

Chapter 5

Study of Hf addition on the microstructure, phase equilibria and oxidation behaviour of two Cr-Si based intermetallic alloys

5.1 Introduction

New high temperature alloys with capabilities beyond those of state of the art Ni based superalloys will require oxidation resistant coatings to operate in the next generation gas turbine engines [108]. Protective scale formation remains a key challenge to the successful implementation of intermetallics alloys for structural application in high temperature environments. Furthermore, the knowledge of how alloy composition and its microstructure can be manipulated to influence the oxidation response of intermetallics is a key factor to design and develop multi-component high temperature coatings.

One approach is to achieve an ideal α -alumina scale by adding of reactive element (RE), such as Y, Zr or Hf to coating and superalloy substrate. Therefore, the Hf addition can improve the oxidation of substrate and/or coating by improving the scale adhesion and reducing the growth rate of α -alumina scale. Moreover, the Hf can also be present in the coating system by elemental inter-diffusion from substrate which has about 2-5 at. % Hf.

The study of the microstructure of alloys suitable for coating systems is of great importance. The latter must be capable of forming in-situ alumina, silica or chromia oxides or mixture of these oxides [6,109,110]. To design and develop oxidation resistant chromia, silica and alumina-forming intermetallic alloys, it is essential to have comprehensive data about phase equilibria, microstructure stability and solidification. The knowledge of phase equilibria is important for optimization of alloy composition and heat-treatment conditions [40]. As was discussed in section 2.17, it is possible to form alloys containing Si and Al rich intermetallic phases in the microstructure but how individual transition metal addition like Hf influence the phase equilibria is not known. There have been some investigations of the phase equilibria in the Cr-Si-Al and Cr-Si-Hf systems [10,13,14,40,43,44], see chapter 2. Yu et al. [40] used the CALPHAD method

to study the Cr-Si-Al ternary system. Gupta [10] reported isothermal sections at 800, 900, 1000 and 1100 °C for the same system. Schoonover et al. [18,45] studied the Cr and Hf rich ends of the Cr-Hf-Si system. To date, there is no published data on the phase equilibria of the Cr-Si-Al-Hf quaternary system. The motivation for the research presented in this chapter was to study the microstructures and oxidation behaviour of the alloys Cr-45Si-5Al-5Hf (AN1) and Cr-25Si-25Al-5Hf (AN2) and understand how the Hf addition affects microstructure development and phase stability in the Cr-Si-Al-Hf system.

5.2 Results

5.2.1 The microstructures of the alloys

The phases present in the as-cast and heat treated alloys AN1 and AN2 were the tetragonal V_6Si_5 -type Hf_6Si_5 , the tetragonal W_5Si_3 -type Cr_5Si_3 , the hexagonal ($CrSi_2$ -type) $CrSi_2$, the cubic (Cr_3Si -type) Cr_3Si and the rhombohedral (Cr_5Al_8 -type) Cr_5Al_8 . In this thesis, the Cr_5Si_3 with Hf and Al in solid solution is referred to as $(Cr,Hf)_5(Si,Al)_3$, and the $CrSi_2$ with Al in solid solution as $Cr(Si,Al)_2$. The Hf_6Si_5 with Al and Cr in solid solution is referred to as $(Hf,Cr)_6(Si,Al)_5$. Likewise, the Cr_5Al_8 with Si in solid solution and Cr_3Si with Al in solid solution are referred to as $Cr_5(Al,Si)_8$ and $Cr_3(Si,Al)$ respectively. The % areas of the phases in the two alloys in the conditions studied are given in Table 5-1.

5.2.1.1 As cast Cr-45Si-5Al-5Hf (alloy AN1-AC)

Data for the compositions of the ingot button and phases in the microstructure of AN1-AC is given in Table 5-2. The data in Table 5-2 summarizes the compositions of the phases in the bulk (centre) of the button. Compared with the nominal composition, the AN1-AC was slightly poor in Si. There was no macrosegregation of Si in AN1-AC.

Table 5-1 Density and data for % areas of constituent phases in the as cast (AC) and heat treated (HT) alloys AN1 and AN2.

Alloy ^a	Density (g/cm ³)	Hf ₆ Si ₅ (%)	Cr ₅ Si ₃ (%)	CrSi ₂ (%)	Cr ₃ Si (%)	Al ₈ Cr ₅ (%)
AN1-AC	4.70±0.01	40.1	34.4	25.5	-	-
AN1-HT1200	-	41.5	37.4	21.1	-	-
AN1-HT1300	-	49.7	26.1	24.2	-	-
AN2-AC	4.88±0.01	31.2	6.1	-	26.9	35.8
AN2-HT1200	-	32.7	14.8	-	18.7	33.8
AN2-HT1300	-	40.6	35.3	-	-	24.1

^a AC=as cast , HT1200 = heat treatment at 1200 °C/100 h, HT1300 = heat treatment at 1300 °C /100 h.

According to the XRD data (Figure 5.1) the $(\text{Hf,Cr})_6\text{Si}_5$, $\text{Cr}_5(\text{Si,Al})_3$ and $\text{Cr}(\text{Si,Al})_2$ phases were present in AN1-AC. The EDX data for the silicides in AN1-AC is summarized in the Table 5-2Ta. The phases in Table 5-2 were identified with the help of the XRD and EBSD (see below) data. In the studied cross section of AN1-AC the microstructure consisted of columnar Hf_6Si_5 and Cr_5Si_3 silicides with growth direction perpendicular to the surface of the water cooled crucible (Figure 5.2). The Cr_5Si_3 was formed either adjacent to the 6-5 silicide or was surrounded by CrSi_2 . In the Hf_6Si_5 there was no solubility of Al (Table 5-2) and the solubility of Hf was in the range 12.9 to 14.4 %. In the Cr_5Si_3 and CrSi_2 there was no solubility of Hf (Table 5-2), and 0.9 and 16.9 % Al had substituted Si, respectively. The microstructure of AN1-AC consisted of 40.1 % Hf_6Si_5 , 34.4 % Cr_5Si_3 and 25.5 % CrSi_2 (see Table 5-1) The EBSD confirmed the phases identified by XRD in the as cast condition (Figure 5.2). Using the channel 5 software there was a strong correlation between proposed and indexed phases with the map obtained from the alloy as very small MAD values (mean angular deviation) were obtained.

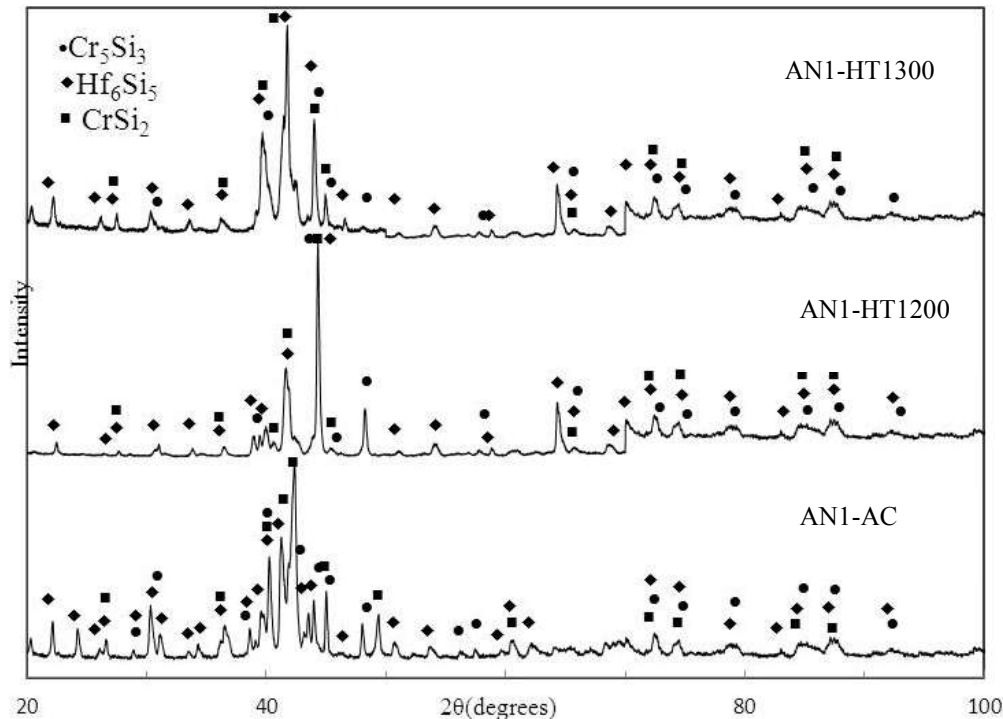


Figure 5.1 X-ray diffractograms of the as cast and heat treated alloy AN1 using card No.01-089-4866 for CrSi_2 , 00-050-1329 for Cr_5Si_3 . (HT1200 = 1200 °C/100h, HT13 = 1300 °C /100h)(HT1200 = 1200 °C/100 h, HT13 = 1300 °C /100 h)

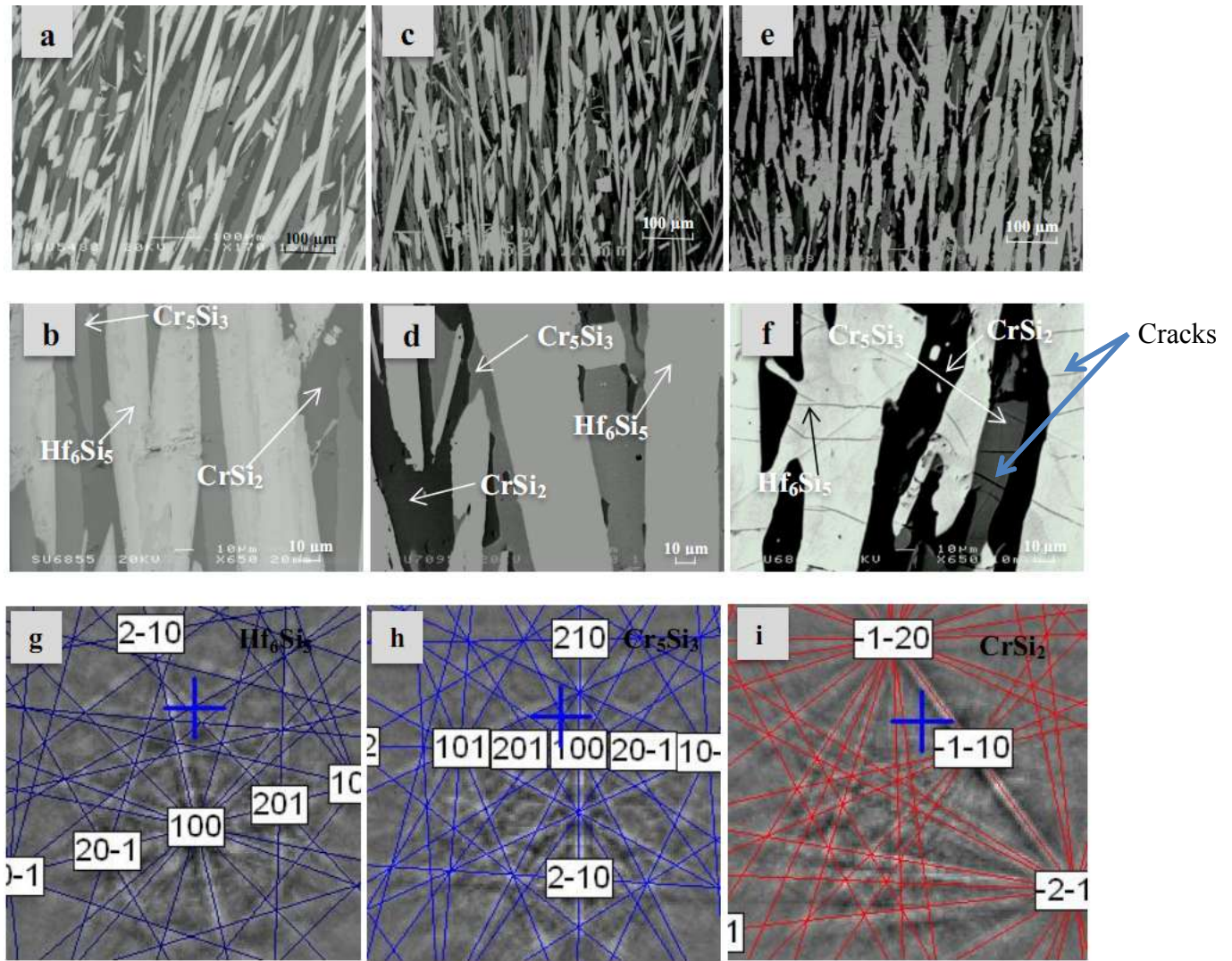


Figure 5.2 Microstructure of alloy AN1 a, b) as-cast condition c, d) heat-treated at 1200 °C for 100 h e, f) heat-treated at 1300 °C for 100 h and g, h, i) EBSD patterns of phases (The Kikuchi lines are indexed as described in section 4.6.1 representing the diffraction band intersection of crystal structure allocated to each of the identified phases)

5.2.1.2 Heat treated Cr-45Si-5Al-5Hf (alloy AN1-HT)

The alloy was given two different heat treatments, namely 1200 °C /100 h, and 1300 °C/100 h. The actual composition of the heat treated alloy at 1200 °C was Cr-46.6Si-3.9Hf-6.1Al (see Table 5-2). According to the XRD data (Figure 5.1) and the chemical analysis data (Table 5-2) the heat treated microstructure at 1200 °C consisted of the Hf_6Si_5 , Cr_5Si_3 and CrSi_2 silicides, i.e., the same phases as in AN1-AC. Typical backscatter electron images of AN1-HT1200 are shown in Figure 5.2. The actual composition of the heat treated alloy at 1300 °C was Cr-47.7Si-4.2Hf-

4.2Al (Table 5-2). Considering the XRD data (Figure 5.1) and the chemical analysis data (Table 5-2), the Hf_6Si_5 , Cr_5Si_3 and CrSi_2 silicides were still present at 1300 °C i.e., the same phases as in AN1-AC and AN1-HT1200. In the Cr_5Si_3 (HT1200 and HT1300), the Si+Al concentration and the Al/Si ratio were essentially the same. In the CrSi_2 (HT1200), the Si+Al concentration was ~ 65.8 % with Al/Si $\approx$ 0.22 and in the CrSi_2 (HT1300), the Si+Al concentration was ~ 66.7 % with Al/Si $\approx$ 0.18 which indicated small changes in the Si and Al contents of this phase. Cracking of the 6-5 and 5-3 silicide was noted in AN1-HT1300, see Figure 5.2.

Table 5-2 Quantitative analysis (at. %) data of the as cast and heat treated (HT) AN1 alloy

Phase	Cr	Si	Hf	Al
AN1-AC ^{a,b}	46.4 $\pm$ 0.3	43.5 $\pm$ 0.4	5.1 $\pm$ 0.5	4.9 $\pm$ 0.3
	46.1-46.8	43.1- 44.0	4.7-5.5	4.5-5.2
$(\text{Hf,Cr})_6\text{Si}_5$	41.8 $\pm$ 0.6	44.5 $\pm$ 1.1	13.7 $\pm$ 0.8	-
	41.3-42.1	43.6-45.7	12.9-14.4	-
$\text{Cr}_5(\text{Si,Al})_3$	59.9 $\pm$ 0.4	39.2 $\pm$ 0.7	-	0.9 $\pm$ 0.2
	59.6-60.4	38.5-39.8	-	0.7-1.2
$\text{Cr}(\text{Si,Al})_2$	33.4 $\pm$ 0.6	49.7 $\pm$ 1.3	-	16.9 $\pm$ 0.5
	32.9-34.1	48.5-50.9	-	16.5-17.4
AN1-HT1200 ^{a,b}	43.7 $\pm$ 0.7	46.6 $\pm$ 0.6	3.9 $\pm$ 0.4	6.1 $\pm$ 0.8
	43.1-44.4	45.9-47.1	3.5-4.4	5.3-6.9
$(\text{Hf,Cr})_6\text{Si}_5$	41.8 $\pm$ 0.4	45.7 $\pm$ 0.7	12.4 $\pm$ 0.6	-
	41.3-42.2	45.1-46.5	11.8-12.5	-
$\text{Cr}_5(\text{Si,Al})_3$	59.7 $\pm$ 0.6	39.1 $\pm$ 0.9	-	1.2 $\pm$ 0.3
	59.1-60.3	38.3-39.9	-	0.9-1.6
$\text{Cr}(\text{Si,Al})_2$	34.3 $\pm$ 0.5	53.8 $\pm$ 0.8	-	12.0 $\pm$ 0.9
	33.9-34.8	53.1-54.6	-	11.1-12.8
AN1-HT1300 ^{a,b}	44.0 $\pm$ 0.5	47.7 $\pm$ 0.8	4.2 $\pm$ 0.3	4.2 $\pm$ 0.6
	43.5-44.5	46.9-48.5	3.9-4.5	3.7-4.8
$(\text{Hf,Cr})_6\text{Si}_5$	45.8 $\pm$ 0.6	44.2 $\pm$ 0.5	10.0 $\pm$ 0.7	-
	45.3-46.4	43.8-44.7	9.3-10.7	-
$\text{Cr}_5(\text{Si,Al})_3$	59.3 $\pm$ 0.4	39.6 $\pm$ 0.5	-	1.1 $\pm$ 0.5
	58.9-59.6	39.2-40.1	-	0.7-1.6
$\text{Cr}(\text{Si,Al})_2$	33.3 $\pm$ 0.7	56.4 $\pm$ 1.1	-	10.3 $\pm$ 0.8
	32.7-33.9	55.2-57.5	-	9.5-11.2

^a Large area analysis from the centre of the button

^b AC=as cast , HT1200 = heat treatment at 1200 °C for100 h, HT1300 = heat treatment at 1300 °C for100 h.

5.2.1.3 As cast Cr-25Si-25Al-5Hf (alloy AN2-AC)

Data for the compositions and microstructures of the button and phases in AN2-AC is given in Figure 5.3, Figure 5.4 (a, b) and Table 5-3. The data in Table 5-3 summarize the compositions of the phases in the bulk button. Compared with the nominal composition, the AN2-AC was slightly poorer in Hf. There was weak macrosegregation of Al in AN2-AC.

According to the XRD data (Figure 5.3) and the EDX data for AN2-AC (Table 5-3), the $(\text{Hf,Cr})_6\text{Si}_5$, $\text{Cr}_3(\text{Si,Al})$, $\text{Cr}_5(\text{Si,Al})_3$ and $\text{Cr}_5(\text{Si,Al})_8$ phases were present in the microstructure of AN2-AC. Due to the complexity of the XRD pattern EBSD was used to aid phase identification in the alloy. The EBSD maps of phases are shown in Figure 5.5. The MAD values were between 0.3-0.8 in the pattern matching process provided by Chanel 5 software.

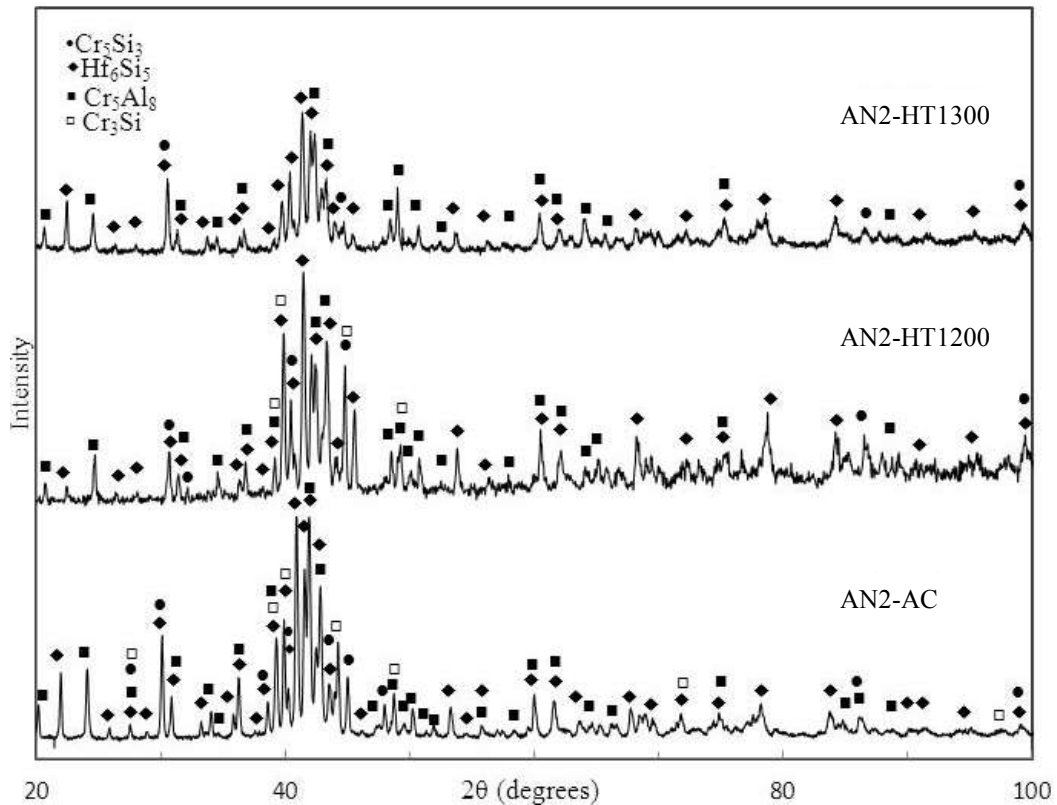


Figure 5.3 X-ray diffractograms of the as cast and heat treated alloy AN2 using card No. 00-050-1329 for Cr_5Si_3 , 00-007-0186 for Cr_3Si and 00-002-1192 for Cr_5Al_8 , (HT1200 = heat treatment at 1200 °C/100 h, HT1300 = heat treatment at 1300 °C/100 h)

The Cr_3Si was formed between Hf_6Si_5 silicide plates. The Cr_3Si was surrounded by Cr_5Si_3 , which is in agreement with the peritectic reaction suggested in [10,40].

The thickness of the Cr_5Si_3 crust around Cr_3Si was different in different areas of AN2-AC. In the Hf_6Si_5 , the solubility of Al was about 4.9 at. % (Table 5-3) and the solubility of Hf was 16.7 at. %. In the Cr_3Si and Cr_5Si_3 silicides, there was no solubility of Hf whereas the solubility of Al was 1.3 and 1.9 at.%, respectively. In the Al_8Cr_5 phase about 7% of Al was substituted by Si. In the microstructure of AN2-AC the area fractions of Al_8Cr_5 and Cr_5Si_3 were about 36 % 6 %, respectively (Table 5-1).

5.2.1.4 Heat treated Cr-25Si-25Al-5Hf (alloy AN2-AC)

The alloy was given two different heat treatments, namely 1200 °C/100 h and 1300 °C/100 h. The actual composition of the heat treated specimen at 1200 °C was Cr-25.4Si-23.9Al-5.8Hf (Table 5-3), close to the nominal composition of the alloy. According to the XRD data (Figure 5.3) and the chemical analysis data (Table 5-3), the heat-treated microstructure (HT1200) consisted of the Hf_6Si_5 , Cr_5Si_3 , Cr_3Si , and Al_8Cr_5 phases. In the microstructure of AN2-HT1200, the crust of Cr_5Si_3 seen in AN2-AC was changed to a lamellar structure and in some areas the Cr_3Si core was fully transformed to a lamellar structure. The contrast in Figure 5.4 (d) suggests a lamellar microstructure containing of Cr_5Si_3 and Al_8Cr_5 .

