MICROSTRUCTURE AND STRENGTH OF MAGNESIA-GRAPHITE REFRACTORY COMPOSITES

A Thesis

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by

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SUMMARY

The relationships between fabrication variables, microstructure and selected properties of carbon bonded magnesia-graphite refractory composite materials have been investigated.

A novel optical microscope method of characterizing the morphology of flake graphites was developed and used to determine distributions of length and thickness and average aspect ratios for the four graphite samples used in the study.

The compaction behaviour of magnesia alone and in combination with the flake graphites has been studied in some detail and the microstructures of the products elucidated. It is shown that the amount of magnesia of small particle size plays a significant role in determining the graphite-graphite contact area in the structure.

An irreversible volume expansion is observed on firing composites, the magnitude of which can be related to the microstructure and the graphite content. A phenolic resin binder restricts this expansion.

It is shown that the carbon binder does not bond to the graphite phase and only weakly, if at all, to the magnesia. Consequently the strengths and moduli are low and show only a small variation with graphite type. The effect of adding graphite to carbon-bonded magnesia is to lower the strength slightly, but increasing the graphite content from 20-30% causes a small increase in strength. Increasing the amount of carbon bond from pitch has little effect on strength at levels of 5-15% whereas over the range 5-13% the resin binder has a more pronounced effect. The most significant factor affecting the strength and modulus of fired composites is the amount of silicon or aluminium,

added as oxidation inhibitors, which react to form carbide and nitride phases.

Finally, a brief study of slag penetration shows that this can be reduced by decreasing the amount of oxide fines in the composite because of the changes in microstructure that result.

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CHAPTER 1

INTRODUCTION

1.1 General Introduction and Literature Survey

About 65% of the total volume of refractories produced in the world is used in the iron and steelmaking industry. Therefore developments in iron and steelmaking processes provide pointers for the future of the refractories industry.

In recent years, the steelmaking process has undergone substantial sophistication such as the increase in continuous casting (concast), increased degassing and other refining processes.[1,2,3] These changes in operation conditions have led to high tapping temperatures, longer molten steel holding time and stirring of slag and molten steel by inert gas bubbling, resulting in shorter life of refractories due to high corrosion and erosion caused by the turbulence of the molten metal and slag.

These high temperatures, usually around 1650°C and above, severely reduce the strength and the chemical stability of the oxide bricks. The reduction in strength is due to the high liquid formation, from the silicate phase in the brick, between and in the interstices of the oxide grains. For instance, the hot strength of a magnesia brick depends on quantity and type of impurity in the brick, such as calcium oxide (CaO), silica (SiO_2), boric oxide (B_2O_3), ferric oxide (Fe_2O_3) and alumina (Al_2O_3). Research over the years has shown that hot strength of a magnesia brick can be controlled by controlling the calcium/silica (C/S) molar ratio. Jackson et al.[4] have shown that hot strength at temperatures greater than 1450°C is highest when the CaO/SiO_2 molar ratio is around 1.8 to 2.8, of course depending on the quantity and type of other impurities (Fe_2O_3, Al_2O_3, B_2O_3) present in the brick. They also showed that the hot modulus was reduced when the test temperature was raised, typically about 40% reduction was observed when the test temperature was raised from 1500°C to 1600°C.

The reason for the decrease in strength as the C/S ratio decreases is associated with a decrease in refractoriness of the silicate phase. On the other hand, the decrease in strength that occurs as the C/S ratio increases is associated with the formation of low melting point ferrites from the small amounts of $Fe_2O_3 + Al_2O_3$ present. The relationship between C/S and the type of phases present in the magnesia brick above 1450°C have been explained in the form of phase assemblage by White[5].

The strength of the magnesia brick is equally lowered if B_2O_3 is present as an impurity in the brick in quantities greater than 0.05%. Taylor et al.[6] showed that this oxide combines with the silicates and reduces their refractoriness by several hundred degrees, to 1000°C-1100°C, the temperature region in which loss of strength was observed to occur.

Great improvements in the brick, in terms of hot strength, erosion/corrosion resistance, etc., were achieved when the boron content in the sea water magnesia raw material, where it is most prevalent, was reduced to less than 0.05%, in addition to the control of the C/S ratio within the required limits.

Although magnesia represents a valuable high refractory structural material, with a melting point of 2800°C, its thermal expansion increases with increasing firing temperature, rising from $12 \times 10^{-6}/°C$ at 300°C to $16.0 \times 10^{-6}/°C$ at 1800°C[7]. This high thermal expansion is directly associated with poor thermal shock resistance observed in the magnesia bricks at steelmaking temperatures.

The literature cited above indicates the vulnerability of the magnesia brick at high temperature both in terms of chemical stability and thermal shock resistance. Similar lines of argument can be followed in explaining the limitations of other oxide refractories, e.g. alumina and zirconia. This is not to mean that the same impurities which affect magnesia will affect the other oxides in a similar manner. Because of this high thermal coefficient of expansion in the magnesia bricks, thermal spalling was a constant problem. In an attempt to eliminate this problem, combinations with chrome ore and dolomite and the use of tar and pitch as bonding or impregnation materials became widespread. Many other studies were also carried out to achieve substantial effects on reducing thermal spalling, but were not sufficient. Therefore various studies were carried out to reduce this problem, and this was achieved by combining the magnesia, and of course other oxides have been used as well, with graphite. This approach was not instant but arose through the accumulation of knowledge and experience through the years and the section below tries to explain how this development came about.

For some time now, the bottom cooling of a blast furnace has been achieved by the use of graphite-containing carbon blocks which have very high thermal conductivity imparted by the graphite[8]. Because cooling of the bottom of the blast furnace is more efficient when the graphite-containing carbon blocks are used, the formation of sumps at the bottom of the furnace is considerably reduced, therefore reducing the wear rate of the hearth floor, which was a persistent problem before this development.

Another problem which was experienced in the operation of the blast furnace was the consistent wearing out of the main trough (iron runner) of the blast furnace. Trials of various materials demonstrated that a satisfactory material for and the construction of the main trough was graphite based monolithic refractories containing alumina. Corrosion resistance against molten pig iron and steel was improved by the addition of alumina. It is not clear from the literature what reasons were advanced for this improvement in corrosion resistance then, but it is now becoming clear that this improvement in corrosion resistance is due to non-wetting behaviour of the graphite by slags while the refractory oxide is not corroded easily by iron or steel as will be explained in later chapters.

In the manufacture of dolomite bricks, tar was used to provide protection of free lime in the brick from hydration. Further, the tar also conferred on the granular mineral matter/tar mixture, sufficient cohesion and plasticity to enable it to be moulded into shapes, which in turn provided sufficient mechanical strength to the product so that it could be handled without deforming. It was observed even in these early days that slag penetration was hindered by the presence of the carbon from tar after coking. This accumulated experience led in the 1960s to the use of pitch or tar impregnated magnesia bricks in the Basic Oxygen furnaces (BOF) and electric arc furnace (EAF) sidewalls in the steelmaking processes. Two methods of introducing the pitch or tar in the brick were used:

(a) The magnesia grains, for instance, were warm mixed with the pitch so as to coat the grains with pitch before pressing them into bricks, to form the so-called pitch-bonded brick.

(b) The fired brick was impregnated with molten pitch or tar in vacuum/pressure vessels.

It was observed that if the carbon in the brick was increased by increasing the amount of binder the coke formed from these binders, this resulted in lowering of the porosity of the brick and therefore improved slag resistance than when the residual carbon was low in the refractory brick[4]. This led to a common practice of enhancing the coke yield from the binder by incorporating carbon black. The advantages which were quoted at the time were:

(i) improved resistance to slag penetration and slag attack;
(ii) resistance to mechanical wear;
(iii) improved thermal shock resistance.

It is clear from above that an increase of the carbon content in the brick would be beneficial and, therefore, ways of increasing the solid carbon content above the levels of those derived from pitch or pitch plus carbon black were sought, and the most significant and probably the most revolutionary one in the refractories manufacture is the addition of natural flake graphite to a carbon-bonded magnesia brick.

Graphite has been recognized as a very promising refractory material for a long time as demonstrated in its use as a constituent in the manufacture of crucibles (plumbago, i.e. clay + graphite) for smelting of non-ferrous metals for decades. Its main drawback is that it oxidizes at temperatures as low as 500-800°C in an oxidizing atmosphere.

The difficulties brought about by the addition of flake graphite to an oxide are enormous because of the differences in physical and chemical characteristics of the two materials. The oxide has more or less equi-axed particles while those of natural flake graphite are platey as Plate 1 shows. Further, Cooper[9] has indicated that graphite presents a surface of very low energy which is not easily wet by both aqueous and organically-based binders, e.g., pitch, while oxides, like magnesia are easily wet by these binders because of their high surface energy, therefore mixing of the oxide-graphite mixtures is difficult. In addition, because graphite is platey, orientation of the graphite during shaping is likely and this can influence the properties of the resulting mixture, henceforth called the composite. The properties of the natural flake graphite are described in detail in Chapter 3 of this thesis. It is, perhaps, important to mention here that the principal reason for the addition of flake graphite is to enhance the thermal shock resistance of the brick in addition to slag resistance offered by carbon as indicated earlier. How this increase in thermal shock resistance comes about is not yet clear, although high thermal conductivity of the brick imparted by graphite, which itself has high thermal conductivity as will be explained in Chapter 3, is being advanced as one of the reasons, due to reduction in temperature gradient in the brick; but it has been shown[9] that "equivalent additions of silicon carbide with almost twice the conductance are far less effective, therefore textural aspects must come into play".

What has not been mentioned so far are the physical properties of the composites, for instance, strength, elastic modulus, thermal expansion coefficient and thermal conductivity. These parameters are fundamental to the understanding of thermal shock resistance of the magnesia-graphite composites which is said to be better than that of oxide refractories. The section below, therefore, summarises some of these properties of the composites known from the literature. The section also tries to describe briefly where these bricks are usually used in the BOF and EAF.

1.2 Properties of Magnesia-Graphite Refractories and Their Uses in the Steel Industry

In the available literature to date (1985), few researchers have published any data concerning a systematic study of the mechanical properties of the magnesia graphite refractories. Mikami et al.[10] investigated the modulus of rupture of magnesia carbon bricks containing various amounts and type of carbon and various types of organic binders. These workers showed that magnesia bricks containing up to 10 ^{w}/o flake graphite and bonded with pitch had strength values (modulus of rupture, i.e. MOR) of about 35 kg/cm^2 (3.4 MPa) and obtained strength values of about 45 kg/cm^2 (4.3 MPa) when a resin binder was used. When the total carbon content was raised to about 20 ^{w}/o the strength did not show any significant change from the values indicated above. This little change in strength when the graphite content is raised from 10 ^{w}/o to 20 ^{w}/o natural graphite was also observed by Fitchett et al.[11] who were studying the effect of tempering (coking) temperature of pitch-bonded magnesia and magnesia-graphite composites bonded with pitch on hot compressive strength. They observed that the compressive strength fell appreciably when 10 ^{w}/o graphite was added to the magnesia bonded with pitch. However when the graphite content was raised to 20 ^{w}/o graphite, the hot compressive strength slightly fell further by an amount of about 5-10% only. It is important to mention that these workers were studying the effect of pyrolysis on hot compressive strength of the magnesia-graphite composites and since the tests were carried out on as-pressed specimens in the case of graphite-bearing specimens, the strength differences were only observed above 500°C when the pyrolysis of the pitch began to produce rigid semi-coke "bond".

Nacamu et al.[12] also carried out experiments on the strength of magnesia-carbon (MgO-C) refractories, by measuring the modulus of rupture of these bricks. Again, these workers found that bricks containing 20 $^{w}/o$ flake graphite showed a strength value of 25 kg/cm^2 (2.45 MPa). The modulus of rupture of the coked MgO-C brick measured at room temperature is very low as cited above compared to the magnesia brick only (28 MPa).[13] Cooper[9] also points out that "refractory bodies containing the quantities of graphite necessary to influence significantly properties such as thermal shock resistance, are generally weaker than more conventional oxide refractories. This is due to the difference in chemistry of the composite phases. When an oxide-graphite composite is fired to steelmaking temperature, for instance during service, diffusion of vacancies can take place within the oxide grain while the graphite will remain effectively inert. Thus there is probably no direct bonding generated in the firing of these composites". The strength of the composite is usually enhanced when the addition of metallic additives such as silicon, aluminium or the combination of the two is made, primarily, as anti-oxidants for the carbon phase. It is not yet clear how these additives improve bonding.

Although the magnesia-graphite brick characteristics are not yet well understood scientifically, these materials are already used in the steelmaking processes because of their durability at high operating temperatures. These bricks were originally developed for use in the EAF walls, replacing, for most parts, fuse cast magnesia-chrome brick in the hot spot areas[12]. The changes that are being carried out in the conventional steelmaking processes, such as pre-treatment of molten iron to achieve desulphurization, dephosphorization and desiliconization, using torpedo cars and ladles as refining vessels before the converter is charged with molten iron, require refractory materials that are resistant to soda ash, iron carbide or iron oxide rich slags. In Japan[14], magnesia-carbon and Al_2O_3-C are used as lining refractories for these vessels.

In the converter vessels, such as Linz and Donnawitz (LD), BOF and Quick or Quiet Basic Oxygen process (Q-BOP), high wear points are the trunnion areas which are located in the rotational axis. The usual BOF steelmaking practice of incorporating a dolomite addition to the after-tap slag for coating the refractory bricks[12] does little or nothing at all to protect the bricks in these areas because of excessive movement of the melts (metal and slag) during charging and tapping operations. The use of magnesia-graphite bricks in these high wear points has extended the lining life of these vessels in addition to lowering gunning maintenance requirements[10]. Typical examples of where these MgO-C bricks are being used in converters are shown in Figures 1.5.1a, b and c. These bricks are used in the metal-slag lines and slag-air interphase, demonstrating clearly the roles being played by both components. At the slag-air interphase, the graphite protects the magnesia from chemical attack by the slag (since graphite is not wet by slags) while the magnesia acts as a diffusion barrier, hence protecting the graphite. Similarly at the metal-slag line, the magnesia protects the graphite from metal attack (graphite dissolves in iron easily) while the graphite protects the magnesia from slag attack as before. The figures also show that the conventional bricks still perform very well in areas where the brick is not in constant contact with slag. Tables 1.5.1a and b are also shown below Figures 1.5.1a and c respectively. Table 1.5.1a shows the types of bricks used in BOF/Q-BOP. .It is perhaps of significance to note that the magnesia-graphite bricks used in the trunnion areas have residual carbon content from 18% to greater than 20%. Further the apparent porosity of these bricks decreases with the increase in carbon content, offering, perhaps, better resistance to slag penetration at high carbon contents. The coked porosity values shown in this table are between 10% to 12%, compared with 15% to 17% for a magnesia brick intended for slag lines and hot spots[15]. The table also shows that MgO-C bricks containing high amounts of graphite have very low strength after coking. These strength values are about 2 MPa for pitch bonded, rising to about 4 MPa when resin is used as a binder.

Similarly, Table 1.5.1b shows the type of bricks used in EAF. This table should be examined with reference to Figure 1.5.1c. From Figure 1.5.1c, it is to be noticed that magnesia-carbon bricks are used in EAF where water cooling of the furnace is practiced. The cooling of the furnace, particularly at the slag line, is enhanced by the high conductivity of the magnesia-graphite bricks.

The strength of the magnesia-graphite is also shown to be about 2 MPa (21-24 kg/cm^2) as already indicated in Table 1.5.1a. Further the bulk density falls with the increase in carbon content.

From the literature above, the important properties of magnesia-graphite refractories for steelmaking applications may be listed as follows:

(a) high corrosion and erosion resistance by molten slags and metals;

(b) high thermal shock resistance and mechanical properties;

(c) oxidation resistance of the carbon phase in the composite;

(d) high thermal conductivity.

The properties are determined by the total composition and microstructure of the refractory product.

1.3 The Manufacture of Magnesia-Graphite Refractories

The methods applied in the manufacture of these bricks are not discussed openly, but what seems to be the practice at present is that the magnesia and graphite both of which can vary in origin, purity and grain size distribution, are mixed together with a binding agent usually pitch or resin, at elevated temperatures of up to about 200°C and then warm pressed into the required shapes. Depending on the binding agent used, the products are heat-treated between 120°C to 400°C to cure the binder, if a resin is used, or to partially carbonize the pitch, if it is the binder, so that the product reaches the necessary strength for handling purposes during transportation and the actual construction of the lining. Complete carbonization of the organic binders is accomplished during the burn-in period of the newly lined furnace.

Although nothing is discussed about the manufacturing techniques of magnesia-graphite bricks, or for that matter any other oxide-graphite products, it would seem that the grain size distribution of the major phases, magnesia and graphite, type and amount of each of these components and type and amount of binder, in addition to the mixing and moulding techniques are the key factors towards producing a good brick. A common problem experienced in the pressing of magnesia-graphite bricks is the laminations in the pressed brick caused by the expansion of the trapped air in the cracks of the graphite flakes when the pressure is released. To overcome this problem, some manufacturers employ vacuum presses, while others apply the method of repeated application of pressure several times before the brick is ejected from the pressing die.

The literature cited above indicates the great potential of magnesia-graphite refractories but not enough scientific information is available to fully exploit the potential of these composites. It is therefore the aim of this work to try to obtain more information concerning these composites and add to what is already known. Therefore the section below presents the objectives of the present work on the magnesia graphite composites.

1.4 Objectives of the Present Study

Among the most significant merits of the presence of graphite in a brick is its ability to impart high thermal shock resistance and hinder the infiltration of the refractory surface by the liquid slag, hence there is improved corrosion resistance, as has been indicated earlier on. How the graphite contributes to all these improved properties is not yet very clear and since the addition of graphite to oxides is a recent development in refractory technology, few researchers have published any data concerning a systematic study of the mechanical and thermal shock properties of these composites. Therefore, in order to explore further the advantages of incorporating graphite in refractory oxides, more fundamental work regarding the addition of graphite to the oxide, evaluation of the physical properties of graphite, such as apsect ratio, physical properties of the composites, such as room and hot temperature strength, thermal expansion, thermal conductivity, elastic modulus, etc., is needed and then jointly interpret the data to try and unravel the various mechanisms at play during service.

The difficulty in carrying out research on oxide-graphite refractories, generally, is the multiplicity of the variables arising from the amounts of both the oxide and graphite, type of magnesia and graphite, size distribution of these two materials, which can considerably vary the microstructural texture, type and amount of binders and, finally, mixing and moulding techniques. These variables can have a fundamental effect on the microstructures giving different physical and chemical properties. It is quite clear, therefore, that the successful manufacture, and ultimately performance of graphite-containing refractories, depends on an understanding of the roles that are played both by the oxide and the graphite in determining texture, chemical relationship between the two materials during service and physical properties which are indicated above. The understanding of this complex system would only come about if some of the many questions which have been raised in the last few years[9] are answered, some of which are listed below:

(i) (a) What is the role of the flakiness (aspect ratio) of graphite and extent of orientation of flakes in influencing the microstructure and hence the properties of the composite?

(b) Since graphite is platey, while the oxide is almost equi-axed, how should the flake graphite be introduced in the oxide matrix when making a composite?

(c) In an attempt to answer question i(b) above, one perhaps needs to raise another question and that is, how should flake graphite used in these composites be characterised in terms of shape, chemical composition, and, further, perhaps is there a need to determine the specific surface area of these flakes?

(ii) (a) What is the binding mechanism in these composites? Does the carbon from the organic binders chemically bond to either of the two major components, oxide and graphite and if not, what role does it play towards the strength of the composite? Then measurement of strength of these composites combined with carbon binders is necessary. Furthermore, what type of contribution does the carbon binder make towards thermal shock resistance and slag attack resistance in the composite?

(b) What is the role and effect of metallic additives (silicon, aluminium, magnesium) in the composite on the binding, the oxidation resistance of the carbon component, the slag resistance and what is their effect on the ceramic oxide in the presence of carbon and melt, slag and/or metal, at steelmaking temperatures? Finally, how is the strength of the composite affected by the presence of these additives at steelmaking temperatures?

(iii) What is the mechanism of dissolution of these refractories by the slags and the effect of composition, texture, porosity and pore size distribution, particle size distribution of the oxide and the graphite and specific surface area of the graphite.

These questions can only be answered by a detailed investigation of the manufacture, texture and other properties, mentioned in the previous sections, of these composite materials, which will result in better understanding of the nature of these refractories and help to clarify their service behaviour at working temperatures. However, because of the limited time in the present study, it is not possible to tackle all these questions, and only certain aspects of the problems have been selected for investigation. Further, the choice was also limited by the availability of the laboratory testing equipment. For instance, hot modulus of rupture, thermal expansion, thermal conductivity and thermal shock resistance at or near service temperature could not be carried out without specialized equipment with a controlled atmosphere.

In an attempt to answer some of the questions raised above, characterization of graphite in terms of its aspect ratio has been carried out. Furthermore, strength determinations and slag resistance examinations have been carried out.

The approach adopted, therefore, was first to characterise the starting materials. This included sieve analyses of magnesia and graphite, oxidation behaviour (not oxidation rates) of graphites and coked binders, ash content determination of the oxides, pyrolysis characterization of the organic binders (pitch and resin) and characterization of four types of graphites in terms of their aspect ratio.

Packing characteristics, strength and dynamic elastic modulus, using ultrasonic method, measurements and microstructure examination of the composites formed the bulk of the investigation. Slag corrosion tests on the composites were carried out by a static reaction test method (cup test method) at 1500°C and 1650°C.

These studies are presented in the subsequent chapters of the thesis along with the review of the relevant literature.

CHAPTER 2

CHARACTERIZATION OF THE STARTING MATERIALS FOR THE FABRICATION OF THE MAGNESIA-GRAPHITE COMPOSITES

2.1 Introduction

In Chapter 1, it has been shown that magnesia and graphite are combined together in various amounts, with small additions of pitch and resin as binders, to produce refractory composites. Packing characteristics, strength, slag resistance, are some of the parameters to be investigated in these composites in the work described in this thesis. Before carrying out measurements of these parameters, however, some basic property evaluation is necessary for the raw materials to be used in the project. These evaluations will be: powder density, sieve analyses, specific surface area, oxidation characteristics of the carbon phases, etc. The density measurement is essential in determining the total porosity of the fabricated specimens as will be described later in this chapter, while surface area measurements and oxidation behaviour of the carbon phase are part of the wider effort of characterizing these materials. Furthermore, the pyrolysis behaviour, at a constant heating rate, of the pitch and resins used in this work has been studied. These studies were used to determine the coking values and give an indication of the rate of evolution of volatiles to be expected at a given temperature and heating rate during the manufacture of the composites. X-ray analyses were also carried out on the crystalline materials, such as magnesia, graphite and the graphite ashes (the residue after the oxidation of graphite) to determine the phases present. The chemical analyses, where available for each material, have been reported as received with the material from the suppliers.

2.2 Sources and General Description of Starting Materials

2.2.1 Magnesia

Magnesia for refractory applications is produced from sea water which contains magnesium salts, and this water is reacted with dolomite or limestone to produce magnesium hydroxide from which magnesium oxide (MgO) is obtained. This is known as the sea water process[16]. For refractory applications, the impurity levels must be very low, as already discussed in Section 1.1 of Chapter 1. For instance, B_2O_3 should be less than 0.05%, $Al_2O_3 + Fe_2O_3 < 1.0\%$, $SiO_2 < 1.0\%$.

Magnesia also occurs naturally in the form of magnesium carbonate. The magnesium carbonate is mined, crushed to liberate some of the impurities, and the magnesium carbonate ($MgCO_3$) is finally separated from gangue using froth flotation methods. The magnesium carbonate is then calcined in rotary kilns or shaft kilns to temperatures of 1600-1700°C before being crushed and sized and ready for use[17]. The impurity levels are also kept very low, e.g. $SiO_2 < 1.0\%$, $Fe_2O_3 < 0.1\%$, $Mn_3O_4 < 0.1\%$, $CaO < 1\%$.

2.2.1(i) Some properties of magnesium oxide (MgO) used as a refractory raw material

Magnesium oxide is a very refractory oxide, melting at 2800°C and it is particularly resistant to attack by iron (FeO)-rich slags. However, refractory bricks made from magnesia alone have poor spalling resistance due to their marked sensitivity to thermal shock because of its high thermal expansion. The effect of high thermal expansion of magnesia on thermal shock behaviour of magnesia bricks is discussed in Section 1.1 of Chapter 1, together with the effect of impurities on hot strength of the brick.

Those properties of fired magnesia bricks which are most affected by the quality of the magnesia grain used in their manufacture are considered to be[4]:

(a) bulk density and porosity;

(b) high temperature strength;

(c) permanent dimensional change on reheating;

(d) slag resistance;

(e) spalling resistance.

Therefore grain bulk density and quantity and type of impurity in the raw magnesia would affect most of the above listed properties. Therefore the need to have high bulk density, low impurity content are fundamental to better performance of the brick at steelmaking temperatures, as already discussed in Chapter 1.

2.2.1(ii) Source of the magnesia used in this work

Two types of magnesia, designated as quality A and B, together with their chemical analyses, were supplied by Steetley Refractories Limited. Quality A was supplied in three sieve cuts, i.e., -5+7, -7+25 and -25 B.S. mesh sieve, while quality B was indicated to have been ball-milled and was only designated as "ball-milled fines". The chemical analyses of the two qualities of magnesia are given in Table 2.3.1(ii) together with the chemical analyses of the graphite ashes, as will be described later.

2.2.2 Natural flake graphite

Natural graphites can be divided into two classes, based on varying modes of formation which account for differences in both physical properties and appearance[18]. The graphite with platey particles is termed "flake graphite". It consists of flat, plate-like particles, as shown in Plate 1, that occur in disseminated form through layers of regionally metamorphosed sedimentary rocks. The size of the particles can range from fractions of a millimetre up to several centimetres. The impurities in the graphite are the associated rock minerals, mainly quartz, micas, feldspar, pyrites and various calcium, aluminium and magnesium silicates, the amounts of which vary from source to source. This is the type of graphite which has been used in this work.

The extremely fine crystalline variety is called amorphous graphite. The description amorphous is a misnomer for this type of graphite since its crystalline structure is well-developed, but the particles themselves are extremely small (cryptocrystalline). This graphite is soft, of dull appearance, in contrast to the flake graphite which has a metallic lustre. It has formed by the metamorphism of coal seams or carbon-rich sediments by magnetic intrusives.

Some of the properties and structure of flake graphite are discussed in Chapter 3, and suffices, perhaps, to indicate that flake graphite exhibits property anisotropy.

In this work, four types of graphite were supplied by GR-Stein Refractories Limited and are designated as A. B, C and D. Graphites A, C and D are of Chinese origin and B is Norwegian.

Very much later, during the course of this work, a fifth graphite sample, of the Malagasy origin, was obtained from Morgan Materials Technology Limited.

This graphite had extremely large flakes compared to those obtained from GR-Stein Refractories Limited. Plate 2.2.2 shows scanning electron micrographs of these five graphites.

2.2.3 Carbon binders

Carbonaceous binders developed from tar or pitch precursors have been used to bond MgO-based refractories, e.g. tar-bonded dolomites, for a long time. Recently, however, there has been a dramatic increase in the usage of carbon and graphite as components of composite steelmaking refractories with oxide phases. Resin binders are finding applications alongside the continued usage of pitch to bind together the two dissimilar phases which do not chemically bond to each other.

The widely used resins in the refractories industry are the phenol-formaldehyde resins. The carbonaceous structure obtained from resins is significantly different from that obtained from pitch precursors. Carbon from pitch can be graphitized at elevated temperatures (> 2500°C) whilst that from resin is non-graphitizing[19].

Any influence that the carbon binder may have on the refractory product that it is contained in, will be related to its volume fraction and distribution as determined by the manufacturing process as well as its inherent physical and chemical characteristics.

The most commonly used resins for binding refractory materials are novalacs and resols. The former are obtained when less than one formaldehyde molecule is reacted with one molecule of phenol, e.g., 0.5:1 or 0.9:1 respectively[20]. If, on the other hand, more than one formaldehyde molecule is reacted with one molecule of phenol, the resultant polymer is a resol[20]. During the manufacture of the resins, hexa methylene tetramine(hexamine)-$N_4(CH_2)_6$ is added to provide methylene linkages to act as crosslinks during thermal curing. In the uncured state both resins are soluble in most solvents.

The type of pitch which is used in binding refractory aggregates is usually coal tar pitch because it is cheap and abundant. Coal tar pitch is a product of the destructive distillation of coal, under pyrolitic conditions, during the carbonization process to make metallurgical coke[21]. This coal tar pitch contains some insoluble particulate matter which is suspended in the tar. These solvent insoluble particles are mostly organic, but some inorganic matter is also included. "The organic matter consists mostly of highly condensed aromatic compounds with as many as 20-25 rings. It also contains some carbon of various forms which is mostly carried over from the coke oven."[19] The solubility of the pitch is determined by quinoline and this matter is therefore called quinoline insoluble fraction (QI).

2.2.3(i) Pyrolyses of these binders

In general, the yield of carbon for both types of binders is determined by the initial carbon content and the extent to which volatile carbon-containing species are produced. Condensation reactions also occur in both resin and pitch precursors and lead to formation of non-volatile aromatic structures that can be converted to carbon.

"During pitch pyrolysis, low molecular weight species evaporate from the melt, the composition of the volatiles being a function of the pyrolysis temperature; at high temperature cracking reactions occur in which aliphatic side groups connected to condensed aromatic hydrocarbons are lost by thermal scission reactions and the free radicals produced may react to form hydrocarbons of increased molecular weight. The cracking reactions lead to species which eventually form carbon.[19]

The decomposition mechanisms of resin are quite complex, with condensation, oxidation, dehydration and decomposition reactions all occurring[20]. Further information on the pyrolysis of resins may be obtained from the references given.

2.2.3(ii) Sources of carbon binders

Two types of binders were obtained for this work; these were coal tar pitch and phenolic resins. The coal tar pitch was supplied by BSC Chemicals while two types of phenolic resins were supplied by Borden (UK) Limited. One resin was a novalac in powder form, code named P41 and the second resin was a liquid resol, code named as PR67 by the suppliers. The powdered resin, P41, did not require any addition of hexamine during use, as this was already done during the manufacturing stage. However, liquid resin PR67 did require the addition of hexamine before thermal curing. The hexamine was supplied together with the resins.

2.3 Experimental Procedures

2.3.1 Sieve analyses of the starting materials

The starting materials, magnesia and graphites only, were sieved into six sieve cuts, namely, -5+7, -7+25, -25+60, -60+100, -100+200 and -200 B.S.S. mesh sieves. These size fractions also correspond to those used to optimize packing of the magnesia-graphite composites as described later in Chapter 4.

Table 2.3.1(i) shows the sieve analyses of the magnesia and the graphites including the Malagasy graphite designated as M and this graphite will be referred to as such throughout the text. The table shows that the graphite with largest flakes was M, followed by A, D, with C well distributed in all the six sieve cuts, and B being the finest of them all.

It is important to point out here that the first raw materials to be received for this work were graphites A, B, C and D, and during aspect ratio measurements, as described in Chapter 3, the sieving of the graphites A, B, C and D was carried out by using 5 sieve cuts, typically +30, -30+60, -60+100, -100+200 and -200 B.S.S. This point will be discussed in detail in Section 3.2.1 of Chapter 3.

The chemical analyses which were carried out on the starting materials by the respective suppliers are reported in Table 2.3.1(ii). The ash contents of graphites A, B, C and D reported in this Table were determined in this work as described in Section 2.3.2. below.

2.3.2 Thermogravimetric analyses of the graphites and the organic binders

Two types of thermogravimetric analysis were carried out on the organic binders, thus their pyrolyses and the oxidation characteristics of the carbonized products were determined at a constant heating rate under non-oxidizing and oxidizing atmosphere respectively. Thermogravimetric oxidation measurements were also carried out on the four graphites.

2.3.2(i) Experimental procedure

The thermogravimetric analyses were carried out using a CI Electronics Mark 3 microbalance, schematically shown in Figure 2.3.2(i). A sample of 100 ±0.1 mg was held in a platinum crucible and then suspended by a fused silica wire hanging from one arm of the balance, and another containing counter weights was hooked on to the other arm. The balance head, which is actually an electronic bridge circuit, was connected, through its control unit, to a double pen chart recorder giving an automatic record of weight change. The other pen was connected to a thermocouple located just below the sample bucket. The temperature of the sample was controlled by a linear temperature programmer connected to a Ni-chrome wound furnace placed around the silica tube in which the platinum bucket containing the sample hung. With this arrangement the pen recorder was able to record simultaneously both weight and temperature at all times during the course of the experiment.

The oxidation of the graphites and coked carbon binders was studied thermogravimetrically at a constant heating rate of 0.3°C/min employing an open system, i.e. the sample holder was open at the top end, in an atmosphere of compressed air at a flow rate of 150 cc/min. However, the pyrolyses of the binders were carried out at a faster heating rate of 1°C/min under a continuous flow of pure nitrogen at a flow rate of 150 cc/min. Other arrangements remained unchanged as described in the oxidation experiments.

The pyrolysis results determined on the binders are plotted in Figure 2.4.4 , while the oxidation results on the graphites and the coked binders are plotted in Figures 2.4.5(i) and (ii) respectively. These figures will be discussed in the Discussion section later.

The resin binders were cured at 120°C in an oven before pyrolyses studies were carried out. In the case of the liquid resin, PR67, 5 $^{w}/_{o}$ hexamine was added to the resin and then thoroughly mixed at about 70°C before being transferred to the oven for thermal curing.

2.3.3 Powder density determinations of the starting materials

In the experiments to follow and described in Chapters 4 and 5, it was essential to determine the total porosity of the compacted and fired composite materials. The total porosity can be determined if the true density, for practical purposes this is equal to powder density, and the bulk density of a specimen are known, i.e.,

$$\% \text{ Total porosity} = \left\{1 - \frac{\text{bulk density}}{\text{true density}}\right\} \times 100 \; .$$

2.3.3(i) Experimental procedure

The determination of powder density involves the use of a fluid that will penetrate and fill the available cavities that are present in the material that is being measured. However, in some particulate materials pores may be enclosed within solid particles, making it impossible for the liquid to fill such pores. To open up such pores, grinding of the material is carried out. In this work grinding of the samples was carried out in a tungsten carbide ball-mill which was then placed in the Glen Creston shaker and left running for 30 minutes before removing the sample. During the course of this experiment, it was found that it was necessary to suspend the sample in acetone, making a thick slurry, during grinding to avoid agglomeration which was observed to occur if magnesia was ground dry. This technique was applied to the graphites which were even more difficult to grind in the dry state because of their slipperiness. Even after suspending a graphite sample in acetone during grinding, the sample had to be reground several times, in between sieving operations, before the whole sample could pass through 200 mesh sieve. The slurries were sieved through 200 B.S. mesh sieve before being dried at 60°C in an oven placed in a fume cupboard. After the acetone had dried the oven temperature was raised to 110°C to remove any residual moisture and the samples were left at that temperature for 24 h before being cooled to room temperature in a desiccator and then transferred into labelled sample bottles after which their bottle tops were screwed tight before being stored away for future use.

For the determination of the powder density of magnesia, it was not possible to use water because magnesia hydrates in the presence of water. Therefore xylene, which has a very high boiling temperature (144.4°C) and hence a low rate of evaporation compared to other low density fluids, was used for density determinations for all those materials that needed density measurement. The density of the xylene was first determined at the temperature to be used for the powder density measurements.

2.3.3(i)a Density determination of xylene

A density bottle (pycnometer) of 25 cc volume was used in the density determinations of both xylene and the starting materials. The bottle was washed clean and then rinsed in distilled water. It was then dried in the oven and weighed repeatedly until there was no weight change. The weight of the dry bottle together with its stopper was noted, then it was filled with xylene. Without inserting the stopper, the bottle was put into the water bath, which was set at 22°C, and left in the bath for 30 minutes to attain the bath temperature. The bottle was then quickly removed from the bath, the stopper gently inserted and the outside of the bottle was wiped dry before being weighed. Now, knowing the weight of the xylene and its volume, i.e. volume of bottle, density of the xylene was determined.

2.3.3(i)b Powder density determination of the materials

The powder densities of the materials were also determined at 22°C. The procedure was similar to the one described above but additional techniques were required as follows:

The required amount of sample, 10 g samples for the magnesia and half that amount for bulky carbon samples, was weighed onto a weighing paper and then carefully transferred into the bottle. The mouth of the bottle was thoroughly wiped clean with a dry tissue paper before the bottle with its contents was weighed again to finally determine the amount of sample in the bottle. Xylene was then poured into the density bottle until its level in the bottle was just above that of the sample. The bottle, without inserting its stopper, was then placed in a desiccator and left overnight. The following day the bottle with its contents was transferred into a desiccator to which a rotary pump had been connected to remove air from the sample slurry to facilitate vacuum impregnation of the powder by xylene. The rotary pump was left to run until no more air bubbles were seen to be coming out of the slurry. This usually took about 10 to 15 minutes before air was let into the desiccator. To accelerate air removal from the sample, the desiccator was gently rocked to and fro by hand while the pump was running.

After the admission of the air in the desiccator, the density bottle with its contents was removed from the desiccator and it was then filled with xylene, taking care that no overflow or spillages took place to avoid loss of fine materials suspended in the liquid at the time of filling. However, all particles settled to the bottom after a short period of time. The bottle without a stopper was then placed in the water bath, set at 22°C, and left there for 30 minutes as before. After this period the bottle was removed quickly, the stopper inserted in position, the bottle surface was wiped dry and then weighed to the nearest milligram. Hence the density of the sample was determined as explained in Appendix, 2.3.3(i)b. Four density measurements were carried out on each sample and these results are reported in Table 2.3.3(i).

It is perhaps important to mention that in the above description of density determinations, it was indicated that after adding a small amount of xylene, the bottle was placed in a desiccator and left overnight. This procedure was followed only after observing that densities determined immediately after weighing the powder were less than those determined after soaking the powder in xylene overnight. This is most likely due to the fact that proper air removal from the powder by the vacuum process was being hindered by the presence of xylene in the powder, hence this soaking period was required. On the other hand, evacuation of dry powders could not be done before admitting xylene because fine powders tended to be sucked out of the bottle, particularly the powders of the carbon samples.

The powder densities of raw resins were determined after curing the resins at 120°C in the oven. This was necessary to render then insoluble in the solvents (see Section 2.2.3). Raw pitch is soluble in most liquids and slightly so in water. Therefore the method of determining powder density as described above could not be applied to raw pitch, instead a mercury balance was used. This was achieved as follows:

A block of pitch was placed on an aluminium foil and then melted at 110°C in an oven. The melted pitch was left in the oven at that temperature for three hours to ensure homogeneity in the melt before being removed and left to cool to room temperature in a desiccator. The temperature chosen for melting the pitch was such that no gases were evolved during melting and this was monitored by checking the weight before and after melting. The cooled pitch block was therefore non-porous or at least near so for practical purposes. Therefore by determining its bulk density, one was effectively determining its true density (see porosity expression in Section 2.3.3). The density of the raw pitch is also reported in Table 2.3.3(i).

2.3.4 Surface area determination of the graphites and coked binders

The specific surface area determinations on the starting materials, particularly graphites, were intended to measure the amount of internal surface which is a measure of the interlaminar cracks (compactness) in the graphites. The specific surface area of a graphite sample was determined before and after grinding the bulk sample. Further, the specific surface areas of various sieve fractions of the same graphite sample were determined to find out whether there were differences in the amount of cracks, hence specific surface area between these fractions.

The same procedure was followed for the coked binders to show the accessible specific surface area before and after grinding.

2.3.4(i) Theory

The surface area of powders can be determined by applying theoretical considerations proposed by Brunauer et al.[22] The BET theory, as it is commonly known in honour of these workers[22], considers the build-up of the adsorbed layer kinetically in terms of a monolayer of the adsorbate, followed by multilayer formation. These workers[22] derived an equation which described the adsorption of a gas upon a solid surface and this equation is given below:-

$$\frac{(P/P_0)}{V[1 - (P/P_0)]} = \frac{1}{V_mC} + [(C - 1)/(V_mC)]P/P_0 \qquad (1)$$

where V is the volume (at standard temperature and pressure, STP) of gas adsorbed at pressure P, P_0 is the saturation pressure which is the vapour pressure of liquified gas at the adsorbing temperature, V_m is the volume of gas (STP) required to form an adsorbed monomolecular layer, and C a constant related to the energy of adsorption.

If a plot of $\frac{P}{V(P_0 - P)}$ against P/P_0 is made, a straight line usually results for P/P_0 values between 0.05 to 0.3. The intercept of the straight line is equal to $\frac{1}{V_mC}$ and its gradient is $\frac{C - 1}{V_mC}$. Then solving for C in each expression and by equating the resulting expressions, V_m can be calculated.

The surface area of the sample, S, giving the monolayer adsorbed gas volume V_m (STP) is calculated from the equation below:-

$$S = (V_m \times A \times N)/V_M \qquad (2)$$

where A is Avogadro's number, V_M is the molar volume of gas, and N the area of each adsorbed gas molecule[23], i.e., molecular cross-sectional area of the adsorbate (in $\mathring{A}^2$) and if nitrogen is used as an adsorbate at liquid nitrogen temperatures, N = 16.2 $\mathring{A}^2$.

The specific surface areas of the graphites and the coked binders were determined in a FlowSorb 2300 and it is schematically presented in Figure 2.3.4(ii)[24] and a brief description of this instrument is given below.

2.3.4(ii) Brief description of the FlowSorb 2300

The instrument determines the specific surface area by the single point adsorption method. The essential elements of this instrument are:

(a) Components for turning on and off gas flow, regulating and directing the flow, and indicating the flow rate.

(b) Attachment points at which the gas is passed through a cold trap for removing traces of moisture that may be present in the gas, points at which the sample is exposed to heated gas to free it of any adsorbed gases and vapours.

(c) A septum by means of which a known amount of gas can be introduced for calibration purposes.

(d) Matched thermal conductivity cells operating at a fixed temperature of 42 ±1°C for gas concentration detection.
It is this concentration difference during the adsorption or desorption of a gas that causes a mismatch in the conductivity of the gas before and after passing over the sample. The instrument uses a mixture of two gases, one which can be adsorbed at its liquid temperature and a carrier gas which cannot be adsorbed at this temperature. In this particular instance, 30 mole% nitrogen and 70 mole% helium mixture was used. It follows then that if nitrogen gas is adsorbed or

desorbed, the ratio of the two gases before entering the sample tube is changed after the gas mixture leaves the sample tube. This causes mismatch in the conductivity of the gas mixture and is detected by the two cells and this difference in thermal conductivity triggers a signal in the electronics of the instrument which rises proportionately to the amount of the gas being adsorbed or desorbed. As less and less gas is being adsorbed/desorbed, the signal also falls, and when the gas mixture ratio is restored, the signal dies down to its threshold level. The resulting curve is integrated[24] to find the area under the curve, which is related to the amount adsorbed, hence to the total surface area of the sample;

(e) a Dewar flask support platform.

2.3.4(iii) Experimental procedure

All samples were dried at 110°C in an oven for a 24 h period before determining their specific surface areas. Those samples which required grinding were ground to less than 75 μm before being dried in the oven.

A clean glass sample holder, in a U-shaped configuration, as shown in Figure 2.3.4(ii) was accurately weighed to the nearest mg. Then the dry sample was put into the tube through one stem, using a spatula. The tube stem was gently tapped to facilitate easy flow of the powder down to the bottom of the tube leaving as little powder as was possible along the inner walls of the stem. The bore of the stem was further cleaned using a pipe cleaner. The sample size used depended on two factors[24]:

(a) "The amount of sample put in should not block the bore of the tube at any point along the tube to enable easy flow of the gas over the sample";

(b) "the results were most accurately and quickly determined if the sample quantity was adjusted, such that its total surface area fell between 0.5 to 25 m^2 limits" .

The two stems of the tube were then inserted into tightenable connectors which joined them with two male connectors. This assembly was then installed at DEGAS position on the instrument (see Figure 2.3.4(ii)) by pushing the male components into female counterparts. A heating mantle was then slid upward about the glass sample and held in place with a flared U-clamp. The heating mantle temperature was then set at 300°C by adjusting the temperature-set register after which the mantle was switched on. The mantle reached temperature in less than 5 minutes, but each sample was left in the mantle at temperature for 20 minutes before being transferred to the test position and left to cool to room temeprature.

Meanwhile, a second sample tube, with a sample, could be placed in the degassing position, if required, while measurements were being carried out on the first one.

When the sample tube in the test position had cooled down to room temperature, a Dewar with liquid nitrogen was brought up about the sample tube and the tube was quickly immersed in liquid nitrogen, up to about 1 or 2 cm below the connectors, using one hand while the other hand was used to bring up a hinged platform to provide support for the Dewar. With the platform in this horizontal position, the instrument automatically collected adsorption data. The Dewar was left in this position until the indicator threshold lamp stopped flushing or its flushing rate reduced to one flush every 15 or 20 seconds, indicating the end of adsorption. The reading on the front panel was the total surface area of the whole sample in m^2 and it was noted. The display was then cleared in preparation for registering the desorption reading.

To obtain the desorption reading, the Dewar around the sample was quickly removed by dropping the platform using a release button, and then promptly immersing the sample tube in a beaker of water at room temperature. The beaker was moved around so that the sample was warmed up as rapidly as possible. The warming procedure was continued until the flowmeter float returned to its position before immersing the sample tube in the water. The beaker was then removed and the sample tube dried. While all this was going on the desorption readings were being recorded by the instrument automatically, since the instrument recorded the desorption values if the platform was dropped. There was no loss of desorption readings during the changeover period from the Dewar to the beaker of water because the sample tube remained essentially at liquid nitrogen temperature for 3 to 6 seconds, which time was adequate for the changeover.

The desorption reading was taken after the indicator lamp flushing rate reduced to one flush every 15 or 20 seconds, as before.

In this experiment the desorption readings were used, because, according to the manufacturers[24], "the adsorption peak is not as sharp and clean as the desorption one and cannot be integrated with the precision of the latter".

Finally, the determination of the specific surface area was obtained by dividing the total surface area read off from the machine by the weight of the sample. Table 2.3.4(iii) shows the specific surface areas determined using this instrument.

The specific surface area measurements obtained using this instrument are more of a comparative nature than being absolute values because of the assumptions made to enable the instrument work out the total surface area[24]. These assumptions are as follows:

(a) since the intercept $\frac{1}{V_mC}$, equation (1), Section 2.3.4(i), is small, its contribution is vanishingly small and therefore may be ignored.

(b) $C >> 1$, therefore $C - 1 \simeq C$.

These approximations reduce equation (1) to $V_m = V[1 - (P/P_0)]$ and substituting this V_m expression in equation (2), Section 2.3.4(i), yields $S = V \times A \times N[1 - (P/P_0)]/V_M$ from which the sample surface area S is readily determined once the volume, V, of gas adsorbed/desorbed is measured.

(c) The calibration is done at room temperature, taken to be 22° C and 1 atm. pressure. The volume used to calibrate the FlowSorb 2300 is multiplied by the ratio $\frac{273.2}{295.2}$ to convert it to standard conditions (0 C and 760 mm Hg)[24]. These experiments were not carried out in a temperature controlled room; therefore the room temperature and atmosphere used in the above conversions were approximations.

(d) P is 0.3 x 760 mm Hg since the gas mixture is 30% nitrogen and the adsorption pressure is atmospheric. However, if this P was measured the result could be different.

(e) P_0, the saturation pressure of liquid nitrogen is "typically a very small amount greater than atmospheric pressure and is averaged at 775 mm Hg"[24]. Again, this assumption could be invalidated if the actual saturation pressure were determined at the time of carrying out the experiment.

2.3.5 X-ray analyses of specimens

The samples to be examined were ground to powder to pass through 200 B.S. mesh, and then examined by X-ray diffraction in order to determine the crystalline phases present. Traces of line intensity against 2θ values were obtained by the use of a Philips PW1730 diffractometer using a graphite monochromator with Cu K_α radiation. From the 2θ values at which reflections occurred, interplanar spacings or "D" values were determined by the use of the Bragg equation, $n\lambda = 2d \sin \theta$ and these values were compared with X-ray Powder Data Files of the A.S.T.M. index. The "d" values with their corresponding relative intensities and the phases present of the materials examined are reported in Tables 2.3.5(i)-(iv) and the results will be discussed in Section 2.4.7.

2.4 Discussion of Results

2.4.1 Sieve analysis of starting materials

Table 2.3.1(i) summarises the weight percent fractions obtained in each material after sieving. These results emphasize the fact that graphite M has the largest flake size of the five graphites shown in this Table, 94 $^w/o$ is retained between 2400 µm and 600 µm. Graphite A is the second most coarse graphite, with 83 $^w/o$ of the flakes being retained on 250 µm aperture. The third most coarse graphite, based on weight percent retained, is graphite D for which 96 $^w/o$ of its flakes is retained on 150 µm, while graphite C is well distributed in all the sieve cuts used; and finally, graphite B is the finest of them all, with about 69 $^w/o$ passing through 150 µm aperture.

2.4.2 Chemical analyses

Table 2.3.1(ii) shows that graphite B and M have the highest ash content, while D has the lowest ash contents with graphites A and C having equal amounts.

The chemical analyses of the ashes show that the ash residue of graphite M has the lowest alkaline contents, K_2O and Na_2O, of 0.90 $^w/o$ and 0.05 $^w/o$ respectively. Graphite B has the highest alkaline content with 5.23 $^w/o$ ($K_2O + Na_2O$) followed by A with 4.61 $^w/o$, then D with 3.77 $^w/o$ and, finally, C with 3.01 $^w/o$. From the alkaline content point of view then, graphite M could be expected to have the highest fusion point, followed by C, D, A and B having the lowest. However, the actual fusing point of a particular ash will also depend on the reactions of other phases in the ash at temperature. For instance, depending on thermal equilibrium conditions, oxides of higher $^w/o$ in the ash may react preferentially with each other and form either high or low melting phases. The oxides which are in large amounts are SiO_2, Al_2O_3 and Fe_2O_3, then followed by MgO and CaO.

The other property which is of refractory interest from Table 2.3.1(ii) is the calcium/silica molar ratios (C/S) of the ashes and the magnesia. The C/S molar ratios of the graphite ashes are low, < 0.1, while the C/S molar ratio of the magnesia fractions is high, > 3. In both cases, separately of course, there is no danger of forming low melting phases were it not for the high alkaline contents in the ashes. However, the possibility of forming low melting phases in the magnesia-graphite composites occurs when the graphite, for example, is oxidized during service and the ash comes in direct contact with the magnesia. This contact at high temperatures can alter the chemistry of the second phases in between the magnesia grains. In the graphite ashes, there is a high amount of silica available while in the magnesia there is a very high amount of calcium oxide available. This situation could lower the calcium/silica ratio of the second phase in the magnesia to 1 to 1.5 in which region low melting phases, like monticellite, can easily form. However, in practice, the ratio in the brick where graphite has been depleted, will not only depend on the ash composition but also on the chemical composition of the slag and the atmosphere at the reaction zone. One other important point to note in the chemical analyses of the graphite ashes is the high amounts of Al_2O_3 and Fe_2O_3. If these ashes come in contact with the magnesia, depending on the ash distribution, the amounts of Al_2O_3 and Fe_2O_3 could be increased in the magnesia, and this, as already discussed in Chapter 1, could reduce the hot strength and corrosion/erosion resistance of the brick at working temperatures. It is equally important to note the absence of B_2O_3 in the chemical analysis of the magnesia, implying that these magnesia fractions are of high quality.

2.4.3 Specific surface area (m^2/g) results

The specific surface area measurements, as already discussed in Section 2.3.4, were intended to determine and compare the interlaminar cracks (compactness), hence surface area, of the graphites between various sieve fractions of the same type of graphite as well as between different types of graphite. The results determined on all the five graphites and the two organic binders, pitch and resin P41, are shown in Table 2.3.4(iii). These results are not absolute but comparative, as already explained in detail earlier on (see page 35, Section 2.3.4(iii).The graphites, except for graphite M do not show a big variation of specific surface area between different sieve fractions of the same graphite. But an increase of the area is evident on flakes which passed through 200 B.S. mesh sieve, with graphite A having the highest surface area in this fraction. Graphite M shows an enormous increase of the specific surface area between its coarse flakes and the fine flakes (-200 B.S.S.). However, when a bulk sample of this graphite was ground, the specific surface area increased only to 21.5 m^2/g compared to 32 m^2/g for its fine fraction (-200 B.S.S.), implying probably that further grinding was required to open up more interlaminar cracks. The other types of graphite, A, B, C and D, showed that their specific surface areas increased when ground, with the highest increases being observed in graphites A and D. It would seem that grinding creates more surface probably by shearing the graphite layers. However, graphites B and C, which had a large proportion of fine fractions, were not very much affected by grinding. Two explanations are possible here:

(a) these two graphites did not have large interlaminar cracks, hence very compact, or

(b) the grinding effect was reduced as the flakes got smaller and smaller, and therefore shearing of graphite layers did not occur at the same extent as in the coarse flakes.

The results demonstrate, generally, that the coarser the graphite flakes the higher the specific area, as shown by graphites M and A, hence they are less compact.

The coked binders also showed that pitch had lower specific surface area than resin P41, but when ground, their specific surface area values were about the same, implying that the total porosity of the two coked binders could be the same up to this coking temperature (1500°C).

The sample labelled "BINDER COKE A200 (1400°C)" was used as a standard sample, whose specific surface area was already known from the Literature (1.33 m^2/g) in the unground state. Therefore it was used to ascertain the reliability of the measurements obtained with the FlowSorb 2300.

2.4.4 Pyrolyses of organic binders

The pyrolysis results of the organic binders are plotted in Figure 2.4.4. The Figure shows that pitch and resin PR67 lose volatiles at lower temperatures than resin P41 at the same heating rate. However, resin PR67 can have its pyrolysis behaviour changed by varying the amount of hexamine added to it before curing[20]. In this experiment, 5 $^{w}/o$ hexamine was added and no attempt was made to vary the amount of hexamine and determine the pyrolysis characteristics with varying quantities of hexamine. Lemon[20] has also shown that the coking value of a resin can be varied by varying the amount of hexamine added before curing the resin and the coking value increases with the increase in hexamine content. In practice, however, the optimum amount of hexamine that can be added to resin PR67 may be between 4 to 10 $^{w}/o$ hexamine[20]. Figure 2.4.4 also shows that resin P41 has a higher coking value (58 $^{w}/o$) than that of pitch (50 $^{w}/o$) and resin PR67 (49 $^{w}/o$). These coking values of these binders were used in determining the total carbon content remaining after coking of the magnesia-graphite composites in which these organic binders were used to bind the composites as will be described in Chapters 4 and 5.

2.4.5 Oxidation of graphites and binders

The aim of the oxidation experiments in this work is an attempt to study, briefly, the characteristics of the starting materials, in this case the oxidation characteristics of the graphites and coked binders at a constant heating rate.

2.4.5(i) Graphites

Figure 2.4.5(i) shows the oxidation behaviour of the four graphites, A, B, C and D studied in this part of the experiment. Graphite B oxidized at lower temperatures than the rest of the graphites and graphite D showed a higher oxidation resistance than the other three graphites.

It has been shown before[25] that "fine graphite flakes oxidize faster than coarse flakes". It is therefore surprising to find that graphite D which has finer flakes than graphite A is more resistant to oxidation than graphite A. However, Thomas[26] has shown that the oxidation rate of graphite, in general, depends on:

(i) the type of impurities in the graphite. He has shown that the metallic impurities can function as very efficient catalysts in the formation of hexagonally shaped holes, which are called etch pits. The etch pits expose the edges of the graphite from which the graphite reacts with the oxidizing gas.

(ii) The amount of surface area available for oxidation reaction to take place.

(iii) the type and number of defects in the graphite lattice, for instance single vacancies and vacancy clusters, dislocations, etc.

It is clear from above that the oxidation of graphite is a very complicated process and the discussion of these oxidation processes of graphite are beyond this scope of this work. It is, perhaps, interesting to note that Table 2.3.4(iii) shows that graphite D has the lowest specific surface area and this could contribute to the oxidation resistance it has shown than graphite A which has a high specific surface area and oxidizes faster than D although it is coarser than D. Further graphite D has less ash content than the other three graphites, which could mean, perhaps, that it contains less impurities which may act as catalysts in the formation of etch pits as described above.

Graphite C which showed an even distribution of flakes in all the sieve cuts (Table 2.3.1(i)) oxidized less at the same temperature than graphite B but faster than the other two graphites. This is not surprising considering the fact that graphite C has 37 $^{w}/o$ of flakes passing through 100 B.S. mesh, sieve (< 150 μm), only surpassed by graphite B in this sieve range; therefore the fine fraction must have oxidized faster than the coarse fraction, resulting in its oxidation behaviour to be in between graphites A and B.

From the above observations, it is apparent that the oxidation of a graphite sample depends on many physical and chemical characteristics, for instance, surface area, amount and type of impurities and their distribution and, finally, the structural defects in the graphite itself.

2.4.5(ii) Oxidation of coked binders

The oxidation of coked pitch and powdered resin P41, after curing at 110°C, was carried out exactly in the same manner as that for the graphites. Figure 2.4.5(ii) shows that the resin oxidized faster than the pitch. It is not quite clear why this is so, but differences in the structure of the resulting carbons from pitch and resin precursors could be a major factor. The carbon from pitch is a graphitizing carbon while the carbon from resin is non-graphitizing. In a review paper, by McEnaney et al.[27], on structure and properties of carbon binder from polymeric resins and pitch, it has been indicated that the nature and extent of the porosity during formation and heat treatment of these carbons is markedly different in non-graphitizing and graphitizing carbons. "Graphitizing carbons have small surface areas, up to about 3 $m^2\ g^{-1}$, whereas the accessible surface areas for non-graphitizing materials can either be very small, because the cross-linked carbon structure prevents access to the internal porosity or be as large as 500 $m^2\ g^{-1}$ (in extreme cases)"[27]. The large surface areas often found for non-graphitizing resin-based carbon exist because porosity is open and microporous (micropores being defined as pores of width up to 2 nm) and these pores can be enlarged by the oxidizing gases; while the low surface areas found for graphitizing carbons and synthetic graphites arise because there is little or no microporosity[27]. During the oxidation process the pitch will continuously present a lower surface to the incoming oxidizing gas than the resin; therefore oxidation should be higher for the carbon obtained from the resin than that obtained from pitch. This is clearly demonstrated in Figure 2.4.5(ii), which shows that the resin oxidized at much lower temperatures than pitch.

Table 2.3.4(iii) shows that the unground coked resin (P41) has almost three times as much specific area as the unground coked pitch at the same coking temperature (1500°C). This is in agreement with the above descriptions that coked resins, in general, have higher porosity than coked pitch. Plate 2.4.5 shows the S.E.M. micrographs of pitch and resin after coking at 1500°C. What is significant from the micrographs is that the physical appearance of the two carbons is different and that the resin shows more open pores than the pitch; this is an indication of the amount of porosity in the coked resin.

2.4.6 Powder density of the starting materials

The powder densities of the starting materials determined in this work are shown in Table 2.3.3(i). Graphites B and M, with high ash contents, showed to have slightly higher densities than the other graphites.

The pitch shows a large increase in density (2.0×10^3 kg/m^3) after coking compared to its raw density (1.3×10^3 kg/m^3). This increase in density could be attributed to the developments of the coked pitch towards a graphitic structure which has little or no micropores enclosed in its structure as discussed in the previous section. In the case of the coked resin, the density increase from the cured state (1.3×10^3 kg/m^3) to the coked state (1500°C) (1.4×10^3 kg/m^3) is small (see Table 2.3.3(i)). This low increase in density is, most likely, as a result of the closing of pores in non-graphitizing carbons during heat treatment (HTT) as described in the previous section. McEnaney et al.[27] in their review paper, have shown that the helium density of non-graphitizing carbons decreases as the HTT increases, and it only begins to increase slightly above 2000°C. This decrease in density is an indication that the open porosity (open to helium gas) is decreasing, i.e., conversion of open micropores to closed micropores, because if pores were being eliminated, density would have been increasing with HTT. In the case of graphitizing carbons, the helium density increases progressively with the HTT, approaching the density of graphite crystals[20].

2.4.7 X-ray analysis

The X-ray analyses were carried out to determine the phases present in the starting materials. Tables 2.3.5(i)-(iii) show the phases present in the materials examined. As much as these results confirm the chemical analyses reported in Table 2.3.1(ii), the X-ray analyses helped to identify the type of oxide or, for that matter, the minerals present in the sample. For instance, in Table 2.3.5(iii), kyanite is shown to be common in the ashes of graphite A, B and D, but not in C. However, the common phases detected in the ashes of the graphites were α-SiO_2 and α-Fe_2O_3. In the ash of graphite B, in addition to α-SiO_2, α-Fe_2O_3 and kyanite detected, tridymite and Mn_3O_4 were also detected. In each graphite ash, a line with a highest d-value (Å) was detected and was found to be of high relative intensity in ashes A, B and C and this could not be indexed as well as those lines of low intensities. The line with the highest D-value in each graphite ash could be due to a complex phase with solid solutions.

Table 2.3.5(i) shows that the magnesia fractions contained minor phases which produced lines of very low intensity and these lines could not be matched by any of the lines listed in the X-ray Powder Data Files of the A.S.T.M. index. Similarly Table 2.3.5(ii) shows the D values (Å) and relative intensities of the phases detected in the graphite samples. Again lines of low intensity were detected and could not be indexed because they did not, as well, match any of the lines listed in the X-ray Powder Data Files.

2.4.8 Summary of the results

From sieve analyses, graphite M had the largest flake size, followed by A and D, with C having distributions in all the sieve cuts, and B was the finest (Table 2.3.1(i)). The specific surface area results show that graphite M has the highest specific surface area, even though it is the coarsest material, again followed by A, and then C, B and finally D.

Graphite B oxidized faster than the other graphites experimented on, while graphite D showed to have the highest oxidation resistance, possibly because of its low specific surface area and low ash content. The coked resin P41 showed a higher rate of oxidation than the coked pitch and had a higher specific surface area (1.30 m^2/g) than pitch (0.45 m^2/g) in the unground state.

The densities of graphites M and B were observed to be slightly higher than those of other graphites. These high density values could be attributed to the high impurity oxide content (ash) in these two graphites.

Finally, the common phases detected in the graphite ashes were α-quartz, hematite (α-Fe_2O_3) and kyanite. This last phase could be a pointer as to the type of area from which the graphites were mined.

The property characterization of the starting materials described above provide a basis for detailed examination of the magnesia-graphite composites, in terms of packing characteristics, strength, slag resistance etc. However, the above determined properties do not in any way indicate the flakiness of graphite. This single physical property makes graphite behave differently from the oxide that it is combined with. For instance, orientation of the flakes can be different depending on the size of the oxide it is combined with and the method of fabrication. In cases where the product is pressed, the graphite flakes may be oriented differently normal and perpendicular to the direction of pressing. It is certain therefore that this flakiness in graphite does affect the packing characteristics of a composite in which it is contained. The question is, how?

In an attempt to understand the effect of flakiness of graphite in composites, further characterization of graphite in terms of its aspect ratio (length/thickness) has been carried out. Chapter 3, which follows, describes in detail how the aspect ratios of the four graphites A, B, C and D, which were received in the first twelve months of this work, were determined.

CHAPTER 3

ASPECT RATIO MEASUREMENTS OF NATURAL FLAKE GRAPHITES

3.1. Introduction

Natural flake graphite, as already pointed out in Chapter 1, is widely used as a constituent in refractories designed to withstand molten slags and metals at steelmaking temperatures, because graphite-containing refractories have higher slag attack resistance and higher thermal shock resistance than oxide refractories alone, e.g. magnesia.

While refractory properties of the magnesia, which is not pure but of sintered grains containing a second phase, are determined by its chemical composition and density[28,29,30], the refractoriness of graphite is well above steelmaking temperatures in a non-oxidizing atmosphere is assured, therefore combining the two materials would almost certainly produce a superior brick. However, combining these two materials is beset with many difficulties arising from their chemical and morphological differences. The graphite flakes are platey and can only be completely defined by their three dimensions, length, breadth and thickness, while magnesia grains can be approximated as spheres and can be defined completely by their radii. Therefore the need to characterize graphite in terms of its aspect ratio (length/thickness) may help in understanding how these dimensions influence packing, strength, thermal shock resistance, etc. of graphite-containing composites. But before describing the experimental procedures used in determining the aspect ratio of the graphites in this work, it is appropriate here to describe some of the general properties of graphite and the section immediately below deals with this.

3.1.2 General Properties of Graphite

The physical and chemical properties of graphite are completely different from those of magnesia. The structure of graphite consists of stacks of layers in which the carbon atoms are covalently linked in hexagonal array forming a large condensed aromatic structure. The distance between carbon atoms in such a plane is 1.42 Å, whereas the interlayer spacing is 3.345 Å. The layers are stacked in an ABAB.... hexagonal unit cell so that there exists an atom above the centre of each hexagon in the plane immediately above, as shown in Figure 3.1.2(a).

Nightingale[31] observed that when some graphites are examined by X-rays, extra lines appear on the X-ray powder photographs and suggested that about 5% of the graphite has a second type of stacking, i.e. ABCAB.... for which the unit cell is rhombohedral. Furthermore, he related the height of the rhombohedral unit cell to that of a normal hexagonal c-axis and found that the height was $^3/_2$c, which gives rise to the extra X-ray lines. However, this structure of graphite is not very stable and it is not usually observed.

Because of the strong binding of carbon atoms in the same sheet, that is Sp^2 hybridization, and the weak binding forces between successive sheets, including possibly Van der Waals forces, the basal plane is the main glide plane; thus gliding should take place between these successive planes. This planar structure results in marked anisotropy in the properties of graphite. It has been established that:

(a) thermal expansion coefficient perpendicular to the planes for single graphite crystal is about 200x ($240 \times 10^{-7}/°C$); that parallel to the basal planes which is actually negative at room temperatures. In both directions ($\parallel$ and $\perp$)

of the basal plane, the coefficient of thermal expansion varies with temperature. For instance, the coefficient of thermal expansion perpendicular to the basal plane, α_C, is given[32] as:

$$\alpha_C = (27.00 \times 10^{-6} + 3.05 \times 10^{-9}\ (T - 273))/K$$

(b) thermal conductivity parallel to the planes is about 200x that perpendicular to the planes; i.e. 250 $^W/(M.K^\circ)$ and 1 $^W/(M.K^\circ)$ respectively. Furthermore, electrical conductivity is also very high along the basal plane, $10^2 - 10^3$ greater than it is perpendicular to the basal plane[32].

(c) compressibility is $10^4 - 10^5$ times greater in the direction perpendicular to the planes.

(d) the rate of oxidation of the edges (parallel to the basal plane) is usually between 4 and 100 times faster than the oxidation rate perpendicular to the surface of the basal planes, depending on purity and the presence of exposed vacancies in basal planes of the graphite. It was shown by Hennig[34] that the edge atoms are actually at least 10^{12} times as reactive as those on the basal plane.

(e) the differences in the atomic binding in the graphite crystals are also reflected in the elastic, plastic and fracture behaviour of both monocrystal and polycrystalline graphite[33].

For an ideal single crystal stiffness of any material, as expressed quantitatively by Young's modulus, is a direct measure of bonding forces between atoms, as Young's modulus is inversely proportional to the thermal expansion coefficient, also to the lattice distance at room temperature[35]. One would, therefore, expect a high Young's modulus in the a-direction of a single crystal graphite with an inter-atomic distance of 1.42 Å and very low thermal expansion of about $-1 \times 10^{-6}/°K$, while obtaining low Young's modulus in the c-direction because of high interlayer spacing of 3.35 Å but high thermal expansion of about $24 \times 10^{-6}/°K$ at room temperature. Applying Hooke's law, that is

$$\sigma = E\,\varepsilon \,,$$

where σ is stress, E is Young's modulus and ε is elastic strain, it follows then that strength is higher in the a-direction than in the c-direction.

Kelly[34] showed that in a perfect graphite crystal, the Young's modulus E in the a-direction, making an angle Φ with a hexagonal axis, Figure 3.1.2(b), is given by

$$\frac{1}{E} = S_{11}(1 - \gamma^2)^2 + S_{33}\,\gamma^4 + (2S_{13} + S_{44})\gamma^2\ (1 - \gamma^2) \,,$$

where $\gamma = \cos\Phi$, S_{ij} are the elastic compliances. When $\Phi = 0°$, i.e. along the hexagonal axis, $\gamma = 1$, therefore $\frac{1}{E_c} = S_{33}$ and when $\Phi = 90°$, i.e. along the basal plane $\frac{1}{E_a} = S_{11}$. Using values given in Table 3.1.2, $\frac{1}{E_c} = 27.5 \times 10^{-12}\ M^2/N$.