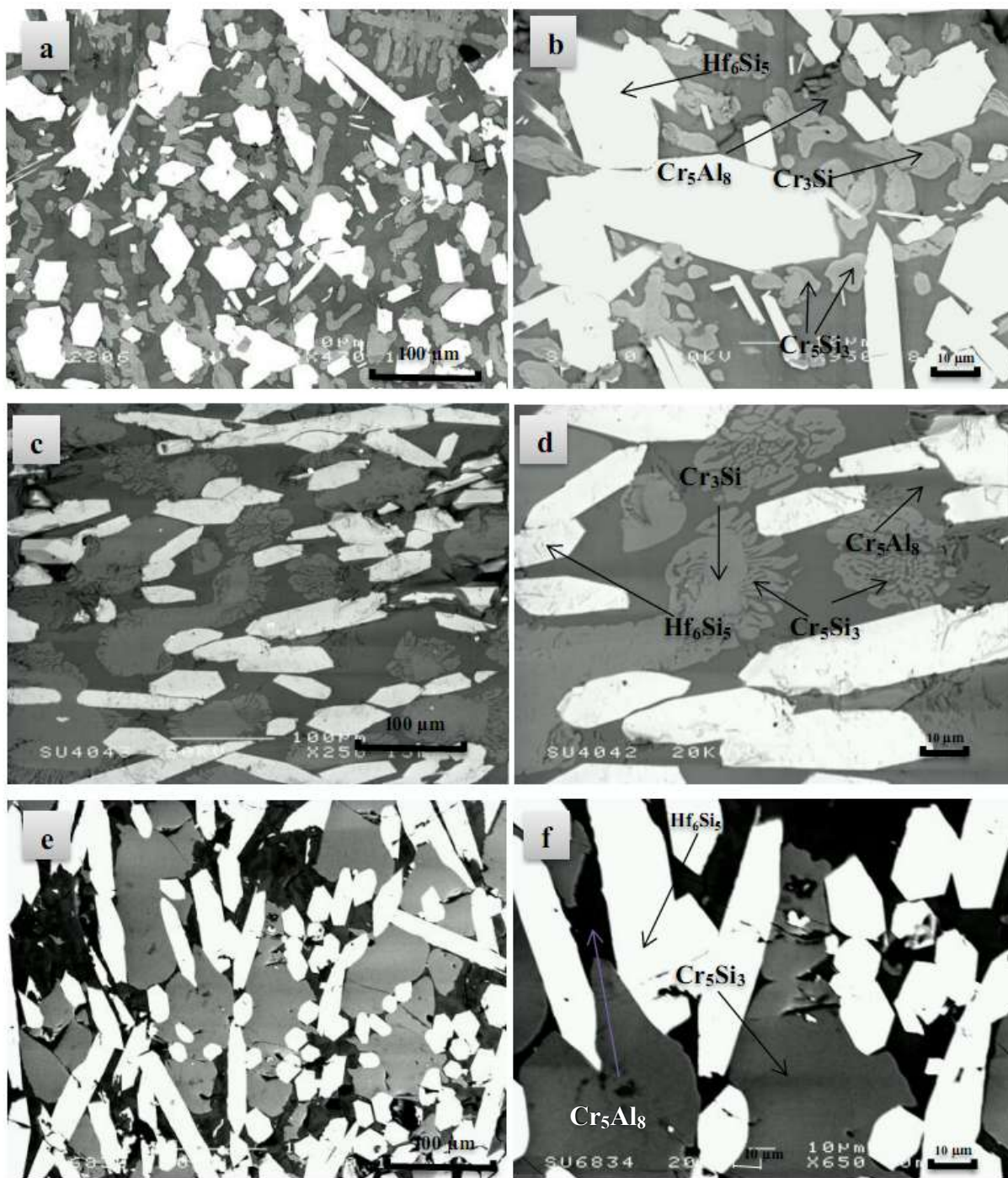


Figure 5.4 Microstructure of alloy AN2 a, b) as-cast condition c, d) heat-treated at 1200 °C for 100 h and e, f) heat-treated at 1300 °C for 100 h

The actual composition of the alloy heat treated at 1300 °C was Cr-32.7Si-16.8Al-6.7Hf. Compared with the nominal composition, the AN2- HT1300 was significantly poorer in Al and

richer in Si and Hf. According to the XRD data (Figure 5.3) and the chemical analysis data in Table 5-3 only Hf_6Si_5 , Cr_5Si_3 and Al_8Cr_5 phases were present in AN2-HT1300.

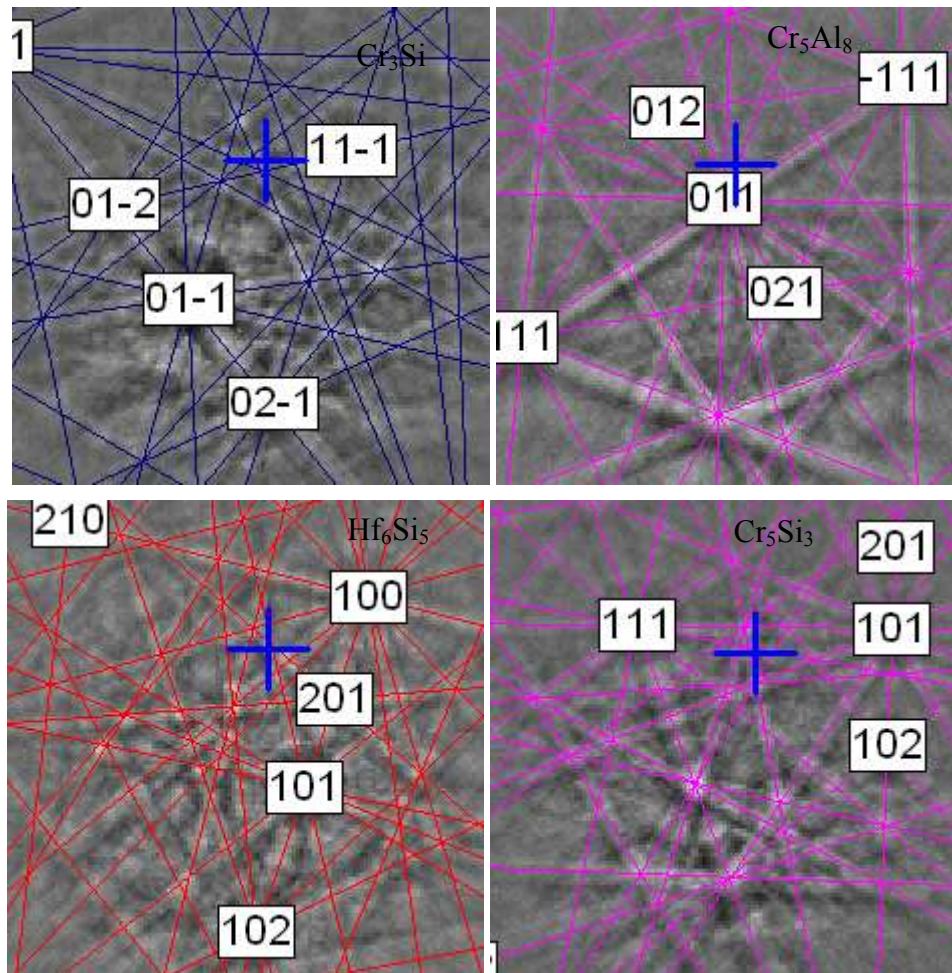


Figure 5.5 EBSD patterns of the Cr_3Si , Al_8Cr_5 , Hf_6Si_5 and Cr_5Si_3 phases in AN2-AC.

Table 5-3 Quantitative analysis (at. %) data of the as cast and heat treated (HT) AN2 alloy

Phase	Cr	Si	Hf	Al
AN2-AC ^{a,b}	44.5±0.6	25.9±0.9	4.1±0.2	26.1±1.1
	43.9-45.2	25.1-26.8	3.9-4.3	25.1-27.2
(Hf,Cr) ₆ (Si,Al) ₅	39.5±0.9	39.0±0.7	16.7±1.3	4.9±0.5
	38.6-40.3	38.4-39.7	15.4-17.9	4.4-5.3
Cr ₅ (Si,Al) ₃	61.4±1.1	36.8±0.8	-	1.9±0.4
	60.2-62.5	36.1-37.5	-	1.5-2.4
Cr ₃ (Si,Al)	74.1±0.9	24.7±1.2	-	1.3±0.6
	73.3-74.9	23.4-25.7	-	0.8-1.9
Cr ₅ (Si,Al) ₈	37.8±1.5	6.9±0.4	-	55.3±1.7
	36.3-39.4	6.5-7.2	-	53.7-57.1
AN2-HT1200 ^{a,b}	45.1±0.6	25.4±0.4	5.8±0.3	23.9±0.5
	44.5-45.6	25.1-25.8	5.4-6.1	23.4-24.3
(Hf,Cr) ₆ (Si,Al) ₅	38.1±0.7	38.9±1.4	17.8±0.7	5.1±1.1
	37.4-38.8	37.6-40.2	17.2-18.5	4.1-6.3
Cr ₅ (Si,Al) ₃	61.4±0.5	36.8±0.8	-	1.9±0.3
	60.9-61.8	35.9-37.6	-	1.6-2.3
Cr ₃ (Si,Al)	74.3±0.9	24.2±0.7	-	1.5±0.4
	73.5-74.1	23.6-24.9	-	1.2-1.9
Cr ₅ (Si,Al) ₈	37.5±1.9	6.1±0.5	-	56.4±1.7
	35.7-39.4	5.6-6.7	-	54.8-58.2
AN2-HT1300 ^{a,b}	44.1±0.4	32.7±0.7	6.7±0.5	16.8±0.6
	43.8-44.5	31.9-33.4	6.1-7.3	16.2-17.5
(Hf,Cr) ₆ (Si,Al) ₅	40.1±0.4	38.3±0.9	16.1±0.6	5.4±0.9
	39.7-40.6	37.5-39.2	15.5-16.8	4.6-6.4
Cr ₅ (Si,Al) ₃	61.5±0.7	36.6±0.5	-	1.9±0.3
	60.9-62.3	36.2-37.1	-	1.5-2.3
Cr ₅ (Si,Al) ₈	36.2±1.1	8.0±0.9	-	55.8±1.3
	35.2-37.3	7.2-8.9	-	54.6-57.1

^a Large area analysis from the centre of the button^b AC=as cast , HT1200 = heat treatment at 1200 °C for100 h, HT1300 = heat treatment at 1300 °C for100 h.

The presence of Cr₃Si was not confirmed in AN2-HT1300 by XRD and EDX. The swelling of the heat treated specimen at 1300 °C, would suggest partial melting of the alloy at 1300 °C due to presence of Cr₅Al₈. The DSC data (Figure 5.6) showed a melting reaction around 1230 °C. In the HT1300 microstructure the lamellar structure was not observed.

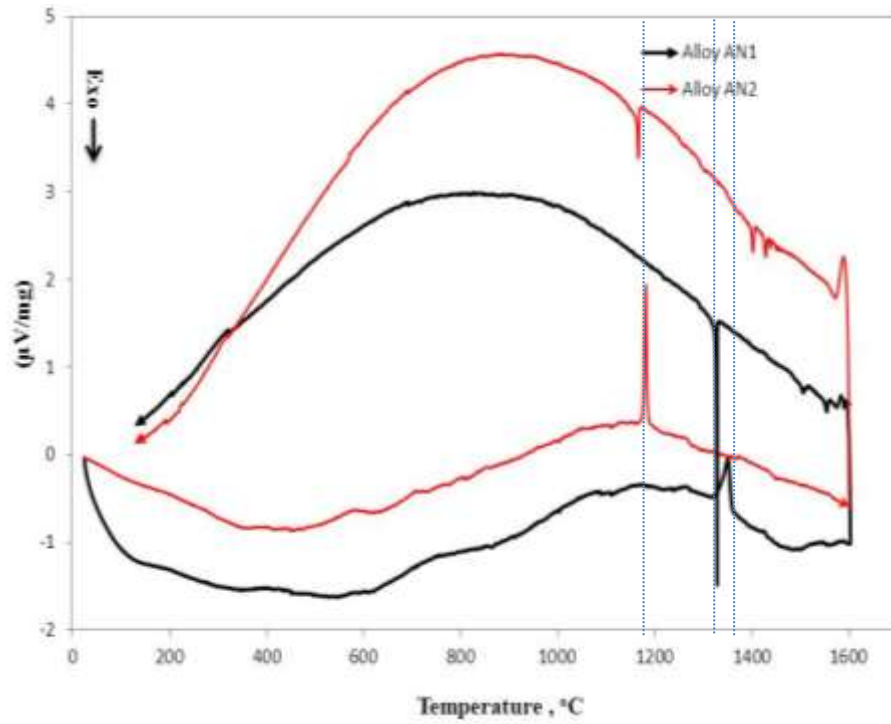


Figure 5.6 DSC traces of the alloys AN1 and AN2 obtained at 20 Kmin⁻¹ heating rate in flowing Argon.

5.2.2 Hardness

The hardness data for the alloys AN1 and AN2 and for the phases present in their microstructure is given in Table 5-4.

Table 5-4 Hardness data (Hv) of the as cast (AC) and heat treated (HT) AN1 and AN2 alloys

Alloy ^a	Macrohardness (10kg)	Microhardness(30g)				
		Hf ₆ Si ₅	Cr ₅ Si ₃	CrSi ₂	Cr ₃ Si	Cr ₅ Al ₈
AN1-AC	683±49	1178±24	1210±32	1035±35	-	-
AN1-HT1200	761±35	1153±14	1143±91	1275±39	-	-
AN1-HT1300	549±39	1200±47	819±10	917±20	-	-
AN2-AC	735±23	1089±35	942±23	-	1013±34	652±15
AN2-HT1200	487±39	1131±47	1016±30	-	795±67	864±64
AN2-HT1300	393±17	767±35	793±44	-	-	566±24

^a AC=as cast , HT1200 = heat treatment at 1200 °C/100 h, HT1300 = heat treatment at 1300 °C /100 h.

5.2.3 Isothermal oxidation of the cast alloys AN1 and AN2

Oxidation experiments were carried out at 800, 1000 and 1200 °C at 20 ml/min air flow. Oxidation kinetics data and the morphology of the oxides are presented in the following sections. Supplementary data about oxidation kinetics is given in the Appendix A.

5.2.3.1 Oxidation kinetics of the cast alloys AN1 and AN2

Figure 5.7 shows the weight change of the alloys AN1 and AN2 versus time at 800 °C, 1000 °C, and 1200 °C and Figure 5.8 shows the oxidation kinetics of the alloys at the three temperatures. In the alloy AN1, the mass gains slightly increased with temperature up to 1000 °C followed by a 6 times increase at 1200 °C, see Table 5-5. This was attributed to the rumpling and corrugating of the scale that formed at intermediate temperature and breakage of the scale and consequent increase of weight.

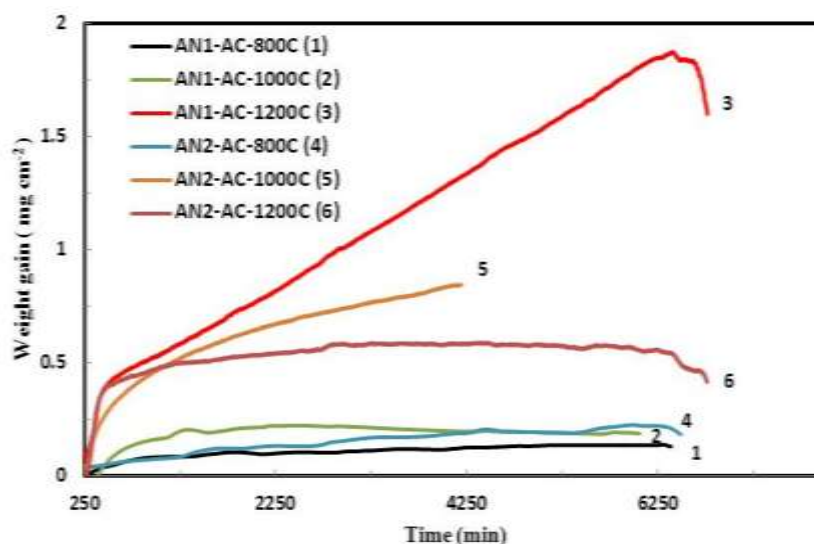


Figure 5.7 Weight changes of the alloys AN1 and AN2 after isothermal oxidation in air at 800, 1000 and 1200 °C

Figure 5.8 (a) shows that the alloys obeyed parabolic ($n=0.5$) oxidation behaviour at 800 °C within the whole exposure time (100 hours). The alloy AN1 exhibited parabolic oxidation behaviour at 1000 °C for the first 35 hours of exposure and exhibited parabolic oxidation behaviour at 1200 °C for a shorter exposure time ($t = 25$ hours) followed by linear oxidation behaviour. In the alloy AN2, the mass gain increased by 8 times at 1000 °C but the weight gain was lower after exposure at 1200 °C. Figure 5.8 (b) shows that the alloy AN2 obeyed parabolic

oxidation for the whole exposure time (100 h) of isothermal oxidation at 800 and 1000 °C and cube oxidation at 1200 °C. Under parabolic oxidation behaviour, the oxidation rate constants of the alloy AN2 (kp) were 1×10^{-13} and $3.3 \times 10^{-12} \text{ g}^2/\text{cm}^4\text{s}$ respectively for 800 and 1000 °C. Under cube oxidation behaviour, the oxidation rate constant of AN2 (Kc) was $2.6 \times 10^{-14} \text{ g}^3/\text{cm}^6\text{s}$ at 1200 °C. According to Figure 5.8 (a), the alloy AN1 exhibited paralinear oxidation behaviour after longer exposure time under isothermal oxidation at 1000 °C.

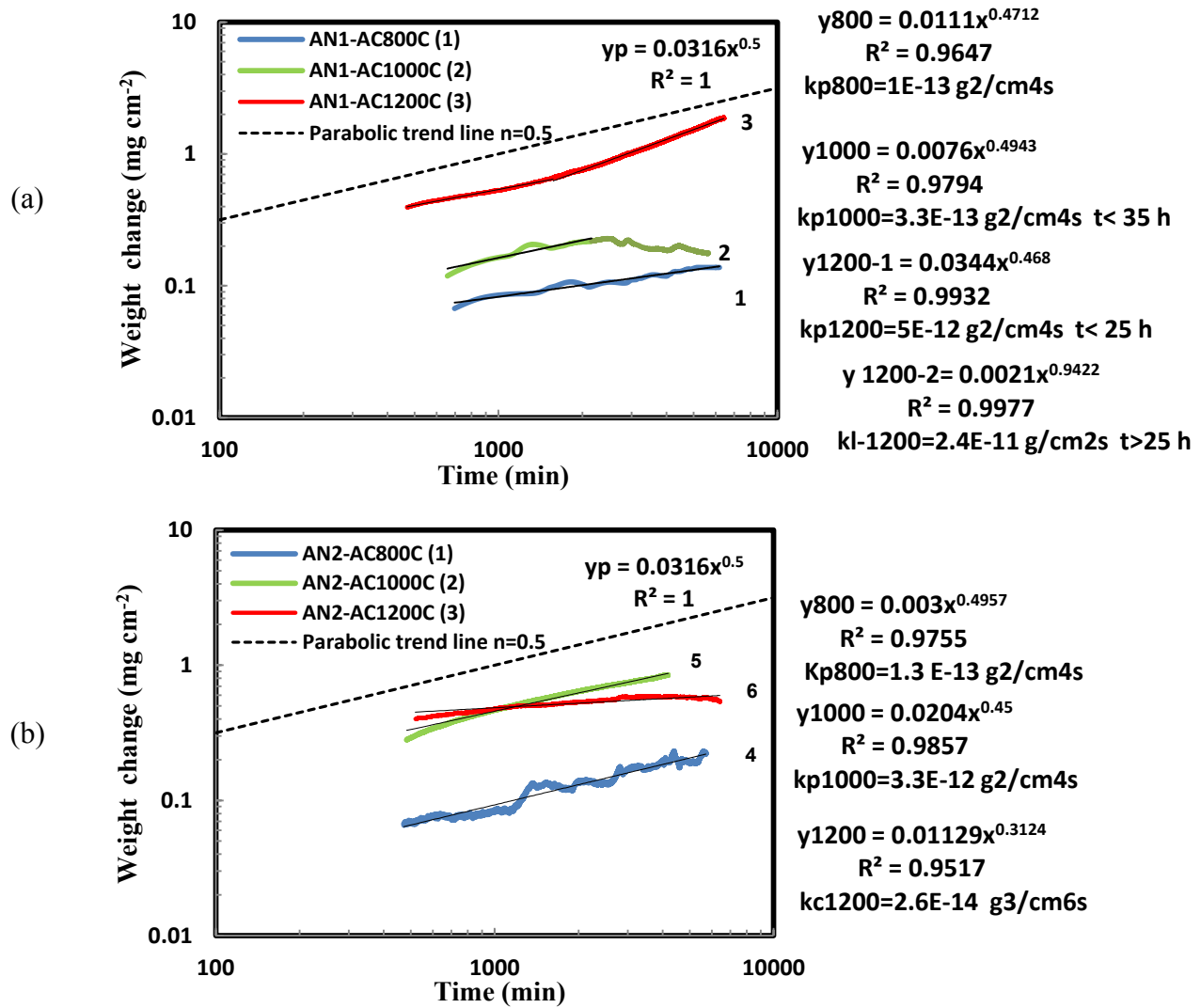


Figure 5.8 Logarithmic plots of weight change versus exposure time for a) the as -cast AN1 and b) as-cast AN2 alloy at 800, 1000 and 1200 °C. The value of the exponent n in equation (2) (in the Appendix A) was obtained from the slop of the plots. Dotted lines show $n=0.5$ (parabolic kinetics).

Table 5-5 Total weight gains and oxidation rate constants of the alloys at 800, 1000 and 1200 °C

Alloy	Weight gain (mg/cm ²)	k_p (g ² .cm ⁻⁴ .s ⁻¹)	k_c (g ³ .cm ⁻⁶ .s ⁻¹)	K_l (g.cm ⁻² .s ⁻¹)
AN1-800 °C	0.15	1×10^{-13} (t = 100 h)	-	-
AN1-1000 °C	0.24	3.3×10^{-13} (t < 35 h)	-	1.7×10^{-13} (t > 35 h)
AN1-1200 °C	0.91	5.0×10^{-12} (t < 25 h)	-	2.4×10^{-11} (t > 25 h)
AN2-800 °C	0.11	1.3×10^{-13} (t = 100 h)	-	-
AN2-1000 °C	0.85	3.3×10^{-12} (t = 100 h)	-	-
AN2-1200 °C	0.59	-	2.6×10^{-14} (t = 100 h)	-

The overall oxidation weight gain in this particular case (paralinear oxidation) was obtained using the equation [111]:

$$(\Delta m/A) = k_p t^{0.5} - k_l t \quad \text{Equation 1}$$

where the k_p (mg²cm⁻⁴s⁻¹) and k_l (mgcm⁻²s⁻¹) are the parabolic and linear oxidation rate constant. In equation (1), the first part on the right hand side is responsible for parabolic weight gain and the second part is responsible for simultaneous weight loss of the alloy.

In this study, for comparison purposes, the parabolic section of the curves was only chosen. The parabolic oxidation rate constants, K_p , of the alloys AN1 and AN2 calculated in Figure 5.8 were used to draw an Arrhenius-type plot for the alloys, see Figure 5.9.

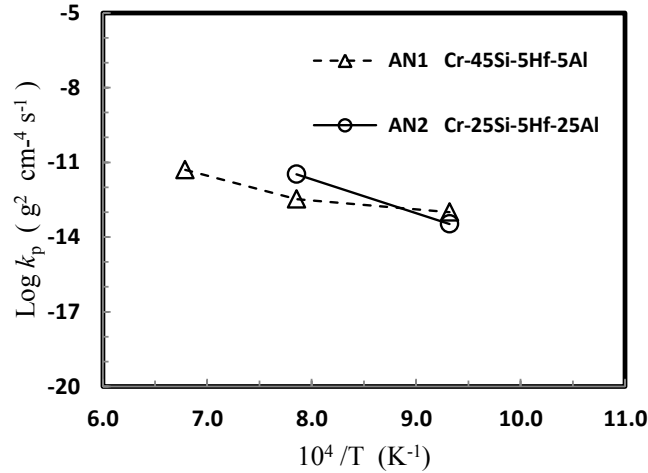


Figure 5.9 Arrhenius plots showing the variation of parabolic rate constants versus temperature for the as-cast alloys AN1 and AN2.