Then $E_c = 0.036 \times 10^{12}\ N/M^2 = 0.036$ T Pa (Tera Pascals)

Similarly $\frac{1}{E_a} = 0.98 \times 10^{-12}\ M^2/N$, giving an E_a value of $1.02 \times 10^{12}\ N/M^2$ = 1.02 T Pa.

For highly anisotropic graphite structure, i.e. fibres and pyrolitic carbon, the Young's modulus drops with increasing temperature in the same way as for metals[35]. In the case of polycrystalline graphite (artificial graphite), Young's modulus is found to increase with increasing measurement temperature and reaches a maximum at about 2000°C with an increase of about 25% of the value obtained at room temperature[35,36].

Several reasons are advanced for this behaviour in artificial graphite. For example, it is thought that the internal stresses which build-up during cooling from the graphitisation temperature, are relieved during reheating to the temperature at which measurements are made, but are then restored again on cooling down from the measurement temperature. This stress relief is thought to be due to the closure of the microcracks (so-called Mrozowski cracks) which are formed on cooling the graphite from the formation temperature. This closure of the microcracks causes the stiffness of the structure to increase, i.e. increasing the bulk modulus. This increase in Young's modulus with temperature has been observed in natural flake graphite [36]. It is important to note that for a perfect crystal Young's modulus falls with increase in temperature[35], therefore the increase in Young's modulus for a polycrystalline graphite or, for that matter natural graphite, with temperature agrees well with the annealing of imperfections in a bulk sample at high temperatures (> 2000°C) as indicated above.

This anisotropy of graphite would undoubtedly affect graphite-containing refractories and there is a need to understand its contribution to the properties of magnesia-graphite composites. The orientation of the graphite phase in the composite can be expected to have a profound effect on properties, such as, strength, thermal conductivity, coefficient of thermal expansion and thermal shock resistance. Before examining some of these property variations brought about by the addition of graphite to the oxide refractory, it is perhaps appropriate to consider the problems brought about by the differences in the morphology of the two materials.

Magnesia grains can be considered to behave almost like spherical particles for packing purposes and the artefacts made from magnesia are isotropic. Natural graphite particles, on the other hand, are platey and therefore all the three directions contribute in the way graphite affects the physical properties of the composite; thus the artefacts are anisotropic. But it is not clear as to how each one of these dimensions affects the physical properties of the artefacts or what rôle each one of them plays in influencing these properties. For instance, distribution of graphite in a composite at a fixed volume fraction of graphite depends on the length/thickness ratio (aspect ratio). If the graphite has a high aspect ratio, long thin flakes, the graphite may form a continuous matrix throughout a specimen because of having long flakes and the properties of the specimen may be influenced by this apparent continuity of the graphite phase. However, if the flakes are short, this continuity observed in long flakes may not occur in the matrix, at the same volume fraction, and there is the likelihood that the microstructure may be different from a specimen containing long flakes and this may affect the physical properties.

In order to establish the rôles played by the graphite dimensions, jointly or individually, their aspect ratios must be determined.

Because of basal plane glide, graphite is very soft and flexible compared to an oxide material. The flexibility of a graphite flake has been demonstrated by Cooper[37] and a bent flake is shown in Figure 3.1.2(c) and graphite flakes can therefore be bent round or easily squashed between the hard oxide grains. Since graphite flakes can easily be bent round hard oxide grains, or, indeed, be squashed between the oxide grains, it is difficult to postulate what rôle the breadth and length of flakes play in the oxide-graphite composites, regarding the properties of the composites. The graphite flakes, as shown in Plate 2.2.2, are irregular in nature and, in some cases, the dimensions across the flake can be approximated to be the same as the dimensions along the flake. In this case then, the effect of graphite on the physical properties may be thought to be affected by length and thickness only and the aspect ratio (length/thickness) determination may help in further understanding how thickness and length of flakes affect the properties of the composites in which graphite is contained in. To the knowledge of the author, there is no standard method of measuring these dimensions. The method of sieve analysis reveals none of these dimensions although minimum breadth may be inferred. However, results so obtained give no indication whatsoever on the thickness of the flakes. In this work, several measurement techniques were devised and attempts to measure the aspect ratios of four types of graphite were made. The techniques involved are:-

(a) the shadowing of the flakes, and by measuring the lengths of the shadow under a microscope, the thickness could be calculated;

(b) polishing the prismatic edges of the graphite flakes mounted in Araldite, and then, using a microscope together with an image analysis equipment, the thickness of the flakes was determined;

(c) graphite flakes were spread on a microscope slide and the maximum length on the flakes was measured using the microscope (direct observation) together with the image analysis system.

The section below describes in detail the experimental techniques used in measuring the aspect ratios of the graphites.

3.2 Aspect Ratio Measurements of Graphite

The measurement techniques indicated above required the use of a microscope and, as already shown in Chapter 2, the graphites contained different flake sizes; therefore the need to determine the aspect ratio in each sieve cut was carried out for two reasons:

(a) to determine whether the aspect ratio varied with flake size fractions;

(b) the need to use one appropriate magnification for each size fraction, since the measurements of dimensions required the calibration of the microscope objective before the measurements were carried out, as described later in the section below.

Four 10 kg samples of natural flake graphite were supplied by GR-Stein Refractories Limited together with their chemical and sieve analyses. The chemical analyses of the graphites are reported in Table 2.3.1(ii). For aspect ratio measurements, sieve analysis on the graphites was necessary and the section below describes the sieving of the graphites.

3.2.1 Sieve Analyses of the Graphites

In order to determine if aspect ratio is a function of the size of the graphite particles (flakes), the four graphites were sieved through five size cuts, namely, +30, -30+60, -60+100, -100+200 and -200 B.S. mesh sieves. These sieve cuts differ slightly from those reported in

Table 2.3.1(i) in that the sieve cuts in that table are from -5+7, -7+25 to -25+60; thereafter the sieve cuts are the same as those used in this part of the experiment. The sieve cuts in Table 2.3.1(i) were determined later than those reported here. This discrepancy arose from the fact that the magnesia fractions were received very much later during the course of this work and the need to sieve the graphites, as shown in Table 2.3.1(i), arose from the fact that large quantities of magnesia grains in the -5+25 B.S. mesh sieve range were supplied and therefore needed to be accommodated in the packing experiments, as described in Chapter 4. This did not affect the aspect ratio measurements of the graphites because the percentage difference of the graphites retained on 30 mesh and 25 mesh is small.

For each sieve operation, 100 g of sample was used and sieved on a sieve shaker for 40 minutes. The choice of both quantity of material to be sieved and the period of sieving were chosen arbitrarily. For practical purposes, the sieve analysis results are always reported together with the indication of the type of equipment, load (quantity of material) and time of sieving. In this work, three sieve operations were carried out on each sample with the same load, time and sieving equipment. The average of the three operations on each sample, in each sieve cut, were determined and the mean in each sieve cut was expressed as a percentage of the mean total load of the three operations and reported as a percentage retained in that sieve cut. The results of these sieve analyses are reported in Table 3.3(i) and will be discussed later in the section dealing with discussions in this chapter.

3.2.2 Specimen Preparation for Aspect Ratio Measurement

Aspect ratio is the ratio of the maximum length of the flake to its thickness and there is no standard method of determining aspect ratio of graphite. In this work several methods were explored in an attempt to obtain the ratio and the methods listed in Section 3.2 were used to prepare the specimens for aspect ratio measurements.

3.2.2(i) The shadowing technique

In principle, the technique involves double shadowing. The slide with flakes is fixed at a given position in an A.E.I. Metrovac coating unit, Type 12, Serial No. P304536, making an angle of elevation θ with a tungsten filament evaporating source from which gold/palladium alloy is evaporated under vacuum of less than 0.5×10^{-5} torr. Using a moveable stage, the height of the sample could be changed without changing its lateral position and its horizontal distance from the base of the evaporating source. The stage was used to change the angle of the source in relation to the position of the slide. Two shadows obtained at two different known angles of shadowing were required, in order to calculate the thickness of a flake producing the two shadows, as described in Appendix 3.2.2(i). This method presented a possibility of measuring thickness, length and breadth of a flake at the same time.

The loose flakes were spread on a glass slide which had been moistened with a thin film of acetone to enable the flakes to adhere to the slide. When the acetone evaporated, however, the flakes could easily be dislodged from their substrate by an air current or a small mechanical vibration. If a flake was dislodged after shadowing, then the remaining shadows were rendered useless, since the length and the breadth of the flake producing the shadows could not be determined, in turn making it impossible to determine the thickness and the length of the flake, hence aspect ratio could not be determined.

This method of measuring the aspect ratio did not work, because the two superimposed shadows could not be distinguished from one another, in addition to the problem of flake dislodgement from the substrate mentioned earlier. Therefore method (ii) was attempted.

3.2.2(ii) Polishing of flakes mounted in Araldite blocks

The loose graphite flakes were allowed to fall freely onto a piece of weighing paper where they rested in their most stable position, i.e. on the plane containing length and breadth. Then a glass slide, which had previously been ground on its edges to stand vertical to the horizontal and smeared with a thin film of Araldite on both sides of its flat surfaces, was placed carefully on the flakes on both of its surfaces alternately. The flakes stuck to the slide surfaces and those which did not stick, were dislodged and those standing on their edges, were forced to lie flat on the slide surface by using an air blower. The slide was left overnight to allow the Araldite film to set, hence fixing the flakes permanently onto the slide. Four such slides were prepared in this way for each sieve cut. The four slides were then mounted into a single block in Araldite while standing on their ground edges, hence putting the prismatic edges of the flakes perpendicular to the surface of the resin block to be polished.

The resin block was surface ground flat on a diamond grinding wheel to expose both the glass slides and the flake edges. To ensure that the glass slides were continually ground flat and at right angles to the horizontal, as when mounted, the block surface was regularly checked with a try square to ensure that the surface of the block was at right angles to its walls, as when mounted. Furthermore, to check the evenness of the grinding on the surface, a simple flatness test was devised and applied at intervals during grinding. The test involves using a flat glass pane in which the ground surface is dried with a tissue paper and then a very small drop of water is dropped at the centre of the ground surface and the block surface is then pressed against the flat glass pane. If the surface of the resin block was flat, the water droplet would spread covering the whole surface, otherwise it would only cover a small area. If the latter happened, the block was ground again. These two simple tests were applied repeatedly until a flat surface which was perpendicular to its side walls was obtained, before moving on to fine grades of silicon carbide papers of 240, 400, 600 and 1200 grits, using water as a lubricant. The block was then polished successively on two Pelon papers and one nylon cloth covered lap impregnated with 6, 3 and 1 micron diamond pastes respectively. Microfin lapping fluid was used as a dispersing agent.

3.2.3 Measurement of Thicknesses and Lengths

(i) Polished block containing prismatic edges of flakes

The polished surfaces were analysed using a Metallux microscope (Leitz Wetzlar) fitted with a TV camera linked to a TV monitor which, in turn, was linked to an Apple II computer with a graphics tablet connected to it. A program written[38] specifically for this work was loaded into the small computer. This program used two other sub-programs supplied by the manufacturers of the system. The sub-programs performed all the commands and functions of the graphics tablet including the activation of a graphics cursor which appeared as two cross-hairs on the TV monitor.

Before making any measurements, the objective of the microscope to be used in the measurements, was calibrated with a 2 mm (2,000 µm) stage graticule. The program allowed this procedure to be carried out before any measurements could be carried out.

The calibration was achieved by placing the graticule under the microscope and then focussing onto the graticule until the millimetre markings on the graticule were clearly visible through the microscope eyepiece. The focussed part of the graticule was then relayed to the TV monitor through the TV camera mounted on the microscope. Then, using the graphics tablet, two markings on the millimetre (mm) marks of the graticule image displayed on the monitor were chosen. The calibration was accomplished by locating the cursor on the screen on one of the two chosen marks and then the tablet pen was pressed on the graphics tablet leaving a small white dot on the screen. The cursor was moved to the other mark, by moving the pen about the tablet, and the pen was pressed again, resulting in a line being drawn automatically on the screen. The actual distance which had just been marked was entered by the operator, as this was allowed for in the program before proceeding further.

The distance used for calibration depended on the objective used. Objectives of high magnification could be calibrated with shorter distances, e.g. 100 µm or less, to increase the accuracy of the measurements when measuring the thickness of very small flakes. This is one of the reasons why the samples were sieve graded so that a suitable objective could be found for each sieved graphite size fraction, and then the calibration could only be carried out once when measuring one particular graphite size fraction.

The prismatic edges of the flakes appeared as long thin bright strips under the microscope, as shown in Plate 3.2.3, as well as on the TV screen. The thickness measurement was accomplished by locating the cursor on the edge of the breadth of the strip, at which point the tablet pen was presesed onto the graphics tablet, leaving a small white dot on the screen. The cursor was then moved to the other side of the flake, at a point directly opposite to the previous point. On pressing the pen for the second time, a line was drawn across the screen. Using the ratio of this distance to that obtained during calibration, and by multiplying this ratio with the real distance value entered at the calibration stage, the thickness of the flake was determined automatically by the machine. Similarly, length was determined by measuring the long ends of the flake (Plate 3.2.3). The program was written in such a way that up to ten measurements could be made on each flake for each parameter, the two averages of thickness and length were determined and stored into two arrays, one for average thickness and the other for average length.

At the end of the measurements, an average of 120 flakes were measured for each sieve cut, the computer programme worked out the aspect ratio, i.e. length/thickness for each flake and stored the value into a third corresponding array to that of length and thickness used in the calculation, before compiling the results into a disc.

Plate 2.2.2 (Chapter 2) shows the four types of graphite (A, B, C and D) used in the aspect ratio determinations and it is clear from the plate that most of the flakes appear as elongated discs, therefore when mounting these flakes on the glass slides for polishing, one does not know whether the flakes were sectioned across the disc, along the longest side of the disc or if it was cut towards the end of the disc during polishing.

Because of these difficulties encountered in length determinations on polished flakes, a different technique of determining length of the flakes was required. In this work, direct observation of the flakes under the microscope and measuring the maximum length of a flake as it appeared under the microscope, was adopted, and the procedure is described below.

3.2.3(ii) Measurement of maximum length of flakes by direct observation method

In order to determine the maximum lengths of the flakes in each sieve cut, flakes were spread on a microscope slide and then observed under the microscope, having the same arrangements as those described in Section 3.2.3(i). The maximum length measurements were obtained in the same way as thicknesses and "lengths" of flakes in the polished blocks were determined, except that, here, the number of length determinations on each flake were kept above seven, up to ten measurements could be carried out on each flake, because a wide flake area was available for measurements; compare Plate 3.2.3 with any of the graphite types in Plate 2.2.2.

The main disadvantage of measuring the length of a flake separately from its thickness was that the advantage of determining the aspect ratio of each particle directly from the two parameters, was lost.

The thickness and length measurements determined in each sieve cut were analysed and the results are discussed in the following section.

3.3 Results and Discussion

The sieve analyses obtained on the four graphites are shown in Table 3.3(i). The interesting point about the table is the similarity of these results with those reported in Table 2.3.1(i), as expected. The results also confirm that most of the particles in graphite A are retained on 60 B.S. mesh sieve (> 250 µm), followed by graphite D which has 40 ^{w}/o retained on 60 B.S.S. and 56% retained between -60+100 B.S.S. (250 µm-150 µm). Graphite C has a lot of fines, with 37 ^{w}/o passing through 100 B.S. (< 150 µm) and graphite B was the finest of the four graphites with 68 ^{w}/o passing through 100 B.S.

The measurements carried out were done on a number of flakes, 120 flakes or more, in each sieve cut, and therefore thickness and length measurements were grouped into pre-determined intervals of each parameter in each sieve cut and the number of flakes in each interval was expressed as a number frequency or percent number of flakes in that particular interval, over the number of flakes measured in that sieve cut. This process was repeated for other sieve cuts of the same sample.

In order to determine the aspect ratio of the graphites, the thickness and length measurements obtained in this work had to be treated in groups of the sieve cuts because thickness and length measurements could only be related to each other in terms of corresponding sieve cuts, since these two parameters were obtained separately.

3.3.1 Percentage Number Frequency Distributions

The first treatment of data was to plot % number frequency against thickness or length in each sieve cut. In this method, no account of the difference in weight percentages in each size cut were considered, although the results shown in Table 3.3(i) demand otherwise.

Figures 3.3.1(i)(a), (b), (c) and (d) show plots of % number frequencies against thickness in each sieve cut for graphites A, B, C and D respectively. A general point to note from the Figures is that the distribution plots are skewed. Log-normal plots were tried but the results did not follow a log-normal distribution.

However, what is immediately obvious from these Figures is that the finer flakes are thinner than the coarse flakes of the same graphite, although some overlapping has occurred.

If these Figures are compared with one another, it is difficult to see which graphite is thinner than the other. However, from Table 3.3.1(iii)(a) it can easily be seen that graphite D is the thickest of all the graphites, and the graphites can be ranked in terms of thickness as below:

mesh range	graphites
+30	D > C > A
-30+60	D > B > C > A
-60+100	D > B > A > C
-100+200	D > B > A > C
-200	D > B > A ,> C

Graphite D was found to be the thickest in spite of the fact that graphite D is finer than A on a sieve analysis basis. Further, graphite B is thicker than graphite A and C, yet graphite B was found to be the finest by sieve analysis. It is therefore clear that thickness cannot be inferred by sieve analysis, as indicated earlier in this chapter.

Figures 3.3.1(ii)(a), (b), (c) and (d) show plots of % number frequencies against maximum length. These Figures appear more symmetrical than those of thickness plots shown in Figure 3.3.1(i). Furthermore, these Figures show clearly that the coarser fraction in each graphite sample has longer flakes than the next coarse fraction of the same sample, as would be expected. For instance, the size fraction retained between -30+60 B.S. has longer flakes than that retained between -60+100 B.S.S in any of the graphite samples. Towards the end of Section 3.1.2 (Page 54), it was suggested that results obtained from sieve analysis may infer minimum breadth only, but from the plots of Figure 3.3.1(ii) it is clear that length is also inferred in the sieve analysis data. This conclusion has been arrived at after taking into account that, in this work, the maximum dimension of each flake, as observed under the microscope, was measured and taken as the length of the flake. Therefore sieve analysis results may infer both length and breadth of the graphite flakes.

From Figures 3.3.1(ii)((a)-(d)), it is clear that graphite B has the shortest flakes amongst the four samples. However, it is not immediately clear from the Figures which of the remaining three graphites has the longest flakes. This is so because the plots assume equal importance of the weight sieve size fractions in all the sieve cuts, contrary to what is shown in Table 3.3(i) and the attempt made in this work to change the number distributions to weight distributions, is discussed in Section 3.3.2, later.

Meanwhile, an attempt to determine the aspect ratios of the graphites from number distribution plots, was made. From the Figures discussed above, the modes (the most occurring) of thickness and length in each sieve cut for each graphite, were determined and these modes are reported in Table 3.3.1(iii)(a). Then plots of mode length against mode thickness in the corresponding sieve cuts were made for each sample and these plots are shown in Figure 3.3.1(iii)(a). A straight line was fitted to these data points using regression analysis. The straight line was a good fit to the data points; hence there was a linear relationship between length and thickness. This means that the aspect ratios of the graphites do not change with the size of the flakes. The aspect ratios of the graphites were determined from the gradients of the straight lines (length/thickness), and the aspect ratio results are given at the bottom row of Table 3.3.1(iii)(a). These aspect ratio results show that graphite A had the highest aspect ratio, followed by B, C and finally D. The results seem to confirm the earlier observations that although graphite D seemed to have similar type of distribution on the length (Figures 3.3.1(ii)) with graphites A and C, Figure 3.3.1(i) shows that graphite D had the thicker flakes, hence lower aspect ratio (length/thickness), assuming that the lengths of the three graphites are about the same on the basis of number distributions, which do not take into account the weight fractions obtained in the sieve cuts.

The other treatment on the raw data was the determination of the arithmetic means of thickness and length in each sieve cut out of the total number of flakes measured in that sieve cut. The results are reported in Table 3.3.1(iii)(b) and plotted as Figure 3.3.1(iii)(b). Again, straight lines were fitted to the data points. As before the straight lines fitted the data well, and the gradients (aspect ratios) were determined. The aspect ratio results are reported at the bottom row of Table 3.3.1(iii)(b) as before. The aspect ratio results from this Table show that graphites A and B have the same aspect ratio, and the aspect ratio of graphite A is very much lower than the one obtained from Figure 3.3.1(iii)(a). Similarly, graphites B and C aspect ratio values have been lowered from 34 to 31 and from 27 to 24 respectively, contrary to that of D, which has increased from 15.5 obtained from mode plots to 17.7 obtained from the arithmetic mean plots. The important point is that the aspect ratio results obtained from the two methods are within the same order of magnitude, except for graphite A. The reason that graphite A gives very different results for aspect ratio by the two techniques, is that the distributions of thickness for graphite A are very skewed and therefore the modes are lower than the arithmetic means. As a result the modes give higher aspect ratios than those obtained by arithmetic means.

As has already been indicated above that the treatment of data described above ignores the weight size fractions obtained during sieving, the results obtained do not give emphasis on those fractions which had the highest weight percentages (see Table 3.3.(i)) although mode values may be indirectly related to the most populace flakes. Therefore, there was need to convert the number distributions to weight percent ($^{w}/o$) distributions so that the distributions are reflected in terms of the sieve fractions. The section below describes the methods attempted in this work to convert % number distributions to weight percent distributions.

3.3.2 Changing Percentage Number Distributions to Weight Percent Distributions

Statistical equations which facilitate the conversion of number frequency to weight frequency distributions, have been derived by Herdan[39] and these equations are given in Appendix 3.3.2. The equations given in Appendix 3.3.2 could not be used to convert the number distributions to weight distributions of the flakes because the volume shape factor (α_V) could not be determined for the graphites in this work. Furthermore, the derivation assumes that the particles being dealt with are spherical.

Figures 3.3.1(iii)(a) and (b) have shown that the aspect ratios of the graphites are constants for all size fractions and that there is a linear relationship between length and thickness of the flakes. Therefore by making several assumptions, the weight distribution in each sieve cut may be determined. The assumptions are:

(a) in order to make use of the linear relationships obtained above and from the shapes of the flakes shown in Plate 2.2.2 (Chapter 2), the flakes may be assumed as thin discs. Therefore, volume of each flake may be calculated as shown in Appendix 3.3.2(a), i.e. volume of a disc is $\pi r^2 T$, where T is the thickness of disc.

(b) in order to determine the weight of each disc using the volume determined in (a), the bulk density of each flake must be known. However, from the specific surface area measurements reported in Table 2.3.4(iii) (Chapter 2), it is shown that the specific area of the graphites A, B, C and D, between different size fractions of the same sample, does not vary very much. Therefore, it can be assumed that the interlaminar cracks of different size fractions of the same sample are about the same. Further, if it is assumed that there are no closed internal cracks in the graphites, the bulk density of the graphite flakes in all sieve fractions is the same.

After making these assumptions, the weight distributions in each sieve cut were worked out as shown in equation (8) of Appendix 3.3.2(a). Then the weight distributions in each sieve cut were grouped in size ranges of the flakes, as was done for number distribution (Table 3.3.2 shows $^{w}/o$ distribution of graphite A as an example). For each graphite sample then, the total weight fraction ($^{w}/o$) in each size range was determined by adding the $^{w}/o$ in that size range (e.g. 0-5 μm for thickness) from all the sieve cuts of that particular graphite. This procedure was repeated for other size ranges for that particular graphite sample and the $^{w}/o$ distributions in each predetermined range were determined in all the graphite samples measured (see Table 3.3.2). The thickness size ranges were varied at intervals of 5 μm, while length ranges were varied at intervals of 50 μm.

Because of the skewness of the thickness number distributions as shown in Figures 3.3.1(i)((a)-(d)), the weight percent distributions ($^{w}/o$) were found to be bimodal except for graphite D, as shown in Figures 3.3.2(i)((a)-(d)). Therefore no particular thickness can be said to be the most occurring (mode) in the sample and the aspect ratio using weight distributions could not be obtained.

Figure 3.3.2(ii) is a plot of weight percent ($^{w}/o$) against length. This Figure shows that the $^{w}/o$ distributions against length are symmetrical except for graphite C. This is what it should be that those graphites with wider sieve distributions should show wider $^{w}/o$

distributions against length, as shown in Figure 3.3.2(ii). (Table 3.3(i) shows the sieve distributions of the graphites.) This again points to the fact that sieve analyses may infer length as well as breadth.

3.3.3 Summary

Graphite A was found to have the largest aspect ratio (1:45) which seems to agree well with the sieve analysis, in that graphite A has the largest amount retained on -30+60 B.S.S. (500 µm-250 µm) as shown in Table 3.3(i). On the other hand, graphite D has the lowest aspect ratio (1:15), yet it has the largest amount retained, up to +100 B.S.S. (150 µm) than graphites B and C. This demonstrates that sieve analysis cannot be used to indicate the aspect ratio of the graphite, as this parameter is a function of thickness, unrelated to sieve analysis, and length.

The method of determining the aspect ratio of graphite should be one that would enable measurements of thickness and length on the same flake, better still, one which will enable breadth measurement as well. Therefore, the method used in this work is inadequate and too slow to obtain results for routine purposes.

From this Chapter and Chapter 2, a reasonable amount of information has been gathered on the characteristics and properties of the materials to be used in making the magnesia-graphite composites. It is therefore appropriate at this point to examine how the magnesia and graphite pack when combined together and investigate how graphite can be introduced in the magnesia considering the fact that graphite is platey, as shown in Plate 2.2.2 (Chapter 2). Furthermore, what effect do the organic binders have on the packing of the composites. The methods of introducing graphite into magnesia mixtures, the packing characteristics of these mixtures, are discussed in detail in Chapter 4, which follows immediately.

CHAPTER 4

PACKING CHARACTERISATION OF MAGNESIA-GRAPHITE COMPOSITES

4.1 Introduction

The mixing of two or more components is frequently practiced in the manufacture of refractory products, and, therefore, an understanding of the properties of the individual components is most important for the manufacturer to enable him select the best possible mixture or range of mixtures in order to obtain the optimum properties that are being sought for in the mixture. In particular, a knowledge of the particle size and shape and the nature of the packing of the components when mixed together is essential to an understanding of the behaviour of the mixture during fabrication processes and is likely to control the properties of the material during service.

It has been suggested that mixtures can be divided into two broad classes[41] :-

(a) single phase systems in which the components are completely miscible or soluble in each other;

(b) multi-phase systems in which the components are insoluble or partially soluble in each other.

Refractory materials usually belong to class (b) above, and especially so the magnesia-graphite refractory composites which are under investigation in this work.

In making attempts to predict the resulting properties of an insoluble heterogeneous mix from the properties of the individual components in the mixture, the distribution, shape and size of the components in the mix must clearly be understood. For example, it is necessary to know:-

(a) which components are continuous or major phase and which are minor phase or dispersed?

(b) what is the shape of the particles of the individual components and how will they pack in a proposed mixture?

(c) if the particles of some or all of the components are not spherical, how are they oriented in the system? and

(d) what kind of interaction occurs at the interfaces within the multiphase system and what is the final optimum packing density of the mixture?

The four questions raised above are some of the questions that need to be answered when dealing with the magnesia-graphite composites in an attempt to better understand the composites and part of question (b) has been answered in Chapter 3 of this thesis. In this work, magnesia is the major phase and graphite and carbon from the organic binders are the minor phases. This work reports microstructural studies of the distribution and the effect of the presence of the graphite flakes in the composite matrix on the relevant physical properties of the composite, such as compaction behaviour, i.e., bulk density and porosity, and strength. This chapter deals with porosity measurements and microstructural studies only and strength of these composites is dealt with in Chapter 5. However, before describing the experimental techniques which have been used in examining the packing characteristics of the magnesia-graphite composites, a review of some of the work previously done on the packing of solid oxide particles is appropriate.

4.1.2 Theory of Dense Gradings of Non-spherical Particles

The packing of spheres has been examined by many researchers, among them, White et al.[42] and Elmes et al.[43] separately derived conditions for maximum packing in systems containing more than one size fraction. Both teams observed that a system of particles tended towards minimum porosity as the breadth of the size distribution increased. In other words, if a system of the same material were graded in many size grains and, say for example, particles of a certain fineness were put into a packing bed, and successive grains of finer particles were put in the same bed, these particles being of size just sufficient to fill the spaces in-between the preceding particles without increasing the total volume of the bed, then the resulting system would have the least porosity.

Although these researchers[42,43] derived conditions for obtaining minimum porosity for spherical particles, these conditions could not be applied directly to non-spherical particles because of the difference in shape factor of the non-spherical particles to that of spheres. Their observation, however, was in total agreement with earlier findings by Skola[44] and Hugill et al.[45]. Skola also postulated that in an ideal system, presumably meaning spherical particles, the voids formed by one size fraction would be filled by the next smaller grains, and so on. Hugill et al.,[45] however, predicted optimum packing by using three two-size systems, namely, coarse-fine, coarse-medium and medium-fine. Further, Hugill's three two-size systems were achieved by gap gradings of -3/16"+4 (4.76-4.00 mm), -18+25 (850-600 μm) and -150+200 (105-75 μm) B.S. mesh sieve, unlike Skola's[44] six consecutive sieve cuts of -4+8 (4.00-200 mm), -8+16 (2.0-1.0 mm), -30+70 (500-210 μm), -70+120 (210-125 μm) -120+250 (125-61 μm) B.S. mesh sieve.

The study of porosity of compacts specifically in relation to particle size gradings was undertaken by Andreasen[46] and Furnas[47] in 1930 and 1931 respectively. Andreasen developed a relationship predicting the quantities of large particles which could be added to the mass of fine particles in order to achieve minimum voids in a continuously graded system. Furnas[47] considered the opposite case of adding finer and finer particles to the coarse particles to just fill the existing voids. He derived laws governing the attainment of dense packing in both gap and continuously graded systems. Both workers[46,47] made a basic assumption that in any continuously graded system, maximum packing will be achieved when the volume ratio between the consecutive sizes is a constant. If the particles are assumed to be spherical, then this assumption means that the diameter ratios of the consecutive sizes must be a constant. If the material in each grading is of the same type, hence same density, weight ratio may be used.

Andreasen's[46] detailed arguments for predicting the quantities of large particles to be added to a mass of smaller particle size in order to achieve minimum voids in a continuously graded system, was as follows:- "Suppose that an addition of coarser and coarser material is to be made in such quantities that they represent in each size class the same fraction 'n' of the quantity which was present before, and if 'y' is the weight percent of material less than size d, and the resulting mixture consists of grain size fractions so that the grain size d of successive classes form a geometrical progression, then one can say that the grain size increases differentially as d(log d)".

"The rate of change of weight with size is then given by $\frac{dy}{d(\log d)}$ and since, according to the condition of the experiment this amount should always be equal to ny, then this becomes an equation:

$\frac{dy}{d(\log d)} = n\, y"$. Integrating this and combining the constants of the indefinite integral, it becomes $y = C\, e^{n \log d} = C\, d^n$, where C is a constant determined by the total quantity of the substance present, set equal to 100 $^w/o$ or $^v/o$; thus $y = 100\left(\frac{d}{D}\right)^n$. D is the largest particle diameter in the system. This expression is identical to that used by Talbot and Richard[48] who studied, among other factors, the strength of concrete in relation to the grading of the aggregates. Some years later, Mong and Adelman[49] found that the reproducibility of the mechanical properties of refractory semi-dry press specimens could be controlled by recombining seven sieve cuts on the basis of Fuller's[50] parabola. They used the expression $P = 100\left(\frac{d}{D}\right)^{\frac{1}{2}}$, i.e. a fixed n-value of 0.5.

The packing of refractory materials was later reviewed by Hughan[51]. He devised experiments to show the degree of control that can be exercised over porosity by the use of Andreasen's and Furnas' distributions by using the equation

$$y = 100\left(\frac{d}{D}\right)^n \qquad (1)$$

given in the previous expression. The n-value was chosen arbitrarily as well as the maximum size D in the system. In his experiments, Hughan observed that distinct minima existed in the porosity curves for silica at n-value close to 0.4 with D = 7 mm. He also observed a minimum porosity at n = 0.33 with D = 3.35 mm for an unfired magnesia compact, but no minima were observed for the fired magnesia compacts.

In the refractories industry the empirical approach to the problem of obtaining maximum density in a refractory product is almost universal. This approach is, apparently, based on Hugill's[45] method of mixing coarse, medium and fine grain size fractions of a refractory oxide. It is clear therefore that each manufacturer is bound to determine his own size ranges that will be referred to as coarse, medium and fine fractions to achieve optimum packing.

Because of this difficulty of having an infinite number of definitions and combinations of coarse-medium, coarse-fine and medium-fine with Hugill's method, the equation (1) derived by Andreasen was used in this work to determine the quantities of the magnesia size fractions required in a set of predetermined sieve cuts, for a given n-value and for a fixed top size, D, of the system, to obtain minimum porosity in the compacts. It is, perhaps, important to always remember that the n-value is the volume ratio of the consecutive sizes in a continuously graded system; in practical terms, the n-value is a parameter which can be varied to control the relative proportion of fine to coarse material in a system.

4.1.3 Application of Andreasen's Method to the Magnesia-Graphite Composites

Whilst the application of the Andreasen technique is useful in obtaining the gradings required for optimum packing of more or less isometric particles like MgO, it is not immediately obvious that this approach, or any other method used in grading refractory oxides, will be useful in evaluating the packing behaviour of highly anisometric particles like graphite flakes and the combination of such flakes with MgO grains is likely to affect the Andreasen predictions. Therefore, in order to make an assessment of the effects which natural graphite flakes of different aspect ratio have on the packing characteristics, the following procedure was adopted. Firstly, the Andreasen approach was applied to the packing of the MgO grain chosen for the study (maximum size of 3.35 mm). Particle size distributions corresponding to different n-values were made up and the packed density determined. The optimum n-values for minimum porosity were evaluated. Then, using the same n-values used to investigate the packing of the magnesia size fraction mixtures only, magnesia size fraction mixtures were prepared into which natural flake graphite was introduced in three different ways to replace some of the magnesia and the effect on the porosity of the composite was ascertained experimentally.

As was shown in the previous chapter, the graphite flakes in the long dimensions were 150-1000 μm which puts them in the category of coarse fractions. However, in the direction across the flake the size is only of the order of 50 μm which is commensurate with the fine grading of MgO. Therefore, it is not immediately obvious how best to introduce the graphite into the MgO. It was then decided to examine this experimentally by adopting three methods of introducing the graphite into the magnesia, in an attempt to try and establish the fundamental question of how flake graphite should be added to an oxide refractory to obtain optimum packing, as well as optimizing other relevant refractory properties of the resulting composite. The approach adopted here was to evaluate the packing of the mixture of magnesia and graphite without binders and then study the effect of binders on the packing density of the composites.

To investigate the packing characteristics of the magnesia-graphite composites using Andreasen's method, a range of n-values was chosen between 0.3 to 1.0 with increments of 0.1. The main effect of changing n from 0.3 to 1.0 is that the amount of fine grain size magnesia in the graded material decreases. Therefore the effect of n-value on packing of the magnesia compacts as well as for the composites, was examined by determining their porosity and bulk density at each n-value before and after firing the samples in a non-oxidizing atmosphere. The total porosity was determined as opposed to open (apparent) porosity, because of the regular shapes of the specimens which enabled not only the determination of total porosity but also the determination of the dimensional changes of the specimens after firing. In any case, the inherent porosity of the magnesia and flake graphite was a constant in specimens which contained equal amounts of the two components in their respective proportions. Hence the variation of the total porosity was attributed only to the variation of the packing behaviour of the particles in the composite or compact.

4.2 Packing Experiments on the Magnesia-Graphite Composites

4.2.1 Packing of Magnesia - Selection of Sieve Cuts

4.2.1(i) Andreasen's method

Andreasen's equation $y = 100\left(\frac{d}{D}\right)^n$, see Section 4.1.2, was used to determine the fractional amount of magnesia required in each sieve cut for each of a number of selected n-values and the efficiency of packing was determined experimentally. Here six sieve cuts, same as those reported in Table 2.3.1(i), were used. Thus six weight percentages were obtained this way and were then combined together to make a 100 $^w/_o$ mixture of different size magnesia fractions. The maximum grain size used in the system was chosen so as to be equal to the largest magnesia grain available in the supplies received (3.35 mm) and this is typical of the maximum size used in the refractories industry for magnesia-graphite refractory composites. The n-value was varied, by increments of 0.1, from 0.3 to 1.0, as already explained above. Appendix 4.2.1(i) shows how the calculations were carried out in determining the weight percentages required in each sieve cut using Andreasen's equation.

4.2.1(ii) Hugill's and Westman method

The prediction by Hugill et al.[45] that optimum packing can be obtained by using three two-size combination systems, was also tested in this work and compared with Andreasen's[46] method. This method predicts that about 72 w/o of coarse material, when combined with about 28 w/o of fine material, for the two-size combination, produces optimum packing. The packing is improved further if the diameter ratio of the coarse material to that of the fine one is very large. A typical example given[45] is that of a mixture of two-size sand fractions with a diameter ratio of 50 giving a void content, by volume, of 18.5%. The void content increases as the ratio of the two-size fractions reduces because fewer of the particles of the fine fractions can go in the interstices of the larger fractions.

Using Hugill et al.'s[45] technique, three mixtures were prepared from three sieve cuts. Here three combinations were arbitraily chosen from three sieve cuts of -5+25, -25+100 and -100 B.S.S. and were coded as coarse, medium and fine grain fractions respectively. These are actually not gap gradings, but suffice to demonstrate the difficulties involved in this method. For instance, if gap gradings were used, the possible number of sieve cut combinations are many, e.g., -5+7, -60+100, -200; -7+25, -100+200, -300 B.S. mesh sieve, etc.

Firstly, the number of sieve cuts chosen depends on the availability of grain size fractions of the material; in industry this depends on the grinding process employed in producing these size fractions. Secondly, there is a difficulty in determining which grain size fractions (gap graded ones) would give the best packing. Because of this difficulty, only three mixtures were made up in this study. This was done by mixing the coarse, medium and fine fractions as shown in

Appendix 4.2.1(ii), presented in the format of a flow chart for ease of presentation. The mixtures are labelled as 1, 2, 3 for identification and will be referred to as such throughout the text of this chapter.

4.2.2 Packing in Magnesia-Graphite Composites

Andreasen's method of determining the fractional amount of magnesia required in each sieve cut for each n-value to obtain better packing of the magnesia fractions, was followed in this section. Three methods of introducing graphite to the efficiently packed mixture of magnesia grain size fractions were explored and these three methods are referred to as Method 1, 2 and 3 throughout the text. The methods are described below.

4.2.2(i) Method 1

In this method, the sieve fractions of the graphites, as reported in Table 2.3.1(i), were weighed out proportionately to the percentages in which they exist in the original bulk sample, so that the total quantity of the graphite would equal the total $^{w}/o$ of graphite required, e.g., 20 $^{w}/o$. Then the amount ($^{w}/o$) of the graphite fraction in each sieve cut was used to replace an equivalent amount of magnesia from the total magnesia fractions in that particular sieve cut, as calculated in Appendix 4.2.2(i). In short, this was a replacement process in which the weight percent graphite in each sieve cut required replaces an equal amount of magnesia in that sieve cut, and the resulting composite contains 80 $^{w}/o$ MgO and 20 $^{w}/o$ graphite, for example. This method assumes that the effective size of the graphite flakes is that determined by the sieve openings, since no account of its shape is taken into account. This replacement method was applied to all the four graphites, i.e. graphite

A, B, C and D. Table 1(b) of Appendix 4.2.2(i) shows how the calculations were carried out.

4.2.2(ii) Method 2

In Chapter 3, Figures 3.3.1(i)(a)-(d) show that all the four graphites used in this work have about 90 $^{w}/o$ of their flakes with thickness less than 45 µm. If thickness values were to be compared with the equivalent diameters of MgO grains, passing through 200 mesh (75 µm), then the graphites, on the basis of thickness alone, could be considered as fines. However, length values of the flakes (Figures 3.3.1(ii)(a)-(d) show that about 80 $^{w}/o$ or more of the graphites have flake lengths greater than 150 µm. But graphite is flexible and can, therefore, be bent round MgO particles. Using these two arguments, graphite could be considered as a fine material as far as packing is concerned. Therefore, the four graphites were separately introduced as fines into the packed different size magnesia fractions by replacing the fine MgO grains at each n-value. The magnesia fractions, passing through 100 B.S. mesh sieve, were also considered here as fines (Section 4.2.1(iii)). Therefore, all the magnesia fractions passing through 100 B.S. mesh sieve in a mixture of different size magnesia fractions, were replaced by the equivalent amount of graphite, on a weight percent basis. Each $^{w}/o$ fraction in each sieve cut of that particular graphite, was present in the replacing quantity, and this was achieved by weighing each weight fraction in each sieve cut separately, as was done for magnesia fractions (see Section 4.2.1(i)). The calculations carried out in Method 2 are shown in Appendix 4.2.2(ii).

The calculations in Table 1(b), Appendix 4.2.1(i), show that as the n-value increases, the total weight percent of fine magnesia grains

(-100 B.S. mesh sieve) decreases and, therefore, the amount of graphite replacing fine magnesia size fractions decreases with increasing n-value in this method. Hence the amount of graphite in each n-value is not a constant in this method as opposed to Method 1 above and Method 3 described below.

4.2.2(iii) Method 3

This method also took into account the fact that the graphites are very thin, very flexible and can easily be bent round the hard magnesia grains. As a result, it could be argued that graphite flakes should enhance the packing of the magnesia fractions in that they would be able to occupy cavities which may not be easily filled by spherical particles on their own because of the way spherical particles pack.

In this method then, graphite was introduced in the mixture of different size magnesia fractions as predicted by Andreasen's method at each n-value. The magnesia fractions were normalized to 80 $^{w}/o$ from 100 $^{w}/o$ so that 20 $^{w}/o$ graphite could be combined with 80 $^{w}/o$ magnesia directly, to make a 100 $^{w}/o$ composite. As in the other two methods, the graphite component (20 $^{w}/o$) contained all the proportions of the weight fractions in each sieve cut obtainable in that particular graphite. This was achieved by weighing each weight percent fraction required in each sieve cut as before. The calculations showing how the graphite component was obtained and then added to the magnesia component in this method, are given in Appendix 4.2.2(iii).

4.2.3 Specimen Preparation

As indicated in the preceding sections, the required mixture of different size magnesia fractions was obtained by weighing out the predicted percentages, using Andreasen's[46] method, in each sieve cut, to ensure that all the predicted size fractions in each sieve cut were present in the mixture at each n-value. If graphite was to be added in the magnesia mixture, the same procedure of weighing out the required percentages in each sieve cut, as determined in the sieve analysis of that particular graphite to be added, was carried out. It is important to point out here that efficient packing prediction of the graphites was not carried out because graphites are anisometric, while Andreasen's method assumes isometric particles. This procedure of weighing out the material for each sample increased the number of weighings, at times reaching 13, for each specimen mixture and, therefore, no more than two specimens were prepared for each n-value.

The weighings were carried out to the nearest milligram on an analytical balance. Two 50 g samples were weighed for each n-value, i.e. n = 0.3 to 1 with 0.1 increments. The 50 g sample was transferred into a sample bottle, after which the bottle top was placed back and screwed tight. The bottle, with its dry contents, was then placed in the Glen Creston shaker and the sample was mixed for ten minutes. The dry mixed sample was then combined with 3 cc of 0.07 $^{w}/o$ solution of polyethylene oxide (M.W. 600,000), which served as a binder while the specimen was still in the green state. The sample was then carefully stirred by hand with a spatula.

Compositions containing organic binders are usually warm mixed, but because of the small quantity of samples (50 g) used here, this technique could not be achieved. Therefore, two methods were used:

(a) When pitch was used as a binder, the mixture of the magnesia size fractions or the composite, was mixed dry as described above. Then the required amount of pitch, which had previously been ground to pass through 200 mesh, was added to the 100 $^{w}/o$ dry mix in the sample bottle after it had been removed from the shaker. The contents were then stirred by hand using a spatula. This technique was adopted when it was observed earlier on that if a mixture containing pitch was mixed dry by shaking the contents in the shaker, some of the pitch adhered to the walls of the sample bottle therefore removing some of the pitch from the mixture.

(b) For composites containing a resin, powdered novalac (P41) resin, with hexamine, as a curing agent, added at the time of manufacture, was used and the technique used for materials without binders was adopted. Several methods of coating refractory aggregates with resins are given by Lemon[20], and the one which was found appropriate for such small amounts in this work, was the one in which he recommended the "use of a solution of novalac in a lower boiling non-toxic non-inflammable solvent (such as water) then evaporate it during coating to increase viscosity to induce 'green' strength." However, water on its own could not be used because of the presence of magnesia, hence the use of polyethylene oxide solution to suspend the resin. The final mixing was then carried out by hand using a spatula as before.

4.2.4 Pressing of Specimens

The specimens used in the packing experiments were pressed in a cylindrical hardened steel die with a bore diameter of about 40 mm. The diameter of the plunger was accurately measured with a screw gauge micrometer and was determined to be 39.998 mm (40 mm). In the pressing process, the whole 50 g sample was transferred from the sample bottle into the cylindrical pressing die and then the die with its contents was transferred to a Denison Compression Testing Machine. On reaching the required pressure, the pressure was held for a period of 15 seconds before letting the bottom platen drop. The pressed specimen was removed by pushing the plunger through the die, in turn, pushing out the specimen.

To determine how much pressure was to be used in this part of the experiment, six samples of magnesia fractions only, at $n = 0.3$, were prepared as described in Sections 4.2.1(i) and 4.2.3(i). Two specimens were pressed at each arbitrary chosen pressure and the green porosities of these specimens were determined as described in Section 4.2.5 below. Three sets, two specimens in each set, were separately pressed at 79, 119.5 and 159.3 MPa. The green porosities obtained on the three sets after pressing at the above pressures, were 17.6, 16.7 and 15.3% respectively. Therefore 159 MPa was chosen as the working pressure on the basis of porosity obtained. Higher pressures were avoided because of the difficulties that would have been encountered in the fabrication of stronger rectangular pressing dies in which reactangular specimens were pressed for modulus of rupture measurements, as described in Chapter 5. Further, the pressure chosen here is of the same order as that used in the refractories industry (159 MPa).

4.2.4(i) Pressing of Specimens Without Carbon Binders

After combining the composite or magnesia size fraction mixture with polyethylene oxide solution, the sample was transferred into the pressing die and pressed as described above. After pressing, all the specimens were dried at 110°C in an oven, for a period of 24 h, to ensure the removal of water from the binder solution. Because graphite has cracks along the flake edges, it is possible that air can be entrapped in these cracks during pressing of specimens containing graphite and, therefore, the air pressure in the specimen could be high enough to force the expansion of the specimen after releasing the pressing load, causing a relaxation of the graphite flakes. Therefore the 24 h period that the specimens were left in the oven was thought adequate to allow any relaxation, if it did occur, of the graphite flakes to take place. The dimensions of specimens determined after this period were thought to be stable at room temperature over a long period of time.

4.2.4(ii) Pressing of Specimens with Carbon Binders

The pressing procedure used in the pressing of specimens without binders was followed here as well, except that the specimens in this case were warm pressed at temperatures of about 130°C for specimens containing pitch and 80°C for specimens containing the resin. At these temperatures, the binders were fluid and acted as lubricants during pressing. The warm pressing was achieved by encasing the cylindrical die in a band heater which was secured by way of a two nut and bolt arrangement at the top and bottom end of the die. To heat up the band heater, a controller set to the required temperature was used, with a control thermocouple inserted between the outside surface of the die and the inside surface of the band heater. If the die was at room temperature prior to switching on the controller, a period of ten minutes was allowed after switching on, before pressing the specimen. After the first specimen had been pressed and ejected from the die as described above, subsequent heating periods were reduced to 5 minutes before pressing the specimens. This period was sufficient since the band heater reached temperature in less than a minute and the extra 4 minutes were allowed to ensure that the specimen itself reached the set temperature.

After pressing, the pressed specimens were left in the oven, set at 110°C for 24 h as before; this time allowed the pitch to soak between the graphite flakes and magnesia grains and also allowed the relaxation of the flakes to take place, as described above, if it did occur. At this temperature, the pitch remained very viscous and did not drain from the bottom of the specimens. The specimens containing the resin were also left in the oven, set at 110°C, for 24 h so as to receive similar treatment with other specimens, even though the resin cured within 20 minutes of putting the specimens in the oven, which was the main objective.

4.2.5 Porosity Determinations of Specimens

As already described in Chapter 2, Section 2.2.3(i), porosity of a specimen can be determined from the relationship:

$$\%\ \text{total porosity} = \left\{1 - \frac{\text{Bulk density}}{\text{True density}}\right\} \times 100\ .$$

For regular specimens like the ones fabricated in this work, bulk density is easily determined by measuring the relevant dimensions of the specimen, in this case diameter and height of the cylindrical disc specimens, and by calculating the volume and knowing the weight of the specimen, then bulk density is the ratio of the weight of the specimen to its volume.

The powder density of the starting materials are given in Table 2.3.3(i) and since the specimens being dealt with in this work are composites, except for the different grain size mixtures of magnesia only, the powder density of the composite specimens can be approximated by using the mixture rule[41], i.e.

$$P = P_1Q_1 + P_2Q_2 + P_3Q_3 + \cdots P_nQ_n \qquad (2)$$

where $P_{1,2,3 \ldots n}$ are the property values of material 1, 2, 3 ... n respectively, in the composite. The property here is powder density, equal to true density for practical purposes, of the material involved, while $Q_{1,2,3 \cdots n}$ are the volume fractions of the materials involved.

Using Table 2.3.3(i) of Chapter 2, and if the volume fractions of the materials reported in this Table 2.3.3(i) are known for a given composite, then the powder density of the composite can be determined by calculation using the above mixture rule expression (2).

4.2.5(i) Green Porosity Determinations

After drying, curing, etc., the specimens were removed from the oven at the end of the 24 h period and left to cool to room temperature before being weighed to determine their green weights. The diameters and the heights of these cylindrical disc specimens were measured using a screw gauge micrometer. Four readings of each dimension were obtained on each specimen and the average value of these four readings was taken as the dimension of the specimen. The diameter measurements had a typical variance from the mean value of 0.02% to 0.07% both in the green and fired state, while the variances in height ranged between 0.07 and 0.13% from the mean, both in the green and the fired state.

Using the procedure described above, the bulk density of the specimen was determined.

4.2.6 Firing of Specimens

After determining the dimension of the specimens in their green state, the weights were again determined before being fired, because some specimens, particularly those without organic binders, had poor abrasive resistance and a very small amount of material (< 0.1 $^{w}/o$), in some specimens only, was lost during dimensional measurements. Therefore the weight loss of a specimen after firing was the difference of this latter green weight and the fired weight of the specimen. Firing of the specimen was carried out in two ways, depending on whether the specimens contained a binder material or not and these firing procedures are described in the section below.

After firing, the bulk densities, hence porosities, of the specimens were determined as described in Section 4.2.5(i) above.

4.2.6(i) Firing of Specimens Without Carbon Binders

The green specimens were placed in a box, with internal diameters of 140 mm x 110 mm x 75 mm, made out of high alumina brick (code named PH85) in which a layer of powdered coke had been spread at the bottom to protect the specimens from oxidation at high temperatures. The specimens were stacked in columns of twos or threes, leaving enough room (10-20 mm depth from the top of the box to the top most specimen) for more coke addition and lid. Up to 16 specimens could be put in the box at a time. The box was then filled with coke and a lid was then placed on top of the box leaving as little gap as was possible. The box with its contents was transferred to a high temperature carbolite furnace raised to temperature at approximately 120°C/h then fired to 1500°C, soaked for 3 h at temperature after which the furnace was switched off and left to cool overnight to room temperature.

4.2.6(ii) Firing of Specimens with Carbon Binders

The initial firing rate of the carbolite furnace, as indicated in the previous section, was too high for specimens that contained binders which emit volatile matter. To avoid pressure build-up in the specimens as volatiles are lost, a two-stage firing process was employed. Firstly, the box and its contents were raised at 0.3°C/min in a muffle furnace up to 850°C and soaked for 5 h then cooled to room temperature before being transferred to a carbolite furnace and fired to 1500°C as described in Section 4.2.6(i).

After firing, both non- and carbon-binder containing specimens were removed from the box and the coke was carefully brushed off from the specimens before being weighed to determine their weights after firing. The dimensions of the specimens were measured as described in Section 4.2.5, and then their porosities were determined.

4.3 Polishing of Specimens for Microscopic Examination

The specimens for microscopic examination were prepared by the usual Araldite impregnation of specimens under vacuum before being polished on various grades of diamond pastes, after which the polished surfaces are examined under the microscope for microstructural evaluation/determination. In this work, however, a slow setting ultra-low viscosity Araldite obtained from Polaron Equipment Limited was used to impregnate the specimens. This Araldite was used after attempts to use the Araldite mixture of 9:1 parts of resin (Araldite M.Y. 753 and hardener H.Y.951) respectively, usually used to impregnate sintered ceramic oxide refractory materials, proved to be a failure because impregnation of the specimens by the Araldite did not occur, as evidenced from the pull-outs of the magnesia fines from the polished section, due, possibly, to the high viscosity of the Araldite which was unable to penetrate the less porous magnesia-graphite composites.

The specimens were impregnated under vacuum with an Araldite prepared from the following component mixture as recommended by the suppliers:

(a)	Hexenyl succinic anhydride (HXSA)	62.9 $^{w}/o$
(b)	Vinylcyclohexene Dioxide (ERL 4206 Resin)	31.5 $^{w}/o$
(c)	Araldite RD2 Resin (DY026)	4.7 $^{w}/o$
(d)	Dimethyl Aminoethanol (DMAE)	0.9 $^{w}/o$

The impregnated specimens were then put in an oven set at 60°C and left for at least 16 h for the resin to set, the minimum temperature and time required for this Araldite to set respectively.

After this period, the specimens were polished using a PLANOPOL machine. The specimens were first ground on 240 grit diamond disc for about 10 minutes before being ground on a 600 grit diamond disc for a further 10 minutes, using paraffin as a lubricant, as water could not be used since the specimens contained magnesia which can hydrate in the presence of moisture. The specimens were then polished on a petrodisc-M (special disc) impregnated with 6 μm diamond spray, for about 20 minutes, using a blue lapping fluid as a lubricant. The specimens were then polished on a disc covered with a nylon polishing cloth impregnated with 3 μm diamond spray for another 20 minutes. Finally, the specimens were polished on another disc covered with a nylon polishing cloth impregnated with 1 μm diamond spray using the blue fluid as a lubricant. Throughout the polishing of the specimens, a constant pressure of about 240 Newtons was applied on the specimens. The main advantage of using this polishing machine over hand polishing is that up to 9 specimens could be polished at one time and that a high degree of planeness is maintained throughout the polishing.

4.4 Results and Discussion

4.4.1 Compositions Studied

The following compositions have been studied in the packing experiments using the methods described above, with n-values that varied between 0.3-1.0 with increments of 0.1:

(1) Different grain size magnesia fraction mixtures only (100 $^{w}/_{o}$ MgO), to investigate how porosity varies with n-value.

(2) 80 $^{w}/_{o}$ MgO + 20 $^{w}/_{o}$ graphite:
  (a) Graphite A
  (b) Graphite B
  (c) Graphite C
  (d) Graphite D

(3) 80 parts MgO + 20 parts graphite (I) + x parts binder where:
  (a) I = A $x = 3,5,7,9,11,15$
  (b) I = B $x = 3,5,7,9,11,15$
  (c) I = C $x = 3,5,7,9,11,15$
  (d) I = D $x = 3,5,7,9,11,15$

N.B: Two types of binders were used separately for each type of graphite in each series of the binder contents shown above, and these were pitch and a powdered novalac resin P41. This was to investigate whether different binders affected the packing of the composites by examining the resulting bulk densities and porosities of composites.

4.4.2 Magnesia Compacts

The percent green and fired total porosities of the specimens were determined as described in Section 4.2.5 and these porosity values of the magnesia compacts are plotted against n-value in Figure 4.4.2. The difference between green and fired porosity, if any, is not evident, but there seems to be a minimum porosity at about n = 0.4 in both curves. At this n-value, the green and fired porosities of the compacts are 14.7% and 15.2% respectively.

This non-existent, or little, difference in porosity of green and fired magnesia specimens, was due to the fact that the specimens were only fired to 1500°C at which temperature sintering of the compacts is minimal. Although the porosity difference between the lowest porosity and the highest is only about 2%, Figure 4.4.2 shows that magnesia size fraction mixutres, or any other oxide, can be combined efficiently using Andreasen's expression

$$y = 100\left(\frac{d}{D}\right)^n$$

to determine empirically the n-value to give the optimum packing of grain size fractions, given the size distributions of the material. Andreasen's method, therefore, provides perhaps a quicker and simpler way of obtaining optimum bulk density, hence lowest porosity of the mixture, than Hugill's method. The n-value, which is the parameter used to change the proportion of the fine to coarse fractions of the material, is varied until a minimum porosity is obtained for a fixed largest grain size fraction (D) in the system.

To show the porosities obtained on magnesia grain size fraction mixtures, both by Andreasen's and Hugill's method, the porosity results obtained by both methods in this work, are reported in Tables 4.4.2(a) and 4.4.2(b) respectively. The porosity values obtained by Hugill's method (Table 4.4.2(b)) are almost the same as those obtained by Andreasen's method. It is important to note that the porosity obtained from Hugill's method is close to those porosity values obtained at n = 0.4 in Andreasen's method, implying that this method can be used. The difficulty, however, lies in establishing the best grain size fraction combination to give optimum packing from a given grain size distribution; and because of the lack of a relationship in Hugill's method from which magnesia grain size fractions could be combined to obtain efficient packing of the different grain size fractions, Andreasen's method of predicting an efficient packing of different grain size fractions of magnesia was used in this work because it was more convenient than Hugill's method and the section below deals with the packing characteristics of the magnesia-graphite composites.

4.4.3 Magnesia-Graphite Composites

As described in Section 4.2.2, three methods of adding graphite to a mixture of different grain size fractions of magnesia were investigated and the packing characteristics of the composites from the three methods are described below, starting with Method 1, 2 and then 3.

4.4.3(i) Method 1

Figures 4.4.3(i)(a) and (b) are plots of green and fired porosities of composites containing 20 $^{w}/o$ graphite against n-value, respectively. In both figures, composites containing graphite B show a definite minimum porosity at about n = 0.5. This minimum porosity occurring in composites containing graphite B, is possibly a result of the size of the graphite flakes used in the composite. It may be recalled from Section 4.2.2(i) that the method used in this particular part of the experiment (Method 1) was to replace an equivalent amount of magnesia from the total magnesia fractions in that particular sieve cut by an equivalent amount ($^{w}/o$) of graphite of the corresponding sieve cut. From Table 2.3.1(i) of Chapter 2, graphite B is the finest graphite amongst the four graphites (A, B, C and D); therefore it is clear that the composites containing graphite B will have less of the magnesia fines (-100 B.S. mesh sieve) than other composites containing the other types of graphites. From this point of view then, it is reasonable to conclude that because different types of graphite replace different size fractions of the magnesia, because of the differences in the size distributions (Table 2.3.1(i)), the packing characteristics of composites made from different types of graphite, using Method 1 described in this work, are bound to be different. The figures above have just demonstrated that.

An attempt to show this difference in packing characteristics microstructurally was made. Plate 4.4.3(i)(a) shows the microstructure of composites containing graphites A, B, C and D at n=0.4. From this plate, the difference in microstructure between the different composites is hard to see, although the composite with graphite B seems to show less magnesia particles between the graphite flakes.

Figures 4.4.3(i)(a) and (b) also show that packing is better at higher n-values than it is at lower n-values. Table 1(b) in Appendix 4.2.1(i) shows that the amount of fine (-100 B.S. mesh) magnesia grains decreases with increasing n-value. Therefore at these high n-values the graphite flakes occupy the cavities between the big magnesia grains, in turn increasing the graphite-graphite contacts. Since the flakes are platey and flexible as well, they can pack more efficiently within the areas they occupy, hence reduction in overall porosity. The most significant observation from the above figures is that when graphite is added to the oxide aggregates, the packing of the resulting composite is better than the packing of the magnesia compacts only. Compare Figures 4.4.3(i)(a) and (b) and Figure 4.4.2.

Plates 4.4.3(i)(b) show how the microstructure of the composite containing graphite D changes with n-value. At n=0.4, the graphite flakes are separated by fine magnesia fractions. As the amount of fine fractions are being reduced, n=0.6, the graphite-graphite contacts increase and, finally, at n=1.0, the big magnesia grains squeeze the graphite flakes into their cavities that they form, since these large sized particles of magnesia do not pack efficiently and the graphite flakes are clearly squeezed together in-between the magnesia grains, and this results in porosity reduction at high n-values compared to the porosities obtained at lower n-values.

The figures discussed above have also shown that the porosity of the specimens increase after firing (note the change of scale limits on porosity axis). This increase in porosity after firing is, perhaps, partly due to the volume increase observed after firing the specimens, and partly due to possible oxidation of some little amount of graphite. The relation between increase in porosity and the observed permanent volume change is discussed later in this section. Meanwhile, Figure 4.4.3(i)(c), shows a plot of percent permanent volume increase after firing against n-value. The figure shows that the expansion of the specimens, in all cases, increase with n-value. This trend is what would be expected as demonstrated in Plate 4.4.3(i)(b) that the graphite-graphite contacts increase with increasing n-values if it is accepted that the expansion is caused by the expansion of the graphite flakes during firing which shrink back into their own cracks on cooling, leaving the oxide matrix in the expanded state which occurred during firing. This can only happen if there is no chemical bond between the oxide and graphite and from the micrographs shown so far there seem to be cracks running along the graphite-magnesia interface, suggesting a non-chemical bond between the two. It is important to remember that the specimens being dealt with in this section do not contain any binder materials, but are made out of magnesia and graphite only, therefore this permanent volume increase may only be attributed to the graphite expansion.

Figure 4.4.3(i)(c) shows that the composite containing graphite B had the highest volume increase, while the composite containing graphite D had the least volume increase. This difference in volume increase between composites containing the same amount of graphite but of different type, hence different size distributions (Table 2.3.1(i) , Chapter 2) could be a direct result of the type of size fractions of the magnesia that each graphite replaces. In the case of composites containing graphite B, which is the finest among the four graphites, more fine magnesia grain size fractions would be replaced than when graphite A, for example, is used in the composite at the same n-value with both composites containing equal amounts of graphite. Therefore the composite with graphite B prepared by Method 1 would have more graphite-graphite contacts than any other composite containing coarser graphite flakes at the same n-value, with the same amount of graphite. Hence higher volume change in the composite containing graphite B after firing, assuming the increase is only due to the expansion of the flakes during firing. In such a case then, the volume increase of a composite will depend both on the graphite-graphite contacts, as well as on the inherent coefficient of thermal expansion of the graphite involved. It is therefore not surprising to find that the composites containing graphite C showed to have the next highest volume increase after firing, as shown in Figure 4.4.3(i)(c), because graphite C has the largest fine fractions (-100 B.S. mesh sieve) after graphite B.

On the basis of the argument that graphites with more fine fractions should have higher volume increase after firing, it would be logical to expect composites containing graphite D to show the next highest volume increase after C, but Figure 4.4.3(i)(c) shows that composites containing graphite A expanded more than those containing graphite D. It is important to note that both graphites, A and D, have very little fractions less than 150 μm (-100 B.S. mesh sieve) Table 2.3.1(i) of Chapter 2, and therefore very little fine (-100 B.S. mesh sieve) magnesia fractions were replaced by these two graphites, hence low graphite-graphite contacts, particularly at lower n-values (see Plate 4.4.3(i)(b)) because fine magnesia particles get in-between the graphite flakes. The higher expansion observed in specimens containing graphite A than those containing graphite D may be attributed to the inherent coefficients of thermal expansions of the two graphites. Presumably graphite D has a lower coefficient of thermal expansion than A. In Chapter 2, Table 2.3.4(iii), it was shown that graphite D had the lowest specific surface area, suggesting that it had the least interlaminar cracks. It could therefore be possible that this graphite has the lowest coefficient of thermal expansion as well.

In an attempt to establish whether this volume increase in specimens containing graphite was largely responsible for the porosity increase observed after firing, a relationship between % permanent volume increase after firing and the porosities before and after firing, was derived and this is shown below:

$$\%\Delta V = P_f \frac{V_{BF}}{V_{BG}} - P_g ,$$

where $\%\Delta V$ is the percent calculated permanent bulk volume change of the specimens after firing, P_f and P_g are the green and fired porosity of a specimen and V_{BF}, V_{BG} are the green and fired bulk volumes of the specimens. The derivation of this expression is shown in Appendix 4.4.3(i). If the increase in porosity is entirely due to volume increase, a plot of measured $\%\Delta V$ against the right-hand side expression of the above equation should be linear with a gradient of 1.

These plots were made for the composites prepared by Method 1 containing the four graphites (A, B, C and D). These plots are shown as Figure 4.4.3(i)(d). From these plots it is clear that the volume increase contributed significantly to the increase in porosity, but it is also true that some of the increase in porosity was due to other mechanisms, such as some oxidation of the graphite, since the gradients of the lines were slightly larger than one with intercepts, which theoretically should be zero, varying between -2.44 to -1.82, except for composites containing graphite D, whose plot gave a gradient of 1.03 with an intercept of 0.83. These straight lines were obtained by linear regression analysis.

Finally, it would seem from Figure 4.4.3(i)(d) that composites with smaller amounts of fine magnesia, thus composites containing graphite B and C, are almost represented by the same straight line, which is not the case with composites containing graphites A and D because, presumably, they replace different magnesia size fractions.

4.4.3(ii) Method 2

It has already been pointed out in Section 4.2.2(ii) that this method is different from the other two methods, 1 and 3, because the graphite content was not kept constant, but decreased with the increase in n-value. Figures 4.4.3(ii)(a) and (b) are plots of percent total green and fired porosities against n-value respectively. Two things are immediately evident from Figure 4.4.3(ii)(a). Firstly, the green porosity increases with n-value, implying that the smaller the amount of graphite (here the amount of graphite decreases with n-value) the lower the packing efficiency of the composite; and, secondly, the green porosity differences, at a given n-value, between composites containing different types of graphite are very small. This implies that, although the graphites are different in their size distributions, their packing characteristics under similar conditions are, probably, the same, hence the small difference in the green porosity.

When these composites were fired and their porosities determined after firing, the relationship between fired porosity and n-value was completely different from that observed in the green state (see Figure 4.4.3(ii)(a)) as shown in Figure 4.4.3(ii)(b). In Figure 4.4.3(ii)(b) all the plots show a trend towards a minimum porosity before the porosity begins to increase at n-values greater than 0.5. This behaviour is difficult to explain because there are several variables in this method. Firstly, the graphite content decreases with the increasing n-value. Secondly, it has already been shown in appendix 4.4.1(i), Table 1(b), that increasing the n-value increases the amount of coarse (-5+25 B.S. mesh sieve) magnesia grain, while the fines (-100 B.S.S.) decrease with increasing n-value. Hence there is a decrease in the graphite content with increasing n-value as already explained above. Therefore, with these two variables changing at the same time, the changes in the packing pattern must be complex and thus difficult to explain.

However, examination of the microstructure at three n-values, 0.3, 0.5 and 0.7, gives an idea of the type of microstructure obtained in this method. Plate 4.4.3(ii) shows typical microstructures obtained in this work at $n = 0.3$, 0.5 and 0.7 for a composite containing graphite A, which is typical of other composites containing other graphites. At the lowest n-value, 0.3, the graphite content is very high (39.4 $^w/o$), hence high fired porosity due to increased volume change caused by graphite. Plate 4.4.3(ii), $n = 0.3$, shows that the magnesia grains are completely surrounded by the graphite flakes. It is also interesting to note how some graphite flakes are bent round the ends of some magnesia grains, demonstrating the flexibility of the graphite flakes in the presence of hard oxide grains. However, at $n = 0.5$, the amount of graphite is reduced, but, possibly, just enough to occupy the cavities formed by the large magnesia grains, as the plate seems to show. Hence, low porosities are observed in Figure 4.4.3(ii)(b). At higher n-values, more cavities are formed by the increased large magnesia grains of almost equal size, but smaller quantities of graphite are available to occupy these cavities. This is again clearly demonstrated in Plate 4.4.3(ii), $n = 0.7$.