Table 5-6 Activation energies for the growth of $\text{Al}_2\text{O}_3/\text{SiO}_2$ scales on as cast AN1 and AN2 alloys

Alloy	Time (h)	(Temperature range oC)	Activation energy (kJmol ⁻¹)
AN1-AC	1-100	800-1000	68.4±3.4
AN1-AC	1-100	1000-1200	211.1± 2.7
AN2-AC	1-100	800-1000	182.8± 4.6

The activation energies for oxidation were obtained using the Arrhenius equation [112]:

$$k_p = k_0 \cdot \exp(-Q_A/RT) \quad \text{Equation 2}$$

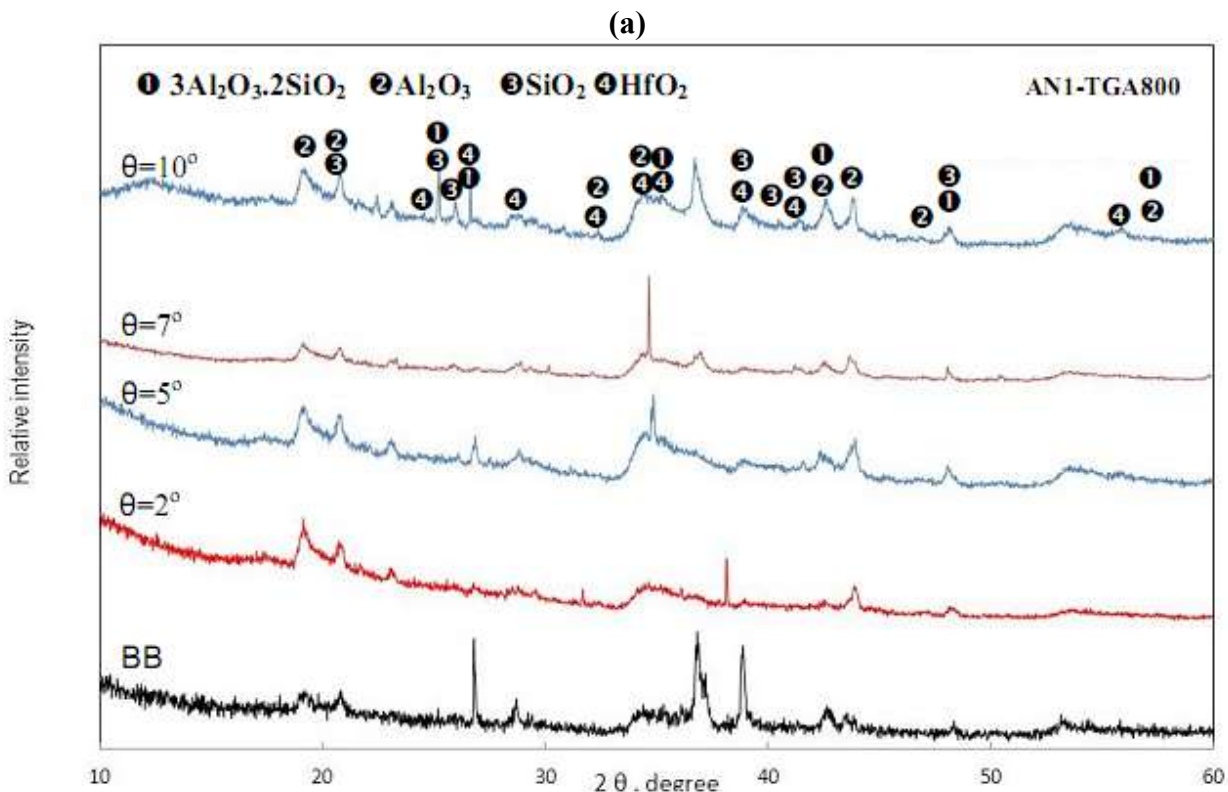
where k_p is the parabolic rate constant ($\text{g}^2\text{cm}^{-4}\text{s}^{-1}$), K_0 is pre-exponential factor, R is the gas constant (8.3144 J/Kmol), T is the absolute temperature and Q_A is the activation energy of overall reaction (kJ/mol).

The data for AN1 in Figure 5.9 indicates that a single mechanism was not operative in the entire temperature range of oxidation. The activation energy of the oxidation reaction of AN2 was 182.8 kJ/mol at 800-1000°C and for the alloy AN1 was 68.4 and 211.1 kJ/mol at the temperature ranges 800-1000 °C and 1000-1200 °C, respectively. The activation energy for the oxidation of

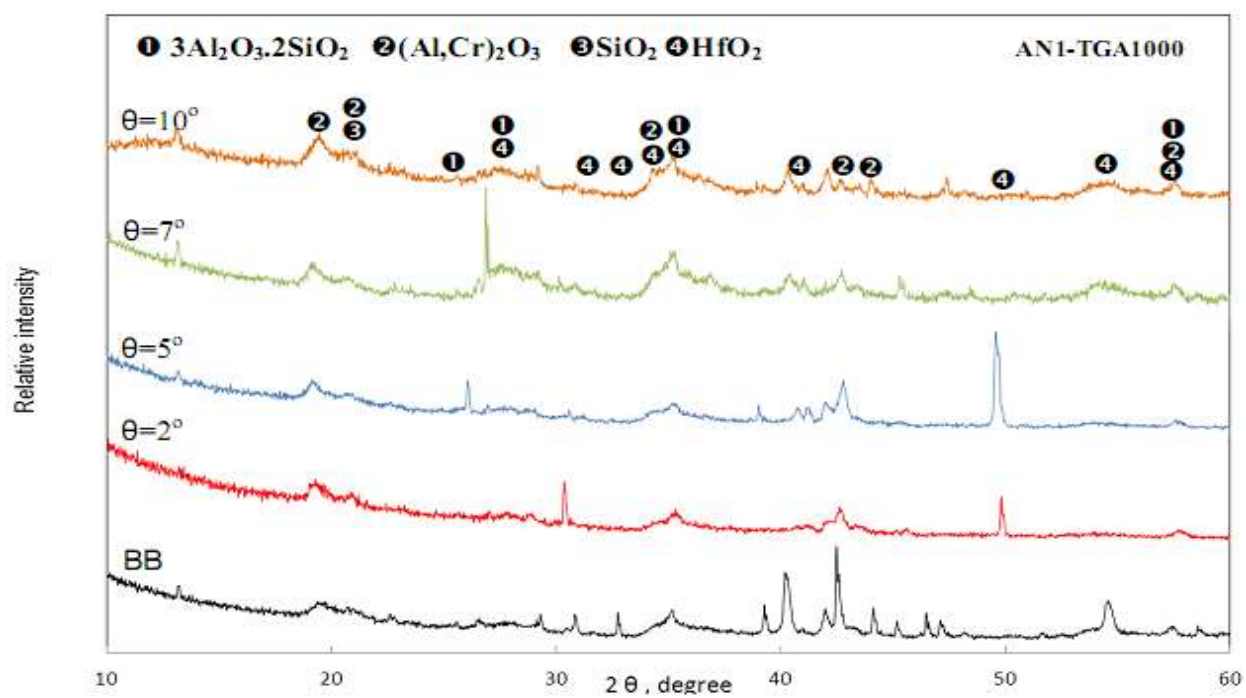
AN1 at 1000-1200 °C was approximately 3 times higher than that at 800-1000 °C. This indicated that the alloy AN1 possessed better oxidation at temperatures below 1000 °C rather than at higher temperatures as it could form scale quickly [113]. The alloy AN2 with activation energy higher than 68.4 kJ/mol exhibited worse oxidation behaviour than AN1 at 800-1000 °C.

5.2.3.2 Oxide scale characterization

The GAXRD data for the specimens of the alloy AN1 and AN2 oxidised at 800, 1000 and 1200 °C is shown in Figure 5.10 and Figure 5.11. Secondary electron (SE) micrographs of the surfaces of the oxidised specimens of alloys AN1 and AN2 are shown in Figure 5.12 and Figure 5.14 for 800, 1000 and 1200 °C. At 800 °C, the alloy AN1 formed a non-uniform alumina oxide along with patches of silica scale where there was HfO_2 formed on the surface of Hf_6Si_5 silicide, see Figure 5.10 (a). The scale was uneven due to different oxidation of the constituent phases. The presence of different oxides was verified by glancing angle XRD by changing the incident beam from 2 degree to 10 degree compared with the Bragg-Brentano geometry, as shown in Figure 5.10 and Figure 5.11.



(b)



(c)

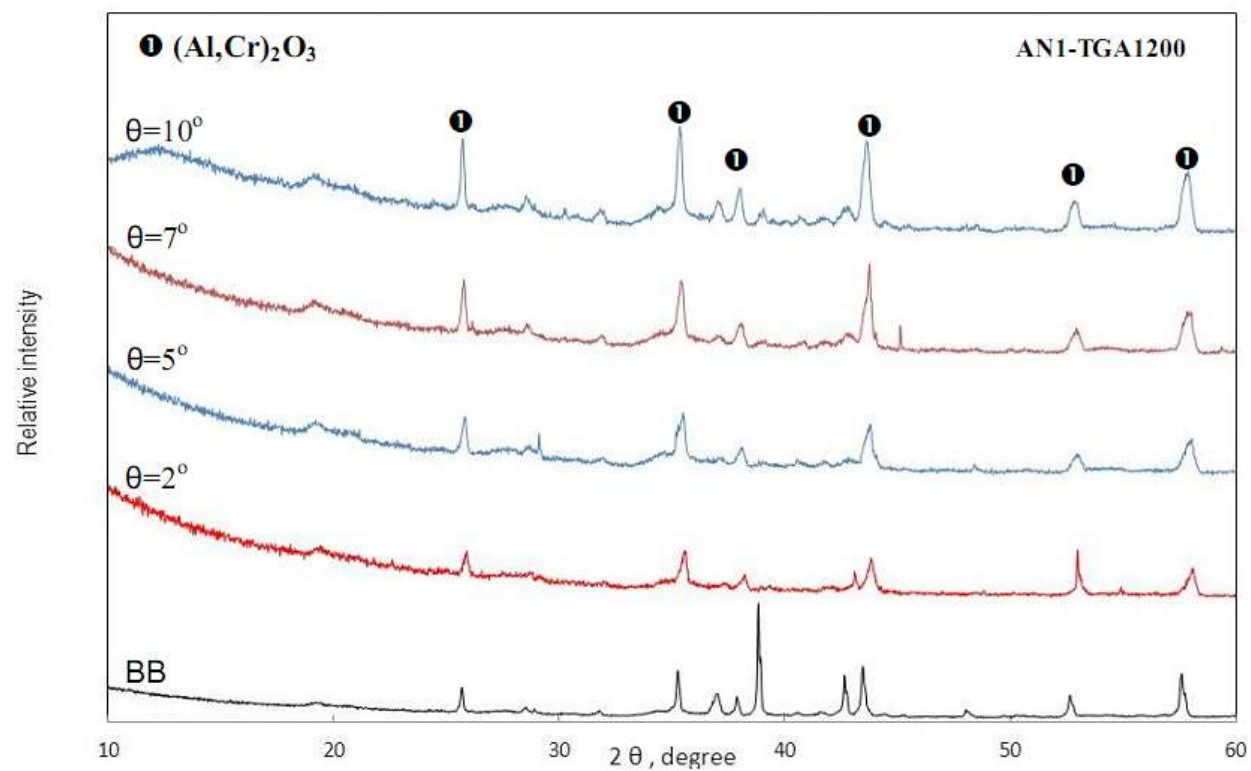
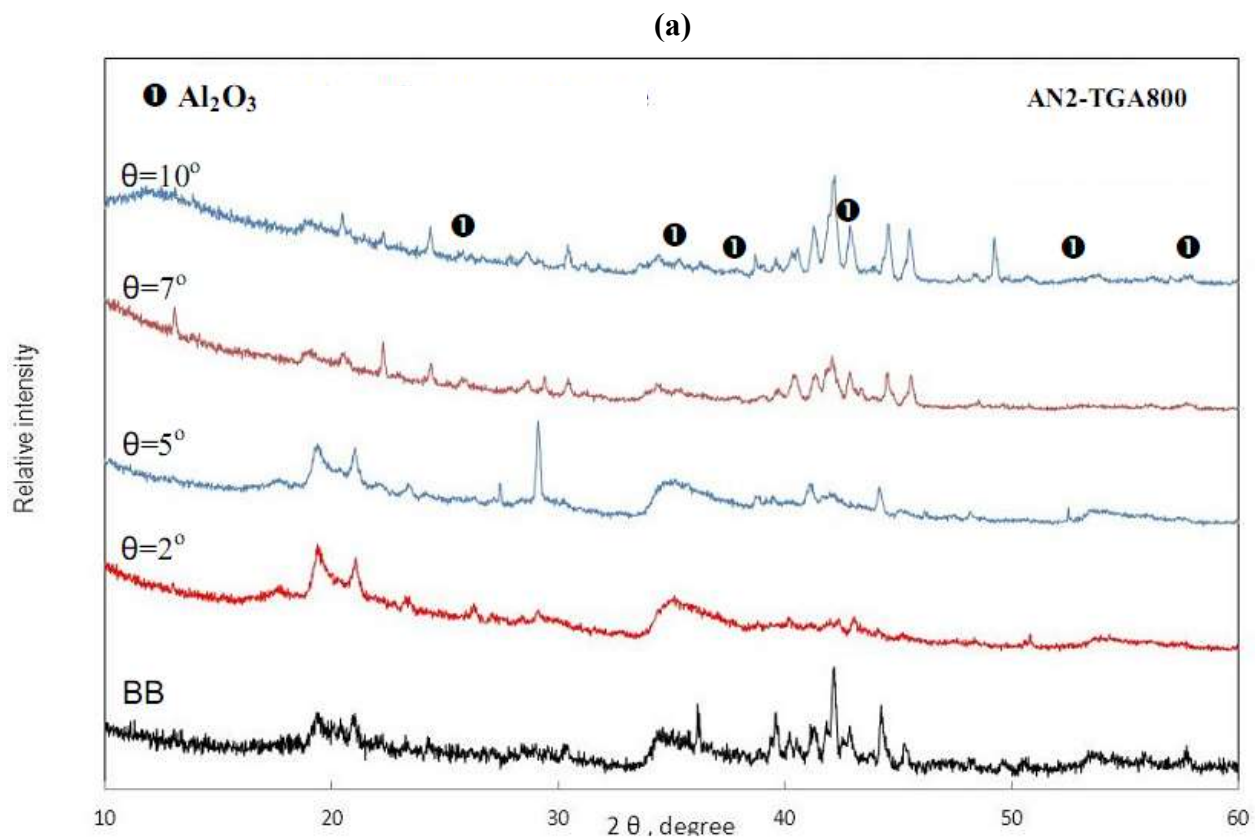


Figure 5.10 Glancing angle XRD data at different incident beam angles (θ) of the scale formed on the oxidized ANI specimen at (a) 800 °C, (b) 1000 °C and (c) 1200 °C (BB refers to Bragg Brentano geometry diffraction pattern taken from TGA cube sample before isothermal oxidation experiment)

Figures 5.12 (a3) and (a4) show dark patches of alumina scale formed in the surface and Figure 5.12 (a5) shows silica oxides with HfO_2 fine particles. At 1000 °C, the scale consisted of continuous alumina oxides (Figure 5.12 (b1) and (b2), the latter shows alumina patch) that spalled during the oxidation experiment either in the isothermal stage or during cooling, Figure 5.10 (b). Pores formed on the substrate are shown in Figure 5.12 (b4). Alumina oxides grains are shown in Figure 5.12 (b5) where HfO_2 oxides particles are dispersed in the scale.



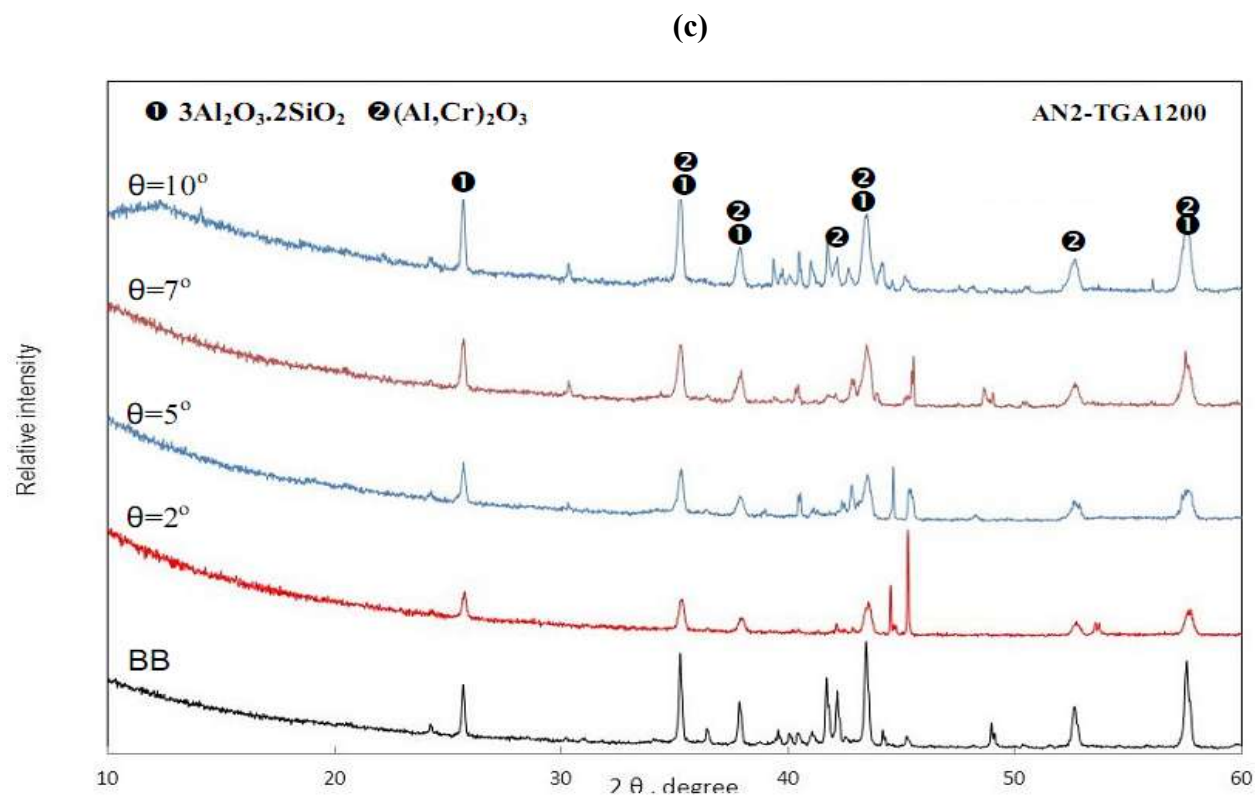
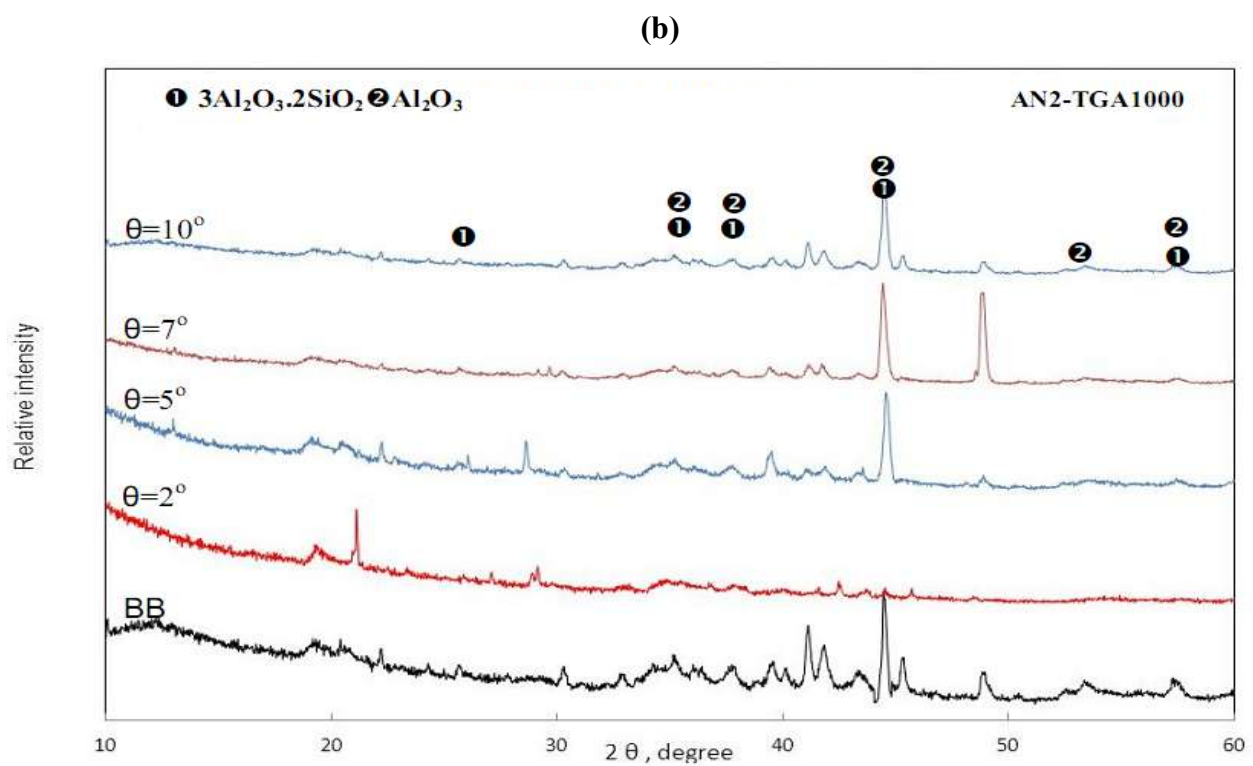


Figure 5.11 Glancing angle XRD data at different incident beam angles (θ) of the scale formed on the oxidized AN2 specimen at (a) 800 °C, (b) 1000 °C and (c) 1200 °C (BB refers to Bragg Brentano geometry diffraction pattern taken from TGA cube sample before isothermal oxidation experiment)

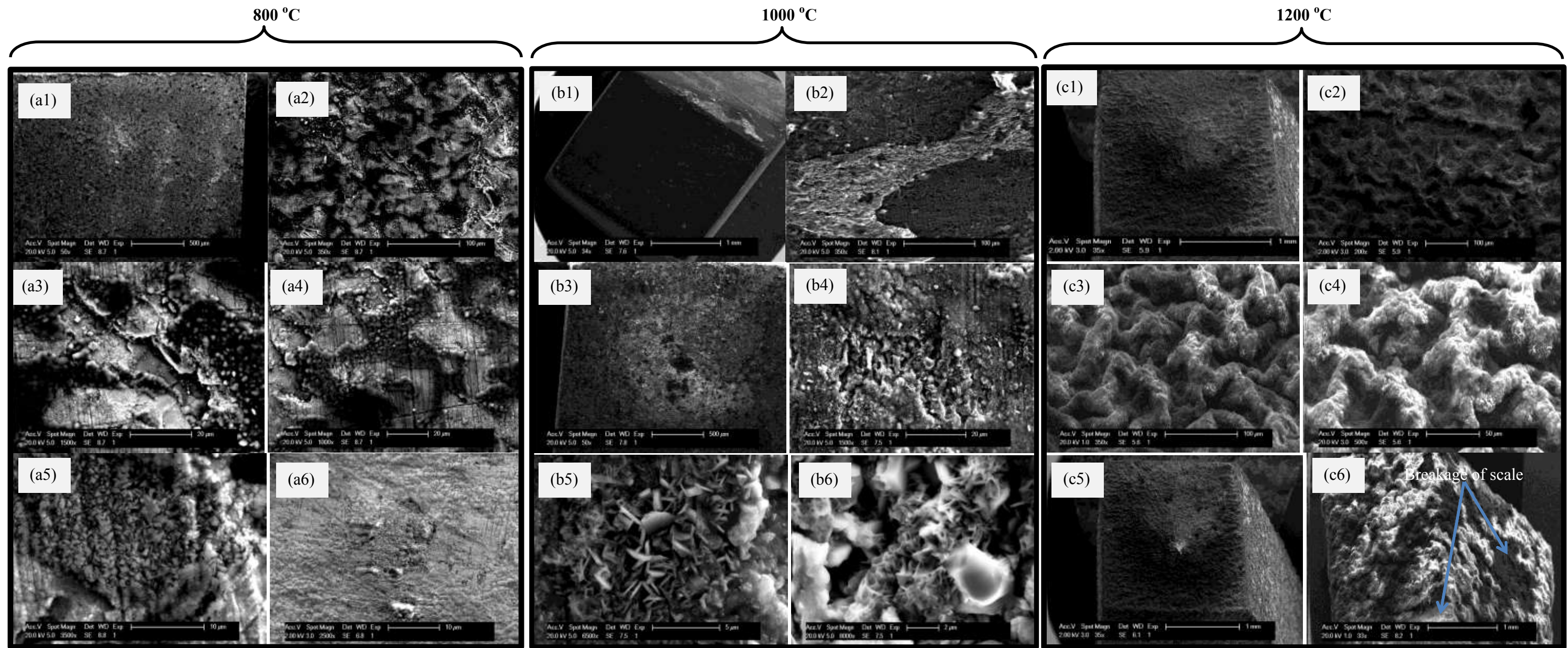


Figure 5.12 SEM-SE images of the oxide scales formed on the cast AN1 alloy after 100 h oxidation in air at (a) 800 °C, (b) 1000 °C and (c) 1200 °C.

The scale formed at 1000 °C was rather uniform compared with that formed at 800 °C. At 1200 °C corrugated (Al,Cr)₂O₃ scale formed (Figure 5.12 and Figure 5.10 c). This could be due to growth stresses that resulted from oxide formation at oxide-substrate interface owing to counter current cation and anion diffusion in oxides and /or thermal contraction mismatch at oxide-substrate interface. Overall the scale exhibited rather good adherence to the substrate but in some areas it was completely spalled; this could have occurred during cooling of specimen to ambient temperature.

The morphology of the scale formed on the oxidized samples of the alloy AN2 is shown in Figure 5.14. At 800 °C, a continuous alumina scale (Figure 5.11 a) was formed on the surface that partially spalled due to the compressive stress induced in the oxide/substrate interface, as shown in Figure 5.14 (a3 and a4) and the elemental map in Figure 5.13. This spallation also occurred because of low supply of Al from the precursor phase that was rich in Cr and Si. Therefore the scale continuity was disrupted due to Al deficit in the interface of substrate and scale. At 1000 °C, the diffusivity of Al and O increased, continuous alumina scale formed (see Figure 5.11 b) on the surface and there was enough Al flux to the interface between substrate and scale to preserve the scale from spallation. Diffusion controlled creep process relieved the growth stresses generated in the scale. There was also whisker formation in the scale (Figure 5.14 b4) that relieved compressive stresses at 1000 °C. The scale was partially spalled near the edges of the specimen and some other regions as shown in Figure 5.14 (b3, b6). At 1200 °C, the alloy AN2 formed a buckled alumina scale (see Figure 5.11 c) as shown in Figure 5.14 (c1- c6). It is suggested that the compressive stress built up due to the lateral growth of the scale or generated during cooling caused the buckling of the scale.

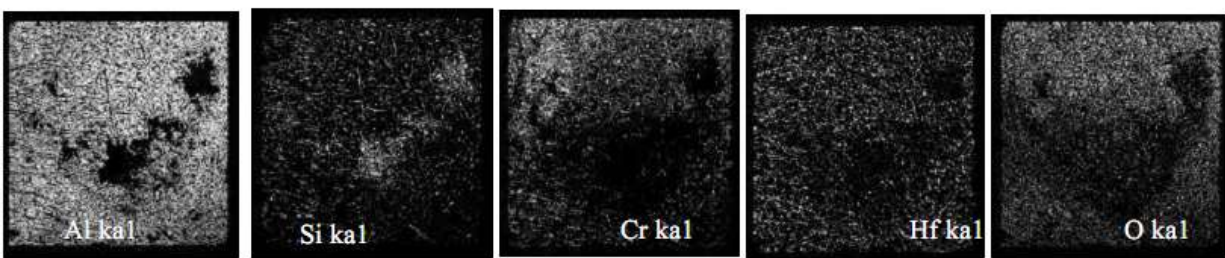


Figure 5.13 surface elemental maps of Al, Si, Cr, Hf and O on the oxidised specimen of the alloy AN1 at 800 °C

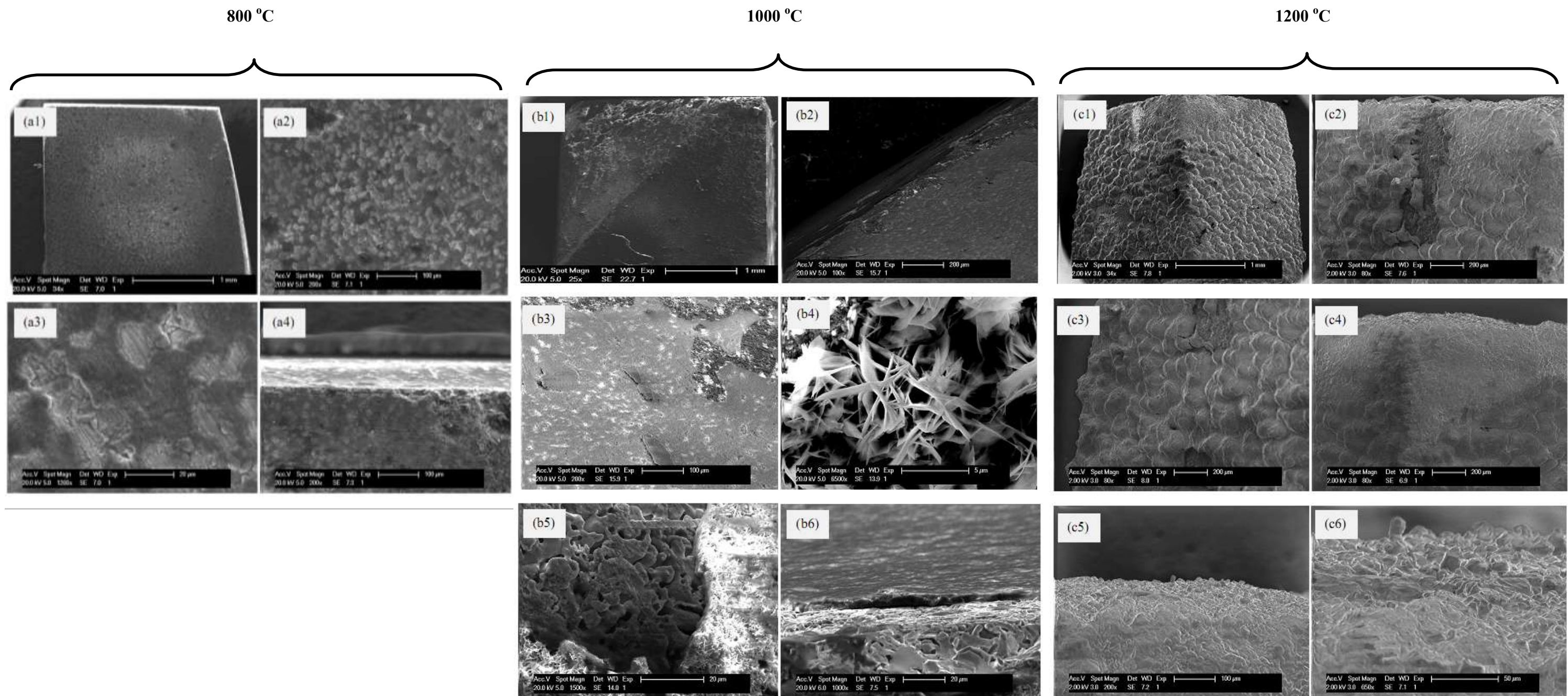


Figure 5.14 SEM-SE images of the oxide scales formed on the cast AN2 alloy after 100 h oxidation in air at 800 °C, (b) 1000 °C and (c) 1200 °C.

5.3 Discussion

5.3.1 Microstructures of Cr-45Si-5Al-5Hf (alloy AN1)

The solidification microstructure of AN1-AC would suggest that the Hf_6Si_5 silicide was the primary phase. Strictly speaking the primary phase is of the M_6Si_5 type or more correctly $\text{M}_2\text{Cr}_4\text{Si}_5$ (see Table 4-3). As we shall see in the following chapters for Cr-45Si-5Al-5M alloys where $\text{M} = \text{Nb}, \text{Ti}$, the 6-5 silicide was observed in those alloys as well. Thus, it was decided to call Hf_6Si_5 the primary phase in AN1-AC in order to emphasise the fact that Hf in synergy with Cr and Si formed $(\text{Cr},\text{Hf})_6\text{Si}_5$ in this alloy. Considering the melting temperatures of Cr_5Si_3 and CrSi_2 , of which that of the former is higher (see Figure 2.1), the solidification path of AN1-AC was $\text{L} \rightarrow \text{L} + (\text{Hf},\text{Cr})_6\text{Si}_5 \rightarrow \text{L} + (\text{Hf},\text{Cr})_6\text{Si}_5 + \text{Cr}_5(\text{Si},\text{Al})_3 \rightarrow (\text{Hf},\text{Cr})_6\text{Si}_5 + \text{Cr}_5(\text{Si},\text{Al})_3 + \text{Cr}(\text{Si},\text{Al})_2$ with $(\text{Hf},\text{Cr})_6\text{Si}_5$ as the primary phase. As the 6-5 primary silicide phase was formed in the melt, the latter became richer in Cr. Thus, in the areas near the primary 6-5 silicide the melt reached a composition with $\text{Cr}/(\text{Si}+\text{Al}) \approx 5/3$ and $\beta \text{Cr}_5(\text{Si},\text{Al})_3$ was formed. Then, the melt in front of the 5-3 silicide became leaner in Cr but richer in Si and Al so that the melt reached a composition with $\text{Cr}/(\text{Si}+\text{Al}) \approx 1/2$ and the $\text{Cr}(\text{Si},\text{Al})_2$ was formed.

The aforementioned solidification path for AN1-AC can be compared with the calculated paths using the Pandat and ThermoCalc SSOL4 databases. The former gives (with comments by the author in parenthesis)

1925 K LIQUID $\rightarrow \text{Hf}_5\text{Si}_4$

1767 K LIQUID $\rightarrow \text{Hf}_5\text{Si}_4 + \text{Si}_3\text{Ti}_5$ (meaning hexagonal 5-3 silicide with prototype Mn_5Si_3)

1733 K LIQUID $+ \text{Si}_3\text{Ti}_5 \rightarrow \text{Hf}_5\text{Si}_4 + \text{Mo}_5\text{Si}_3$ (meaning tetragonal 5-3 silicide with prototype W_5Si_3 , i.e., isomorphous with Cr_5Si_3 , see section 2.2)

1627 K LIQUID $+ \text{Mo}_5\text{Si}_3 \rightarrow \text{Hf}_5\text{Si}_4 + \text{CrSi}$

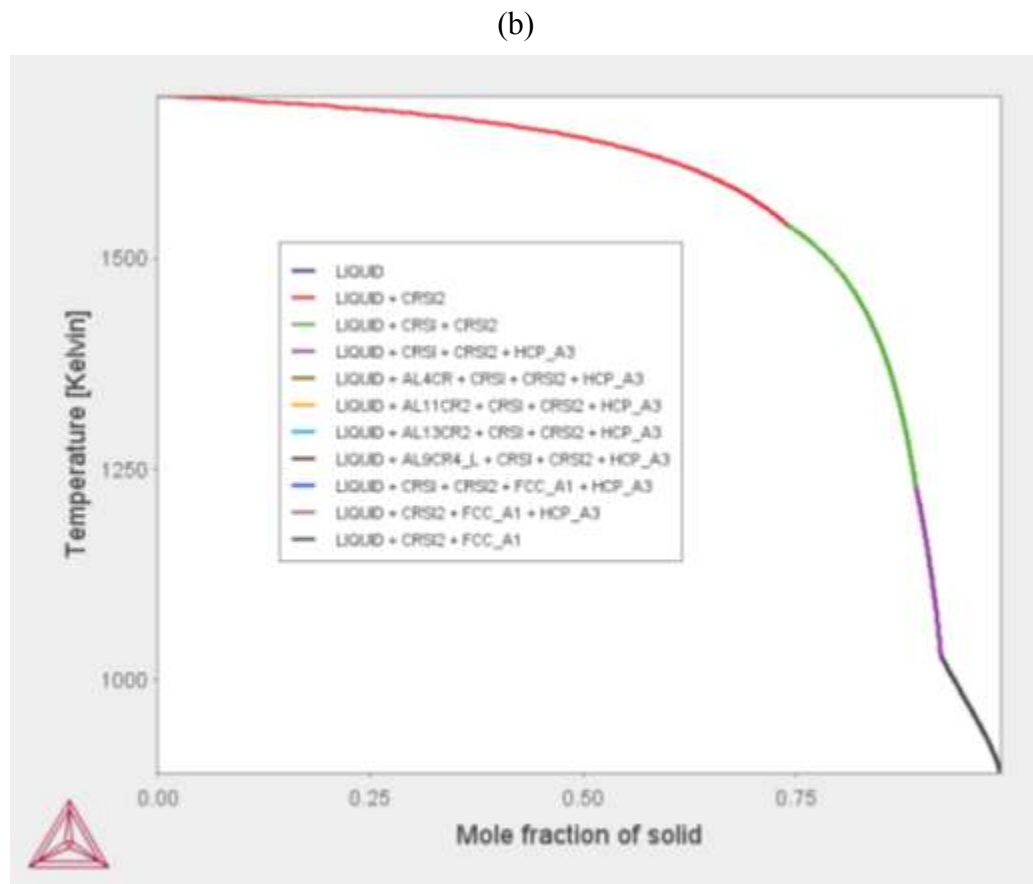
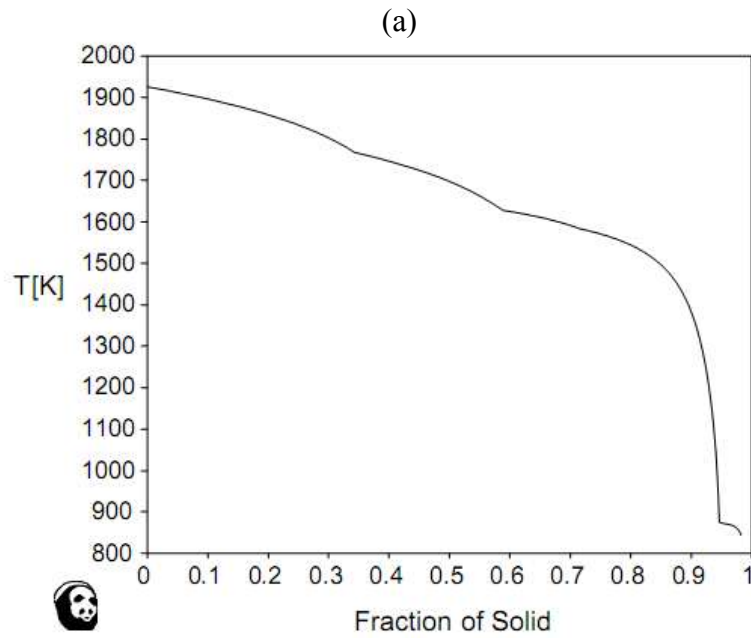


Figure 5.15 Solidification path for the alloy AN1-AC using a) Pandat database b) ThermoCalc SSOL4 database

1582 K LIQUID $\rightarrow$ Hf₅Si₄ + CrSi + CrSi₂

870 K LIQUID + Hf₅Si₄ + CrSi $\rightarrow$ FCC_Al + Mo₅Si₃

842 K LIQUID + Hf₅Si₄ + FCC_Al + Mo₅Si₃

According to Pandat the primary phase in AN1-AC should be the tetragonal Hf₅Si₄ and hexagonal 5-3 silicide, CrSi and Al should form during solidification. The calculated path correctly predicts formation of tetragonal 5-3 silicide not as primary phase, an Hf silicide as the primary phase (but not the one identified in the alloy) and can account for the formation of CrSi₂.

The solidification path of AN1 using ThermoCalc is shown in Figure 5.15(b). According to ThermoCalc, the CrSi should be the primary phase, and during solidification hexagonal Hf, Al₄Cr, Al₁₁Cr₂, Al₁₃Cr₂, Al₉Cr₄ and fcc Al should form. The calculated path correctly predicts formation of CrSi₂ but cannot account for the formation of the 6-5 and 5-3 silicides.

The above data shows that the two databases are not accurate enough, in particular ThermoCalc SSLO4.

If we were to consider Cr and Hf as equivalent and Al and Si as equivalent so that the alloy AN1 can be considered respectively as Cr-45Si-5Al or Cr-50Si-5Hf then the Pandat database gives for the former alloy composition the solidification path as follows (Figure 5.16 a):

1541°C LIQUID $\rightarrow$ Si₃Ti₅ (meaning hexagonal 5-3 silicide with prototype Mn₅Si₃)

1481°C LIQUID + Si₃Ti₅ $\rightarrow$ Mo₅Si₃ (meaning tetragonal 5-3 silicide with prototype W₅Si₃, i.e., isomorphous with Cr₅Si₃, see section 2.2)

1372°C LIQUID + Mo₅Si₃ $\rightarrow$ CrSi

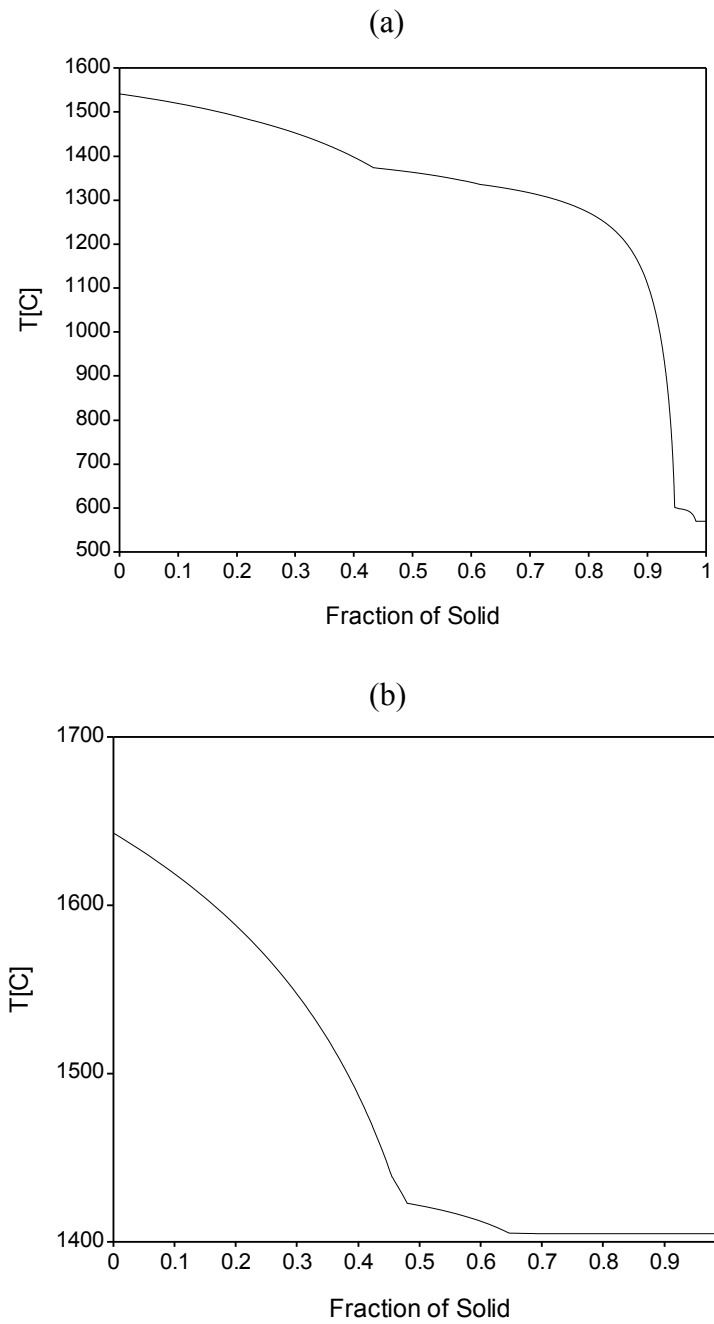


Figure 5.16 Solidification path for the alloy AN1-AC using Pandat database a) Cr-45Si-5Al (Cr and Hf as equivalent) b) Cr-50Si-5Hf (Al and Si as equivalent)

1334°C LIQUID $\rightarrow$ CrSi + CrSi₂

600°C LIQUID + CrSi₂ $\rightarrow$ CrSi + FCC_A1

597°C LIQUID + CrSi $\rightarrow$ FCC_A1 + Mo₅Si₃

569°C LIQUID $\rightarrow$ FCC_A1 + Mo₅Si₃ + BCC_A2

and for the latter composition the solidification path is as follows (Figure 5.16 b):

1643 C LIQUID $\rightarrow$ Hf₅Si₄

1438 C LIQUID $\rightarrow$ Hf₅Si₄ + Mo₅Si₃ (meaning tetragonal 5-3 silicide with prototype W₅Si₃, i.e., isomorphous with Cr₅Si₃, see section 2.2)

1422 C LIQUID + Mo₅Si₃ $\rightarrow$ Hf₅Si₄ + CrSi

1422 C LIQUID + Hf₅Si₄ $\rightarrow$ CrSi

1422 C LIQUID $\rightarrow$ CrSi

1405 C LIQUID $\rightarrow$ CrSi + CrSi₂

1404 C LIQUID $\rightarrow$ CrSi + CrSi₂ + Hf₅Si₄

The above data and its comparison with the experimental results for AN1-AC would thus suggest that the synergy of Al, Si and Hf in AN1 suppressed the formation of CrSi and stabilises an M_6Si_5 type silicide rather than an M_5Si_4 one.

In the AN1-AC in the $(Cr,Hf)_6Si_5$ there was no solid solubility of Al. In the 5-3 silicide the Si was substituted by Al, in agreement with [10] and other work on M_5Si_3 silicides in TM-Si-Al based alloys, where TM is transition metal(s), with Si + Al = 40.1 at%, in agreement with the composition of $Cr_5(Si,Al)_3$ (Figure 2.1). In the $Cr(Si,Al)_2$ the Si + Al = 66.6 at%, the Si was also substituted by Al, in agreement with [10,43,44,114-116] and the solubility of the latter in $Cr(Si,Al)_2$ was significantly higher compared with $Cr_5(Si,Al)_3$. There was no solubility of Hf in $Cr_5(Si,Al)_3$ and $Cr(Si,Al)_2$.

The same phases were present in the alloy AN1 after the two heat treatments. After the heat treatment at 1200 °C, the area fraction of the primary Hf_6Si_5 in AN1-AC was very close to that of AN1-HT12 (Table 5-1) and no coarsening of the Hf_6Si_5 had occurred. The % area of the 5-3 and 1-2 silicides had increased and decreased respectively, probably because of the slightly different components of the AN1-HT1200 specimen (Table 5-2). No coarsening of the primary phase Hf_6Si_5 was observed after the heat treatment at 1300 °C and its area fraction had increased compared with the AN1-HT12 and AN1-AC. The % area of the Cr_5Si_3 and $CrSi_2$ had increased and decreased respectively compared with AN1-HT1200. This would suggest that, at 1300 °C, the three phase field corner had shifted, compared with that at 1200 °C. After the heat treatments the solubility of Hf in the 6-5 silicide decreased slightly. The composition of $Cr_5(Si,Al)_3$ was essentially unchanged and the solubility of Al was reduced in $Cr(Si,Al)_2$, in agreement with data reported in [10,40], but always the Si + Al content was as expected for $CrSi_2$ (Figure 2.1).

5.3.2 Microstructures of Cr-25Si-25Al-5Hf (alloy AN2)

The solidification microstructure of AN2-AC would suggest that the Hf_6Si_5 silicide was the primary phase. Strictly speaking, the primary phase is of the M_6Si_5 type (Table 2-6) or more correctly $M_2Cr_4Si_5$ (see Table 4-3). As the 6-5 silicide formed, the surrounding melt became lean in Si and rich in Al, thus the Cr_3Si formed making the melt richer in Al, then the Cr_5Si_3 formed

making the melt lean in Si and richer still in Al, such that eventually the Al_8Cr_5 intermetallic formed from the Al rich and Si poor melt. Considering the melting temperatures of Cr_3Si , Cr_5Si_3 , of which that of the former is higher (see Figure 2.1), and the melting temperature of Al_8Cr_5 (see figure 2.2), which is lower than that of Cr_5Si_3 , it is suggested that the solidification path of AN2-AC was $\text{L} \rightarrow \text{L} + \text{Hf}_6\text{Si}_5 \rightarrow \text{L} + \text{Hf}_6\text{Si}_5 + \text{Cr}_3\text{Si} \rightarrow \text{L} + \text{Hf}_6\text{Si}_5 + \text{Cr}_3\text{Si} + \text{Cr}_5\text{Si}_3 \rightarrow \text{Hf}_6\text{Si}_5 + \text{Cr}_3\text{Si} + \text{Cr}_5\text{Si}_3 + \text{Al}_8\text{Cr}_5$, with the crust of Cr_5Si_3 around Cr_3Si (Figure 5.4b) suggesting a peritectic reaction between Cr_3Si and Cr_5Si_3 . Such a reaction does not exist in the binary Cr-Si (Figure 2.2), where the peritectic $\text{L} + \text{Cr}_5\text{Si}_3 \rightarrow \text{CrSi}$ and the eutectic $\text{L} \rightarrow \text{Cr}_3\text{Si} + \text{Cr}_5\text{Si}_3$ exist, respectively at 1440 and 1675 °C. The co-existence of Cr_5Si_3 and Al_8Cr_5 in the microstructure is in agreement with the results of Gupta [10], who suggested the presence of $\text{Cr}_5\text{Si}_3 + \text{Al}_8\text{Cr}_5$ phase field in the Cr-Al-Si ternary, see section 2.11.