Figure 4.4.3(ii)(b) also shows that composites containing graphite C had the highest porosity at $n < 0.4$ and $n > 0.6$ after firing followed by composites containing graphite B, then A over all n-values and D showing the lowest porosity increase as it did show in Method 1, Figure 4.4.3(i)(a)

Figure 4.4.3(ii)(c) is a plot of % permanent volume increase of specimens after firing against n-value. The Figure shows that the volume increase decreases with the decrease in the graphite content, i.e., increase in the n-value.

The volume increases of the composites obtained in Method 2 show that composites containing graphite C had the highest expansion after firing, as shown in Figure 4.4.3(ii)(c), followed by B, while A and D seem to have equal expansion. This is in total agreement with the observations made on specimens made from graphite only, which showed that the % volume increases of the specimens made from graphite A, B, C and D were 5.7, 5.6, 8.5 and 5.4% respectively after firing at 1500°C. However, the expansions observed on composites containing equal amounts of graphites A, B and D are not the same, although the graphite expansions are the same, because this volume increase observed in the composites depends on many factors, such as coefficient of thermal expansion of the individual graphite, distribution and orientation of these graphites in the composite.

To investigate whether the porosity increase after firing in this method was also largely due to volume increase of the specimen after firing, the expression in Section 4.4.3(i) was used here as well, i.e.,

$$\%\Delta V = P_f \frac{V_{BF}}{V_{BG}} - P_g \ .$$

Figure 4.4.3(ii)(d) is a plot of measured % volume increase after firing (%ΔV) against calculated %volume change after firing ($P_f \frac{V_{BF}}{V_{BG}} - P_g$). The meaning of the symbols are given in appendix 4.4.3(i). A straight line was fitted to each set of data points for each composite using regression analysis as before. The interesting thing to notice from the figure is that all the points from the four composites lie within the same region, implying that the relationship between measured % volume increase and calculated %volume increase is the same in all the composites. But, perhaps the most important point from the figure is that the gradients of the four lines (representing the four composites) had gradients of one, and intercepts almost equal to zero, as predicted by the expression, except for the composite containing graphite B, which had an intercept of -1.35 and a gradient of 1.05. From Figure 4.4.3(ii)(d), it would be reasonable to argue that the porosity increase in this method (2) was largely but not entirely due to increase in volume after firing.

Using Figures 4.4.3(ii)(a) and (d) the minimum porosity observed in Figure 4.4.3(ii)(b) can now be explained. From Figure 4.4.3(ii)(a), the green porosity increases with increasing n-value as explained in the earlier part of this section, while the porosity increase due to the graphite expansion, decreases with n-value. This is deduced from Figures 4.4.3(ii)(c) and 4.4.3(ii)(d) which show that the calculated %volume change[†] decreases with n-value (%ΔV V's n-value). Therefore the result of the two opposing porosities, i.e., porosity due to compaction (green porosity) and porosity due to the expansion of the flakes on firing, with n-value produce a minimum porosity. As already mentioned before, this minimum porosity occurs at different n-values for each composite containing a different type of graphite (Figure 4.4.3(ii)(b)).

4.4.3(iii) Method 3

This is the method where the graphite was introduced in the mixture of different size magnesia grain fractions, as predicted by Andreasen's method at each n value, as described in Section 4.2.2(iii). The magnesia-graphite mixture was kept constant for all n-values at 80 $^{w}/_{o}$-20 $^{w}/_{o}$ respectively.

Figures 4.4.3(iii)(a) and (b) are plots of green and fired porosity of the composites against n-value respectively. Figure 4.4.3(iii)(a) shows

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[†] % volume change is directly porportional to % porosity change.

that the porosities of the composites fall with increasing n-value. This shows that the composites pack better when the amount of fine (-100 B.S. mesh sieve) magnesia is reduced. This behaviour can again be argued in terms of the microstructure at different n-values. Plates 4.4.3(iii)(a), (b) and (c) show the microstructure of a composite containing 20 $^{w}/o$ graphite B at n = 0.3, n = 0.5, and n = 1.0 respectively. One immediately notices from the plates that as n increases, the graphite-graphite contacts increase, as has been shown in Method 1. Therefore, graphite flakes fill the interstices between the magnesia grains more efficiently at high n-values than at lower n-values where the flakes are separated by fine magnesia grains which go in-between the flakes. Each plate has two micrographs showing the orientation of the flakes in the direction of pressing and perpendicular to the direction of pressing. The orientation of the graphites in the two directions at n = 1.0 is not evidence, because here the large magnesia grains control the microstructure while at lower n-values, the graphite controls the microstructure since the system is not rigid but fluid during pressing and the graphite flakes easily impose their anisotropic behaviour without hindrance.

Plate 4.4.3(iii)(d) is for a composite containing graphite D at n = 0.3. This plate has been included to show that the microstructure of the composites containing different types of graphite is similar at the same n-value for the same method of fabrication.

Figure 4.4.3(iii)(a) shows that these composites have lower porosities than those shown in Figure 4.4.3(i)(a) (Method 1). This implies then that the magnesia grain size fraction mixtures, as predicted by Andreasen's method, are not upset by the addition of the graphite in their packing characteristics but rather enhanced actually. At any given n value, the difference in total green porosity, between a composite giving the lowest porosity and that of highest porosity is only about 1%. Therefore, the packing characteristics of the composites containing these graphites are almost the same, at least in their green state. This phenomenon was also observed in Method 2, Figure 4.4.3(ii)(a), where the mixtures were identical, except for the type of graphite, at each n-value. The porosity differences of composites in Figure 4.4.3(i)(a) (Method 1) are different because each type of graphite replaced different amounts of magnesia grain size fractions, therefore the composites packed differently.

In Method 3, graphite C gave better packing in the composite than other graphites, as demonstrated in Figure 4.4.3(iii)(a) which shows that the composite with graphite C has the lowest green porosity. The composite with graphite A has the highest porosity, while those containing graphite B and D are in-between these two extremes.

When these specimens were fired, there was porosity increase, as has been found in the other two methods, and the amount of porosity increase after firing for each composite at each n-value is the same as that found with composites prepared by Method 1. However, the total porosities of the composites, even after firing, are lower in Method 3 than in Method 1. This can be deduced easily from the differences in the scaling of the porosity axes of the figures. Figure 4.4.3(i)(b) (Method 1) has higher porosity scale limits than Figure 4.4.3(iii)(b) (Method 3).

Although the porosity differences between composites containing different types of graphite are small (about 2%), as shown in Figure 4.4.3 (iii)(b), it still shows that these graphites pack differently and therefore it is likely that these composites have different physical properties which can result into differences in the way each composite behaves at service temperatures. This difference is exemplified in Figure 4.4.3(iii)(c) which shows that the % volume increase (after firing) against n-value for each composite is different. It is clear from Figure 4.4.3(iii)(b) that each graphite packs optimumly at different n-values; for instance, the optimum packing for the composite containing graphite B is around n = 0.4, C and D at n = 0.7, while A is about n = 1.0. This then shows that the size of the graphite (hence aspect ratio) is important.

To investigate whether the porosity increase after firing was due to the volume increase, plots of measured % bulk volume increase against calculated %volume change, were made as was done in the previous methods, and Figure 4.4.3(iii)(d) shows these plots. Here the scatter of points is high and the fitted straight lines may not represent the real relationships between the two parameters. The slopes for composites containing graphites B, C and D, are similar to those obtained in Figure 4.4.3(i)(a) (Method 1) (1.2, 1.4, 1.3 respectively). The composite containing graphite A has a slope of 0.45 with an intercept of 1.45. This implies that the porosity increase in this composite was not largely due to volume increase as the relationship in Section 4.4.3(i) predicts. The weight losses of these composites after firing were between 1.2% to 1.7%, similar to those obtained in Method 1 and within the expected range for a composite containing no organic binders. However, emphasis should not be laid on determining which mechanism (oxidation of the graphite or volume increase) was largely responsible for the porosity increase because the increase in porosity was only about 3 to 4%; therefore both mechanisms could have contributed to this increase.

In Method 3 then, composites containing graphite A and C showed large scatter (Figure 4.4.3(iii)(d)) of data points and the porosity increase may not have been solely due to volume increase of specimens after firing, while composites containing graphites B and D show that there is a direct linear relationship between measured % bulk volume change and calculated %volume change; hence porosity increase was largely due to volume increase.

4.4.4 Composites Containing Varying Amounts of Binders at a Fixed n-value (n = 0.6) and at a Fixed Magnesia/Graphite Ratio

From the three methods of introducing graphite into a magnesia mixture of different grain size fractions, Method 3 gave lower porosity values at all n-values for composites containing the same amount of graphite. Therefore this method was chosen to study the effect of varying the amount of binder addition to the composite on the packing of the composite. The composites prepared by this method showed to have minimum porosity at different n-values containing different types of graphite, Figure 4.4.3(iii)(b). But considering the fact that the porosity difference between composites was small and that the porosity difference between composites with the lowest porosity and those with the highest porosity was only about two percent, any of the n-values could have been used in this part of the experiment. However, an inspection of the curves in Figure 4.4.3(iii)(b), one notices that the minimum porosities for the composites occurred between n-values of 0.4 to 0.8, therefore n = 0.6 was chosen for being the mid-point between the two extreme n-values at which the minimum porosities occurred in two composites. In this part of the experiment, all composites were prepared by using Method 3 at n = 0.6. Figures 4.4.4(i)(a) and (b) are plots of percent total green and fired porosity against percent raw binder added. Figure 4.4.4(i)(a) shows that the green porosity decreases with the increasing pitch content, as expected, because the pitch fills the holes between the solid particulate matter in the composite and it also acts as a lubricant during pressing, hence the decrease of porosity with the increase in the binder content. The binder axis includes a zero point so as to include the points when the composites contained no pitch.

On firing these composites, the porosity increased with the increasing pitch content. It is also interesting to note that the fired porosity decreases slightly at low pitch contents before it begins to increase.

In Figure 4.4.3(i)(b) the lowest porosity occurs at a pitch content of 3 $^{w}/o$. Furthermore, the figure also shows that porosity differences between different composites at the same binder content is very samll. This again confirms the earlier suggestion that these graphites do not pack very differently from each other, on the basis of porosity values obtained, although composites containing graphite A have consistently shown to have higher porosities than other composites.

Figure 4.4.4(i)(c) is a plot of % bulk volume increase after firing against % raw pitch content. The obvious feature in this figure is that the composite with graphite A had the highest volume increase after firing than the other composites. This is a little bit misleading, because it could be interpreted to mean that graphite A caused high volume increase, yet the reason is that this set of specimens was fired at a higher heating rate of 1°C/min instead of 0.3°C/min up to 850°C (see Section 4.2.6(ii)) by error, hence the high volume increase was caused by the high evolution of volatiles from the pitch. If the volume increases in Figure 4.4.4(i)(c) are compared with Figure 4.4.3(iii)(c) at n = 0.6 only, one finds that the pitch binder exacerbates the volume increase of the composites after firing.

Figures 4.4.4(ii)(a) and (b) are plots of percent total green and fired porosities against raw resin content respectively. Figure 4.4.4(ii)(a) shows also that the green porosity decreases with the increasing resin content. The decrease in green porosity is almost certainly due to the fact that the resin flows into the holes between solid particles since these are warm pressed specimens and acts as a lubricant during pressing, since composites containing binders were warm pressed (see Section 4.2.4(ii)). However, it is clear that the resin is not as effective as pitch is in filling the holes between solid particles, since this resin P41 does not go into a fluid state as pitch does at its softening temperature (~ 70°C) but behaves like a plastic mass and therefore it may not efficiently fill the holes between the particles of the composite. Furthermore, it may not act as a good a lubricant as pitch does; compare Figure 4.4.4(ii)(a) and 4.4.4(i)(a).

When these composites were fired, the fired porosity of the composites increased with the increase in the resin content, as shown in Figure 4.4.4 (ii)(b), caused, most likely, by the increased amount of volatiles being given out as was found with the composites containing pitch. However, the porosity increase with the resin content was not as high as it was with composites containing pitch at the same initial binder content by weight because, perhaps, the resin gives out less volatile matter than pitch, as shown in Figure 2.4.4 of Chapter 2.

To investigate the effect of the binder content on the volume increase of the specimens, a plot of percent bulk volume change after firing against binder content (resin) was made and this is shown in Figure 4.4.4(ii)(c). The reduction in volume increase when small resin additions are made to the composite is apparent. Furthermore, the overall volume increase is lower in composites containing a resin than other composites (compare Figure 4.4.4(ii)(c) with Figures 4.4.4(i)(c), 4.4.3(iii)(c) and Figure 4.4.3(i)(c)).

The way the two binders (pitch and resin P41) affect the % bulk volume increase after firing can be explained by the way these two binders pyrolyse. The pitch passes through a liquid phase, during pyrolysis, between its softening temperature up to about 450°C when the viscosity begins to increase as the liquid crystals (mesophase) in the pitch begin to coalesce and more volatile matter is lost. Most of the volatiles are lost by the time the temperature reaches ~ 800°C, except for hydrogen and sulphur which continue to come out of the now solid carbon up to about 1500°C. Therefore, during the time the pitch is in liquid state, the composite matrix can easily be pushed apart by the expansion of the flakes or by the volatiles coming out from the pitch.

However, the resin cures at low temperatures (110°C) and therefore composites containing a resin contain rigid solid binding particles which continue to interlock the matrix in this solid state throughout the firing. So even during the pyrolysis, the resin particles provide the keying effect in the composite matrix throughout their firing and, therefore, the matrix is not free enough to expand freely as it possibly does in the presence of liquid (pitch is in liquid form between 70°C-450°C within a reasonable time period).

4.4.5 Summary of the Results

Andreasen's[46] method of determining the amounts of magnesia grain size fraction mixtures required to obtain efficient packed magnesia grain size fractions of six sieve cuts has been used in this work. The optimumly packed magnesia size fractions were then determined experimentally by varying the n-value in the equation

$$y = 100\left(\frac{d}{D}\right)^n$$

(see definitions of these parameters in Section 4.1.2.)
The maximum size (D) used in the mixtures was fixed at 3.35 mm throughout this work and six sieve cuts were used to obtain the necessary different magnesia grain size fractions. The mixture of magnesia grains containing a maximum particle size of 3.35 mm has been found to give minimum porosity at n = 0.4 (see Figure 4.4.2) using six sieve cuts shown in Table 2.3.1(i) of Chapter 2.

Of the three methods of adding graphite to the magnesia grain size mixture investigated, Method 3, in which the required amount of graphite was added to a mixture of different grain size magnesia fractions, has been found to give better packing characteristics. All the composites containing the same amount of the four different types of graphite had about the same total percent porosity for a given n-value, the difference being about 2% between the composite with lowest porosity and that with the highest porosity.

On the basis of packing experiments described in this chapter, it is not possible, at a glance, to say whether the graphite with the highest or lowest aspect ratio produced the best or worst packing in the composite as composites containing different types of graphite were found to give the lowest porosity at different n-values for each method. Although composites containing graphite A showed to have slightly higher porosities than other composites in all the three methods.

All composites containing different types of graphite were found to have a permanent volume increase after firing, resulting in a total porosity increase. When a binder was added to the composite, the green porosity, as expected, was reduced depending on the amount of binder added. However, on firing, the porosity increased with increasing binder content, with the highest increases being observed in composites containing pitch. The resin was found to have a reducing effect on the permanent volume increase of the composites.

The experiments described above have shown that all four graphites examined pack slightly different from each other, using porosity as an index to monitor packing variation. On examining Figure 4.4.3(iii)(b) closely, where the plotted values were obtained from fired specimens prepared by Method 3, it is observed that the porosity minimum for each composite containing a different type of graphite occurred at a different n-value. The composite containing the finest graphite, B, had fired minimum porosity between n = 0.4 to 0.5, and that with the coarsest graphite, A, had a fired minimum porosity around n = 0.8. Further, fired composites of fixed n- value (n = 0.6) and magnesia/graphite ratio, with varying amounts of binder content, showed increasing fired porosity with increasing binder content, as expected. Porosity variation with any variable of the product is a clear indication of the variation of the microstructure with that variable. This microstructural variation in a composite result in a variation of the physical properties and, in most cases, chemical properties as well. One such property which is affected by the microstructural variation is strength, and strength, in general, is paramount in any structural design. Hence the control of this property under service conditions is crucial to the performance of a structure. In refractory applications, the importance of strength depends on where the brick, for example, is going to be used. The magnesia-graphite composites are presently being used in hot spots in electric arc furnaces and the high wear areas of the BOF, therefore hot strength and erosion resistance are of paramount importance in these composites.

To examine further, therefore, the effect of varying the above parameters, e.g. proportions of fine to coarse grain fractions of magnesia, n-values, the amounts and type of graphite, orientation of graphite, binder content and type, etc., at a fixed magnesia/graphite ratio, on the physical properties of the magnesia-graphite, one such property which can be chosen is bend strength. Because of the relative ease with which it can be measured, bend strength has been determined on the magnesia-graphite composites and the effect of the variables indicated above on strength are evaluated. Further, the addition of metallic elements, silicon and aluminium, which are usually added as anti-oxidants in the magnesia-graphite refractory composites, into the composites was made and their effects on strength and also the resulting microstructure after firing, were evaluated. Chapter 5, below, describes in detail the measurements that have been carried out in this work.

CHAPTER 5

MECHANICAL AND ELASTIC PROPERTIES OF MAGNESIA-GRAPHITE COMPOSITES

5.1 Introduction

The susceptibility of refractory materials to fracture from rapid heating and cooling is a critical problem in refractory technology. Rapid temperature changes produce temperature gradients within a refractory brick which restrain free expansion of volume elements giving rise to thermal stresses.[52,53] These thermal stresses may result in thermal spalling of the brick at its working surface during service and erosion of the brick by the molten liquids (slags/metals) may easily take place. Therefore a high strength of a refractory brick at service temperature improves the erosion resistance of the brick, although erosion resistance may equally be enhanced by controlling the chemical stability of the brick at service temperature.

Factors such as strength, elastic modulus, coefficient of thermal expansion, fracture surface energy[†54] and thermal conductivity have considerable effect on thermal shock resistance of refractory materials.

Kingery,[55] using thermal elastic properties, proposed a parameter, R′, which would indicate whether a ceramic material would resist crack initiation, i.e., resist fracture initiation, by thermal stresses or not. The parameter is as follows

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[†] The fracture surface energy is defined as "the work done to create unit area of new fracture face".[54]

$$*R' = \frac{K\,\sigma_f\,(1 - \mu)}{E\,\alpha} \qquad (1)$$

where σ_f is the tensile strength of the specimen, K is its thermal conductivity, α is thermal expansion coefficient, E is the modulus of elasticity and μ is Poisson's ratio.

The thermal shock resistance, resistance to crack initiation, is said to be high if R' is high and vice versa. This can be appreciated if the parameters in the R' expression are considered. R' is high if K and σ_f are high while E and α should be low. When K is high, the temperature gradient in the brick (article) is low, hence low thermal stresses. The relationship between σ_f and E is given by Hooke's law, i.e.,

$$\sigma_f = E\,\varepsilon \qquad (2)$$

where ε is elastic strain. It follows then that if σ_f is high and E is low, then strain is high. This means that if the body is stressed, the stresses can be relieved by yielding, since ε is large. Finally, α should be low for high R' because during sudden temperature changes, the body will have minimum differential thermal expansion which, if large, can cause stresses in the body.

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* This parameter, R', can be used to compare[56]:

(a) The maximum allowable heat flux through a body under conditions of steady heat flow.

(b) The maximum allowable temperature difference to which a body can be subjected under convective heat transfer.

(c) The maximum allowable heat flux in steady-state heat conduction in a solid containing non-conducting holes or cavities.

Therefore R' is the maximum heat flux, for steady flow, allowed in the body to resist fracture initiation.

However, in refractory bricks and other refractory products, the presence of cracks is not in question, but restraining the extent of their propagation and the resulting change in the physical behaviour is fundamental to prolonging the service life of the brick. Therefore efforts have been devoted to establishing the driving force for crack propagation in the absence of an external force. Hasselman[57] proposed that to reduce the probability of fracture propagation and subsequent changes in physical properties, material properties should be selected so as to maximize the "thermal stress crack stability" parameter, R_{st}, defined by

$$*R_{st} = \left(\frac{\gamma_{wof}}{E\,\alpha^2}\right)^{\frac{1}{2}} \tag{3}$$

where R_{st} is a thermal stress crack stability parameter, γ_{wof} is the work of fracture, α is the thermal expansion, and E is the modulus of elasticity. In direct analogy to the derivation of thermal stress parameters, $\frac{K\,\sigma_f\,(1-\mu)}{E\,\alpha}$, Hasselman[57] introduced the role of thermal conductivity on crack stability by multiplying thermal conductivity, K, with R_{st} giving:

$$**R'_{st} = R_{st} \times K = \left(\frac{K^2\,\gamma_{wof}}{E\,\alpha^2}\right)^{\frac{1}{2}} \tag{4}$$

For high thermal shock resistance, R_{st} and R'_{st} must be high. This then means that γ_{wof} must be high and E and α must be low as already explained above.

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* The physical meaning of R_{st} is that it is the maximum allowable temperature difference required to propagate "long cracks" under severe thermal stress conditions.[56]

** R'_{st} is the maximum allowable temperature difference required to propagate "long cracks" for mild thermal stress conditions.[56]

In order to understand possible service characteristics of the brick and for design purposes as well, a detailed knowledge of the parameters defining R_{st} and R'_{st} is essential. In an attempt to improve thermal shock resistance and other physical properties, an understanding of factors affecting this parameter, such as strength, Young's modulus, thermal expansion, thermal conductivity, etc., is necessary. This thesis describes a first attempt to investigate, in a systematic way, some of these properties contributing to thermal shock resistance. This work has been limited to investigation of bend strength and Young's modulus determined from sonic velocity measurements due to limited time.

Before describing the experimental work carried out on strength and elastic modulus, it is appropriate to examine briefly the fundamental theories in the failure behaviour and the elastic properties of brittle materials, of which refractory materials are part of this group.

5.1.1 Fracture Mechanics of Brittle Materials

Ceramic materials fracture in a brittle manner because of the absence of significant plastic flow at low temperatures. The materials do not appreciably deform to the same extent as metals because the dislocations in their structure are relatively immobile compared to metals, which is a direct consequence of their ionic or covalent bonding. Moreover, the presence of flaws caused by the heterogeneous nature of these materials leads to their low tensile strength and, therefore, severely limits their mechanical use.

5.1.1(a) Theoretical strength considerations of ceramic materials

Theoretical tensile strength (σ_{th}) of an ideal single crystal of a material depends on the chemical and physical forces holding it together, for instance, the bonding forces between atoms. This tensile strength (σ_{th}) can therefore be estimated from the energy function for bonding between atoms in an isotropic material. Orowan[58] derived an approximate expression relating stress in the material to atomic displacement:

$$\sigma_{th} = \left[\frac{E\,\gamma_0}{r_0}\right]^{\frac{1}{2}} . \tag{5}$$

where E is the elastic modulus, γ_0 is the surface energy and r_0 is the equilibrium distance between the two atoms. He argued that the work done in stressing the material to stress σ_{th} must at least be equal to the energy required to produce the two new fracture surfaces.

However, in practice, the strength of materials is 50 to 200 times less than the theoretical strengths that can be estimated from the above relationship, approximated at 0.1 E [59], where E is Young's modulus. This difference between theoretical and practical strengths lies in the presence of defects in real materials, such as cracks, pores, dislocations, etc. The explanation of this strength discrepancy was offered by Griffith.[60] He assumed that in a brittle material, there are many cracks and that at the tip of such cracks there is a strong concentration of stress. Therefore a smaller stress than the theoretical stress is required to cause failure. Griffith [60], therefore, developed a new theory of fracture to explain his observation: "That if fracture occurs it must involve a continuous reduction in potential energy when passing from the original to the ruptured state". This then implies that a crack will start propagating and will continue to propagate as long as the eleastic energy released from the stress field surrounding the crack is as great or greater than the energy required to supply effective surface energy. Further, a propagating crack which is being slowed down can also derive energy from the kinetic energy accompanying the crack. This is Griffith's energy balance theory from which he derived a relationship to relate the strength, the effective surface energy, elastic modulus, crack length, etc., as given below

$$\sigma_m = \left(\frac{2\gamma E}{\pi c}\right)^{\frac{1}{2}} \tag{6}$$

where σ_m is the maximum stress that the material may withstand up to failure, γ is the effective surface energy, and c is the crack length.

The measurements and discussion of γ and c are beyond the scope of this work and it will suffice to say that these details can be obtained from the literature [59,60,61,62,63]. The measurement of stress (strength) σ_m and elastic modulus is the subject of this chapter and will be discussed in detail later.

From the above cited literature, it is clear that the strength of ceramic materials depends on many factors, such as:

(1) nature of the bond in the matrix;

(2) type of defects, such as cracks arising from fabrication processes;

(3) amount of pores, size and its distribution.

In order to understand fully the fracture characteristics of these ceramic materials, the above information must be supplemented by the knowledge of, among other properties, such as, thermal conductivity, thermal expansion etc., the Young's modulus of these materials. The section below, briefly reviews the basic principles involved in the determination of Young's modulus of these materials.

5.1.1(b) Elastic modulus of polycrystalline materials

The elastic properties of ceramics determine the mechanical behaviour of the material and the properties are directly dependent on crystal structure and bonding. Stiffness or Young's modulus is a direct measure of these bonding forces between two atoms in a single crystal. However, in a polycrystalline material, Young's modulus is very dependent on porosity, dislocation and other defects.

Most ceramic materials are composed of mixtures of several solid phases together with voids. Therefore the resulting elastic modulus of the body depends on the composition of the body - that is, the proportions of the individual components, the elastic modulus of these individual components and phase interaction. It has been shown[59] that the elastic properties of a two-phase isotropic material must lie between those of the components. Consider this material to be made out of two components of hard and soft slabs and have a sandwich-type construction to represent a homogeneous composite, as shown in Figure 5.1.1(b). When the stress is applied parallel to the slabs, the strain in each slab is a constant. Young's modulus for this composite is given by the approximate formula

$$E_{\parallel} = E_1 V_1 + E_2 V_2 \qquad (7)$$

where $E_{\parallel}$ is the elastic modulus of the composite derived from considerations when stress is applied parallel to the slab (see Figure 5.1.1(b)), E_i and V_i are the moduli and volume fractions of the two types of slabs making the sandwich material in Figure 5.1.1(b) respectively. The relationship given in equation (7) gives the highest Young's modulus (upper bound[64]) one would expect to get on such a sandwiched material. When the stress is applied normal to the slabs, the stress in each slab is constant, and the corresponding Young's modulus $E_{\perp}$ is given by:

$$E_{\perp} = \frac{E_1E_2}{E_2V_1 + E_1V_2} \tag{8}$$

and this gives a lower bound[65]. In practice, Young's moduli of materials fall between these two limits.

The model described above assumes that the two phases have finite stiffness. However, if the second "phase" is porosity, which is always present in most heterogeneous ceramic materials, then one phase, porosity, has zero stiffness. Many workers have proposed equations to relate elastic constants to the amount of porosity. The equations are in the form[59] $E = E_0(1 - f_1P + f_2P^2)$ as summarized by Watchman[66]; where E_0 is the modulus for fully dense material, P is the pore volume fraction and f_1 and f_2 are constants which measure the rate of change in the modulus relative to change in porosity. This relationship assumes spherical pores. Further it was shown by Knudsen[67] that elastic modulus of hot pressed porous polycrystalline alumina at room temperature varied exponentially with porosity and used the general equation proposed by Spriggs[68] that

$$E = E_0\, e^{-bP}$$

where E = Young's modulus of a porous polycrystalline body;

E_0 = Young's modulus of a non-porous polycrystalline body;

P = fractional pore volume of the body; and

b = an empirical constant.

Spriggs[69] suggested that the parameter b may be due to the fabrication technique and the resultant pore phase structure. However, predictions of elastic modulus of a material which do not include assumptions of phase geometry were examined by Hashin et al.[70] who observed that exact solutions could be obtained only when further factors, such as the statistical details of the phase distribution, were evaluated. It would therefore seem that the calculation of elastic modulus without taking into account the geometry and distribution of all the phases in the system, gives an approximate value. However, if comparison of the elastic modulus of two bodies is required, the relationship proposed by Wachtman[66] can be applied.

The section below describes the techniques which have been used to measure strength and elastic modulus of the magnesia-graphite composites fabricated in this work.

5.2 Strength and Elastic Measurements of Magnesia-Graphite Composites

The magnesia-graphite refractories (graphite content $\geqslant 10$ $^{w}/o$) are used, presently, in high wear areas of the steelmaking furnaces such as metal-slag line in the Electric Arc Furnace (EAF) and trunnion areas of the Basic Oxygen Furnace (BOF), because conventional refractories such as magnesia-chrome, tar bonded or tar-impregnated magnesia bricks are no longer chemically/mechanically stable due to increased temperatures required in the continuous casting of steel and tapping temperatures ($\geqslant 1650^{\circ}$C) required in the refining of high grade steel. The magnesia-graphite bricks have higher slag resistance and higher thermal shock resistance than the ordinary basic bricks. The high thermal resistance of the magnesia-graphite composite is a result of adding the graphite component to the magnesia and it is not clear at present how this parameter is influenced by:

(a) the graphite level (or magnesia/carbon ratio);

(b) type of graphite;

(c) type of bond, if any, between magnesia and graphite or a third bonding phase;

(d) interaction, orientation and distribution of the graphite in the composite;

(e) type and size of magnesia.

Although this study is not about determining the thermal shock resistance (TSR) itself, determination of some of the parameters which influence TSR may help in elucidating the characteristic behaviour of the composites at service temperatures; therefore strength and elastic moduli of the composites have been studied. Since composites are developed so that the desired properties of each phase are accentuated and the undesirable properties suppressed, a range of composites defined by the list immediately above was studied and the actual compositions are listed in Section 5.3.5.

5.2.1 Strength Measurements

The classical tensile testing technique used in metal testing cannot be applied to ceramics because of their brittle nature which prohibits the use of grips, which may cause failure at grip points. Therefore tensile testing of these materials is usually carried out using bend test methods which do not require any grips.

The bend test measurement method is based on a long thin beam, of uniform cross-section, supported at two points and loaded at one or two points positioned centrally between the supports. Both types of arrangement are shown in Figure 5.2.1. These arrangements are three- and four-point bend tests. On applying the load to break the test piece, the stress distribution resulting within the material varies linearly from tensile at the convex face to compressive at the concave face. Failure is therefore most likely to occur from a point on or near to the convex surface. Furthermore, the stress between loading and support point increases linearly, reaching a maximum at the loading point[71]. In three-point bend test, the maximum stress is therefore at the convex surface opposite the loading point of contact. In four-point bend test, the surface stress is uniform between the two loading points, over a larger surface area than in three-point bend test, using the same support span. The load required to break a specimen and the dimension of the test specimens are used to calculate the failure stress, known as 'flexural strength', 'bend strength', or modulus of rupture (MOR). The relationships between MOR, load required to break the specimen and specimen dimensions are given below for rectangular section beams:

(a) Rectangular beam

Three-point bending: $$\sigma_{max}\ (\mathrm{MOR}) = \frac{W\ell h}{8I_z} \qquad (9)$$

Four-point bending: $$\sigma_{max} = \frac{W\ell' h}{4I_z} \qquad (10)$$

where dimensions are defined in Figure 5.2.1, W is the applied force, and I_z is the cross-sectional moment of inertia, which for a rectangular section beam of width b and depth h is:

$$I_z = \frac{bh^3}{12} \qquad (11)$$

Substituting I_z in the above equations (9) and (10), gives

$$\sigma_{max} = \frac{3W\ell}{2bh^2} \quad \text{for three-point bending} \qquad (12)$$

and

$$\sigma_{max} = \frac{3W\ell'}{bh^2} \quad \text{for four-point bending} \qquad (13)$$

There is a number of essential points to consider when using the equations indicated above and these points are outlined in Appendix 5.2.1. In deciding which method would be practicable in this work, it was important to note point (d) in Appendix 5.2.1, namely, "that the ratio of the separation distance between the loading and support point (ℓ') to depth (h) for four-point or (ℓ) to (h) for three-point bending, should exceed 4:1 (symbols ℓ', ℓ and h are defined in Figure 5.2.1)", because the validity of the equations indicated above ((12) and (13)) depend on satisfying these conditions.

In this work, three-point bending was used because:

(a) only small rectangular specimens that were long enough to meet the 4:1 ratio requirement could be fabricated by the pressing method;

(b) a commercially fabricated three-point bend flexure jig was available and satisfied most of the requirement for test jigs outlined in Appendix 5.2.1;

(c) the simplicity of the method.

The disadvantage with three-point bending is that only a small area of the specimen surface is subjected to the maximum stress and, further, stress gradients exist both along the bar and the thickness of the specimen[59]. Because only a small area of the specimen surface is sampled, for defects causing failure, by the applied stress in three-point bending, strength values obtained tend to be higher by 15-25% than strength values of the same specimen (same material) obtained by other tensile strength test measurements. An ideal method would be the one in which the whole specimen between support points is uniformly stressed, because only such a loading system would enable larger portions of the specimen to be stressed and therefore when failure occurs it will occur from the most highly stressed defect. In three-point bending, however, failure usually occurs at the loading point and yet the defects at that point may not necessarily be the likely ones to cause failure in the specimens if larger portions of the specimens were tested. In this work, though, it is not the absolute strength of the composites that is being sought, rather their comparative values when any of the variables listed in Section 5.2 is changed.

Since a spread of strength values is always obtained due to differences in defect sizes, their distributions, geometry etc., when a batch of nominally identical test specimens of a brittle material is tested, as described in Section 5.2.1, many specimens of the same batch were required to enable the determination of the dispersion of the test results (standard deviation). The spread (distribution) of strength results is affected by, among other factors, the way the specimen is made, the surface finish produced and the frequency of occurrence of large microstructural defects which, in most cases, cause large strength variations and therefore have profound effect on the reliability of the product.