The aforementioned solidification path for AN2-AC can be compared with the calculated paths using the Pandat and ThermoCalc SSOL4 databases. The former gives (with comments by the author in parenthesis)

2066 K LIQUID $\rightarrow$ Si_3Ti_5 (meaning hexagonal 5-3 silicide with prototype Mn_5Si_3)

1926 K $\text{Si}_3\text{Ti}_5 \rightarrow$ LIQUID + Hf_3Si_2

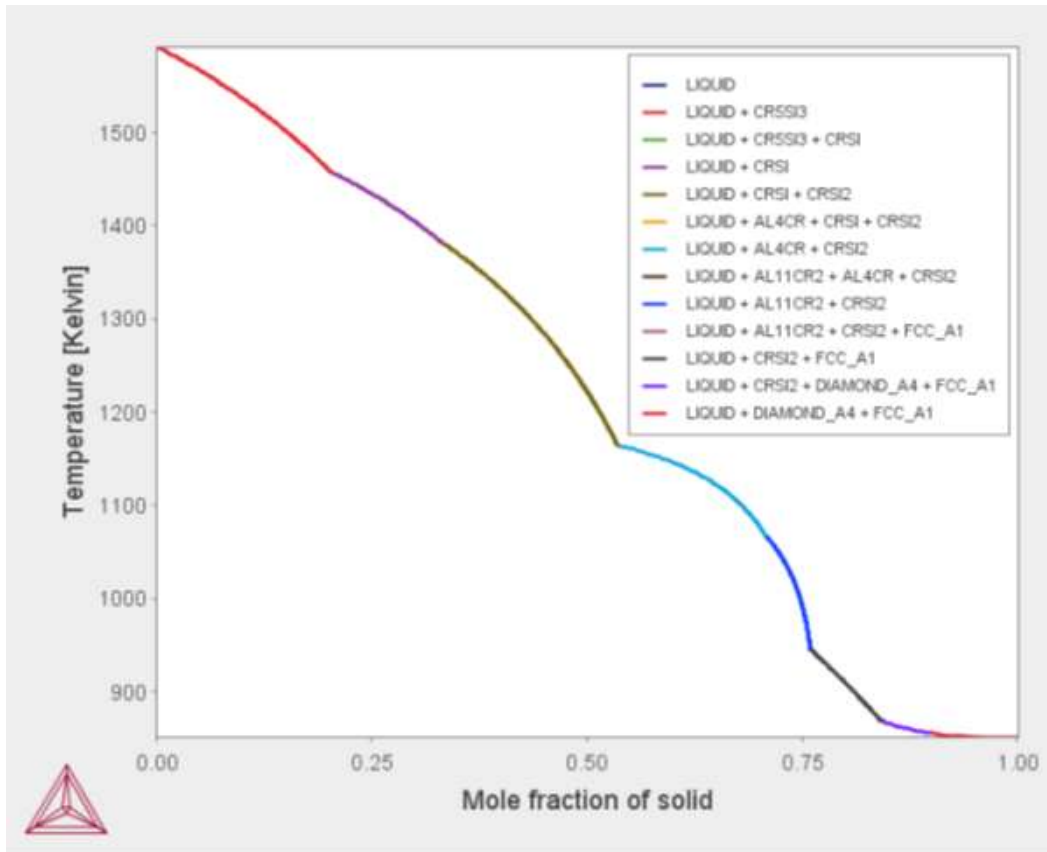
1733 K LIQUID + $\text{Hf}_3\text{Si}_2 \rightarrow$ Hf_5Si_4

1705 K LIQUID + $\text{Hf}_5\text{Si}_4 \rightarrow$ Si_3Ti_5

1687 K LIQUID $\rightarrow$ Si_3Ti_5 + A15_Nb₃Al (meaning Cr_3Si as this is also an A15 phase)

1663 K LIQUID + $\text{Si}_3\text{Ti}_5 \rightarrow$ A15_Nb₃Al + Mo_5Si_3 (meaning tetragonal 5-3 silicide with prototype W_5Si_3 , i.e., isomorphous with Cr_5Si_3 , see section 2.2)

(a)



(b)

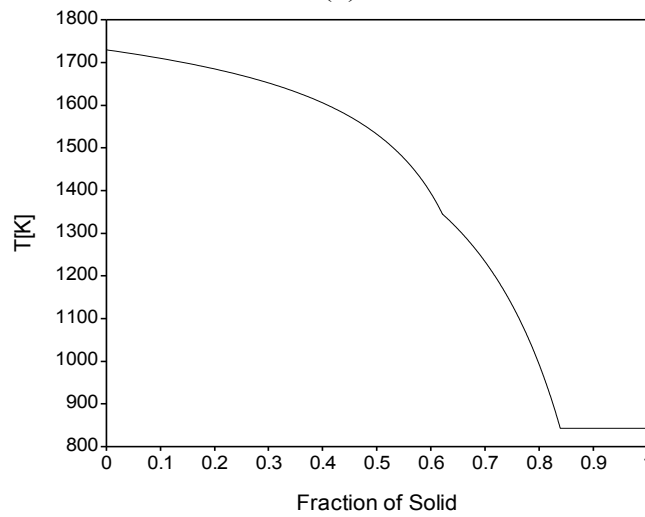


Figure 5.17 Solidification path for the alloy AN2-AC using a) ThermoCalc SSOL4 database (b) Pandat database and consider AN2 as Cr-25Si-25Al (Cr and Hf as equivalent)

1663 K LIQUID $\rightarrow$ A15_Nb₃Al + Mo₅Si₃

1344 K LIQUID + A15_Nb₃Al $\rightarrow$ Mo₅Si₃ + BCC_A2

1344 K LIQUID $\rightarrow$ Mo₅Si₃ + BCC_A2

1177 K LIQUID + Mo₅Si₃ + BCC_A2

According to Pandat the primary phase in AN2-AC should be the hexagonal 5-3 silicide, then the tetragonal Hf₃Si₂ and Hf₅Si₄ should form before Cr₃Si, then tetragonal 5-3 silicide and then bcc Cr. Thus, the calculated path correctly predicts formation of A15 Cr₃Si and tetragonal 5-3 silicide and the sequence of formation of these intermetallics, it also predicts that Hf-Si intermetallics should form before Cr₃Si but cannot account for the 6-5 silicide as the primary phase and the formation of the Al₈Cr₅ phase.

The solidification path of AN2 using ThermoCalc is shown in Figure 5.17(a). According to ThermoCalc, solidification should start with Cr₅Si₃ as the primary phase followed by formation of CrSi and CrSi₂ and then Al₄Cr, Al₁₁Cr₂, and Al and Si. The calculated path cannot account for the formation of the 6-5 silicide as the primary phase, and the Cr₃Si and Al₈Cr₅ intermetallics.

The above data confirms the inadequacies of both data bases, which are found to be not accurate enough, in particular ThermoCalc SSLO4.

If we were to consider Cr and Hf as equivalent so that the alloy AN2 can be considered as Cr-25Si-25Al then the Pandat database gives for this alloy composition the solidification path as follows (Figure 5.17 b):

1729 K LIQUID $\rightarrow$ Mo₅Si₃ (meaning tetragonal 5-3 silicide with prototype W₅Si₃, i.e., isomorphous with Cr₅Si₃, see section 2.2)

1690 K LIQUID $\rightarrow$ Mo_5Si_3 + A15_Nb₃Al (meaning Cr_3Si as this is also an A15 phase)

1344 K LIQUID + A15_Nb₃Al $\rightarrow$ Mo_5Si_3 + BCC_A2

842 K LIQUID $\rightarrow$ Mo_5Si_3 + BCC_A2 + FCC_A1

The calculated solidification path cannot account for the 6-5 silicide as the primary phase and the formation of Al_8Cr_5 ; it predicts formation of the tetragonal 5-3 before Cr_3Si , as well as formation of bcc Cr and fcc Al.

The above data and its comparison with the experimental results for AN2-AC provides further support that the synergy of Al, Si and Hf suppresses the formation of CrSi and stabilises an M_6Si_5 type silicide.

In AN2-AC, in the 6-5 silicide about 5 at% Al was in solution (Table 5-3) substituting Si, with Si + Al = 44 at%, i.e., essentially the same as the Si content in the 6-5 silicide in AN1-AC (see Table 5-2). The data for AN2-AC would thus suggest that in the 6-5 silicide the solubility of Al depends on the Al concentration in the alloy. There was no Hf in solution in the 5-3 silicide, in agreement with the results for AN1-AC, and with Si + Al = 38.7 at%, which is also in agreement with the binary system (Figure 2.1). In the Cr_3Si there was solubility of Hf, the solubility of Al was in agreement with [40,43] but not [10], with Si + Al = 26 at% (in agreement with the Cr-Si binary, figure 2.1) and in the Al_8Cr_5 there was no solubility of Hf and the Al and Si concentrations were in agreement with the results of Gupta [10].

After the heat treatment at 1200 °C the same phases were present in AN2-HT1200 as in AN2-AC, with slight changes of the volume fractions of Hf_6Si_5 and Al_8Cr_5 and an increase and decrease of the volume fractions respectively of the Cr_5Si_3 and Cr_3Si , which is consistent with evolution of the peritectic micro-structure towards equilibrium. The microstructure shown in figure 5.4b would also suggest a eutectoid type transformation, with the product probably being

$\text{Cr}_5\text{Si}_3 + \text{Al}_8\text{Cr}_5$, possibly the reaction $\text{Cr}_3\text{Si} \rightarrow \text{Cr}_5\text{Si}_3 + \text{Al}_8\text{Cr}_5$, in other words the reduction in the volume fraction of Cr_3Si being the result of both the peritectic reaction moving towards completion and the aforementioned eutectoid. The compositions of the phases were essentially unchanged, particularly when considering their Al + Si contents. There was no solubility of Hf in the Cr_3Si , Cr_5Si_3 and Al_8Cr_5 intermetallics.

After the heat treatment at 1300 °C no Cr_3Si was present in the microstructure, the compositions of the remaining phases in AN2-HT1300 were not changed significantly compared with AN2-HT1200 (Table 5.3) and there was further increase of the volume fraction (and size) of the Cr_5Si_3 (as would be expected with the microstructure evolving towards equilibrium via the reactions mentioned in the previous paragraph) and respectively increase and decrease of the volume fractions of the Hf_6Si_5 and Al_8Cr_5 , consistent with the establishment of three phase equilibria. The DSC data for AN2 showed an endotherm between 1200 and 1300 °C. The Al_8Cr_5 intermetallic has the lower melting temperature (~ 1350 °C in its unalloyed form, figure 2.2) of the phases present in AN2, and according to Gupta [10] the Cr_5Si_3 can be in equilibrium with Al_9Cr_4 (melting temperature ~ 1170 C, Figure 2.2), or Al_8Cr_5 or with both of these Al rich intermetallics. Given that there was weak macrosegregation of Al in AN2-AC, and that the Al_8Cr_5 and Al_9Cr_4 can be alloyed with Si (as confirmed in this work for the former and for both by Gupta [10]) it is likely that the endotherm was due to the decomposition of some metastable Al-Cr-Si rich phase to $\text{Cr}_5(\text{Al},\text{Si})_8$ that was present in AN2-AC and not detected by XRD and EDX.

5.3.3 Hardness

Table 5-4 shows that the macrohardness of the alloy AN1 increased by $\sim 11\%$ after the heat treatment at 1200 °C, and decreased by $\sim 20\%$ after the heat treatment at 1300 °C compared with the as cast condition. The macrohardness of the alloy AN2 decreased after both heat treatments by $\sim 34\%$ after the heat treatment at 1200 °C and by $\sim 46\%$ after the heat treatment at 1300 °C compared with the as cast value. The microhardness of Hf_6Si_5 in the alloy AN1 was essentially unchanged after the heat treatments which is consistent with its unchanged composition. The microhardness of Hf_6Si_5 in AN2 could suggest a weak softening effect for Al for the as cast condition and after the heat treatment at 1200 °C and a stronger effect after the heat treatment at

1300 °C. However, in AN2 the Hf_6Si_5 had essentially the same composition in the three conditions. Thus, the low microhardness at 1300 °C cannot be linked with the Al content. If we compare the Hf_6Si_5 in the alloys AN1 and AN2, its microhardness in AN2-AC was slightly lower than in AN1-AC but almost the same in AN1-HT1200 and AN2-HT1200. Thus, an argument that the microhardness of Hf_6Si_5 is affected by its Al content must be weak. What has changed is the Si/Hf ratio in Hf_6Si_5 , which is lower in the alloy AN2. In AN1 the hardness of Hf_6Si_5 increased as the Si/Hf ratio increased and in AN2 the hardness decreased as the Si/Al ratio decreased. The microhardness of Cr_5Si_3 was higher in AN1 compared with AN2 where the Si+Al content of the silicide was lower. In both alloys the microhardness of Cr_5Si_3 decreased after heat treatment at 1300 °C compared with the as cast condition with the highest % reduction observed for AN1. Compared with the as cast condition, the microhardness of the CrSi_2 silicide in AN1 increased after the heat treatment at 1200 °C and then decreased at 1300 °C. The measured microhardness values in the as cast and HT1200 conditions were very close to those of the unalloyed CrSi_2 [1150, 1085 Hv] reported in [117,118]. The increase of the macrohardness of AN1 HT1200 was attributed to the increase of microhardness of CrSi_2 in this condition. The microhardness of Cr_3Si decreased by ~ 21% after the heat treatment at 1200 °C. The microhardness in the as cast condition was in good agreement with the values reported by Shah et al., Newkirk et al. and Raj [119-121]. The trend in the variation of the microhardness of Al_8Cr_5 was similar to that of the Cr_5Si_3 silicide. The measured microhardness of the Al_8Cr_5 at 1200 °C was very close to that reported by Neto et al. [122].

Table 5-7 Calculated hardness (HV) of the as cast (AC) and heat treated (HT) alloys AN1 and AN2.

Alloy ^a	Law of mixtures	Pythagorean type rule	Inverse type rule
AN1-AC	1152	683	1148
AN1-HT1200	1175	696	1173
AN1-HT1300	1032	671	1003
AN2-AC	903	497	858
AN2-HT1200	961	516	942
AN2-HT1300	728	440	714

^a AC=as cast , HT1200 and HT1300= heat treatment at 1200 °C and 1300 °C respectively for 100 h .

The calculated macrohardness of the alloys using the law of mixtures ($H_v = \sum V_i H_{vi}$), Pythagorean type rule ($H_v^2 = \sum (V_i H_{vi})^2$) and inverse type rule ($1/H_v = \sum V_i / H_{vi}$) is given in Table 5-7 where V_i is the area fraction of a constituent phase (Table 5-1) and H_{vi} is its microhardness (Table 5-4) [123]. The measured average hardness values of the alloys AN1 and AN2 (shown in Table 5-4) were in good agreement with those calculated values using the Pythagorean type rule. Similar agreement with the Pythagorean type rule was reported in [123,124].

5.3.4 Oxidation of alloys AN1 and AN2

The two alloys consisted of different silicides and aluminides with different volume fractions depending on the alloy Al/Si ratio and alloy condition. The alloys were evaluated for their oxidation behaviour in their as-cast condition. Qualitative and quantitative EDX analysis, elemental X-ray maps and GAXRD were used to study the scales.

A summary of the scales formed on the alloys AN1 and AN2 is given in Table 5-8. The alloys did not show any signs of accelerated or pest oxidation, but instead gained small weight and formed either mixture of oxides or a uniform scale (Table 5-8). For the three isothermal exposures, the morphology of the scale changed from cells to whiskers to ridges or buckled

Table 5-8 Summary of textures of the scales formed after isothermal oxidation at 800, 1000 and 1200 °C

Alloy	Temperature		
	800 °C	1000 °C	1200 °C
Cr-45Si-5Al-5Hf (AN1)	Cells, Al ₂ O ₃ patches SiO ₂ and HfO ₂ Mullite No spallation No uniform scale	Cells/whiskers SiO ₂ -(Al,Cr) ₂ O ₃ -HfO ₂ Mullite Spallation	Continuous scale (Al,Cr) ₂ O ₃ Corrugated scale Partially spalled
Cr-25Si-25Al-5Hf (AN2)	Cells Continuous Al ₂ O ₃ scale Silica islands No spallation.	Cells Al ₂ O ₃ and Mullite Continuous scale Partially spalled	Cells, whiskers (Al,Cr) ₂ O ₃ and mullite Buckled scale Partially spalled in ridges

scales. The alloy AN1 suffered from scale spallation at higher temperatures (1000-1200 °C). The scales grown on the alloy AN2 developed a convoluted morphology.

According to the Cr-Si-O [125] and the Hf-Si-O [126] ternary systems, the Cr silicides are in equilibrium with silica up to 1000 °C (Figure 5.18 a) whereas Hf silicides are in equilibrium with HfO₂ oxide (Figure 5.18 b). There is equilibrium between silica and hafnia oxides at higher oxygen partial pressure ($O_2 > 0.66$ at.%) where the hafnia is in equilibrium with Hafnium silicate and quartz is in equilibrium with hafnium silicate, as shown in Figure 5.18 b.

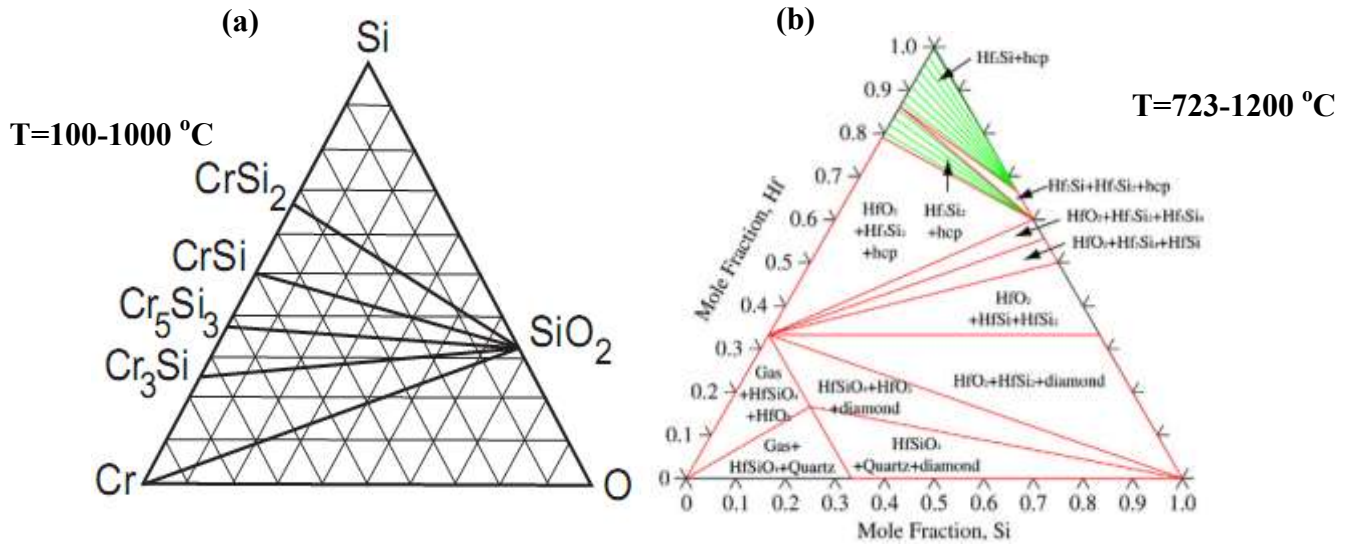
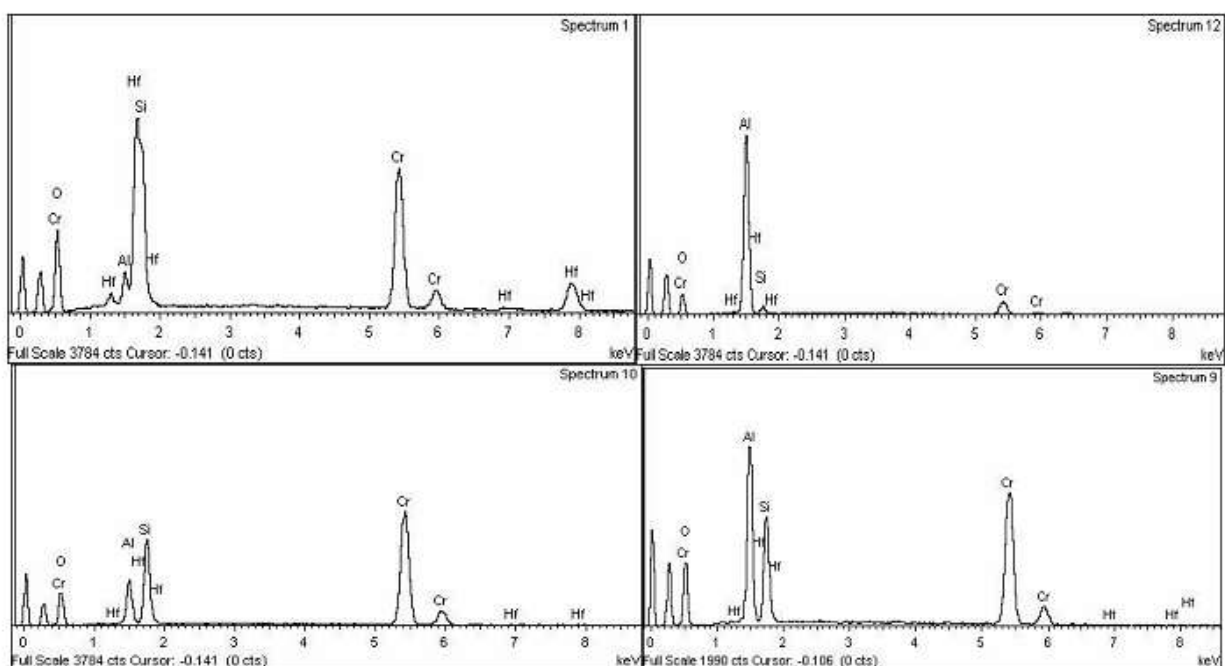
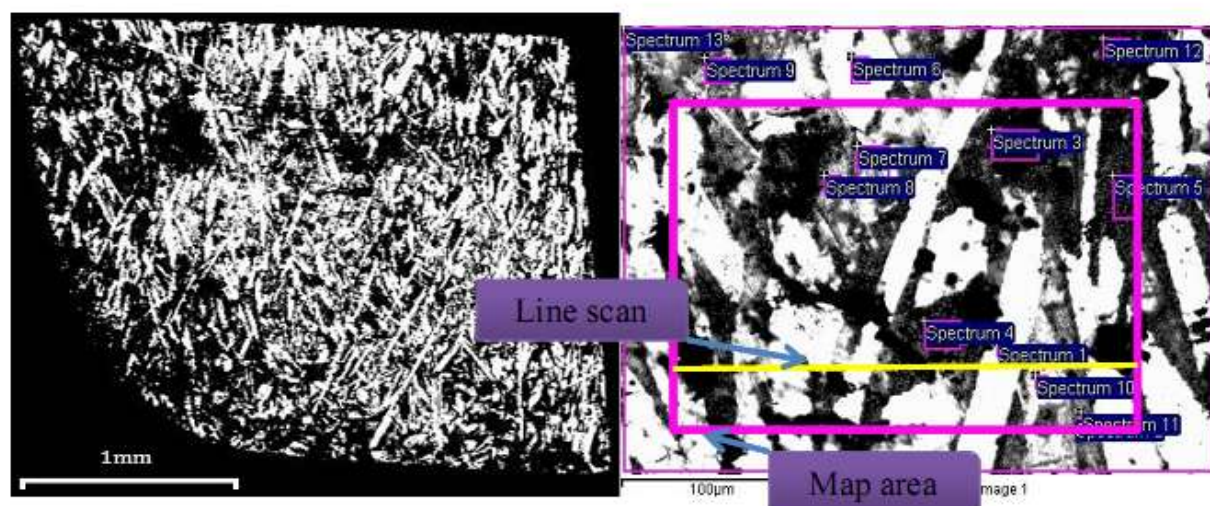


Figure 5.18 Isothermal sections of the Cr- Si-O and Hf-Si-O ternary systems [125,126]

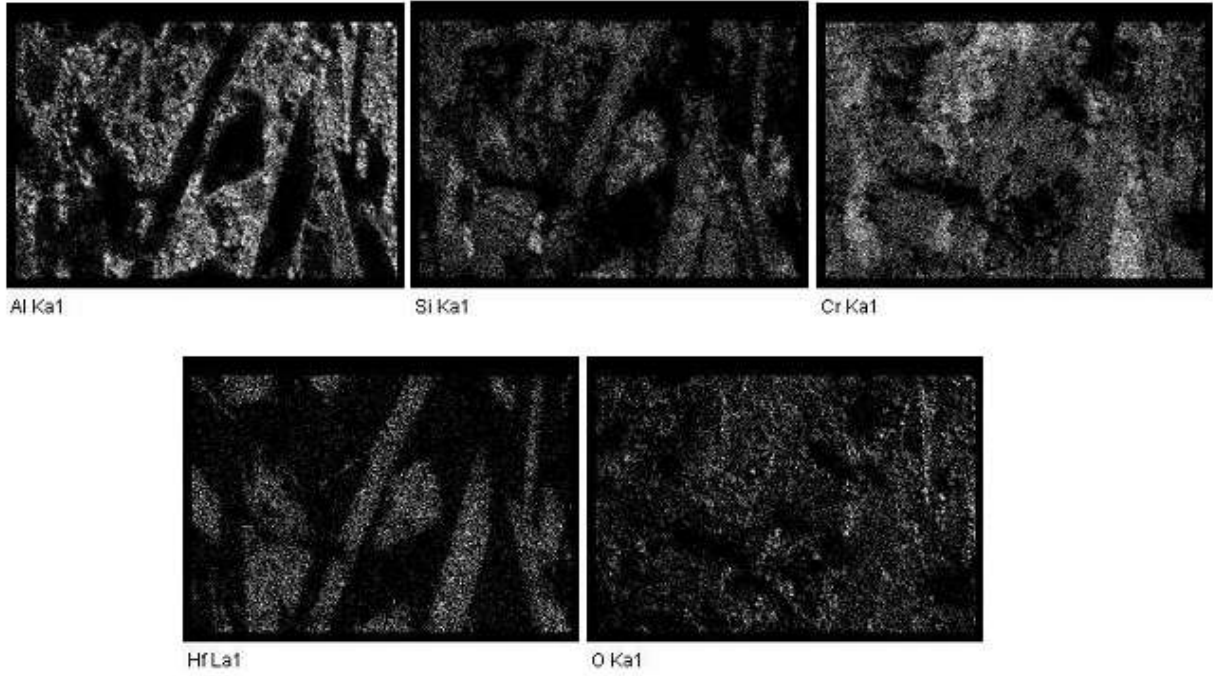
The microstructure of alloy AN1-AC consisted of the (Hf,Cr)₆Si₅, Cr₅Si₃ and Cr(Si,Al)₂ intermetallics and was stable between 800 and 1200 °C based on the results for the heat treated alloy. Depletion of Al, Cr and Hf could occur during oxidation leading to phase transformations and decompositions in the alloy and/or intermixed oxides subscale. Cross sections of the oxidised specimens were not studied in this thesis. Characterization of the top scale with glancing angle XRD at different incident angles gave information about what was present

beneath the scale (see section 5.2.3.2). A more detailed study of the scale would require TEM studies in addition to the GAXRD.

(a)



(b)



(c)

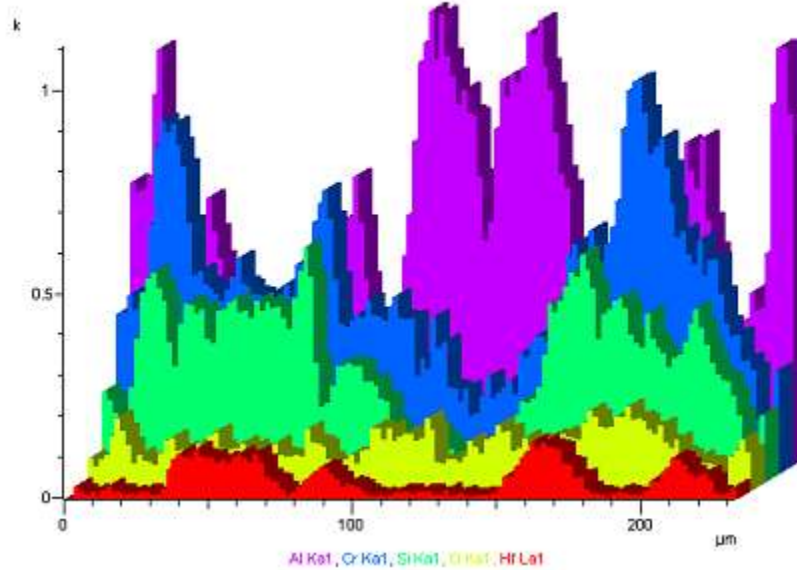
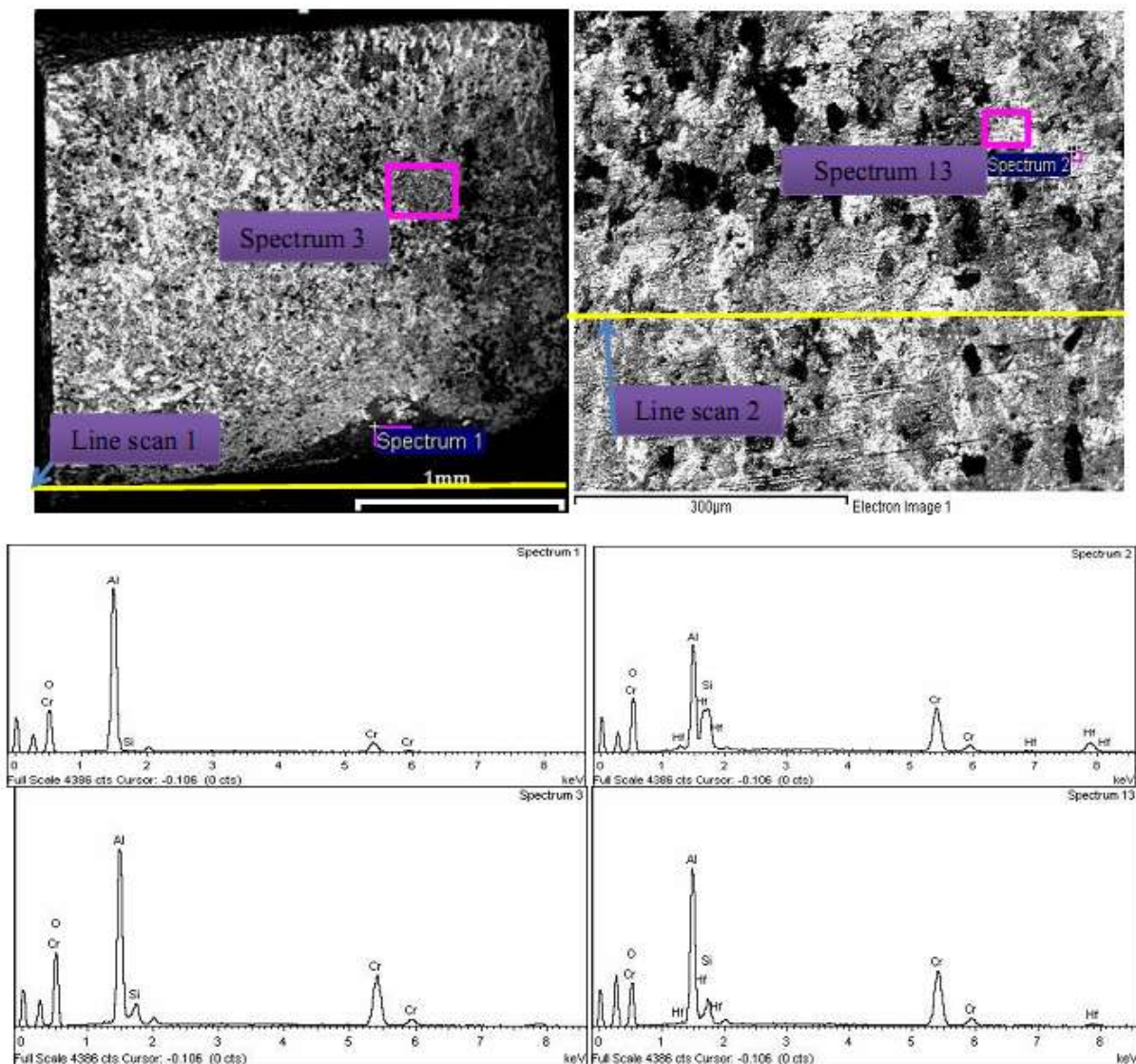


Figure 5.19 a) Surface SEM-BSE image of oxidized AN1 specimen at 800 °C with EDX spectra from the indicated areas and/or spots b) surface elemental maps of Al, Si, Cr, Hf and O c) line scan of the oxidized specimen at 800 °C as indicated in (a) (yellow line).

The data obtained from EDX analysis of the scales formed on the oxidized specimens of the alloy AN1 is shown in Figure 5.19, 5.20 and 5.21. The GAXRD data for AN1 was shown in Figure 5.10. Figure 5.19 shows a low magnification BSE image of the oxidised specimen of AN1 at 800 °C and a higher magnification image taken from this area from which spot analysis spectra, X ray elemental maps and a line scan were taken. The EDX spectra confirmed the presence of phases rich in Cr and Si (spectra 1 and 10), in Al (spectrum 12) and in Al, Cr, Hf and Si (spectrum 9), supported by the X-ray maps for Al, Cr, Hf, Si and O and consistent with the presence of Al_2O_3 , SiO_2 , $3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ and HfO_2 oxides suggested by the GAXRD of the same specimen (Figure 5.10a). Figure 5.20 shows a low magnification BSE image of the oxidised specimen of AN1 at 1000 °C, and areas studied using spot analyses, X-ray elemental maps and line scan. The spectra confirmed the presence of Al and Cr in the scale (spectra 1 and 3) as well as Al, Cr, Hf and Si (spectra 1 and 13). The line scans confirmed the presence of these elements and the data is consistent with the presence of $(\text{Al,Cr})_2\text{O}_3$, $3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$, SiO_2 and HfO_2 in the scale as identified by the GAXRD of the same specimen (Figure 5.10b). Figure 5.21 shows a low magnification BSE image of the oxidised specimen of AN1 at 1200 °C, a higher magnification image of the convoluted scale, line scans confirming that the latter is rich in Al, which is also supported by the GAXRD data of the same specimen (Figure 5.10c). The data shows that mixture of oxides was formed on the surface of the alloy AN1 at 800 and 1000 °C and a continuous alumina scale at 1200 °C. At 800 °C the alloy AN1 formed composite scale where the different precursors in the microstructure formed different oxides owing to the different oxygen diffusion rates and the variation of the Al, Si, Cr, and Hf activity in each constituent. The oxidation products formed on the alloy AN1 at 1000 °C were similar to those at 800 °C and consisted of a composite scale formed on the different constituents of the alloy which had different Al, Si, and Cr activity. The scale formed at 1200 °C was partially spalled and some cracks had propagated on its surface. The spallation of the scale was attributed to thermal expansion mismatch between the alloy substrate and alumina scale, but could also be due to internal oxide formation beneath the scale. The oxidation kinetics of the alloy at 1200 °C showed that it exhibited different oxidation behaviour during isothermal oxidation (Table 5-5). Parabolic behaviour was observed for the first 25 hour of the isothermal oxidation whereas the oxidation of the alloy became linear during the rest of the isothermal experiment. The substrate was in a direct contact with the oxidizing environment through the crack formed on the scale and gained

0.91 mg/cm² weight after 100 hours. Subsurface depletion of Al driven by selective oxidation to form the alumina scale could trigger phase transformation(s) in the alloy just below the evolving oxide scale to less oxidation-resistant intermetallic phases that could prevent the re-formation of the spalled alumina scale.

(a)



(b)

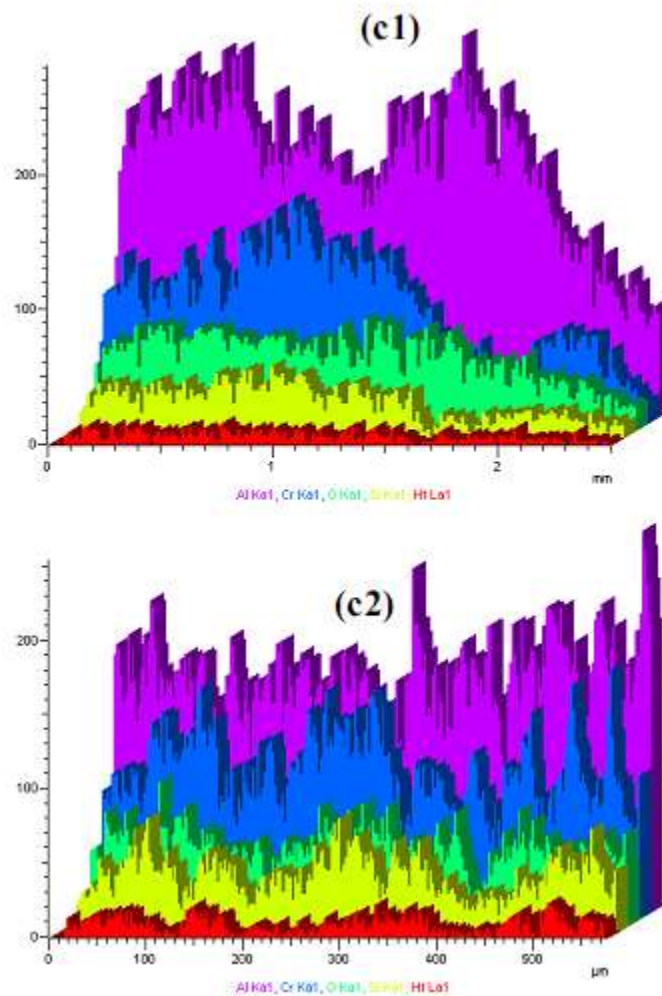
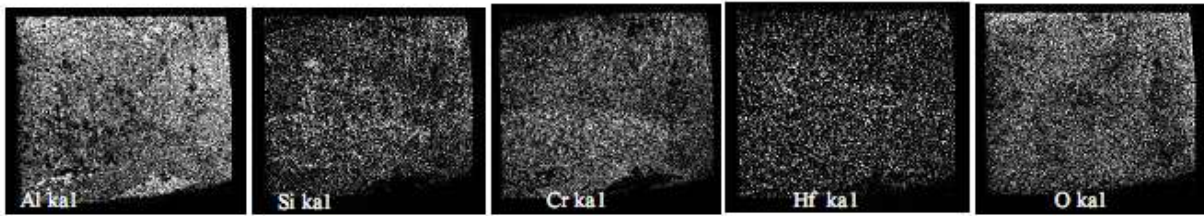
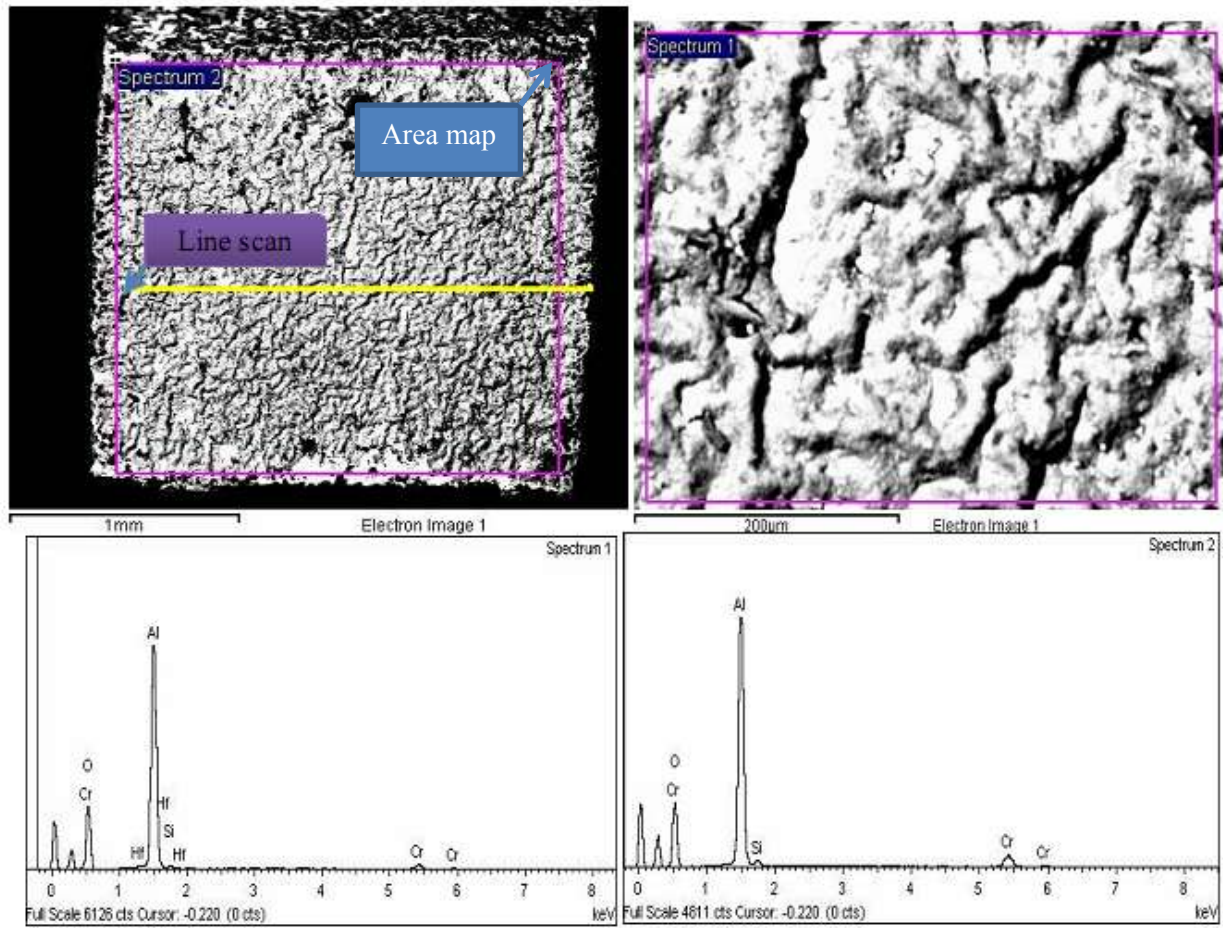
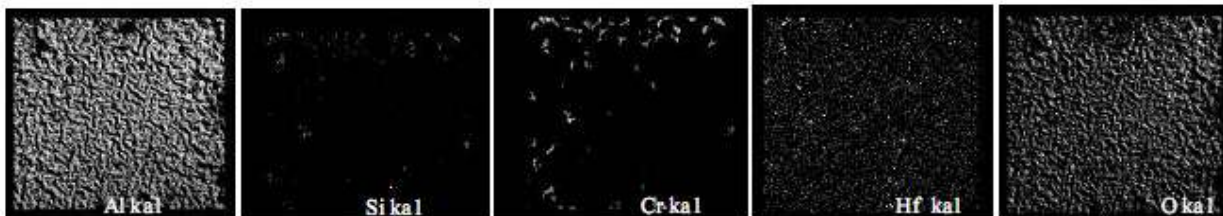


Figure 5.20 a) Surface SEM-BSE image of oxidized AN1 specimen at 1000 °C with EDX spectra from the indicated areas and/or spots b) surface elemental maps of Al, Si, Cr, Hf and O c1,c2) line scans of the oxidized specimen at 1000 °C as indicated in (a) (yellow lines)

(a)



(b)



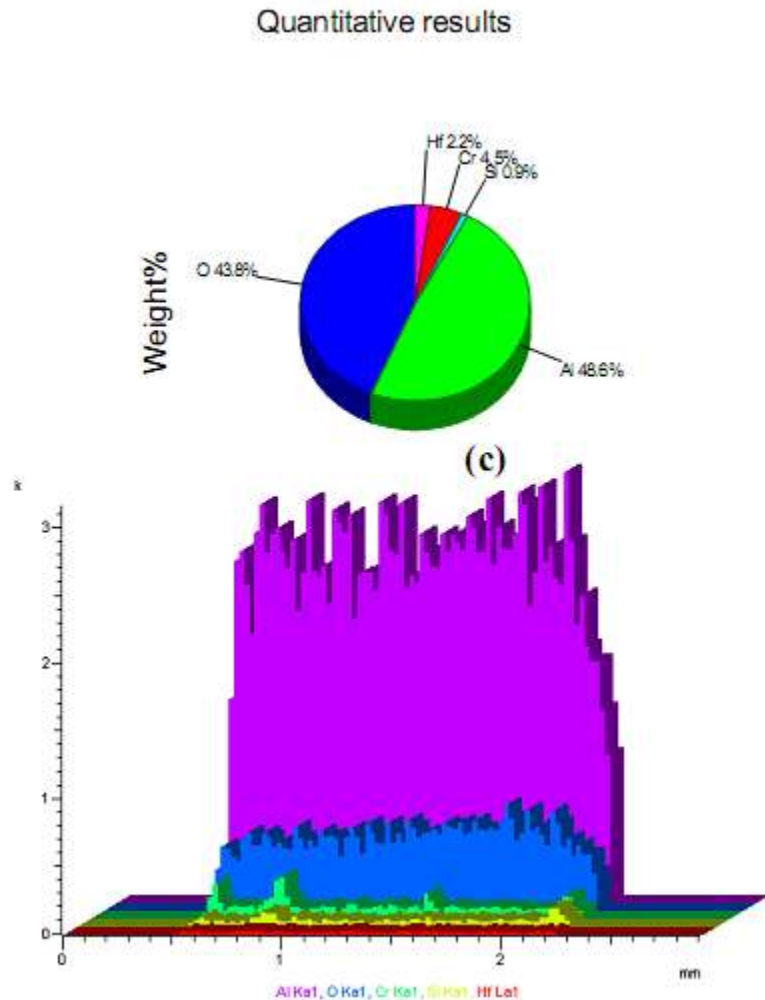
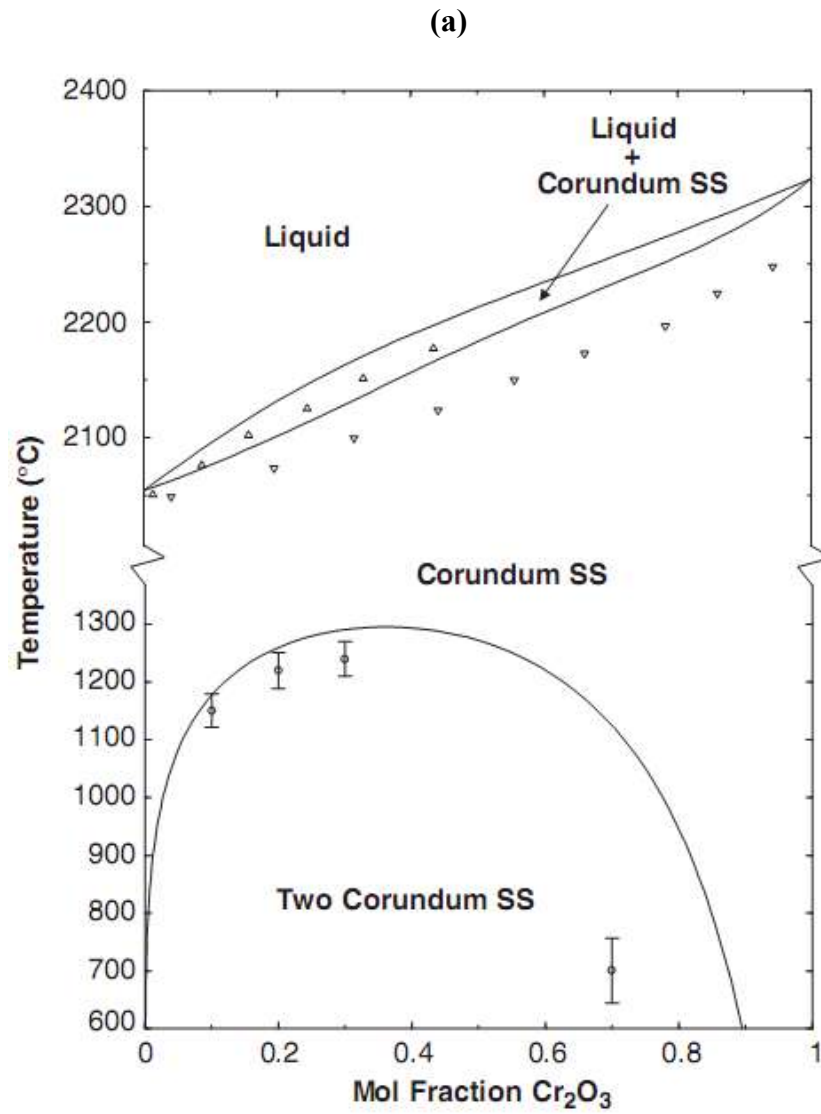


Figure 5.21 a) Surface SEM-BSE image of oxidized AN1 specimen at 1200 °C with EDX spectra from the indicated areas and/or spots b) surface elemental maps of Al, Si, Cr, Hf and O c) line scan of the oxidized specimen at 1200 °C as indicated in (a) (yellow line)

According to the binary $\text{Cr}_2\text{O}_3\text{-SiO}_2$, $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$ and $\text{SiO}_2\text{-Al}_2\text{O}_3$ systems, the oxides are not miscible and soluble in one another with the exception of alumina –silica where mullite can exist at 800 °C. The composition of the scale formed at 800 °C on the $\text{Cr}(\text{Si},\text{Al})_2$ precursor is shown in Figure 5.22 contained 14.1 % mullite, 27.7 % silica and 58.2.% chromia. Likewise, the scale

formed on the Cr_5Si_3 precursor, is shown in Figure 5.22. The scale contained 10.9 % mullite, 25.9 % silica and 63.2 % chromia.