5.2.2(a) Elastic modulus measurements

In ductile materials, destructive tensile testing of specimens to determine Young's modulus is frequently applied because of the appreciable plastic deformation of the material. Therefore the measurement of tensile strain (change in length due to the applied force), ε, is easily achieved. For a uniform rod, of cross-sectional area A, subjected to a tensile force F, the tensile stress $\sigma = F/A$, is related to Young's modulus E and the tensile strain ε by:

$$\sigma = E\,\varepsilon \,. \tag{14}$$

However, brittle materials do not show appreciable plastic deformation, as discussed earlier, and are not usually tested in tension, in the literal sense, but by bending. Therefore the deflection of the beam is normally measured, but because these displacements are very small, they are extremely difficult to measure. The difficulties encountered in determining Young's modulus using the static methods are avoided by using an ultrasonic method.

5.2.2(b) Ultrasonic measurements

The propagation of ultrasonic waves in a material is related to the elastic properties of the material and the homogeneity of its structure, namely, the magnitude of velocity of an ultrasonic wave travelling in a material is related to the density and Young's modulus of the material [72]. This therefore involves, among other things, the determination of the time taken for the wave to pass through the material and if longitudinal wave velocity (C_L) is determined, the relationship between this velocity and Young's modulus is given by: [73]

$$C_L = \left\{\frac{E(1-\nu)}{\rho(1+\nu)(1-2\nu)}\right\}^{\frac{1}{2}} \qquad (15)$$

where C_L is the longitudinal velocity, E is Young's modulus, ρ is the bulk density of the material and ν is Poisson's ratio. No criterion is known that gives a minimum sample dimension for a particular accuracy, but it would appear that as long as dimensions, both lateral and along the pulse, are greater than a few wavelengths of the pulse in the material, then any departure in the measurement of velocity from the body-wave value is negligible [72,73,75]. Further, it has been shown [74] that the longitudinal wave velocity detection is enhanced if $\lambda << 2a$: where λ is the wavelength of the pulse in the material and 2a is the diameter of the transducers. Figure 5.2.2(b) shows the variation of the longitudinal wave field with wavelength. When the wave length is very much greater than the diameter of the transducer ($\lambda >> 2a$) the ultrasonic field is made of longitudinal, transverse and surface waves. When $\lambda \simeq 2a$, the field of both the transverse and surface wave decrease with respect to the longitudinal wave field. With further decrease in wavelength, i.e. $\lambda << 2a$, the surface and transverse waves disappear, whilst the longitudinal wave field gradually increases.

In this work the limiting factors on the dimensions of the specimens and the transducers were taken into consideration during the determination of the longitudinal velocities of the test specimens, as discussed later.

The elastic constants, as obtained from wave velocity measurements, are called dynamic constants, as opposed to the static constants determined from static stress-strain measurements.

5.2.2(c) Velocity measurement

There are several methods that can be used to determine longitudinal and transverse wave velocities in a solid and these are discussed elsewhere[73]. In this work, longitudinal velocities of the test specimen were measured by measuring the delay of ultrasonic pulses. In this method the ultrasonic pulses are propagated in the material by a transmitter and picked up by a receiver at the opposite side of the specimen. Simultaneously, with the transmission of a pulse, the time base of an oscilloscope or, in this case, a Portable Ultrasonic Non-Destructive Digital Indicating Tester (PUNDIT) is triggered and the time delay of the received pulse, in relation to the beginning of the time base, is equal to the time of travel of the waves through the material and it is indicated on the display panel. Therefore, the velocity $C_L = \ell/t$, where ℓ is the dimension of the specimen and t is the time taken by the wave to travel through the specimen. The actual measurement techniques will be described in the sections below.

5.3 Experimental Techniques

5.3.1 Starting Materials

The materials described in Chapter 2 and used in the packing experiments described in Chapter 4, were also used in fabricating specimens for strength and elastic modulus measurements, discussed in this chapter. The sieve analyses of those materials which required sieving, were carried out using the same sieve cuts reported in Table 2.3.1(i) of Chapter 2. The coal tar pitch was ground and sieved through 200 B.S.S. mesh sieve, while the powdered resin P41 did not require any grinding as it readily passed through 200 B.S.S. mesh sieve.

The silicon and aluminium metals used as additives in the composites were obtained from BDH chemical suppliers.

The aluminium metal needed grinding, and was ground to pass through 300 B.S.S. mesh sieve, while silicon was found to pass through a 300 B.S.S. mesh sieve without further grinding.

5.3.2 Apparatus

In the packing experiments, Chapter 4, the specimens were mixed dry in a sample bottle by shaking the bottle with its contents in a mechanical shaker for a period of ten minutes. This method of mixing was satisfactory because the samples mixed at a time were in small batches of 50 g each. However, when a powdered binder (< 75 μm) was added and mixed as described in Section 4.2.3(i) of Chapter 4, to a composite used to make a specimen and when such a specimen was fired to

1500°C as described in Section 4.2.6(ii), the specimen showed some pin (blow) holes after firing. The number and size of the holes increased with increasing binder content. The size and the distribution of these pin holes would affect the strength of the composites. The areas where these holes appeared were areas, presumably, where the binder was concentrated because of lack of proper distribution during mixing. It is true that these holes occur even if the binder was well distributed in a composite, but the holes themselves will be distributed and, possibly, uniform in size throughout the sample. Therefore their effect on strength may be less severe than in a composite containing large holes in some parts. In the refractories manufacture, warm mixing of oxide aggregates, or for that matter oxide-graphite composites, containing binders, is carried out to coat all the particles with the binder as well as avoiding the formation of large pin holes caused by the evolution of volatiles from the binder.

As already mentioned in the last paragraph of Section 5.1.2, it is necessary to fracture many specimens to obtain one statistically significant strength measurement for a given variable. This means that large amounts of material were required to be prepared in the same way for fabricating the number of specimens required for one strength measurement value. This was achieved by mixing the necessary ingredients in one operation. Therefore, a mixer was designed for mixing the composites with the binders at elevated temperatures of 70°C-130°C, depending on the type of binder used to a chieve its liquid state.

In the packing experiments described in Chapter 4, cylindrical disc specimens were used to determine the porosity and bulk density of various composites. Therefore a cylindrical die was used. However, the shape of specimens required in the three-point bend test in this work, were rectangular bars and this necessitated the design of a rectangular pressing die.

5.3.2(i) The warm mixing equipment

The details of the mixer are shown in Figure 5.3.2(i), and this mixer essentially consisted of:

(a) a 4 litre capacity heating mantle with a variable power supply.

(b) a 4 litre capacity stainless steel Kenwood Chef bowl, and

(c) a variable speed laboratory stirrer, with a maximum jaw chuck of 12 mm and a purpose fabricated stainless steel paddle consisting of a flat blade and a stem. The blade had 12 holes of five different diameters drilled through it and its profile matched that of the inner shape of the Kenwood Chef bowl. The matching of the profile of the paddle blade to that of the inner shape of the bowl was vital when mixing materials containing a binder, because only this arrangement would ensure the continuous scraping of the walls of the bowl by the blade during mixing which, in turn, ensured that no binder material stuck to the walls of the bowl. The drilled holes through the blade had a similar effect as that of a multiple blade stirrer, since, during the mixing operation, different amounts of material at different heights went through the holes, while some were carried forward with the blade. This produced randomness in the mixing of the material.

(d) Ni/Cr v Ni/Al compensated thermocouple to measure the temperature in the mixing chamber.

5.3.2(ii) Rectangular pressing die

To enable the porosities obtained during packing experiments and those obtained from strength test specimens to be compared, the same pressure, used in pressing the cylindrical discs for packing characterization of composites, was also used to press strength test specimens, i.e. 159 MPa. This required a strong rectangular die that was small enough to minimize pressure variations along the bar during pressing. Several possible designs were explored and, finally, a split pressing die was chosen and fabricated. The die was made of two long rectangular hardened steel pieces of equal dimensions, two short spacers and another fifth piece which served as a base. These pieces were assembled using three toughened screws at each end. The base was secured by way of six toughened screws.

5.3.2(iii) The Denison Compression Testing Machine

This was used to press the test specimens and the details of the operation of the machine are described in Section 4.2.4 of Chapter 4.

5.3.2(iv) Gas furnace

Strength test measurement specimens were fired in a gas fired furnace at 1500°C. The change to a gas fired furnace from the carbolite furnace was necessitated by the frequent failure of the carbolite elements experienced during the firing of specimens used in the packing experiments.

The gas furnace had an ogival arch shaped chamber measuring about 350 mm and 450 mm of minor and major axis respectively, with a 300 mm depth. Two burners were positioned to direct the flame tangentially to the walls of the furnace. The furnace was lined with mullite bricks. The temperature of the box containing the specimens and flame temperature were measured using a Pt 13%Rh/Pt thermocouple and a potentiometer. The temperature varied very little (±5°C) from the required temperature after 20 to 25 minutes of reaching the set temperature on the control panel. The flow rate of the gas/air mixture was controlled by an electronic control box.

5.3.2(v) The Instron Tensile (Compression) Testing Machine

The Instron Machine, Model No. TT-CM-L, was used to determine the strength of the fired specimens using a three-point flexure jig -2810-004.

5.3.2(vi) The PUNDIT

A Portable Ultransonic Non-Destructive Digital Indicating Tester, PUNDIT, manufactured by CNS Electronics Limited, was used to determine the longitudinal sonic velocities of the test specimens. Two transducers were used, one as a transmitter and the other as a receiver, since direct coupling with a specimen was used, a coupling media (grease) was applied on the faces of the transducers.

The transducers consisted of lead zirconate titanate (PZT_4) ceramic piezo electric elements mounted in stainless steel cases. The elements were tightly held onto the inside face of the case to provide highly efficient acoustic transmission. The pulse generator caused the transmitting transducer to be shock-excited by a peak voltage of 1000 volts operating for 1.5 micro-seconds. Pulses were generated at a repetition frequency of 10 per second and caused the transducer to oscillate mechanically at its design frequency. Two pairs of transducers which could be used with the PUNDIT were available at the time with frequencies of 150 KHz and 500 KHz.

5.3.2(vii) Scanning Electron Microscope (SEM)

A Philips PSEM 500 scanning electron microscope was used to examine the fracture surfaces of the test specimens as well as to examine whether the composites developed any kind of chemical bond after firing at test temperature.

5.3.3 Specimen Preparation

In deciding how many specimens would be required to determine the strength of a composite for a given variable, three factors were considered:

(a) the number of specimens for each strength determination must be statistically significant with eight (8) being at the lower end of the scale and the top scale being only limited by practicality.

(b) Because of the possible preferential alignment of flake graphite within the composite, it was decided to double the number of test specimens and test them normal and perpendicular to the pressing direction.

(c) To reduce the possible pressure variations on the specimens during pressing, it was important that the specimens should be small and short but still satisfying the three-point bend test requirements indicated in Section 5.2.1(a), and yet large enough (64 mm x 13.5 mm x 14 mm) to contain all the different grain size magnesia fractions of the composite, taking into account that large magnesia grains, up to 3.35 mm, were to be present in the specimens.

Considering all the three points outlined above, it was proposed that each strength measurement at each chosen variable be carried out on 20 specimens, 10 for each side ($||$ and $\perp$ to the direction of pressing) and that each specimen would be made from a 30 g batch of material. Therefore a 600 g batch was required in each mixing operation.

5.3.3.1(a) Testing the effectiveness of the mixer

In Section 5.3.2, it was indicated that the strength of the composite can be affected by the type and distribution of porosity which results from how the volatiles of the binder are given out; therefore the need to study and ascertain that the binder was well distributed. Furthermore, this was a study, in itself, on the effectiveness of the mixer.

There are several techniques that can be applied to determine the variation of composition from one specimen to another made from the same batch material. Chemical analysis is used if chemical composition of the specimen is to be determined. Reflected light microscopy can be used to determine the distribution of solid phases in a specimen. The latter method, which can be used to determine the distribution of a phase, was not used because it involves a colossal amount of work to obtain an accurate result. Instead the difference in the oxidation temperatures of the raw binders to those of the graphites was exploited.

Figure 2.4.5 (i) shows that these graphites begin to oxidize around 500°C in a current of air, while no information is available on the oxidation characteristics of the raw binders. Therefore, a temperature was determined at which all the binders (pitch and resins) were completely oxidized while the graphites were not at all oxidized and this temperature was determined to be 485°C.

Since the temperature at which the binder can be oxidized completely without oxidizing the graphite is known (485°C), then a number of specimens, containing known quantities of magnesia, graphite and an organic binder, could be prepared from the same batch and the amounts of the three components in each sample could be determined by oxidizing out the carbon components intermittently and weighing the specimens in-between these firings. This technique was used to determine the effectiveness of the mixer designed as described below.

5.3.3.1(b) Trial mix

To get an idea of mixedness that could be obtained from the mixer described in Section 5.3.2(i), a composite with a large particle size variation was thought to be ideal for such a test. Composites with n-value of 0.3 and prepared by using Method 3 (see Chapter 4, Section 4.2.2(iii)) have a large size variation of MgO grains and these composites were chosen for this test. Further, 5 $^{w}/o$ pitch was used as a binder and all the materials were weighed to an accuracy of ±10 mg. In this test, the composite contained 80 parts MgO, 20 parts graphite B and 5 parts pitch, giving a total batch weight of 630 g.

This batch was then charged in the mixer after which a lid was placed on the mixer to avoid spillage of material during mixing, and was stirred at a speed of 100 rev/min and then increased to 200 rev/min on reaching the desired temperature. A thermocouple was inserted in the mixing chamber to measure the temperature during mixing.

After one hour period of mixing, the stirrer was stopped and the contents were immediately discharged into a container at room temperature. This procedure was adopted after observing that material stuck to the bowl walls if the contents were left to cool down to room temperature inside the bowl. The disadvantage with discharging the mixed composite containing pitch is that pitch can be oxidized slightly even at low temperatures as 120°C if exposed to an oxidizing atmosphere, e.g. air.

It is also known that the pyrolysis behaviour of pitch and the resulting carbon from pitch can be altered by oxidizing the pitch slightly in the early stages of pyrolysis[76]. But since this procedure was followed throughout this work, then this error was constant in all the mixtures, therefore any variation of the property measurement due to this error was the same for all the specimens.

The mixed batch was then weighed out into 20 batches of 30 g each and 20 cylindrical discs were pressed at a pressure of 159 MPa using the Denison Compression Testing Machine as described in Section 4.2.4, Chapter 4. Any other shape of specimens could have been used in this part of the experiment. After pressing, the discs were left in the oven, set at 60°C for 24 h and then removed to cool down to room temperature. The discs were then weighed to an accuracy of ±10 mg. During weighing, the discs were arranged in such a manner that the first disc to be weighed was coded as No. 1 and the last one as No. 20. This coding was carefully observed during subsequent experiments on this batch as well as in the subsequent specimens made for strength measurements.

The specimens were then placed on a ceramic bat and then the bat was placed in a muffle furnace. Through the door spy-hole of the muffle furnace, a recrystallized alumina tube was pushed into the muffle chamber while the other end of the tube was connected to an oxygen gas cylinder by way of plastic tubing. Because of the large size of the muffle chamber, a high rate of oxygen flow (> 200 cc/min) in the chamber was maintained. The furnace was heated at a rate of 0.3°C/min up to 850°C and held at that temperature for 24 h before the furnace was switched off and left to cool to room temperature before the oxygen flow was turned off. Air was tried at the initial stages of this experiment and it was found that the binders oxidized at a slower rate than they did in pure oxygen. The weights of the discs before and after firing were compared in their respective order and the weight difference was attributed to weight loss of the binder due to oxidation since it has already been indicated in Section 5.3.3.1(a) that there was no weight loss of graphites used in this work at 485°C in a current of oxygen, and this weight loss was noted. The discs were placed back on to the bat and then fired to 850°C in the same furnace using an oxygen atmosphere. This time the furnace heating rate was raised to 1°C/min. The specimens were soaked for 24 h at temperature before switching off the furnace and left to cool to room temperature. On removing the specimens from the furnace, it was observed that the specimens were too weak to be handled and those which were tried to be removed from the bat for weighing, crumbled between finger tips. This weakness in the specimens, which now contained magnesia grains only, was caused by the oxidation of the graphite which seems to have provided an interlocking or keying mechanism when present. The undamaged specimens still on the bat were carefully transferred to a high firing carbolite furnace and fired to 1300°C to enable the specimens to develop a ceramic bond. The specimens were soaked for 3 h at temperature before switching off the furnace. The weight difference of each specimen between the weight after oxidizing the pitch at 485°C and the weight after oxidizing the graphite at 1300°C, is the weight of graphite in that specimen.

The results obtained from 13 specimens containing 80 parts magnesia, 20 parts graphite B and 5 parts pitch, are shown in Table 5.3.3.1(b). The table shows that the variation of pitch content in each specimen was very small, typically ±0.2 $^{w}/_{o}$. The graphite content variation between the specimens studied was equally small, ±0.5 $^{w}/_{o}$. The expected weight loss of the specimens, without pitch, due to graphite oxidation, is about 18.5 $^{w}/o$, taking into account that graphite B has 11.6 $^{w}/o$ ash as residue and that 0.5 to 1 $^{w}/o$ of the graphite could have been oxidized at 485°C used to oxidize the pitch, the oxidation results obtained agree with the expected weight loss.

Using the pitch and graphite distributions determined above as mixing indices, then the designed mixer for this work was considered suitable to carry out warm mixing of the composites containing binders. In this part of the experiment, it was not possible to determine the distribution of pitch and graphite in each specimen.

5.3.3.2 Preparation of Specimens for Strength Measurements

Specimens for strength determination of the composites were prepared using Method 3 in which graphite was introduced into a mixture of different size magnesia grains, as described in Section 4.2.2(iii). A 600 g batch made out of different size magnesia grains and graphite, in the required proportions, was weighed out with an accuracy of ±10 mg. The mixture of the two materials made a total of 100 $^{w}/o$ of the composite, to which all additives made were based on 100 $^{w}/o$ of this mixture. To minimize possible confusion, these mixtures will be described in terms of parts; for example, 80 parts magnesia plus 20 parts graphite plus 5 parts pitch.

5.3.3.3(i) Addition of binders and metallic additives

(a) Pitch

When pitch was used as a binder for the composite, the powdered pitch, which in this case did not necessarily need to be fine because of warm mixing, was weighed out in the required amount, as a percentage of the 100 $^{w}/o$ magnesia graphite mixture. Then this mixture, together with the pitch, was charged in the mixing vessel, and the mixing was carried out as described in Section 5.5.3(ii).

(b) Resin

In the packing experiments described in Chapter 4, resin P41 was mixed with the composites by dissolving it in a 0.07 $^w/o$ solution of polyethylene oxide. This method was not followed here because it was thought to be inadequate, judging from the porosity values obtained in the packing experiments. It was, therefore, proposed that the powdered resin, P41, be dissolved in the liquid resin, PR67. But, as discussed in Chapter 2, resin PR67 can only be thermally cured after adding hexamine (hexamethylene tetramine $N_4(CH_2)_6$).

The amount of hexamine determines, among other things, the amount of residual carbon after coking. The determination of the optimum hexamine required to obtain high carbon yield was not carried out in this work, but after a private communication with the suppliers of the resins, it was proposed that 7.5 parts hexamine to 100 parts liquid resin PR67 only could be tried, and this ratio was used whenever PR67 was used.

To dissolve the powdered resin P41, which did not require the addition of hexamine, into the liquid resin, PR67, the amount of binder, in this case the resin, required in the composite, was calculated. Then the ratio of PR67 to P41 was arbitrarily chosen, which was 7.6:1 respectively, and the proportions of each resin were then calculated. This ratio was kept constant in experiments which were intended for investigating the effect of the resin content on strength.

The proportion of resin PR67 was weighed out and then charged in the mixing vessel set at 70°C ±5°C. Then 7.5 parts of hexamine to

100 parts of resin PR67 were charged in the vessel and mixed until all the hexamine dissolved in the liquid resin which was now very fluid at this temperature. The proportion of the powdered resin, P41, was then charged into the vessel and mixing continued until all the resin, P41, was dissolved. Finally, the magnesia/graphite mixture was added and mixing was carried out as described in Section 5.3.3.2.

The addition of hexamine together with resin P41 into PR67 was attempted in the early stages of making the resin mixture, but it was found that nodules were formed during mixing and did not dissolve easily in the liquid resin PR67, hence the method described above was adopted.

It will become clear later, from Section 5.5.2, that most of the work described in this chapter was carried out with pitch as a binder, not with a resin, unless a comparision of the effect of one binder as opposed to the other, was necessary on a particular property. The reason is that the mixed resins required greater temperature control and were actually messy to handle. For instance, if the temperature went above 85°C, the resin would thicken such that mixing was impossible, or it could actually set and the only way to remove the contents and clean the mixing bowl was to oxidize the resin at 500-700°C. Pitch, on the other hand, has a large temperature range (115°C-130°C) in which it remains in liquid form without giving out a lot of volatile matter.

(c) Metallic additives

When metallic additions were made to a composite, their weight percent added were based on 100 $^{w}/o$ magnesia/graphite mixture. During mixing, all the ingredients were charged in the mixing vessel at the same time, since pitch was used as a binder here.

5.3.3.3(ii) Pressing of specimens

After mixing, 30 g batches were weighed out and pressed in rectangular bars (slabs) using the rectangular pressing die. Specimens used in strength test measurements contained organic binders and were therefore required to be warm pressed, as was done during the packing experiments for those specimens containing organic binders. Previously, warm pressing was achieved by wrapping a band heater around a cylindrical pressing die. This method could not be adopted here because of the difficulty in attaching any sort of a heater around a rectangular die. Therefore, warm pressing was achieved by heating the die with its contents in an oven set at 120°C, if pitch was the binder, and set at 70°C if the resin was used. The die was left for 20 minutes at temperature before it was quickly transferred to the Denison pressing machine. The load was applied fairly quickly to reach the desired pressure within 40-50 seconds. This was to ensure that the composites were pressed at or near the oven temperature at which the binders were in their fluid state, therefore acting as lubricants. The same pressing procedure, as described in Section 4.2.4 of Chapter 4, was used in pressing the rectangular specimen bars (slabs). Heating of the samples in the die took about 20 minutes to reach oven temperature. Therefore to speed up the pressing operation, three dies were used so that when one die was being used for pressing, the other two were being heated up in the oven ready for the next operation.

After pressing, the bottom of the die was unscrewed and the specimen was ejected in the usual manner. The pressed specimens were then put into the oven set at 110°C, if pitch was the binder, to allow the pitch to soak in the composite matrix and allow the relaxation of the graphite flakes, and set at 120°C if the resin was used as the binder. This latter temperature was high enough for the thermal setting of the resin. In both cases, the specimens were left in the oven for 24 h. After this period, the specimens were then removed from the oven and left to cool to room temperature and then their weights before firing were determined.

5.3.3.4 Firing of the Specimens

The specimens were fired in the same manner as described in Section 4.2.6(ii) of Chapter 4, when the composites contained an organic binder, but this time up to 40 specimens, each weighing about 30 g and measuring approximately 64 mm x 13 mm x 14 mm could be packed in the box and covered with coke breeze, compared to 16 cylindrical discs, each weighing about 50 g. This is due to the fact that the rectangular bars packed more efficiently. Further, after firing the specimens at 850°C in the controlled heating furnace, the box and its contents were transferred into a gas fired furnace and then fired to 1500°C and soaked for 3 h. The specimens were carefully removed from the box, taking note of their arrangement and then weighed. The weight, after firing, was used to determine the bulk density of the specimen, as described below. It was also used to check whether a specimen had been oxidized during firing by comparing the weight of the specimen before firing and its weight after firing. This was approximated by first taking into account the known weight loss due to loss of volatile matter from the binder and weight loss due to loss on ignition in an inert atmosphere of both magnesia and graphite.

The calculation was achieved as follows:

(a) Let the expected weight loss of a specimen due to evolution of volatile matter in the binder = W_V.

(b) Let the expected weight loss of a specimen due to loss on ignition of both the magnesia and the graphite = W_S.

Then the total expected weight loss of the composite

$= W_V + W_S = W_{L.O.I.}$

If the green weight of the specimen is W_g, then the weight of the specimen after firing is $W_g - W_{L.O.I.} = W_F$, where W_F is the weight after firing. Therefore, if $W_F < W_g - W_{L.O.I.}$ then some oxidation occurred and the weight loss, due to oxidation, is $= (W_g - W_{L.O.I}) - W_F$.

5.3.4 Measurements of Specimens

5.3.4.(i) Specimen dimension determinations

After determining the weights of specimens after firing, the breadth, height and length of the individual slabs were measured using a screw gauge micrometer, taking three measurements for each side and the average of these three was taken as the dimension of that particular side. The variations of these measurements were about ±0.2%. Using these dimensions and the calculated powder densities of the composites, the porosity of the individual slabs was calculated. The average porosity for twenty specimens at each n-value or any other variable, for instance, binder content etc., had a standard deviation of about 0.5% porosity.

5.3.4(ii) Strength test measurement

A specimen was placed in a flexture jig and supported at each end of an adjustable 50 mm-200 mm span by a yoke suspended from the load cell coupling of the Instron machine. A second interlocking yoke, connected to the moving cross-head, applied the flexing force to the top of the specimen at the centre of the span. Bearings attached to the second yoke were guided by slots in the first yoke to ensure that the force bears exactly, or at least near so, on the centre of the sample. The support rods on the supporting yoke had shallow 14 mm breadth circular grooves cut into them. The breadth and height of the test specimens were about 14 mm, enabling the specimens to be placed at the centre of the span.

Throughout the bend strength measurements carried out in this work, the rate of applying the breaking load was kept constant by using a constant cross-head speed of 0.2 cm/min. In order to investigate possible variations in the breaking characteristics of specimens in the same batch, for different n-values, or specimens containing different types or contents of graphite, etc., the chart speed and the sensitivity were also kept constant at 40 mm/min and 10 mV respectively.

5.3.4(iii) Sonic velocity measurements

After strength measurement tests were carried out on a set of 20 specimens, eight of the broken specimens were randomly chosen from the set and sonic velocity measurements were carried out, using the PUNDIT apparatus described in Section 5.3.2(vi), on a section of each broken specimen about 10 mm away from the fracture point and about the same distance from the other end.

After working out the wavelength of the pulse through the specimens, it was found that the 500 KHz transducers with diameters of 6.5 mm were appropriate for the specimen sizes tested. For instance, specimens containing magnesia only had a pulse velocity of about 5.4 x 10^3 m/sec equivalent to a value of λ of 11 mm. For a material with 5 parts of pitch as a binder to 100 parts MgO, the highest velocity measured was 2.97 x 10^3 m/sec giving a λ value of about 6 mm and all composites containing flake graphite, irrespective of quantity used, the highest velocity recorded was about 1.84×10^3 m/sec, giving a λ value of about 4 mm. These transducers could therefore be used to measure the sonic velocities of the specimens used in strength measurements, since specimens' breadths and heights ranged between 13 mm to about 14 mm, satisfying the requirements described in Section 5.2.2(b), that the dimensions of the specimen, both lateral and along the pulse, should be a few wavelengths greater.

When an ultrasonic transducer is placed on the surface of a material to be tested, it will rest on a layer of air, even though the surfaces of the transducer and the material may appear to be very smooth. Because the characteristic impedance of a solid medium is about 100,000 times that of air, almost total reflection occurs at the transducer-air boundary and the waves do not enter the test specimen, therefore coupling media are used[77]. In this work, grease was used as described in the calibration of the PUNDIT immediately below.

A reference bar was used to calibrate the instrument. The pulse time for the bar was 26.3 micro-seconds, engraved on the bar. The transducer faces were smeared with a medium bearing grease before placing them on the opposite ends of the bar. The instrument was adjusted by the "Set-Ref" control until the reference bar transit time was obtained on the instrument read out. For maximum accuracy, 0.1 micro-second read out range was selected which could display transit times of up to 99.9 micro-seconds. After this procedure, the instrument was calibrated.

Velocity determinations on the specimens were carried out in a similar manner to that described in the instrument calibration. The mean value of the display reading was taken when the last digit moved between two adjacent values. The same dimensions used in the calculation of strength, namely, height and breadth of the specimen were used to calculate the sonic velocity after the transit time had been determined, using the relationship, velocity (V) = $\frac{\text{Path length (L)}}{\text{Transit time (T)}}$. If the transit time was measured across the breadth, the velocity was appropriately indicated $V_{\perp}$, velocity perpendicular to the direction of pressing, and if transit time was measured across the height of the specimen, the velocity was indicated as $V_{\parallel}$, velocity parallel to the direction of pressing.

The compositions used in the study of strength and dynamic elastic modulus of magnesia-graphite composites are described below. However, before going into details of the compositions studied, it is appropriate here to indicate that most of the work reported in the literature on the magnesia graphite composites is based on commercial specimens. Therefore, the compositions chosen in this part of the work were deliberately widened so as to try and identify the most likely potential areas of the composite characteristics and properties for detailed study in the future. As a result, some of the trends observed in this work have not been explained because more work is required to understand the factors influencing the mechanical properties of these composites.

5.3.5 Compositions Used in Determining the Mechanical Properties of Magnesia-Graphite Composites

The composites studied in this part of the work were constituted using Method 3 described in Section 4.2.2(iii) of Chapter 4 and the methods of preparing and testing the specimens were those described in the above sections of this chapter. Below is a list of the type of compositions used in the study of the physical properties of composites. All physical property measurements on the specimens were carried out after firing the specimens at 1500°C.

(i) Composites in which the n-value was varied, n = 0.3 to n = 1.0

(a) Specimens containing different size magnesia grains only.

The purpose in this part of the experiment was to study the effect of varying different size magnesia grains on strength and Young's modulus. This was achieved by determining these parameters at different n-values.

(b) Specimens containing 100 parts magnesia and 5 parts pitch.

Here, in addition to studying the effect of varying the grain size, the effect of pitch addition to the magnesia on strength and modulus was studied at various n-values.

(ii) Effect of varying graphite content at various n-values on strength and elastic modulus of the composites

(a) Specimens containing 90 parts magnesia + 10 parts graphite A + 5 parts pitch.

(b) Specimens containing 80 parts MgO + 20 parts graphite A + 5 parts pitch.

(c) Specimens containing 70 parts MgO + 30 parts graphite A + 5 parts pitch.

(iii) Effect of graphite type on strength and elastic modulus

Specimens containing 80 parts magnesia + 5 parts pitch + 20 parts graphite:

(a)	B
(b)	C
(c)	D

(iv) Study of the effect of varying the binder content in a fixed magnesia/graphite ratio on the physical properties of the composite at a fixed n-value

(a) Composites containing 80 parts MgO + 20 parts graphite A + varying amounts of pitch (3 parts to 15 parts of pitch with increments of 2 parts).

(b) Using the same MgO/graphite ratio as above, (iv(a)), but this time with a resin. The resin content being varied between 3 parts to 13 parts with increments of 2 parts as was done in pitch additions. The resin content was not raised to 15 parts because of the difficulties experienced in pressing the specimens when the resin content was being increased.

(c) To investigate whether the two resins influence the strength of the composites differently, the ratio of the resin was varied, but the total resin content was fixed at 5 parts resin to 100 parts of composite of a fixed magnesia graphite ratio, i.e., 80 parts MgO to 20 parts graphite A.

(v) Effect of metal additives on strength and sonic modulus of fired composites measured at room temperature

In this part of the work, the magnesia/graphite ratio was kept constant at 80 parts to 20 parts respectively.

(a) The aluminium metal additive was varied, at increments of 3 parts, from 2 to 11 parts of aluminium to 100 parts of composite.

(b) The silicon metal additive was varied, at increments of 3 parts, from 2 to 11 parts metal to 100 parts composite.

(vi) Effect of varying the maximum grain size of magnesia in the composite

Throughout the above listed compositions, the maximum grain size of the magnesia was fixed at 3.35 mm, thus the term, D = 3.35 mm in the equation $y = 100\left(\frac{d}{D}\right)^n$, (Section 4.1.2 of Chapter 4), was fixed. To investigate the effect of changing D on the mechanical properties of the composites, two sets of specimens were made from composites with D = 600 μm and D = 250 μm.

5.4 Calculation of Results

5.4.1 Strength

The bend strength of rectangular specimens was calculated from equation (12) of Section 5.2.1(a) for three-point bending, given in Section 5.2.1.

i.e.
$$\sigma_{max} = \frac{3WL}{2bh^2} \quad .$$

The force W = L x 9.81 N, where L is the breaking load in kg.

5.4.2 Dynamic Modulus

Equation (15) of Section 5.2.2(b) was used to calculate the dynamic elastic modulus.

Thus,
$$C_L = \left\{\frac{E(1-\nu)}{\rho(1+\nu)(1-2\nu)}\right\}^{\frac{1}{2}} \tag{15}$$

Rearranging this

$$\rho C_L^2 = Ef(\nu)$$

where

$$f(\nu) = \frac{(1-\nu)}{(1+\nu)(1-2\nu)}$$

In this work Poisson's ratio, ν, of the composites was not determined because of the difficulty in obtaining reproducible results on such a small value, using sonic velocity measurements techniques [73]. However, Poisson's ratio could be estimated by using Paul's [78] argument as follows:

(a) If the composite material is assumed to be uniform and homogeneous, i.e. each small section of the composite contains the same proportions of the two materials involved, and that

(b) the constituents are distinct and are capable of separation by mechanical means, then the following arguments can be used to determine the Poisson's ratio of the composite.

If ν_1, ν_2 and ν denote respectively the Poisson's ratio of the major phase, the minor phase and the composite, then a relationship between the volume fraction, $V_{n=1,2}$ of the constituents and Poisson's ratio may be found as follows:

$\nu = \nu_1$ when $V_1 = 1$ and $\nu = \nu_2$ when $V_1 = 0$, where V_1 and V_2 are volume fractions of the major and minor phase in a two-component composite respectively.

$$\therefore \qquad V_2 = 1 - V_1$$

The simplest relationship satisfying these conditions is that which results when it is assumed that both constituent materials contribute to the composite's Poisson's ratio in proportion to their own Poisson's ratio and fractional volume. Thus,

$$\nu = \nu_1 V_1 + \nu_2 V_2 \qquad (16)$$

This turns out to be the principle of predicting a property of a mixture of components as proposed by Nielsen[41] as shall be demonstrated later.

Therefore, if Poisson's ratio of graphite is taken to be 0.5, the maximum value[79], although this parameter changes with temperature for graphite and that of magnesia[80] as 0.25, then Poisson's ratio of the composite of known quantities of magnesia and graphite can be calculated using equation (16) above. However, the problem arises when a binder phase is present. It is known that the Poisson's ratio of polycrystalline graphites is low[79], about 0.2, then the Poisson's ratio of carbon derived from pitch can be approximated to be 0.2. Therefore, if the volume fractions of the components making up the composite are known, then Poisson's ratio of the composite can be calculated. For instance, a fired composite containing 80 parts magnesia, 20 parts graphite A and 5 parts pitch, would have Poisson's ratio of $\nu = 0.32$; and using $\nu_m = 0.25$, $\nu_g = 0.5$ and $\nu_p = 0.2$ for magnesia, graphite and pitch respectively, the value of $f(\nu) = 1.39$.

It is, however, important to note that

$$f(\nu) = \frac{(1-\nu)}{(1+\nu)(1-2\nu)}$$

is valid when $\nu \neq 0.5$.

In this work, bulk density and longitudinal sonic velocity of the specimens were determined, and from equation (15), Section 5.2.2(b), i.e.,

$$C_L^2 = \frac{E}{\rho} f(\nu)$$

it is clear that the dynamic (elastic) modulus, E_r, larger by a factor of $f(\nu)$, henceforth called relative elastic modulus, can be determined, i.e.,

$$\rho C_L^2 = E\, f(\nu) \quad ,$$

and since ν for all the materials used in this work is less than 0.5, $f(\nu)$ will vary between, perhaps, 1 and 1.5.

If the variation of f(ν) is very small between composites containing equal amounts of graphite, but of different types, then ρC_L^2 values can be used to compare the variation of dynamic modulus with different types of graphite used in the composite.

In this work, therefore, it is Ef(ν) which has been used to describe the behaviour of the relative elastic modulus of composites as described in the sections that follow below. The units are in giga pascals (GPa) since

$$\rho = x \text{ g/cc} = x \times 10^3 \text{ kg/m}^3$$

$$C_L^2 = y^2 \times 10^6 \text{ m}^2/\text{sec}^2$$

$$\therefore \quad \rho C_L^2 = \text{m}^2/\text{sec}^2 \,.\, \text{kg/m}^3 = (\text{kg} - \text{m/sec}^2)/\text{m}^2$$

$$= x\, y^2 = x\, y^2 \times 10^9 \text{ N/m}^2 = x\, y^2 \text{ GPa},$$

where x and y represent the actual figures of density (g/cm^3) and sonic velocity measured (m/sec) respectively.

In this chapter, as has been done elsewhere in this thesis, the curves have been drawn through the experimental points using the best polynomial fit, and most curves have been drawn by using a cubic parabola. However, where this method has not been satisfactory, hand fitting of the points has been used.

5.5 Results and Discussion

5.5.1 Magnesia Compacts

Figure 5.5.1(a) shows a plot of strength and porosity against n-value. The fall in strength is accompanied by the rise in porosity as expected of a fired ceramic body. However, the increase in porosity is also a clear indication of poor packing of the compacts at high n-values as observed in the packing experiments described in the previous chapter (see Figure 4.4.2).

The magnesia used in this work was sintered magnesia, which is generally carried out around 1650°C. Therefore these magnesia compacts would not be expected to develop much solid-solid bonding at 1500°C, the temperature at which they were fired. It would then seem that most of the bonding was due to the glass phase formed from the silicate system in the magnesia, implying that the interparticle bonds will be weaker than they would have been if solid-solid bonding occurred between the particles. Since the interparticle bonds are weak, then the strength of such compacts may be related directly to the critical load bearing area which is transversed by an irregular cross-sectional surface passing between grains[81]. At lower n-values, i.e., with a large proportion of magnesia fines, the number of magnesia-magnesia contacts is increased by the presence of many fine grains in the interstices of larger magnesia grains. In this way, the residual glass phase bonding, even if it is very low per individual grain, increases the total load bearing area of the compacts because of the large number of contacts, hence the increase in strength.

The effect of fine fractions on strength is exemplified if the strength difference between $n = 0.3$ and $n = 0.5$ in Figure 5.5.1(a) is compared with the difference in the amount of fine magnesia grains ($< 150\ \mu m$) which is 39.4 $^{w}/o$ at $n = 0.3$ and 21.2 $^{w}/o$ at $n = 0.5$ as reported in Appendix 4.2.1 (Table 1(b)) of Chapter 4. To demonstrate that the load bearing area decreases with increasing n-value, specific surface areas of the magnesia grain size mixtures were estimated from the relationship given below:

i.e.,

$$S = \frac{6}{\rho\ d} \qquad (17)$$

where S is the specific surface area (m^2/g), ρ is the density in g/cc and d is the diameter of the particles in microns.

The diameter of the particles in each sieve range was estimated by taking the mean size aperture of the two sieves and the density used was the powder density of the magnesia (3.44 g/cc = 3.44×10^3 kg/m^3) reported in Table 2.3.3(i) of Chapter 2. This density was used after assuming that the bulk density of the grains is about the same as that of the powder density of the magnesia, i.e., the grains were assumed not to contain any closed pores.

Figure 5.5.1(b) is a plot of the calculated specific surface area against n-value. The specific surface area (SSA) decreases with increasing n-value as expected, because as n-value increases the amount of larger particles increases (see Appendix 4.2.1, Table 1(b) of Chapter 4). With this decrease in SSA with increasing n-value, it is not surprising that strength falls with the increasing n-value as shown in Figure 5.5.1(a) because, as already discussed above, the strength of these magnesia compacts depends on the number of particle-particle contacts. When this number is high the strength is high as well. Figure 5.5.1(c) is a plot of strength of the compacts against SSA and a linear relationship was obtained. This figure confirms the earlier argument that the strength of these compacts depends on load bearing area in addition to the size and distribution of pores, and other defects in the compacts, such as cracks, etc.

Figure 5.5.1(d) is a plot of relative elastic modulus Ef(ν) (see Section 5.4.2) V's n-value. The variation of Ef(ν) against n-value is identical to that of strength shown in Figure 5.5.1(a). This implies that there should be a linear relationship between the modulus and the strength. The arguments advanced for the lowering of strength with increasing n-value also apply to the relative elastic modulus, because at lower n-values, the number of grain contacts is high, and therefore there are fewer defects which affect the propagation of the waves than at higher n-values at which there are larger defects, mostly voids (porosity increases with increasing n-value, Figure 5.5.1(a)) which have to be circumvented by the sonic waves resulting in low velocities, hence lower relative modulus.

Figure 5.5.1(e) is a plot of elastic modulus and porosity against strength of the compacts. The porosity falls to a minimum and increases slightly again in the region where strength increases. It is important to emphasize here that this particular plot does not mean that porosity depends on strength but vice versa.

The elastic modulus-strength plot shows a linear relationship as suggested earlier on in this section. If the straight line is extrapolated to zero strength, there would be a residual relative elastic modulus. This is not surprising because if magnesia, graded in the same way as in this work, was pressed, the assemblage would almost have zero strength except for frictional forces between particles. However, the elastic (dynamic) modulus can still be determined this way because of the intrinsic modulus of the solid particles. The nearest to this situation is to determine the elastic (dynamic) modulus of green specimens, but this was not done here because the specimens were too weak to be handled.

A high intercept value can also arise from errors in the actual measurements, such as improper contact between the specimen and transducer surfaces, misalignment of the transducers at the opposite surfaces of the specimens being measured, etc. Furthermore, the equations given in Section 5.4.2 are only valid by assuming that, "the stress applied in sonic velocity measurements is very small, therefore Hooke's law can be applied, because with such small stresses only elastic deformation may occur to the material and that the quantities of stress σ and Poisson's ratio, ν, are constants during the period of measurement"[73]. This may not necessarily be true that σ and ν are constants during the propagation of the sound waves, particularly σ, which depends on how the transducers are held against the specimen.

To study further the effect of porosity on the relative elastic (dynamic) modulus ($Ef(\nu)$), plots of the modulus against porosity of fired compacts were made as shown in Figure 5.5.1(f). The relationship between the two parameters is not clear. From Figure 5.5.1(d), the highest modulus occurs at n = 0.3 with a porosity value of 16.4 and the next highest modulus occurs at n = 0.4 with a slightly lower porosity of 16.1 before the porosity begins to increase while the modulus continues to fall. The plot in Figure 5.5.1(f) is not a real relationship that the modulus passes through a maximum and then falls again as porosity increases. Therefore the effect of porosity on the relative modulus is not obvious in this case.

5.5.2 100 Parts Magnesia + 5 Parts Raw Pitch

The strength, relative elastic modulus ($Ef(\nu)$) and porosity measurements against n-values are plotted as Figures 5.5.2(a) and (b) respectively. The curves show that over the range of n-values the magnitudes of the strength and elastic moduli are reduced by factors of the order of 10 and 4 respectively compared to the strength and modulus values shown in Figures 5.5.1(a) and Figure 5.5.1(d). However, there is also a noticeable porosity increase of about 6% for all n-values compared with the values shown in Figure 5.5.1(a), but the porosity difference between the lowest and the highest porosity value is still about 3% as before.

The fall in strength when pitch is added is by a factor of about 12 to 10 in the increasing n-value respectively. For instance, when $n = 0.3$ strength = 2.1 MPa for specimens containing pitch, that is after coking the specimens at 1500°C, while specimens containing magnesia only, show a strength of 25 MPa for the same n-value. Similarly at $n = 1.0$, the strength of specimens containing pitch is 0.8 MPa while those specimens containing magnesia only have a strength of 7.8 MPa. The other point to note from Figure 5.5.2(a) is that the fall in strength between $n = 0.3$ to $n = 0.5$ is very small compared with that observed from the "direct bonded" magnesia in Figure 5.5.1(a). The lowering of strength when pitch is added to the magnesia may be understood in terms of the bonding, if any, between magnesia and carbon. Cooper[37] has indicated the problems encountered in the manufacture of oxide-graphite composites. One such difficulty is the lack of bonding of graphite to an oxide. This non-bonding behaviour of these two is due to differences in the chemistry of the two materials. For instance, at temperatures at which sintering of the oxide takes place the graphite is effectively inert (graphite does not melt but sublimates at temperatures > 3000°C). Under these conditions, therefore, bonding between the refractory oxide and a carbon cannot be expected to take place. Plate 5.5.2(a) shows a fractured surface of a fired specimen made from 100 parts MgO + 5 parts pitch. The magnesia grains are completely coated with pitch coke. The shrinkage cracks of the pitch are very much in evidence on the magnesia grains. Plate 5.5.2(b) shows the pitch coked at 1500°C. The cracks in the coked pitch are identical to those shown in Plate 5.5.2(a). The important features of Plate 5.5.2(a) are that the magnesia grains have pitch carbon around them. This invitably destroyed the liquid phase sintering which took place in the carbon-free magnesia because the liquid so formed will not penetrate through the carbon layer covering the individual grains to link-up with the other grains to form a bond since the carbon is not wetted by the liquid. Further, the solid-solid contacts are now separated by a thin layer of carbon which itself does not make a firm contact with the magnesia because it does not bond with the oxide. This factor, together with the loss of the liquid sintering, reduces the loading bearing area further, due to increased number of cracks around MgO grains, hence the drastic fall in strength. The fall in strength can therefore be attributed to loss of the ceramic bond and the structure is only held together by the physical contacts and interaction of the particles, in addition to the keying effect of the pitch provided for in-between the magnesia grains.

The strength of a material is affected by Young's modulus, E, effective fracture surface energy (or work of fracture), γ, and defect size (crack size or length), C. These factors are related to each other in Griffith's[60] equation (6) given in Section 5.1.1(a) as follows:

$$\sigma_m = \left(\frac{2E\gamma}{\pi C}\right)^{\frac{1}{2}} .$$

According to this equation, strength can only come down if E and γ fall or the crack length, C, increases. In this work, work of fracture γ and crack length, C, were not determined, making it difficult to explain precisely why strength falls when pitch is added. However, the values of relative elastic modulus may particularly help to explain this fall in strength. Therefore a plot of relative elastic modulus ($Ef(\nu)$) against n-value is made in Figure 5.5.2(b). This Figure shows that the elastic modulus has also dropped but to a less degree than strength did. Here the modulus has dropped by a factor of about 3 to 5 over the various n-values, since the modulus also falls when pitch is added, this fall in E is one of the contributing factors in the fall of strength, but this may not be the major factor because its fall is only by a factor of about 4 while the strength fall is by a factor of 10. Therefore parameters such as γ and C may have been the major factors in the fall of strength.

Figure 5.5.2(b) also shows that the relative modulus increases with n-value, passes through a maximum before it begins to fall again at higher n-values. The fitted curve to data shows that the maximum modulus occurs around $n = 0.8$. However, the scatter of points is found to be as high as 30%. This phenomenon where the modulus passes through a maximum is surprising, because at lower n-values the number of particle to particle contacts is expected to be high and therefore the modulus should have been highest. Further, if it is argued that the surface area at lower n-values is high such that there is not enough pitch to coat all the magnesia grains and residual MgO-MgO bonding took place which is consistent with the strength plot against n-value, Figure 5.5.2(a), then the modulus should have been high at lower n-values and decreasing with the increasing n-value. On the other hand, if it is argued that the size of cracks between magnesia grains coated with pitch increases with n-value because of the increase in the grain size, then modulus must fall with the increase in n-value without passing through a maximum. The trend observed in Figure 5.5.2(b) is more complex and the need to understand how the sound waves are propagated through such a chemically unbound matrix need to be understood. Obviously, the sound waves are affected by the number of discontinuities, size of defects, shape and their distribution in the propagating medium. It is clear from the above discussion that to understand fully the variation of elastic modulus with grain size (n-value) in a chemically unbonded system, a more detailed study is required, as already suggested. Perhaps the best approach would be to study the fracture behaviour of such materials at selected n-values in addition to studying the elastic modulus. Such a study would involve determining the work of fracture by determining the stress-intensity factor [59], K_I, also known as fracture toughness. This may help to find out whether the crack sizes in the system vary with n-value, and, if so, how do these crack sizes vary with the measured moduli at these n-values.

Fracture toughness can be related to the applied stress, σ_S, and crack length, C, by

$$K_I = \sigma_S \, Y \, C^{\frac{1}{2}}$$

where Y is a dimensionless term determined by the crack propagation and loading geometry[59]. "Comparing with the Griffith equation" (Section 5.1.1(a), equation (6)) "reveals the following equalities:

$$\sigma_S = \frac{1}{Y}\left(\frac{2EY_0}{C}\right)^{\frac{1}{2}} = \frac{K_{Ic}}{YC^{\frac{1}{2}}} \qquad (18)$$

where K_{Ic} is the critical value of K_I for fracture" [59].

When a plot of Ef(ν) against strength was made, the modulus passed through a maximum before it began to fall, as shown in Figure 5.5.2(c). The relationship between Ef(ν) and strength is completely different from that obtained in Figure 5.5.1(e). This is not surprising in that Ef(ν) behaves differently as n-value is varied as shown in Figure 5.5.2(b). Therefore, a plot of Ef(ν) against strength does not prove anything. However, the plot of porosity against strength shows that the porosity falls slightly with increasing strength, implying that the strength may be affected by porosity, as expected.

Finally, a plot of elastic modulus against porosity is shown in Figure 5.5.2(d). As previously found in Figure 5.5.1(f), the modulus passes through a maximum and then falls at high porosity values. As has been shown above, the elastic modulus does not depend on porosity at least in these chemically unbonded materials. The plots of elastic modulus against porosity do not show any particular trend because they are independent of each other and such plots when found to behave similarly to those in Figures 5.5.1(f) and 5.5.2(d) will not be reported any further.

5.5.3 Composites Containing 90 Parts MgO + 10 Parts Graphite A + 5 Parts Pitch

To try to understand further the effect of increasing the carbon content on strength and the relative elastic modulus, Ef(ν), 10 parts of graphite A was added to 90 parts of magnesia containing 5 parts pitch as a binder. It is important to note that the addition of graphite was made not to try to increase the binding effect but rather to investigate how the presence of graphite in various amounts, as described later, would affect the properties of the composite. Therefore the results of strength, elastic modulus, in terms of $Ef(\nu) = \rho C_L^2$ as shown in Section 5.4.2, and porosity of composites containing 10 parts graphite against n-value, are plotted as Figures 5.5.3(i)(a) to (c).

Figure 5.5.3(i)(a) is a plot of strength, parallel and perpendicular to the direction of pressing of the tested specimens and porosity against n-value. The figure shows that there is a further reduction in strength when graphite was added, compared to specimens containing pitch only (see Figure 5.5.2(a)). The further lowering of strength when graphite is added will be discussed later in this section. Figures 5.5.3(i)(b) and (c) have been included to show the variances (±S) of strength at each n-value (S = standard deviation of strength of ten specimens measured at each point plotted). The addition of graphite has also reduced the porosity, bringing it down almost to the same levels of porosity of specimens containing magnesia fractions only. Figure 5.5.3(ii)(a) is a plot of elastic modulus against n-value. Similarly here there has been a further reduction of elastic modulus. In this figure it can also be seen that the difference between elastic modulus measured in the direction of pressing to that measured perpendicular to the direction of pressing, is evident. This obviously is the effect of orientation of the graphite flakes during pressing. The difference in orientation of the graphite flakes in the direction and perpendicular to the direction of pressing, is shown in Plate 4.4.3(iii)(a)-(b) of Chapter 4. The modulus in the direction of pressing (‖) is lower than that perpendicular to the pressing direction. Two reasons can be advanced for this difference: (i) the first one is, possibly, due to practical limitations of the method used to determine relative elastic modulus, thus the surfaces parallel to the direction of pressing (opposite surfaces of breadth) which were used to measure the modulus perpendicular to the direction of pressing were a lot more smooth than the surfaces perpendicular to the pressing direction which were used to determine the modulus parallel to the direction of pressing. This means that the contacts between the transducers and specimen surfaces were more firm when measuring the velocity perpendicular to the direction of pressing. Therefore, there could have been less scatter of sound waves at the interface than there was, possibly, at the opposite surface. This may have resulted in high velocities being obtained. (ii) The second reason is, most likely, due to the differences in the orientation of the graphite. If it is argued that in the direction of pressing there are more flakes with the surfaces containing length and breadth lying normal to the direction of wave propagation, then it is likely that the number of waves scattered due to large cracks between magnesia and graphite flakes (there is no bonding between the two) is very high. Further, the graphite flakes themselves have large interlaminar cracks which will also hinder the smooth propagation of the waves. These two factors alone, could reduce the velocities of the waves in the direction of pressing. However, if it is assumed that there are more graphite flakes orientated in such a way that they present their prismatic edges perpendicular to the direction of pressing, then the contact area between MgO and the flakes is very small, therefore the cracks along the contact points is small indeed, their size (crack size or length) being determined by the flake thickness and grain size at the point of contact. Such small cracks may not scatter a large number of sound waves at the same extent as a large crack formed by the flake surface and a MgO grain at the contact point. Furthermore, the interlaminar cracks of the graphite flakes if lying parallel to the direction of wave propagation, may not have the same scattering effect as they would if lying normal to the direction of propagation. From these two arguments then, relative modulus perpendicular to the direction of pressing must be higher than it is in the direction of pressing.

The fall in both strength and elastic modulus may be described in terms of the microstructure. In Section 5.5.2 above, it has been shown that when magnesia grains are coated with pitch, the grains are separated by thin films of pitch at contact points and no bonding of magnesia grains takes place, hence the lowering of strength and relative elastic modulus. The addition of 10 parts of graphite to 90 parts magnesia containing 5 parts pitch reduces the strength further, as already shown above. Using the same argument that there is no chemical bond between carbon and magnesia, for that matter any other oxide, the introduction of graphite introduces larger cracks along the magnesia-graphite interphase. If an ideal situation is assumed and applying Griffith's[60] equation (6)

i.e.,

$$\sigma = \left(\frac{2E\gamma}{\pi C}\right)^{\frac{1}{2}}$$

then it becomes clear that when C is large, other parameters being the same, strength, σ, is reduced. Of course, the strength of a material in practice is determined by many factors, such as size, distribution, shape, and position of defect, testing conditions etc. It would seem reasonable to argue that the addition of graphite (~ 10 w/o) introduces larger cracks, possibly equal in size with the flake length.

Plates 5.5.3(i)-(iii) show the microstructural characteristics of some of the specimens, containing ~ 10 w/o graphite A tested in this work for n = 0.3, n = 0.5 and n = 1.0. Clearly, the graphite flakes are dispersed in the matrix particularly at lower n-values. Therefore, wherever there is a flake, there is crack of the same length as the flake. At n = 1.0, however (Plates 5.5.3(iii)(a)-(b)), the graphite-graphite contacts have increased, but then the amount of large magnesia grains has increased as well implying that the MgO-graphite interface, hence the size of cracks, has increased, and the strength is also reduced further as Griffith's equation predicts.

The lowering of the elastic modulus from the MgO/pitch specimens is, perhaps, a result of two factors:

(a) The increased crack sizes by the introduction of graphite flakes as discussed above. At the magnesia-graphite interface the sound waves experience a high scatter because of differences in the impedance of the two materials. They also suffer a further scatter because there is always a crack associated with the MgO-graphite interface, or the propagating wave may have to circumvent the long crack resulting in longer time of travel. Plates 5.5.3(iv)(a) and (b) show the non-bonding of a graphite flake to the magnesia grains in the composite bonded with pitch, and the non-bonding of MgO-MgO particles when coated with a carbon phase respectively. Both micrographs show the same field of view but at different magnifications. In Plate 5.5.3(iv)(a) the crack along the bottom part of the flake is evident, (the bright long phase in the middle of the micrograph is a graphite flake.

(b) The graphite itself has a lower relative elastic modulus as shown in Table 5.5.3. Using the Voigt[64] model (which assumes constant strain and gives an upper bound for Ef(ν)) and the Reuss[65] model (which assumes constant stress and gives a lower bound), the term Ef(ν) for the composites containing 90 parts MgO + 10 parts graphite A + 5 parts pitch was calculated at each n-value according to equation (7), Section 5.1.1(b) for elastic modulus E, and this method of determining the upper bound can be extended to other calculations, thus:

$$\rho C_L^2 = \rho_m C_L^2 V_m + \rho_g C_L^2 V_g \qquad \text{(Voigt[64])}$$

and using the same analogy as given in equation (8) of Section 5.1.1(b), the lower bound (Reuss[65] model) can be calculated, i.e.

$$\frac{1}{\rho C_L^2} = \frac{V_m}{\rho_m C_L^2} + \frac{V_g}{\rho_g C_L^2}$$

where the term $\rho_m C_L^2$ is that obtained experimentally from the magnesia-pitch mixture given in Table 5.5.3, $\rho_g C_L^2$ is the relative elastic modulus term also given in the same Table and V_m and V_g are the volume fractions of MgO and graphite respectively and $\rho C_L^2 = Ef(\nu)$ is the relative elastic modulus of the composite.

The calculated upper and lower bounds against n-value of the composite are plotted in Figure 5.5.3(ii)(b). The measured values of the composite (Figure 5.5.3(ii)(a)) are close to the lower bound curve of Ef(ν). This simple calculation demonstrates that the lowering of the modulus when graphite is added to the magnesia is also as a result of the lower modulus of the graphite, in addition to the increased number and size of cracks in the composite.

Finally, the increase in modulus towards high n-values (Figure 5.5.3(ii)(a)) is, perhaps, a result of increased graphite-graphite contacts, thus providing a continuous phase for efficient wave propagation.

Plots of elastic modulus normal and perpendicular to the pressing direction and porosity against strength are shown in Figures 5.5.3(iii)(a) and (b). The elastic modulus falls with increasing strength. This is in agreement with Figures 5.5.3(i)(a) and 5.5.3(ii)(a) which show decreasing strength and increasing relative elastic modulus with increasing n-value respectively. Furthermore, the porosity shows an increase with the decreasing strength .

In this section it has been shown that a small amount of graphite (approx. 10 $^w/o$) reduces strength as well as elastic modulus. To investigate further the effect of graphite on the composite, the amount of graphite was increased to about 20 $^w/o$ and the section below discusses the results.

5.5.4 Composites Containing 80 Parts Magnesia + 20 Parts Graphite A + 5 Parts Pitch

Similar data treatment as that carried out for the composites containing 10 parts graphite A was followed here.

A plot of strength and porosity against n-value is shown in Figure 5.5.4(i)(a). The plot is for the mean values only, for clarity, while Figure 5.5.4(i)(b) and (c) are the same plots, strength parallel and perpendicular to the direction of pressing, respectively, but include the variances (± standard deviation) of strength.

Figure 5.5.4(i)(a) shows that the strength of the composite increases slightly when the graphite content is raised to ~ 20 $^{w}/o$ from ~ 10 $^{w}/o$ graphite (see Figure 5.5.3(i)(a)). Furthermore, the strength difference between strength values obtained from the two directions of testing seems to have increased, but it is so small that it may not be significant when variances are taken into consideration.

The increase in strength can be explained by examining Plates 4.4.3(iii)(a)-(c) of Chapter 4. Note should be taken that the plates show the microstructure of a composite containing 20 parts graphite B, not A. As has been indicated in Section 4.4.3(iii) that the microstructural texture of composites containing the same amount of graphite but of varying types, is similar, therefore the plates can be used to explain the effects on strength and modulus of composites containing the same amount of graphite A as that of B.

Plates 4.4.3(iii)(a)-(c) show the texture variation of the microstructure with n-value. If these Plates are compared with Plates 5.5.3(i)-(iii), it is clear that the number of graphite-graphite contacts in Plates 4.4.3(iii)(a)-(c) is more than in Plates 5.5.3(i)-(iii) at each corresponding n-value. This increased contact seems to have two effects:

(a) the magnesia-magnesia contacts are, possibly, reduced, but the large amounts of graphite now available have taken over the keying effect provided for by the pitch when very little or no graphite was present in the matrix, as discussed in the previous two sections. Since the graphite flakes are larger and elongated particles than coked pitch particles, their keying effect, if this is the mechanism which provides strength to the composite in the absence of bonding, is more effective because they would act as a fibrous continuous matrix in the composite.

(b) the porosity of the composite has further been reduced from that obtained when graphite content was only about 10 $^w/o$, underlining the fact that the presence of more graphite has further filled the cavities between the magnesia grains and therefore the graphite is becoming more continuous in the matrix than it was when only ~ 10 $^w/o$ was added.

The elastic modulus, on the other hand, has not changed very much from that obtained in composites containing ~ 10 $^w/o$ graphite A, and Figure 5.5.4(ii) is a plot of relative elastic modulus against n-value. If this Figure is compared with Figure 5.5.3(ii)(a) it is clear that the modulus has dropped further by the addition of more graphite. This overall reduction in modulus when graphite is increased can be attributed to the increased graphite content which has a lower modulus than MgO as argued in Section 5.5.3 in which the expected lower and upper bound were calculated, using Reuss[65] and Voigt[64] models respectively.

Figure 5.5.4(ii) shows that the modulus passes through a maximum before it begins to fall, as was observed in Figure 5.5.2(b). The reason why the modulus passes through a maximum is not clear and a detailed study of various parameters, as suggested in Section 5.5.2, may help to clarify this phenomenon. The slight increase in strength when the graphite content is increased, has been attributed to the interlocking mechanism of the graphite flake in the composite. If this is true, it would mean that a further increase in graphite content should increase the strength of the composite. The section below discusses the results obtained when this was done.

5.5.5 Composites Containing 70 Parts MgO + 30 Parts Graphite A + 5 Parts Pitch

Following the same pattern of plotting the results as in Figures 5.5.3 and 5.5.4, Figure 5.5.5(i)(a) is a plot of strength and porosity against n-value, while Figures 5.5.5(i)(b) and 5.5.1(i)(c) are plots of strength with its variances normal and perpendicular to the direction of pressing, respectively, against n-value.

Figure 5.5.5(i)(a) shows that the strength of the composite in the two directions tested (normal and perpendicular) is about the same. The intertwining of the curves is, possibly, a confirmation that the orientation of the graphite flakes does not have a profound effect on strength, as argued in the previous two sections immediately above. The plot of porosity against n-value is shown in the same Figure, and as has been observed in the previous composites described in Sections 5.5.3 and 5.5.4, porosity here also falls with increasing n-value.

Figure 5.5.5(i)(a) shows that the strength of the composite has increased markedly (relative to the composites containing less graphite) from a strength value of about 2 MPa for composites containing about 20 $^{w}/o$ graphite A at n = 0.3, to 4 MPa when the graphite content was increased to ~ 30 $^{w}/o$ at the same n-value. Similarly, the strength has increased from about 1.0 MPa at n = 1.0 to greater than 2 MPa at n = 1.0

when ~ 30 $^{w}/o$ graphite was added. This increase in strength is now almost certainly due to the keying effect suggested earlier on. The porosity has increased slightly, not possibly due to poor packing but due to increased volume fraction of the graphite which has inherent porosity, much higher than the magnesia grains. This porosity increase is only about 1% (actual porosity value) higher than porosity values obtained from composites containing less graphite content at all n-values.

Figure 5.5.5(ii) is a plot of relative elastic modulus, Ef(ν), against n-value. The elastic modulus, normal and perpendicular to the direction of pressing is almost a constant. This constant value of elastic modulus with n-value seems to suggest that the graphite is now continuous at both ends of the n-value. Furthermore, the modulus parallel to the direction of pressing in Figure 5.5.5(ii) is, probably, higher than the modulus obtained in the same direction for composites containing ~ 20 $^{w}/o$ graphite. However the modulus measured perpendicular to the direction of pressing is evidently higher than that obtained from composites containing less graphite. It is also interesting to note that the difference in modulus between the modulus obtained parallel to the direction of pressing and the one obtained perpendicular to the direction of pressing has almost doubled compared to the differences in Figures 5.5.3(ii)(a) and Figure 5.5.4(ii). This increased difference in the two directions of measurement is due to increased orientation of the flakes, as discussed in Section 5.5.3.

Plates 5.5.5(i)(a)-(d) show that at both ends of the n-value, the graphite contacts have increased compared with composites containing less graphite (see Plates 4.4.3(iii)(a)-(c) and 5.5.3(i)-(iii)). Judging from the microstructure and Figure 5.5.5(ii), graphite is now the main propagating medium of the sonic waves (30 $^{w}/o$ graphite A $\simeq$ 50 $^{v}/o$) since the graphite makes the continuous matrix while the magnesia grains are more separated from each other as Plates 5.5.5(i) (a)-(d) show.

The information obtained above is vast and it is perhaps appropriate at this point to summarize what is known so far before discussing the possible implications of adding graphite to magnesia on thermal shock resistance (TSR) and the section below summarizes the results and the possible implications on TSR are discussed after summarizing the results.

5.5.6 Summary of the Observations Made on the Magnesia-Graphite Composites When the Amount of Graphite A was Varied and the Implication on Thermal Shock Resistance

The observations can be summarized best, perhaps, by plotting various parameters against graphite content. This, for instance, is shown in Figure 5.5.6(i) where strength of the composite at various carbon content is plotted against n-value. The composite containing 10 parts graphite A + 90 parts magnesia and 5 parts pitch shows the lowest strength, magnesia + pitch together with the composite containing ~ 20 $^{w}/o$ graphite have about the same strength. The superiority in strength of the composite containing ~ 30 $^{w}/o$ graphite is clearly seen in the Figure.

To demonstrate further the effect of graphite content in the composite on strength at each n-value, the latter is plotted against the carbon content (residual coke from pitch + graphite), Figure 5.5.6(ii). The strength values of magnesia only have not been included because they are significantly higher than those of the composites. The addition of a small amount of carbon (pitch) reduces the strength of the magnesia grain size mixture by a factor of about 9 to 12 (see Section 5.5.2), an addition of about 10 ^{w}/o graphite reduces the strength, but further addition of graphite results in a strength increase again. This strength increase is more significant as the amount of graphite is raised from ~ 20 ^{w}/o to ~ 30 ^{w}/o graphite.

Figure 5.5.6(iii) is a plot of porosity against ^{w}/o carbon in the composite and shows that the addition of pitch increases the porosity; this porosity rise is, possibly, due to evolution of volatile matter during coking which does not happen in the magnesia compacts only. However, when 10 ^{w}/o graphite is added the porosity is reduced, implying better packing. With further addition of graphite (20 ^{w}/o A), porosity decreases further while strength increases, as already shown above. When the graphite content is raised to 30 ^{w}/o (50 ^{v}/o), the porosity begins to increase again. This increase in porosity is due to increased inherent porosity of the graphite, in addition to an increase in the permanent volume change when the amount of graphite is increased. This volume increase was observed in the composites studied in Chapter 4 and the porosity increase after firing was attributed, partly, to this volume change. This was first proposed by Mrozowski[82] after observing that dense graphitic bodies could not be produced. He proposed that, after firing, the flake graphite in bulk structures does not contract in a manner which will cause the body to shrink, but opens up through its cleavage planes. Cooper[37] indicates that in a typical refractory containing about 50 ^{v}/o graphite, some 5% of the porosity could arise in this manner. It seems, from the arguments presented above, that volume expansion caused the porosity increase rather than poor packing.

Figure 5.5.6(iv) is a plot of elastic modulus, $E \times f(\nu)$, against carbon content in the composite. The figure shows that the elastic modulus is greatly affected by the addition of small amounts of pitch as shown in Figure 5.5.1(a). The modulus falls further by adding 10 $^{w}/o$ graphite in the composite. Further addition of the graphite does not change the elastic modulus. The lowering of elastic modulus when graphite is added is almost certainly due to the introduction of large cracks as a result of non-bonding of graphite-magnesia at the interface, therefore cracks as large as the interface exist along the contact points, Plate 5.5.3(iv)(a). Furthermore, graphite itself has shown to have lower relative elastic modulus due to, perhaps, the presence of widely distributed Mrozowski[82] cracks in the graphite flakes.

The most significant observation from Figures 5.5.6(ii) and (iv) is that when graphite is increased to 30 $^{w}/o$ from 20 $^{w}/o$, the strength increases while elastic modulus remains constant. Assuming an ideal situation again, Griffith's[60] equation (6), Section 5.1.1(a), may be used to explain the strength increase, i.e.,

$$\sigma = \left(\frac{2E\gamma}{\pi C}\right)^{\frac{1}{2}} .$$

From this equation then σ can increase if E and γ go up or at least one of them, or C, is reduced. In the present situation (composites containing 30 $^{w}/o$ graphite), E is a constant and it is difficult to say whether C has been reduced, increased or remains constant, when graphite content is raised from 20 $^{w}/o$ to 30 $^{w}/o$. Since it is not possible to decide which of the two parameters (γ or C) has changed, an examination of the fracture surfaces (fractography) may help because high work of fracture in graphite composites is attributed[37] to various factors, viz:

(a) A tortuous crack path and crack branching caused by graphite. Plate 5.5.6(i) shows a tortuous crack on one of the specimens containing ~ 20 $^{w}/o$ graphite tested in this work. Such a crack path would require more energy to propagate once started, compared to a straight crack initiated in oxide refractories where bonding is of the chemical nature.