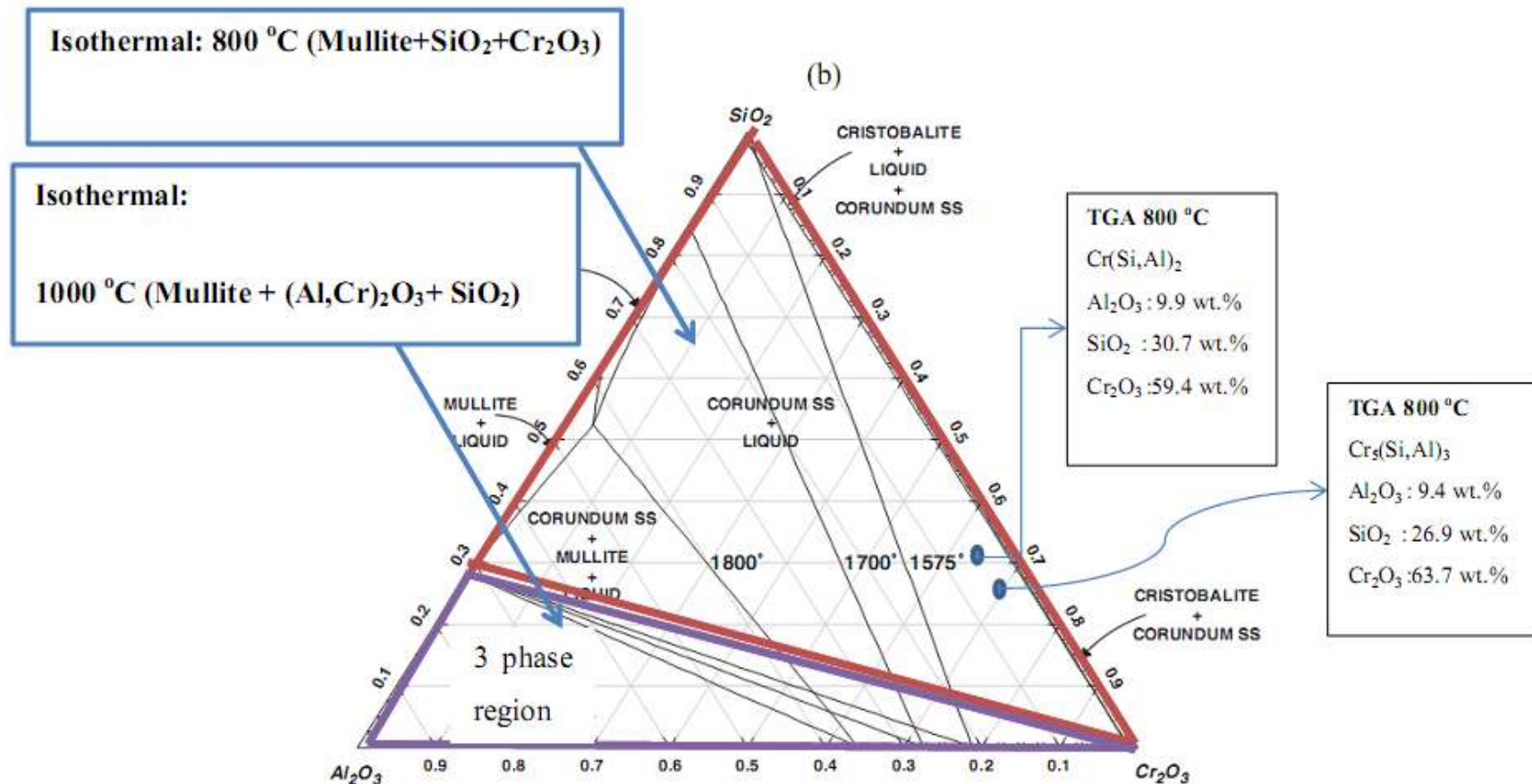


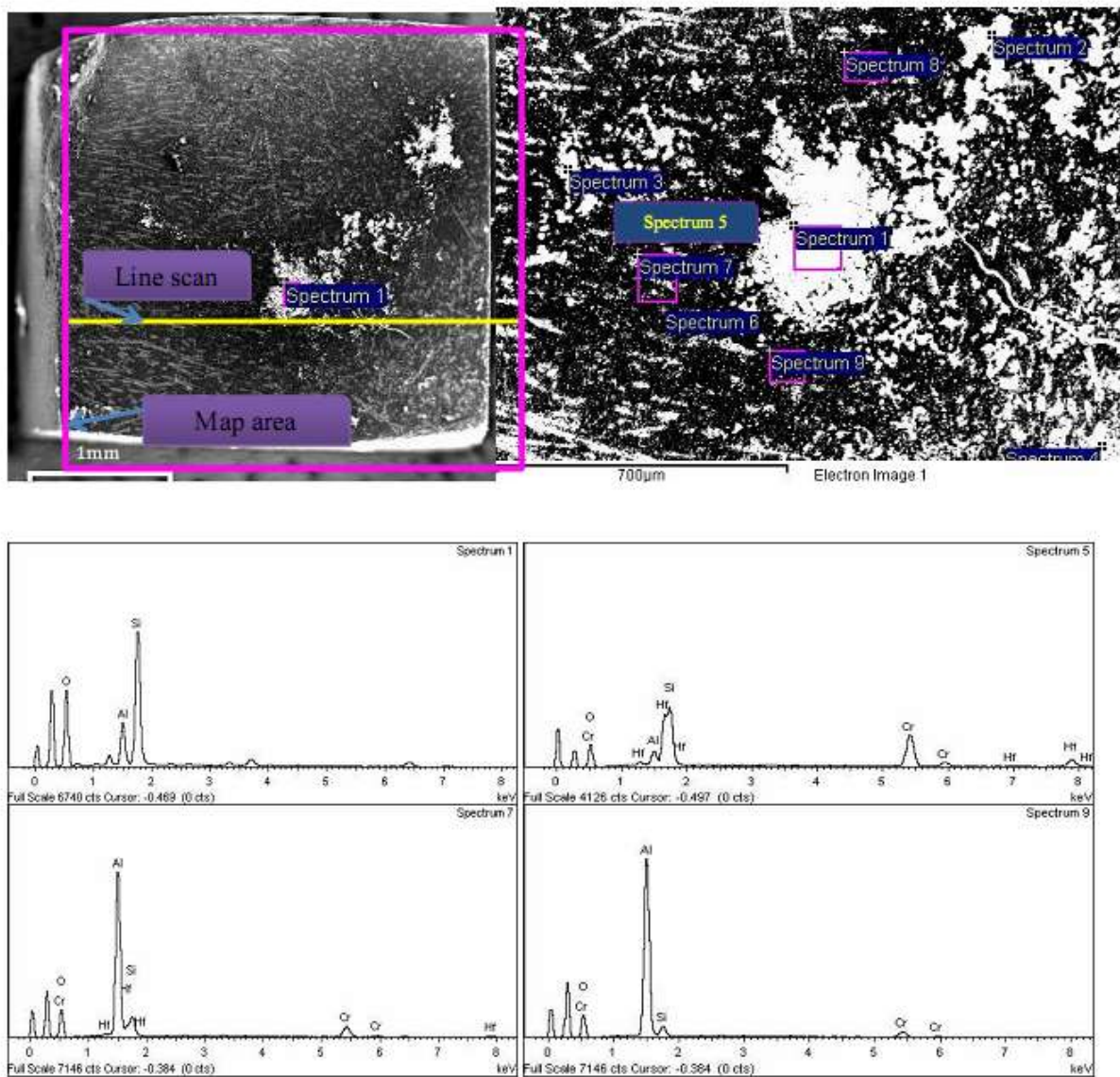
Figure 5.22 (a) computed $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ system phase diagram with the experimental solidus (∇) and liquidus (Δ) values of Bunting and the miscibility gap determination of Sitte (O) (b) computed ternary phase diagram for $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3\text{-SiO}_2$ indicating isothermal data at 1575, 1700, and 1800 °C (composition is given in mass fraction to allow comparison with published diagram) [127].

The scale formed on AN1 at 1000 °C was also a composite scale that formed on $\text{Cr}(\text{Si},\text{Al})_2 + \text{Cr}_5\text{Si}_3$ precursors and had composition 86, 8 and 6 wt.% alumina, silica and chromia respectively, and lies in the three phase region in Figure 5.22 where mullite, alumina and chromia are stable with fractions 33, 60 and 7 wt.% respectively. According to Figure 5.22, in the alumina rich side of the ternary system, the mullite and corundum solid solution are the stable phases but at lower temperature ($T < 1250$ °C) the corundum solid solution transforms to Al_2O_3 and Cr_2O_3 . The results for the oxidation of the $\text{Cr}(\text{Si},\text{Al})_2$ and Cr_5Si_3 precursors are in agreement with the results reported in [127]. Composite scale also formed at 1000 °C on the Hf_6Si_5 precursor consisted of chromia, silica and hafnia. In the ternary Cr_2O_3 - SiO_2 - Al_2O_3 phase diagram, the composition of the spalled composite scale formed on the Hf_6Si_5 is placed on the right hand side of the ternary where the alumina content is almost negligible and the HfO_2 has no solubility either in the Cr_2O_3 or SiO_2 (at 1000 °C [126]). Therefore the scale was a mixture of corundum and silica and Hafnia that subsequently spalled. At 1200 °C continuous alumina scale formed on the surface although the alloy suffered from partial spallation of the scale (see above).

In cooperative oxidation, the Al, Si or Cr rich second and third phase particles maintain the growth of the protective scale whereas in the independent mode of multiphase oxidation, all the constituents participate in the oxidation and a composite surface rather than an exclusive, continuous layer of the protective scale, is formed [6]. The oxidation behaviour of the alloy AN1 at 800 °C and 1000 °C conformed to an independent mode of oxidation whereas at 1200 °C, the phases reacted cooperatively to form a single phase continuous scale despite of the adhesion issues. However, kinetic factors play a significant role in determining which of the oxide phases continue to grow. During the very early stages of oxidation virtually all oxides which are thermodynamically stable are formed. As oxidation continues diffusion begins to take place and the displacement reactions begin to occur. The important diffusing species are oxygen into the alloy precursors and the outward diffusion of elements in the alloy. In the case where oxygen diffuses rapidly compared with the metallic elements, the volume fraction of oxide is approximately equal to that of the element in the alloy because the element is converted to oxide in situ with virtually no diffusion. On the other hand, when oxygen diffusion is slow compared with that of elements in the alloy, the volume fraction of the oxide can be substantially greater

than that of the elements in the alloy because of the diffusion of the elements from the interior toward the oxidation front [128].

(a)



(b)

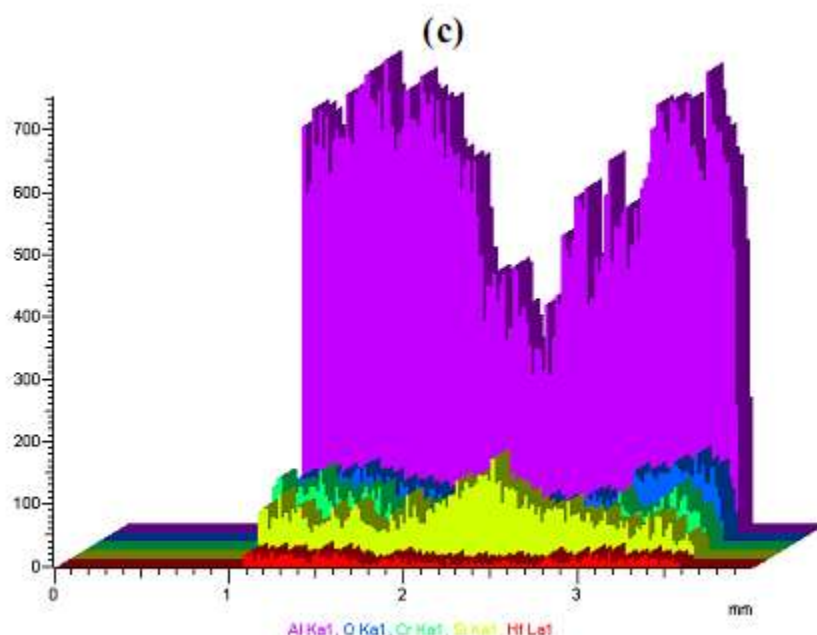
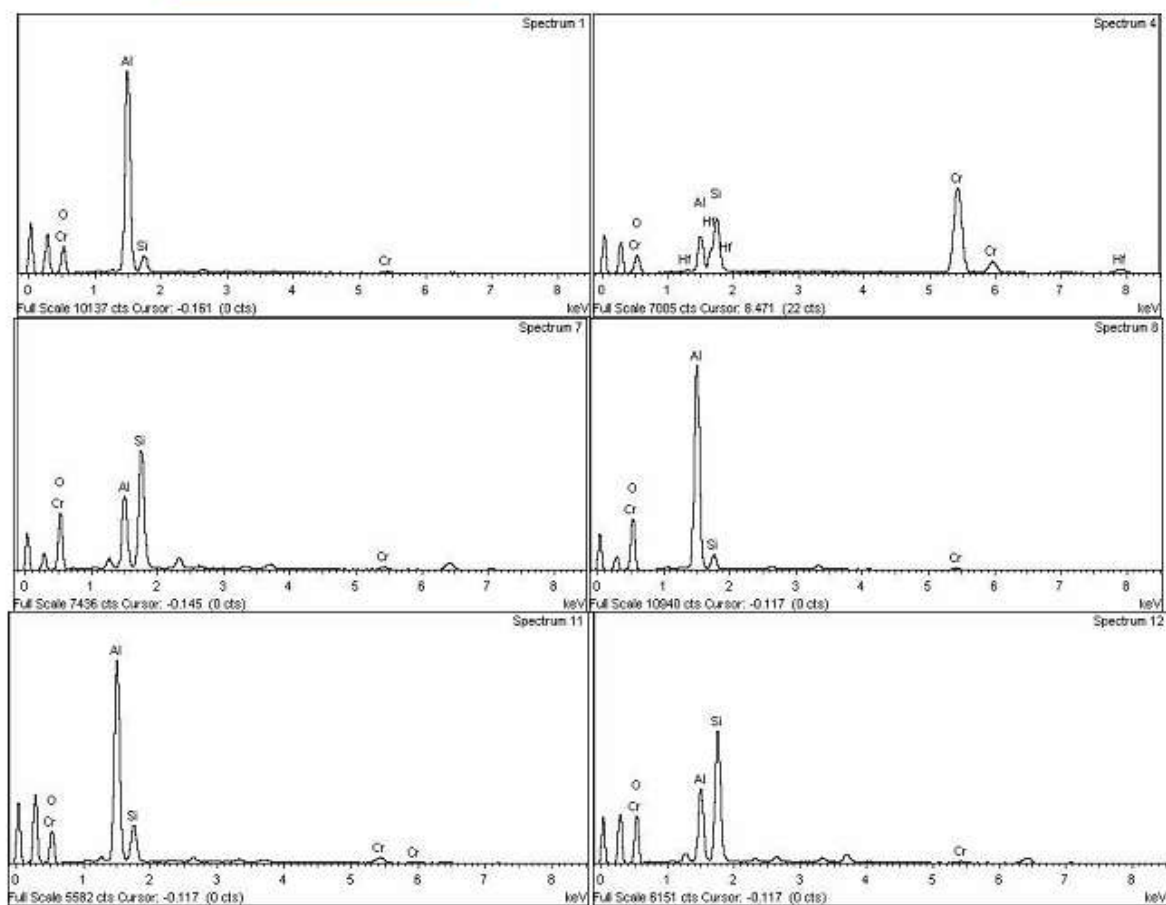
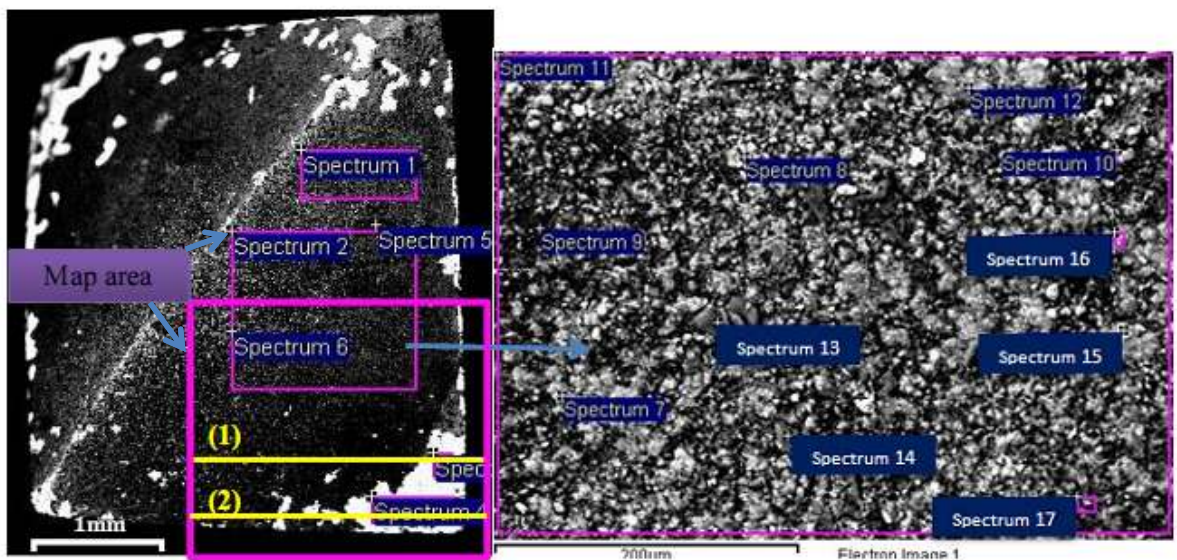


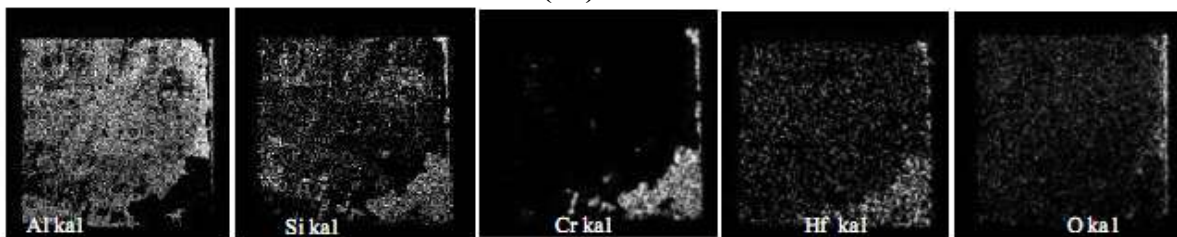
Figure 5.23 a) Surface SEM-BSE image of oxidized AN2 specimen at 800 °C with EDX spectra from the indicated areas and/or spots b) surface elemental maps of Al, Si, Cr, Hf and O c) line scan of the oxidized specimen at 800 °C as indicated in (a) (yellow line)

Figure 5.23 shows a low magnification BSE image of the oxidised specimen of AN2 at 800 °C and a higher magnification image taken from this area from which spot analysis spectra, X ray elemental maps and a line scan were taken. The EDX spectra confirmed the presence of Al rich scale (spectra 7 and 9), and Si rich islands (spectra 1 and 5), supported by the X-ray maps and consistent with the presence of Al_2O_3 oxides suggested by the GAXRD of the same specimen (figure 5.11a). Figure 5.24 shows a low magnification BSE image of the oxidised specimen of AN2 at 1000 C, and areas studied using spot analyses, X-ray elemental maps and line scans. The

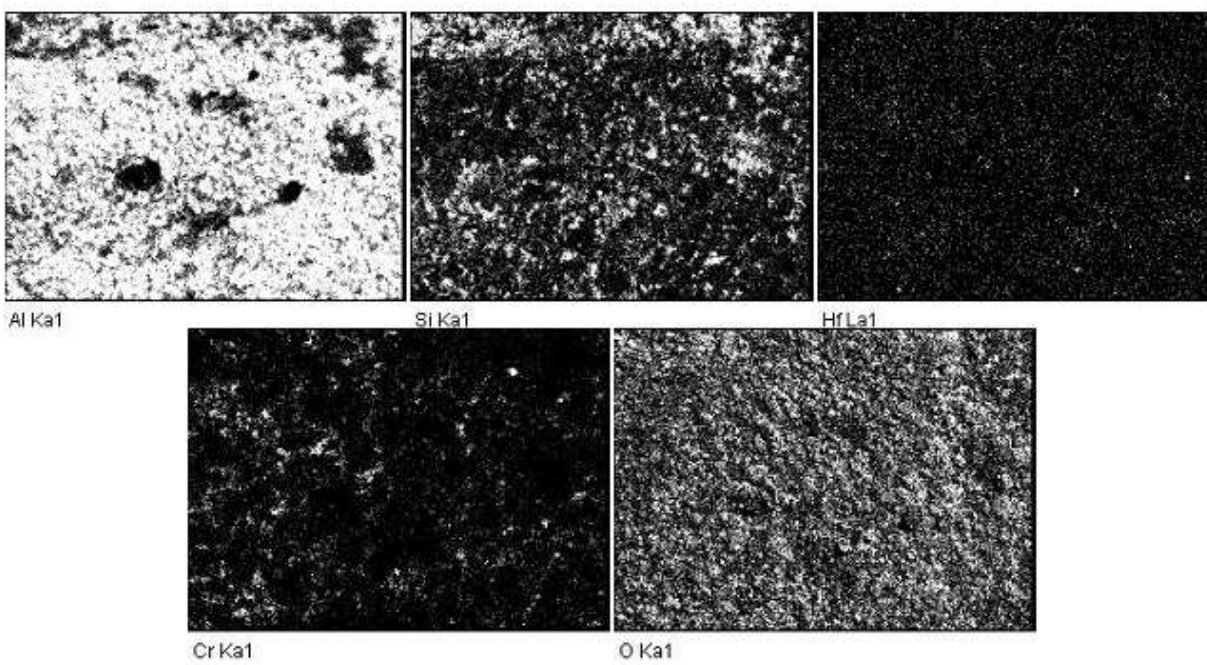
(a)



(b1)



(b2)