(b) Graphite can act as a plate-like reinforcement, absorbing energy either through pull-out or actual plate fracture. Plates 5.5.6(ii) and 5.5.6(iii) show the flakes being pulled out from one half of the specimen.

(c) Graphite has the ability to absorb energy through basal plane slip. Plate 5.5.6(iii) exemplifies this point. This would therefore mean that some of the energy would go into creating new surfaces.

From these factors described above and the evidence given in the plates, it is almost certain that the strength increase when graphite content is being increased, greater than say 10 $^w/o$ in the composite, is due to increased surface energy, i.e., work of fracture. Landy et al.[52] showed that work of fracture increases with increasing graphite content. For instance, three types of commercial carbon-magnesia bricks, all special chemically bonded type, containing 18 $^w/o$, 28 $^w/o$ and 37 $^w/o$ total carbon, were found to have work of fracture (γ_{wof}) of 63, 87 and 108 J/m^2 respectively. These workers[52] did not, however, observe an increase in strength with the increasing residual carbon content as has been observed in this work. In fact, they observed a slight decrease in strength with increasing carbon content. For instance, when the carbon content levels were 18.3, 28.0 and 37.0, the strengths (MOR) were 11.3, 10.7 and 10.4 MPa respectively for these special chemically bonded commercial bricks. It is important to note that these strength values cannot be compared directly with those obtained in this work because of:

(a) difference in bonding phase used;

(b) the gradings and type of magnesia used by these workers are unknown; and

(c) type of graphite used.

Using Griffith's equation (6) then strength has increased because γ has increased when graphite content is raised to 30 $^w/o$, assuming C has not increased since the load bearing phase, graphite, is continuous.

Davidge et al.[61] have shown that the area under the curve of a stress-strain curve obtained from a notched specimen is directly proportional to total work, U, done during the test. For a three-point bend test on a rectangular notched specimen, the fracture energy, γ_F, is given[61] as:

$$\gamma_F = \frac{U}{2b(d-c)}$$

where b = breadth, c = crack depth, d = specimen depth and U is the total work done to fracture the notched specimen. Therefore the variation of area under the stress-strain curve gives a direct indication of how the work of fracture varies. Figure 5.5.6(v)(a) shows the stress-strain curves of composites containing varying amount of graphite (~ 0 $^w/o$, 10 $^w/o$, 20 $^w/o$ and 30 $^w/o$) at n = 0.3. The area under the stress-strain curves of specimens containing magnesia and pitch is very small compared to that of specimens containing 10 and 20 $^w/o$ graphite. Clearly, the work of fracture increases as the graphite content increases. However, for the composites containing 30 $^w/o$ graphite, the area under the curve is larger than it appears (should be twice as much) because the full scale load (20 kg) deflection on the chart is twice that used for specimens containing less graphite (10 kg). Therefore, the work of fracture is very high for specimens containing 30 $^w/o$ graphite.

Figure 5.5.6(v)(b) shows the stress-strain curves of the same composites discussed above but at n = 0.7. The immediate noticeable feature is that the curves are more rounded at the failure tips than those at n = 0.3, suggesting deformation of specimens before complete failure occurred. It is difficult to say whether the area under the curve has increased because as much as the curves have widened, their heights have been reduced, because the specimens are weaker at high n-values.

Figure 5.5.6(v)(c) shows the stress-strain curves of the same composition at n = 1.0. Clearly, the failure tips of graphite containing specimens are more rounded than previous, indicating more graphite flakes are being stressed because only graphite flakes can relieve stresses in these composites through flake slip or graphite flakes being pulled out of the matrix, i.e., acting like a fibre in the matrix. This can only happen if the graphite component in the composite is continuous. The other interesting feature in this figure is the apparent inherent strength of the composite containing 30 $^{w}/o$ graphite after failure. This non-catastrophic failure in such a material should show high thermal shock resistance because of higher strain.

Equation (3) of Section 5.1.1 relates work of fracture, elastic modulus and coefficient of thermal expansion to thermal shock parameter, R_{st}, as:

$$R_{st} = \left(\frac{\gamma_{wof}}{E\alpha^2}\right)^{\frac{1}{2}} .$$

Further it has been indicated in the same section that for the material (product) to have very high thermal shock resistance, R_{st}, must be high to hinder any possible fracture propagation. From the above discussion, it is now apparent why magnesia-graphite composites have high thermal shock resistance. Firstly, the work of fracture γ_{wof} increases with graphite content and secondly, the elastic modulus is very much lower than it is in the oxide materials on their own. The thermal expansion of graphite containing refractory composites is said to be negligible "probably due to the presence of 'Mrozowski'[82] cracks, which introduce porosity into which graphite moves on expansion"[37]. All these three parameters are in favour of increasing R_{st}, hence higher thermal shock resistance. From the results discussed above, it is evident that high thermal shock resistance can be obtained if the graphite component in the composite makes a continuous matrix, apparently the graphite content in the composite must be greater or equal to 20 $^{w}/o$ graphite to realize high TSR, because only at these levels of graphite does work of fracture increase significantly.

The composites discussed in this section contained a fixed amount of binder pitch, therefore there was need now to study the effect of type and binder content on strength and modulus of a composite of a fixed magnesia/graphite ratio and at a fixed n-value. The section below discusses the results obtained on such composites.

5.5.7 Composites Having a Fixed Magnesia/Graphite Ratio (80 Parts MgO + 20 Parts Graphite A) and n-value (0.6), but Varying the Binder Content

In an attempt to study the effect of binder content and type on strength and elastic modulus of the composites, the binder contents were varied in the composite containing 80 parts magnesia and 20 parts graphite, and strength and elastic modulus determinations were carried out at each binder content. The results are discussed below.

In Figure 5.5.7(i)(a) and (b), plots of the strength of the composite against raw binder content and that of carbon remaining from the binder after coking, respectively, are shown. Both figures show that an increase in pitch content did not increase the strength of the composite significantly. However, when the resin, which was a mixture of 7.6 parts of liquid resin, PR67, itself containing 7.5 w/o hexamine based on the weight of the liquid resin and 1 part of powdered resin, P41, was used, the strength increased significantly with increasing resin content. Figure 5.5.7(i)(b) shows that the amount of carbon remaining after coking from the resin mixture is about half that of pitch. This is in direct contradiction with the results shown in Figure 2.4.4 of Chapter 2, which show that the carbon content from resin PR67 after coking, is about the same as that of pitch. The low carbon yield was possibly due to chemical degradation of the liquid resin PR67, which was said to have short life span, according to the suppliers (Borden (UK) Limited) and this resin was used two years after it was received. In the pyrolyses experiments of binders, the hexamine level used for PR67 resin was 5 w/o, based on the weight of the liquid resin. In this part of the experiment, 7.5 w/o hexamine was used as described in Section 5.3.3.3(i)(b). It is unlikely that such a small difference in the hexamine addition should reduce the carbon yield by almost half. In any case, it has been shown[20] that the carbon yield in a resin increases with the hexamine content.

Figure 5.5.7(i)(b) shows that composites bonded with resin have a higher strength rise for the same residual carbon increase than those bonded with pitch. Therefore, if the carbon yield is raised in the resin, it is likely that composites bonded with resin could have higher strength than those bonded with pitch.

The ratio used in mixing the resins was arbitrarily chosen, but resin P41 (powdered resin) gives higher carbon yield than both pitch and resin PR67, see Figure 2.4.4 of Chapter 2. To test whether strength could have been improved if the content of P41 was raised in the mixture, two more mixtures were tried in the ratios, by weight, of 7.6:7 and 7.6:10 of PR67:P41 respectively, at a fixed resin mixture content of 5 parts (~ 5 $^w/o$) to the 80 parts MgO + 20 parts graphite A. The results of strength against the ratios are plotted in Figure 5.5.7(i)(c) and an increase of strength with increasing amount of P41 is apparent. At 7.6:10 ratio, the strength of the composite is about 1.5 MPa giving the same strength value as composites containing 5 $^w/o$ pitch. Assuming the same strength rise as observed at 7.6:1 ratio (see Figure 5.5.7(i)(b)), it can be inferred that composites bonded with a resin mixture (7.6:10 of PR67:P41 respectively) would be stronger than those bonded with pitch.

Figure 5.5.7(i)(d) is a plot of elastic modulus against binder content ($^w/o$ carbon after coking). The elastic modulus changed little with increasing binder content, implying that the binder content does not very much affect the propagation of sound waves. Although the modulus goes through a minimum with increasing resin content, the modulus difference between the lowest and the highest is only 0.7 GPa while the variance at the lowest point is 0.5 GPa (2.7 ±0.5 GPa) and at the highest point is 0.8 GPa (3.4 ±0.8 GPa). Therefore this minimum is not real, but possibly due to experimental errors. The scatter of data points is also high for pitch bonded composites.

Figure 5.5.7(ii) is a plot of % total fired porosity against $^w/o$ residual carbon from binder after coking. The porosity increases with increasing binder content because of the increased volatiles evolved. This is consistent with Figures 4.4.4(i)(b) and 4.4.4(ii)(b) of Chapter 4 which showed porosity increase with increasing binder content. This figure also shows that the composites bonded with a resin mixture (7.6:1) had higher porosity than those bonded with pitch, consistent with low carbon yield shown in Figure 5.5.7(i)(b) for equal raw binder addition (pitch and resin).

The effects of graphite content and binder on strength and elastic modulus have been examined as discussed in the above sections and the section below discusses the results of strength and elastic modulus of composites containing a fixed amount of pitch and graphite, but of different types added to the magnesia separately. The amount of pitch used was ~ 5 $^{w}/_{o}$ as was done in composites containing varying amounts of graphite. Furthermore, Figure 5.5.7(i)(b) shows insignificant strength increase over a range of pitch content, therefore this amount was used.

5.5.8 Composites Containing 80 Parts Magnesia + 20 Parts Graphite + 5 Parts Pitch, but Changing the Graphite Type

(i) Composites containing 20 parts graphite B

Figure 5.5.8(i)(a) is a plot of strength, normal and perpendicular to the direction of pressing, and porosity against n-value. The strength values at each n-value are, generally, higher than those of the composite containing graphite A for the same graphite content (see Figure 5.5.4(i)(a)). However, the general trend of falling strength with n-value is the same, as has been shown with composites containing graphite A. Figure 5.5.8(i)(b) and (c) are plots of strength parallel and perpendicular to the direction of pressing against n-value, respectively.

Figure 5.5.8(i)(d) is a plot of elastic modulus against n-value. The change in elastic modulus with increasing n-value is very small, unlike the composites containing graphite A whose modulus passed through a maximum, as shown in Figure 5.5.4(iii).

The strength and elastic modulus of composites containing ~ 20 $^{w}/_{o}$

graphite B are marginally higher than those composites containing the same amount of graphite A. This, probably, can be attributed to the fineness of the flakes which, presumably, do not introduce large cracks in the matrix. This factor can be appreciated more if it is recognized that the relative elastic modulus, Ef(V), of graphite B on its own, is lower than that of graphite A after firing (see Table 5.5.3), therefore the composite modulus could be lower if both graphites introduced the same size of defects in the composite.

(ii) Composites containing 20 parts graphite C

Figure 5.5.8(ii)(a) is a plot of strength, normal and perpendicular to the direction of pressing, and porosity against n-value. The strength in these composites is less than that reported in Figure 5.5.5(i)(a) but about the same as that of composites containing ~ 20 W/o graphite A, Figure 5.5.4(i)(a). It may be recalled that graphite C has an evenly flake size distribution in the sieve cuts used for grading of both the magnesia and the graphites (see Table 2.3.1(i) of Chapter 2) and considering the fact that graphite C has about 37 W/o of flakes less than 150 μm, and assuming that the lowering of strength is largely dependent on the size of cracks brought about by the introduction of graphite, and since no bonding takes place between MgO and graphite, it could have been argued that composites containing graphite C should have higher strength than those containing graphite A because graphite C contains less large flakes than graphite A, hence less larger cracks than when graphite A is used. But strength of a material depends on so many factors, such as, distribution, size, shape and position of defect, among other factors as discussed in Section 5.5.2 above. Figures 5.5.8(ii)(b) and (c) are plots of strength in the two testing directions against n-value. The variances (±S, S = standard deviation), of strength of the composite at each n-value are also plotted.

Figure 5.5.8(ii)(d) is a plot of elastic modulus against n-value. The change of elastic modulus with n-value is small and increases linearly with increasing n-value. These elastic modulus values at each n-value are almost the same as those shown in Figure 5.5.4(ii), except that these do not pass through a maximum.

(iii) Composites Containing 20 parts (~ 20 ^{w}/o) graphite D

As has been done in the above compositions, Figure 5.5.8(iii)(a) is a plot of strength (normal and perpendicular) against n-value, while Figures 5.5.8(iii)(b) and (c) are plots of strength normal and perpendicular to the pressing direction against n-value, respectively, but showing the scatter of strength measurements. The strength values obtained in the composite containing graphite D are not very different from those obtained from composites containing graphite A and C, but perhaps slightly higher than the latter composites.

Similarly, a plot of elastic modulus against n-value did not show significant differences from the previous plots of other composites containing the same amount of graphite. The plot of elastic modulus against n-value is shown in Figure 5.5.8(iii)(d), but shows a subtle maximum at n = 0.9 before it begins to fall.

(iv) Composite Containing 80 Parts MgO + 20 Parts Graphite M + 5 Parts Pitch

The values of strength and porosity versus n-value are plotted in Figure 5.5.8(iv)(a) and Figures 5.5.8(iv)(b) and (iv)(c) are individual plots of strength normal and perpendicular to the pressing direction, including their variances, against n-value respectively. The graphite used in this composite has the largest flakes than A, B, C and D, yet the strength of the composite is not very different from composites containing these other graphites. As argued in Section 5.5.8(i), composites containing larger flakes should show low strength on the basis that they introduce large cracks since crack sizes should approximately equal the length of the flakes, at least in some sections of the specimen, assuming that some of the flakes make continuous contacts with the magnesia grains, but not chemically bonded to each other, hence the cracks, Plate 5.5.3(iv)(a). As discussed already, the size or amount of cracks is not a sufficient condition to predict precisely what the strength of the body would be as strength depends on many more factors (see Section 5.5.2). Figure 5.5.8(iv)(d) is a plot of modulus V's n-value and the trend is similar to other composites discussed above.

To compare directly the effect of the type of graphite used on strength and elastic modulus of the composites containing a fixed amount of graphite, plots of each of these parameters for composites containing different types of graphite against n value are made on one graph but, perhaps, best discussed in the summary section below.

5.5.9 Summary of the Effect of the Type of Graphite on the Physical Properties of a Composite Containing a Fixed Pitch Content and Magnesia/Graphite Ratio (80/20 Parts Respectively)

(i) Strength

Strength values obtained on the composites containing a fixed amount of graphite but of different types (A, B, C, D amd M) are plotted in Figure 5.5.9(i)(a) and (b) as strength, normal and perpendicular to the pressing direction, against n-value, respectively. The figures show that composites containing graphite B, which was the finest among the five graphites (see Table 2.3.1(i) and Plate 2.2.2), have the highest strength, but marginally. The strength differences between the other composites are not significant, although composites containing graphites C and M show lowest strength values between n-values of 0.5 and 0.7, Figure 5.5.9(i)(a) and (b). Figures 5.5.9(i)(c)-(e) show stress-strain curves of composites containing the same amount of graphite (~ 20 $^w/o$) but of different types at n = 0.3, n = 0.7 and n = 1.0. It is clear from the figures that the stress-strain curves of composites containing the same amount of graphite but of different types, are not different at each n-value. What is different, however, is that the stress-strain curves show to have increased strain at high n-values, which is a clear demonstration of the fact that the graphite flakes are the load bearing matrix because their matrix is continuous at high n-value. This increased strain is due to the fact, already mentioned earlier, that flakes can relieve stress through flake cleavage, pull-out as fibres do, etc. The strength, however, falls at high n-values because flakes can easily be cleaved. The stress-strain curves do not show, at least in this work, that large flakes fracture differently from fine ones. Surely they show slightly lower strength, as already discussed above, and this is also shown, barely, on the stress-strain curves, particularly at higher n-values (full-scale detection was the same for all the tests).

The differences in strength of composites, normal and perpendicular to the pressing direction, the latter being higher, may be due to differences in the crack geometry due to the orientation of graphite. If more flakes are loaded on their prismatic edges, they may not cleave easily as they would if loaded on their surfaces. Furthermore, such orientation puts the interlaminar cracks parallel to the loading direction and cracks oriented in this way may only act as minute cracks than they would act if oriented at right angles to the testing direction, i.e., when loading direction is normal to the flake surfaces. Therefore, what is likely to affect the strength here is the geometry of the cracks as seen from two directions of testing. Equation (18) of Section 5.5.2 above, includes the geometrical factor Y, which is determined by crack configuration and the loading geometry[59] of the test-piece, i.e.,

$$\alpha = \frac{1}{Y}\left(\frac{2E\gamma_0}{C}\right)^{\frac{1}{2}} .$$

Therefore a crack between a magnesia grain and an orientated graphite flake could seem to be geometrically different when the test specimen is loaded normal and when loaded perpendicular to the pressing direction.

(ii) Relative elastic modulus

The elastic moduli of composites containing the same amount of graphite but of different types, are plotted as a function of n-value in Figure 5.5.9(ii)(a) and (b). It is seen from these figures that the difference in elastic modulus between composites containing the same amount of graphite but of different types, is also very small. However, the difference between the elastic modulus, normal and perpendicular to the pressing direction, is large for the same composite over all n-values. Factors which, probably, give rise to this phenomenon have been discussed fully in Section 5.5.3. Suffice to mention here, that cracks between magnesia grains and graphite flakes may scatter the sonic (sound) waves differently from the two testing directions, the interlaminar cracks in the graphite if oriented parallel to the direction of wave propagation may not affect the wave travel as they would if oriented perpendicular to the direction of propagation.

Finally, the elastic moduli increase towards high n-values, because, as discussed in earlier sections, the number of dissimilar contacts which hinder efficient propagation of waves, decreases with increasing n-values as the graphite-graphite contacts increase, making a continuous matrix and, therefore, the graphite phase becomes the propagating medium. It may be recalled from Chapter 4 (Appendix 4.2.1, Table 1(b)), that the amount of fine (< 150 μm) magnesia grains decreases with increasing n-value, meaning that the graphite flakes are less separated by the fine magnesia, hence the increase in graphite-graphite contacts.

The general conclusions that can be made on the effect of different types of graphie on composites containing equal amounts of graphites are:

(a) The strength difference of composites containing different types of graphite is very small, although the composites containing fine graphite showed to be slightly stronger than the rest.

(b) The moduli were also slightly different for each type of composite, particularly moduli normal to the pressing direction.

(c) The stress-strain curves of composites containing different types of graphite showed similar fracture characteristics for the same n-value. However, the fracture modes were different at various n-values for the same composite.

(d) The strength decreases with increasing n-value for all composites while the relative modulus increases.

In Chapter 1, it was indicated that in magnesia-graphite refractories addition of metallic elements, such as aluminium and silicon, improves hot modulus of rupture and the reaction which takes place between the carbon phase and the metal at service temperatures, hinder oxidation of the carbon phase. To investigate the effect of adding these metallic elements to the composites on strength, additions of various amounts of silicon and aluminium in a composite of a fixed magnesia/graphite ratio and n-value were made. The section below discusses the results of these additions.

5.5.10 Effect of Metallic Additives on Magnesia-Graphite Composites

Watanabe et al.[83] found that the hot modulus of rupture of magnesia-graphite bricks is increased if aluminium or silicon metal or both, in varying proportions, is added to the composite. The level of metallic additive ranges between 5 $^{w}/o$ to 10 $^{w}/o$. Further, Yamaguchi[84] suggests that these same metallic additives act as anti-oxidants to the carbon phase at furnace operating temperatures. Short experiments were, therefore, conducted to investigate the effect of metallic additive on the strength of fired magnesia-graphite composites. The MOR tests were carried out at room temperature on fired composites containing 80 parts MgO + 20 parts graphite + 5 parts pitch, in the green state. The first experiment was to examine the effect of adding a fixed amount of the metallic elements and varying n-value. The second part was to fix the n-value and vary the amount and type of the additive, separately.

5.5.10(i) Aluminium and silicon metal additions to composites of fixed magnesia/graphite ratio (80 parts MgO + 20 parts graphite A) and 5 parts pitch

Figure 5.5.10(i)(a) shows the plots of strength normal to the pressing direction, against n-value, for the composites containing pitch only, 5 parts aluminium + 80 parts MgO + 20 parts graphite A and

5 parts aluminium metal + 5 parts pitch + 80 parts MgO + 20 parts graphite A, with strength increasing in that order. From the figure it is shown that when a fixed amount (5 parts) aluminium metal was added to a composite bonded with pitch, the strength doubled compared with the strength obtained from the composite without aluminium additive. However, when the same amount (5 parts) aluminium was added to the same composite but this time without pitch, the strength was lower than when pitch was also present.

The increase in strength when aluminium is added to the composite can be explained in terms of the microstructure of the composites after firing. Plate 5.5.10(i)(a) shows a fracture surface of a test specimen containing 5 parts aluminium. Using X-ray analysis, the dominant phases in the composite were shown to be graphite, magnesia (MgO), aluminium nitride (AlN) and aluminium carbide (Al_4C_3). The increase in strength is, almost certainly, due to the fibrous phase shown in the plate which increases the interlocking mechanism in the composite. The fibrous phase is that of aluminium nitride, after comparing this structure with that obtained by Schevetz [86] when making experiments on the production of AlN and Al_4C_3 in which he showed that the fibrous phase in his specimens was that of AlN and the granular phase was that of Al_4C_3. The granular phase in Plate 5.5.10(i)(a) was also thought to be that of Al_4C_3, confirmed by X-ray analysis.

Figure 5.5.10(i)(b) shows a plot of elastic modulus in the direction of pressing against n-value. Also plotted, in the same graph, is the elastic modulus, in the same direction, of the same composite but without aluminium additive. The modulus of the composite containing aluminium and pitch is higher than the moduli of composites containing aluminium without pitch and pitch without aluminium.

Figure 5.5.10(i)(c) is a plot of porosity against n-value. The figure shows that the composite with pitch only has the lowest porosity, followed by that with aluminium only, and the composite with pitch and aluminium has the highest porosity. Clearly, the addition of aluminium upsets the packing more so when aluminium is added together with pitch. However, care should be exercised on this figure, because when calculating the porosity of the composites containing aluminium, the calculated powder density of the composite was based on the assumption that the resulting phase, after firing, was assumed to be AlN. Therefore, knowing the amount of aluminium added, the amount of AlN formed was calculated. Then, using the powder densities of MgO, graphite and pitch, and then the known density of aluminium nitride (AlN), the composite density was calculated. However, it has already been shown above that Al_4C_3 was also formed. But the proportion of Al_4C_3 to AlN was not known, hence the assumption above. Strictly speaking, the porosity values are not correct. From Figure 5.5.10(i)(b) and Figure 5.5.10(i)(c) it is seen that the relative elastic modulus seems not to be affected by porosity as has been shown in the earlier sections.

Figure 5.5.10(ii) is a plot of strength against $^{W}/o$ metallic additive. The composites with equal amounts of silicon and aluminium have about equal strength while strength increases with increasing amount of metal. This equality in strength is hardly surprising, at least for these composites, because of the similarities in their microstructure. Plate 5.5.10(ii)(a) shows the microstructure of a composite containing ~ 5 $^{W}/o$ silicon and this microstructure is similar to that shown in Plate 5.5.10(i)(a). Here, also, the fibrous phase is silicon nitride (Si_3N_4) and the granular phase is silicon carbide. These phases were confirmed by X-ray analysis and were also compared with those of Mori et al.,[85] who were working on producing nitrides and carbides using various techniques and were found to be similar. Plate 5.5.10(ii) (b) shows cubic crystals of silicon carbide lying on a graphite flake. No such definite shape was observed for aluminium carbide phase.

The formation of nitrides from both metals is not surprising since the atmosphere in which the specimens were fired was rich in nitrogen. The formation of the carbides could have been formed by a reaction of the metals with carbon from CO_2 or CO gas due to slight oxidation of the coke covering the specimens or the graphite, although from weight change determinations of the specimens before and after firing was negligible, therefore oxidation of graphite was unlikely. In fact, there was weight increase of 0.5 $^w/o$ to 2 $^w/o$, when a metal addition to the composite was made. This increase in weight was almost certainly due to nitrogen pick-up during the formation of the nitrides.

One other observation on fired specimens containing aluminium was that, if left in an open atmosphere or even in an oven set at 60°C, the specimens disintegrated after several days. Plate 5.5.10(iv) shows two specimens which were previously fractured during the bend test and left in the oven at 60°C for one week. Specimen No. 1 contained 80 parts magnesia + 20 parts graphite + 5 parts pitch and 5 parts aluminium in the green state and specimen No. 2 contained the same amount of non-metallic materials as in No. 1 but 5 parts of silicon were used instead of aluminium. Specimen No. 1 disintegrated while specimen No.2 did not react. It would seem, therefore, that one of the compounds formed in the composite containing aluminium, hydrolyzes in moist air. It is most likely that the phase which reacted with moist air is Al_4C_3, since some carbides are known to hydrolyze in moist air[87], suggesting the presence of aluminium carbide.

The effect of Al or Si addition on thermal shock resistance of the composite, due to consequential increase in strength and elastic modulus, is not clear. However, from stress-strain curves obtained when testing these specimens, their shapes were the same as those obtained in composites containing ~ 20 $^{w}/o$ graphite, see Figures 5.5.9(i)(c)-(e) and, therefore, these curves have not been shown. This being the case, that the area under the curve of the stress-strain curve of the composite containing a metal is not reduced, hence γ_{wof} is not reduced, then thermal shock resistance would not have been drastically changed from that which would have been expected from composites without a metal additive. However, coefficients of thermal expansion and thermal conductivity could have been altered drastically, hence changing the thermal shock parameter, R_{st}.

Throughout this work, the maXimum grain size fraction of magnesia in all composites, has been fixed at 3.35 mm. To study the effect of changing the maximum grain size fraction of magnesia in the composites on strength, two sets of specimens having 600 μm and 250 μm maximum grain size fraction were prepared and strength and modulus measurements were carried out. The results are discussed in the section below.

5.5.11 Composites Containing 80 Parts MgO + 20 Parts Graphite A + 5 Parts Pitch in Which the Maximum MgO Grain Size in the Composite is Reduced From 3350 μm to 600 and 250 μm

Strength and modulus were determined on composites containing 80 parts MgO + 20 parts graphite + 5 parts pitch, which were constituted using Method 3, as described in Chapter 4, that the required amount of graphite is added to a mixture of different grain size fractions of magnesia. The size fractions are determined using Andreasen's equation:

$$y = 100\left(\frac{d}{D}\right)^n$$

where y is the amount of magnesia ($^w/o$ fraction) of size d to obtain efficient packing in the system with a top size D, and in this part of the experiment two sets of mixes were made at a fixed n-value for D = 600 µm and 250 µm. The n-value was arbitrarily chosen as 0.7.

Figure 5.5.11 shows a plot of strength and porosity against dimeter of the largest magnesia grain fraction. The increase in strength when D is reduced is analogous to reducing the n-value which increases the amount of fine magnesia grains, hence the increase in the particle-particle contact, as well as increase in the specific surface which results in an increase in the load bearing area which, in turn, results in an increase in strength when the amount of fine magnesia grains is increased, as discussed in Section 5.5.1. The figure also shows that the porosity increases inversely with D, in the same way as strength does. This indicates then that the packing is upset when D is reduced at n = 0.7. Therefore, to find where optimum packing of the composite occurs, it would be necessary to vary n-value for each D investigated. This was not done here because of limited time. The fact that porosity increases, together with strength, when D is reduced, implies that there is not a dependent relationship between the two. Perhaps the strength of graphite containing composites is not affected by porosity in the same way as a ceramically bonded body is, see Figure 5.5.1(e).

5.6 Summary of the Results on Mechanical Properties of Magnesia-Graphite Composites Studied in this Work

The results discussed in this chapter have shown that the magnesia-graphite composites are very weak compared to the ceramically bonded magnesia bricks generally including magnesia compacts examined in this chapter. This is due to non-bonding of the magnesia to the carbon phase. Furthermore, even a small amount of carbon, as little as 2.5 ^{w}/o, derived from an organic binder, coated around magnesia grains, inhibits bonding of the magnesia grains at their contact points. This has been shown in this work where the strength of the magnesia compacts fired to 1500°C fell by a factor of about 10, when similar compacts, fired to the same temperature, were made from magnesia grains which were coated with ~ 5 ^{w}/o raw pitch at the fabrication stage. This non-bonding behaviour has been reported by other workers[9].

An addition of ~ 10 ^{w}/o graphite to the magnesia grains containing pitch reduces the strength of the composite further than when magnesia grains are coated with pitch because the dispersed graphite in the matrix introduces large cracks in the composite as a result of non-bonding between the oxide and graphite. However, the porosity is reduced because graphite, being flexible, occupies the cavities which cannot be filled by isometric magnesia grains. Further addition of graphite to 20 ^{w}/o improves the strength slightly and porosity decreases again. The strength increases because the graphite phase becomes a continuous phase and it is providing enough interlocking mechanism in the composite. When graphite is increased to 30 ^{w}/o (≃ 50 ^{v}/o), the strength is twice that of the composites containing 20 ^{w}/o graphite and the porosity increases slightly. The increase in strength is a result of effective interlocking mechanism provided for by the graphite which is now a continuous matrix in the composite, as exemplified in Plates 5.5.5(i)(a)-(d). This phenomenon is shown in Figure 5.5.6(i)-(iii).

The relative elastic modulus has been found to decrease drastically when a small amount of carbon, up to 10 w/o graphite, is added because the sonic waves are affected by the number of discontinuities caused by dissimilar phases at the particle interface due to lack of bonding. It is not surprising, therefore, that the relative modulus does not change very much when the graphite makes a continuous matrix (graphite contents > 10 w/o) as shown in Figure 5.5.6(iv), because the graphite becomes the propagating medium for the sound waves.

When the binder contents were varied in a composite containing a fixed magnesia/graphite ratio and n-value of 0.6, the strength did not change very much with the binder content when pitch was used as a binder. However, the strength of the composite increased significantly with increasing resin content. This is shown in Figure 5.5.7(i)(b).

There were insignificant strength differences between composites containing different types of graphite but with the same amount, at the same n-value. It could, however, be inferred that composites containing the finest graphite, B, were slightly stronger than composites containing coarser graphites, while the composite containing the coarsest graphite, M, together with graphite,C, gave the lowest strength between n-values of 0.5 and 0.7. This is shown in Figures 5.5.9(i)(a) and (b).

The strength and elastic modulus values, normal and perpendicular to the pressing direction, are constantly different for all graphite-containing composites because of the orientation of the graphite flakes which present different geometries from the two testing directions. The defects associated with graphite affect the strength of a composite from the two testing directions (normal and perpendicular to the direction of pressing) differently because of flake orientation. These points are discussed fully in Sections 5.5.3 through to 5.5.8. To appreciate the strength difference from the two testing directions, Figure 5.5.9(i)(a) should be compared with Figure 5.5.9(i)(b) in which the lower limit of the strength axis of the former is lower than that of the latter figure. Similarly, Figures 5.5.9(ii)(a) and (b) show the differences in the same way. The results from this work also show that the relative elastic modulus does not depend on the porosity of the composite. This may be a result of small variation of porosity in each composite investigated, over a range of n-values.

In this work it has been shown that an addition of 5 parts aluminium or silicon to a composite containing 80 parts MgO, 20 parts graphite and 5 parts pitch, doubles the strength. Furthermore, strength was found to increase with increasing metal content. These two phenomena are shown in Figure 5.5.10(i)(a) and (b).

Perhaps the most important observation from the strength studies described in this chapter is that unless graphite is present as a continuous phase in the matrix, strength of the composite is extremely low. This observation could be extended to thermal conductivity, thermal expansion and, most important of all, thermal shock resistance of the composite. It has been shown in this work that increasing the graphite content increases the area under the stress-strain curve, see Figures 5.5.6(v)(a)-(c), which is proportional to work of fracture (see Section 5.5.6), resulting in possible increase in thermal shock resistance.

From the literature[52,37] and from the results discussed in this chapter, the magnesia-graphite composites are not chemically bonded, but are held together by some keying or interlocking mechanism of the components, particularly the flake graphite phase which may be acting like a fibrous material in the composite. If this picture is accepted, it may be argued that the strength of the composites at room temperature may be similar to that at the working temperatures, in the absence of metallic additives. But this may not be true because at higher temperatures the graphite flakes expand, and this may tighten the composite structure at these temperatures and strength could increase this way. The increase in hot strength [87] when metallic additives are made to the composite is, possibly, due to the formation of high temperature melting carbides.

Finally, the increase in thermal shock resistance of the magnesia-graphite composites is, among other factors, due to increased work of fracture as discussed in the literature,[37,52] and the decrease in the coefficient of thermal expansion is due to "Mrozowski"[82] cracks when graphite is added to an oxide. Furthermore, the cracks along the magnesia-graphite interface may also help to relieve thermal stresses in the composite, in addition to increased thermal conductivity, imparted by the graphite, i.e. reducing thermal stresses in the composite product.

The strength results obtained in this work are similar to those obtained by Mikami et al.[10] in which they found that the strength of graphite containing sintered magnesia composites bonded with pitch or resin, with graphite contents of about 18 to 22 w/o varied between 1.5 MPa to 3.1 MPa. Similarly Lalama et al.[88] worked on magnesia-carbon composites containing various types of carbon and found that the strength (MOR) of composites containing 19 w/o flake graphite was 2.5 MPa in total agreement with the previous workers[10] as well as has been reported in this work, although the gradings of the magnesia and the graphite may have been different in all the three cases being compared.