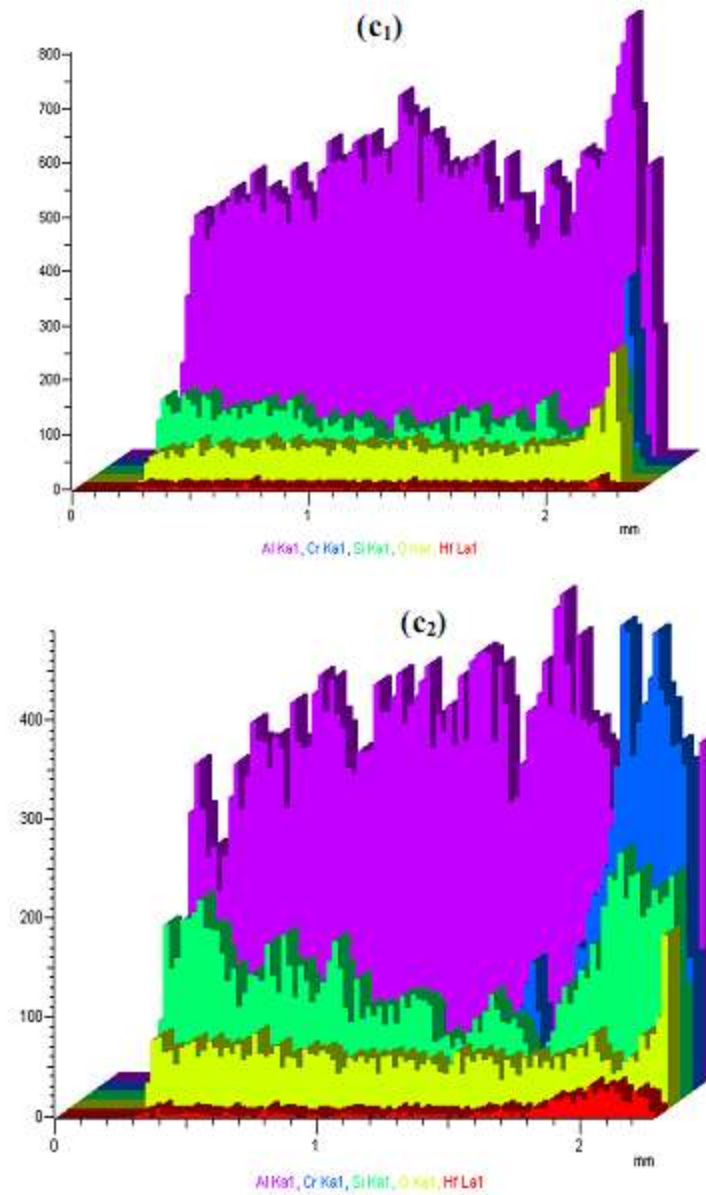
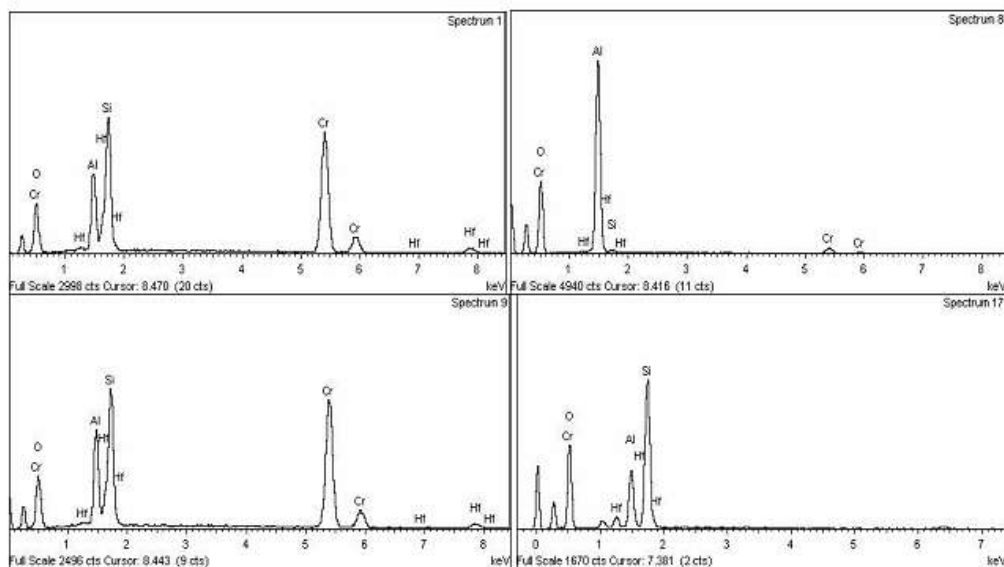
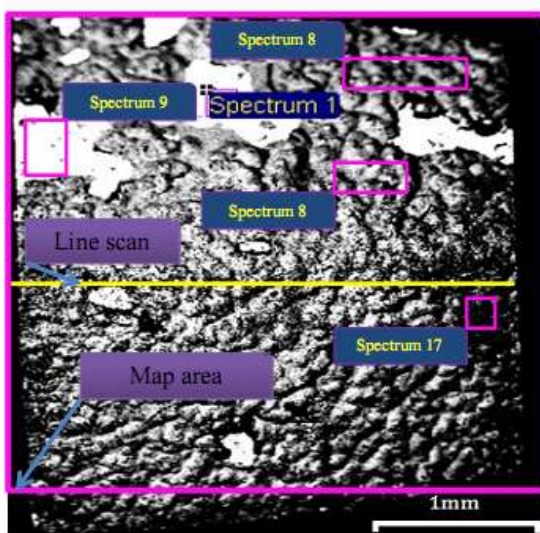


Figure 5.24 a) Surface SEM-BSE image of oxidized AN2 specimen at 1000 °C with EDX spectra from the indicated areas and/or spots b1,b2) surface elemental maps of Al, Si, Cr, Hf and O c1,c2) line scans of the oxidized specimen at 1000 °C as indicated in (a) (yellow lines)

spectra confirmed the presence of Al rich scale (spectra 1, 8, 11), the presence of Cr (spectrum 4) and Si in the scale (spectra 4, 7, 12). The line scans confirmed the presence of these elements and the data is consistent with the presence of Al_2O_3 and $3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ in the scale as identified by the GAXRD of the same specimen (figure 5-11b). Figure 5.25 shows a low magnification BSE image of the oxidised specimen of AN2 at 1200 °C, spot analyses of the scale, X ray maps and line scan confirming that the latter is rich in Al (spectrum 8), and confirming the presence of Cr and Si in the scale (spectra 1, 9, 17), and support the GAXRD data of the same specimen (figure 5.11c).

(a)



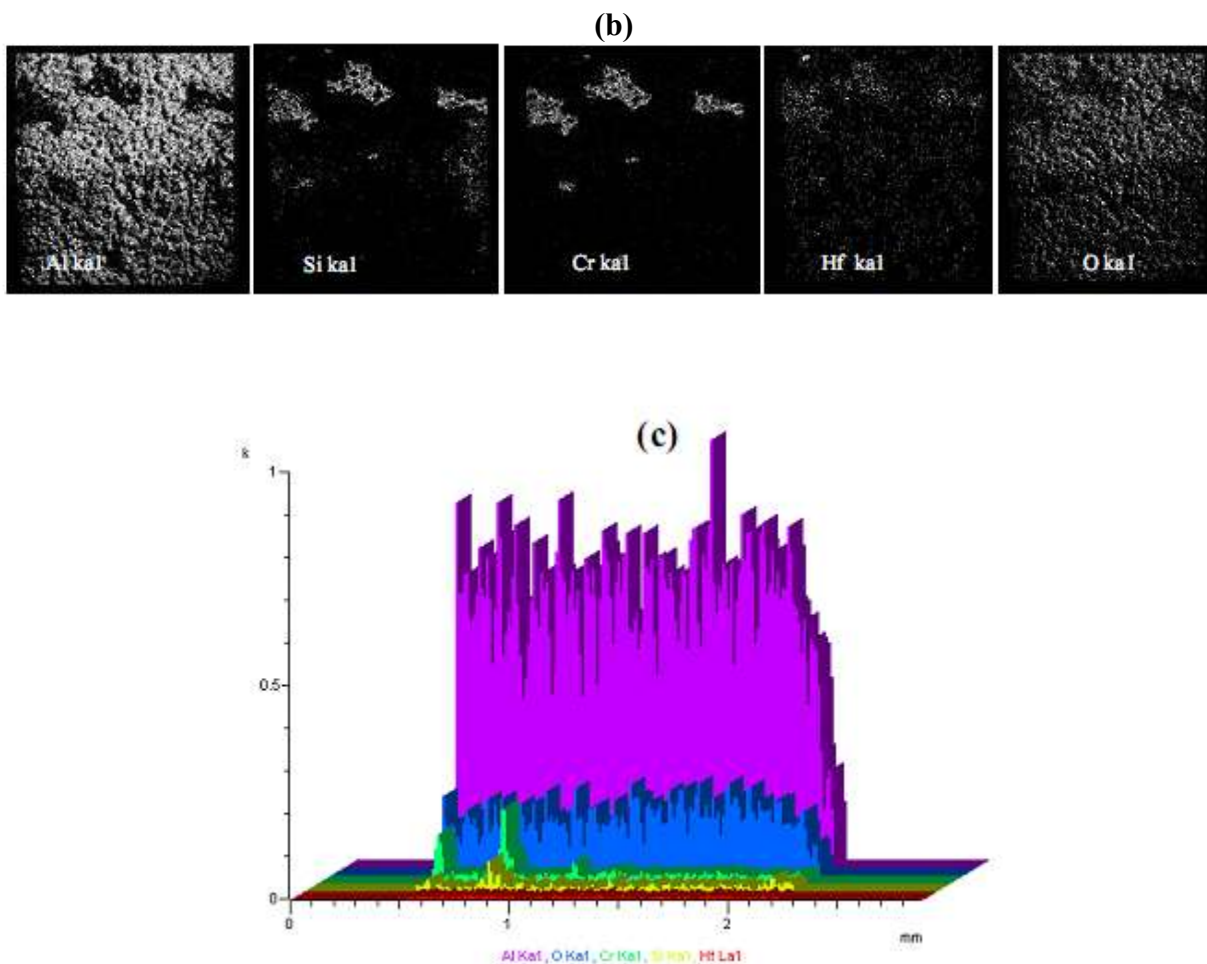


Figure 5.25 a) Surface SEM-BSE image of oxidized AN2 specimen at 1200 °C with EDX spectra from the indicated areas and/or spots b) surface elemental maps of Al, Si, Cr, Hf and O c) line scan of the oxidized specimen at 1200 °C as indicated in (a) (yellow line)

The microstructure of the alloy AN2 consisted of $(\text{Hf,Cr})_6\text{Si}_5$, Cr_5Si_3 , Cr_5Al_8 and Cr_3Si precursor phases (see Table 5-1) of which the sum of volume fraction of its aluminide was 52.6 % and 47.4 % wt. of the alloys contains the Cr and Hf silicide (Table 1). Unlike the alloy AN1, there was aluminide precursor and thus the activity of the Al increased and the alloy AN2 was more capable of forming a single phase scale rather than a composite scale. However, the concern about phase transformations was stronger for this alloy as Al depletion just below the evolving oxide scale could lead to formation of less oxidation resistant, lower Al-containing intermetallic phases, which can prevent the establishment of, or cause subsequent loss of, protective scale

formation. According to the EDX and GAXRD data for alloy AN2 at 800 °C, the alloy formed a continuous composite scale with silica island in the scale (Figure 5.11 a, Figure 5.23), with composition 91, 6 and 3 wt.% respectively Al_2O_3 , Cr_2O_3 and SiO_2 . Considering the Al_2O_3 - Cr_2O_3 - SiO_2 system (Figure 5.22), the scale composition lies in the 3-phase region where the mullite, alumina and chromia are stable. The alloy precursors reacted cooperatively to form an exclusive single composite scale. The composition of scale formed in this condition was very close to that of the scale formed on the alloy AN1 at 1000 °C. The % volume of alumina, mullite and chromia in the composite scale formed on the alloy AN2 at 800 °C were 82, 11, 7 % respectively.

The scale of the oxidized alloy AN2 at 1000 °C consisted of a mixture of alumina and mullite. The growth of the scale was rather uniform on all faces and spallation of the scale was seen in some region. It is suggested that the weak adhesion of the scale to the substrate could be due to the formation of pores beneath the scale either by aluminium consumption and/or phase transformation beneath the scale which can cause subsequent loss of protective scale formation.

The alloy AN2 at 1200 °C formed a buckled scale with cracks that propagated alongside the ridges on the scale, as shown in Figure 5.25. According to the heat treatment data for the alloy AN2, the volume fractions of phases in the microstructure of the alloy changed at this temperature compared with the cast alloy. This caused a change in the oxidation behaviour of the alloy (Table 5-5). In this particular condition, during isothermal oxidation, the alloy was confronted (i) by changes in its microstructure driven to reach equilibrium and (ii) by Al depletion beneath the scale. By assuming constant volume fraction of aluminide in the microstructure (Table 5-1), an increase in the fraction of the 5-3 silicide could have positive effect on the oxidation of the alloy by forming silica protective scale on the Cr_5Si_3 precursor during oxidation. Si rich phase can be soluble in the alumina scale as a solid solution. The scale formed on the alloy AN2 at 1200 °C was mostly corundum solid solution $(\text{Al,Cr})_2\text{O}_3$ and mullite formed in some area in the ridges where the corundum was spalled (Figure 5.11 c).

To summarise, the alloys AN1 and AN2 exhibited parabolic oxidation behaviour for the whole exposure time (100 hours) at 800 °C whereas the alloy AN1 followed parabolic oxidation behaviour only during the early stages of oxidation at 1000 and 1200 °C and exhibited linear

oxidation kinetic after 25 and 35 hours respectively. Unlike the alloy AN1, the alloy AN2 exhibited parabolic and cube oxidation kinetic for the whole exposure time at 1000 °C and 1200 °C, respectively. The weight gain of the alloy AN1 at 800 °C was 0.15 mg/cm² followed by an increase to 0.24 mg/cm² after oxidation at 1000 °C and finally the alloy weight gain increased to 0.91 mg/cm² at 1200 °C . In the alloy AN2, the weight gains were 0.11, 0.85 and 0.59 mg/cm², respectively at 800, 1000 and 1200 °C. The data for 1000 and 1200 °C could suggest that microstructure of cube specimens used for the TGA experiment might had been different regarding the volume fractions of phases.

Oxidation rate data obtained from this study is plotted together with data for Ni, Fe, or Pt based intermetallics in Figure 5.26. As shown in Figure 5.26, the alloy AN1 is amongst those alumina forming intermetallic alloys following parabolic oxidation behaviour with oxidation rate constant (kp) between 6×10^{-12} and 5×10^{-11} g²/cm⁴s at 1200 °C. The oxidation rate of the alloy AN2 is not plotted in this figure due to different oxidation behaviour of the alloy at 1200 °C (cube oxidation rate). The alloy AN2 contained high volume fraction of the aluminium rich precursor Al₈Cr₅ (Table 5-1) that is capable of forming alumina, subsequently the alloy formed a continuous alumina scale on its surface with total weight gain less than the alloy AN1. In addition, the alloy AN2 showed relatively poor oxidation behaviour at 1000 and 800 °C compared with AN1 and the other alloys included in Figure 5.26.

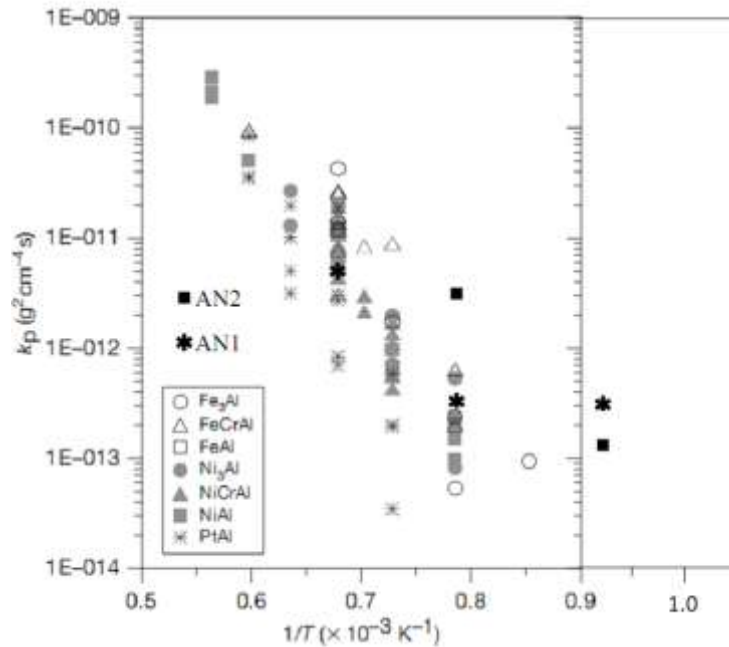


Figure 5.26 Parabolic rate constants showing the Al_2O_3 scale growth rates on different Fe, Ni, and Pt-based alloys [61]. The results of the present study are indicated.

The oxidation rate constants of the alloys AN1 and AN2 are plotted together with chromia, silica and alumina forming alloys in Figure 5.27. At 800 °C, the alloys AN1 and AN2 are placed out of the alumina /chromia forming alloy zone, have better oxidation resistance than chromia forming alloys and worse oxidation behaviour than alumina forming alloys. At 1000 °C, the alloy AN1 moves to the alumina forming region in which the oxidation rate constant of the alloy is almost the same as that at 800 °C whereas the alloy AN2 is approaching to alumina/chromia stability interface. At 1200 °C, the alloy AN1 is still in the alumina-forming band. Compared with the results of Zamoum et al. [129], the oxidation rate constant of the alloy AN1 is close to that of M_7Si_6 silicide at 1200 °C.

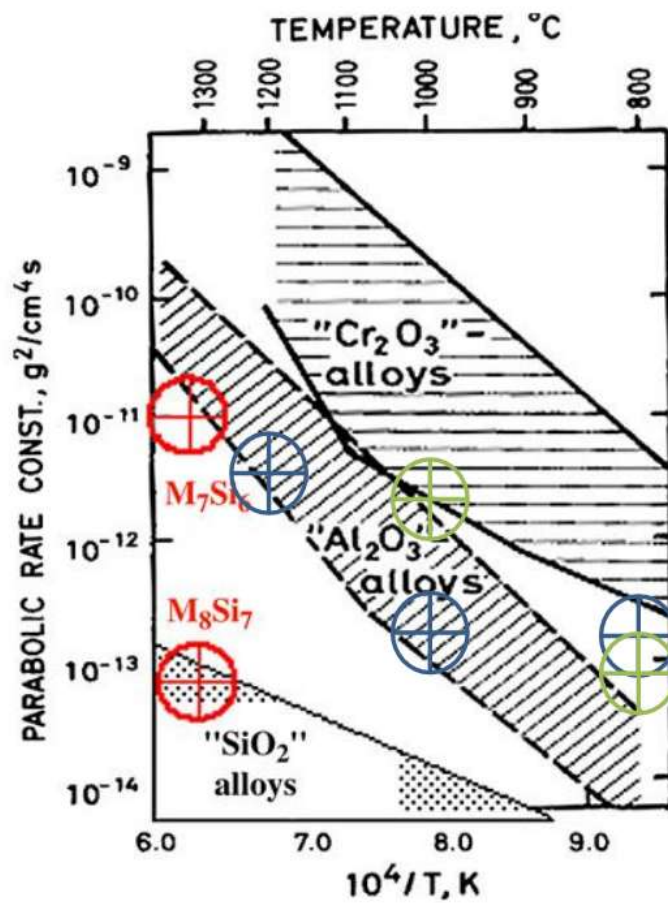


Figure 5.27 Fields of k_p values for chromia, silica and alumina-forming alloys. The oxidation rate constants of the alloy AN1 and AN2 are indicated by blue and green crosses respectively. Red crosses show oxidation rates of silicides studied by Zamoum et al. [103,129].

5.4 Summary

- I. The microstructures of the as cast and heat treated alloy AN1 consisted of the $(\text{Hf,Cr})_6\text{Si}_5$, $\text{Cr}_5(\text{Si,Al})_3$ and $\text{Cr}(\text{Si,Al})_2$ phases. In the alloy AN2, the $(\text{Hf,Cr})_6\text{Si}_5$, $\text{Cr}_5(\text{Si,Al})_3$, $\text{Cr}_3(\text{Si,Al})$ and $\text{Cr}_5(\text{Al,Si})_8$ phases were present in the as cast and heat treated condition at 1200 °C and the $\text{Cr}_3(\text{Si,Al})$ was absent after the heat treatment at 1300 °C.
- II. The Hf addition destabilized the CrSi in the alloy AN1 and stabilized the Cr_3Si in the alloy AN2. and the 6-5 silicide in both alloys.
- III. There was no solubility of Hf in Cr_5Si_3 and CrSi_2 in AN1 and Cr_5Si_3 , Cr_3Si and Al_8Cr_5 in AN2. There was Al solubility in the 6-5 silicide only in AN2. Aluminium substituted Si in the silicides
- IV. The solidification path of the alloy AN1 was
 - a. $\text{L} \rightarrow \text{L} + \text{Hf}_6\text{Si}_5 \rightarrow \text{L} + \text{Hf}_6\text{Si}_5 + \text{Cr}_5\text{Si}_3 \rightarrow \text{Hf}_6\text{Si}_5 + \alpha\text{Cr}_5\text{Si}_3 + \text{CrSi}_2$
- V. The solidification path of the alloy AN2 was
 - a. $\text{L} \rightarrow \text{Hf}_6\text{Si}_5 \rightarrow \text{L} + \text{Hf}_6\text{Si}_5 + \text{Cr}_3\text{Si} \rightarrow \text{L} + \text{Cr}_3\text{Si} + \text{Cr}_5\text{Si}_3 \rightarrow \text{Hf}_6\text{Si}_5 + \text{Cr}_3\text{Si} + \text{Cr}_5\text{Si}_3 + \text{Al}_8\text{Cr}_5$
- VI. The macrohardness decreased after thermal exposure of the alloys AN1 and AN2 as the Si/Al ratio in the alloy decreased. The measured macrohardness values of both alloys were in better agreement with the calculated hardness values using the Pythagorean type rule.
- VII. The microhardness of Hf_6Si_5 depended on the Si/Hf ratio in this phase.
- VIII. The alloy AN1 formed a composite scale at 800 and 1000 °C. The scale consisted of alumina, mullite, silica and hafnia at 800 °C and $(\text{Al,Cr})_2\text{O}_3$, mullite, silica and hafnia at 1000 °C. The alloy AN1 formed a continuous $(\text{Al,Cr})_2\text{O}_3$ scale at 1200 °C.

- IX. The alloy AN2 formed a composite scale at 800 °C that consisted of alumina and some silica island and had rather good adhesion to the substrate. Alumina and mullite were formed on the alloy AN2 at 1000 and 1200 °C and the scale was partially spalled at these temperatures. The scale was smooth and uniform at 1000 °C but was buckled at 1200 °C.
- X. The alloy AN1 obeyed parabolic oxidation kinetics at 800 °C for the whole exposure and only for the first 35 hours and 25 hours respectively, at 1000 °C and 1200 °C.
- XI. The alloy AN2 followed parabolic oxidation kinetic for the whole exposure time at 800 and 1000 °C and cube oxidation kinetic at 1200 °C.
- XII. Oxidation rate constants of the alloy AN1 were comparable to those of Fe, Ni and Pt-based alloys at 1000 and 1200 °C. The alloy AN2 had higher oxidation rate constant at 1000 °C compared with other Al rich intermetallics.
- XIII. The activation energies for oxidation for the alloy AN1 indicated that no single mechanism was operative in the temperature range 800 to 1200 °C.

The evidence for alloys AN1 and AN2 would thus suggest that in the Al rich alloy AN2 with Hf addition the CrSi_2 is not stable while the Al_8Cr_5 is stable. However, the latter phase is undesirable as it could lead to liquation in the microstructure above 1200 °C. Furthermore, the data for AN1 shows that with Hf as quaternary addition it is possible to form alumina in the scale up to 1200 °C without having a high concentration of Al in the alloy and achieve oxidation rate constant that are comparable to those of Ni and Pt based intermetallic alloys. The addition of Hf does reduce slightly the solubility of Al in CrSi_2 but this phase was not destabilized by the quaternary addition of Hf in the alloy AN1 (low Al content) and is believed to play a key role in the formation of alumina scale owing to its volume fraction in the Al poor alloy AN1. The microstructure of Alloy AN1 is also desirable because the intermetallics in the Cr-Si system are expected to be exhibiting good oxidation behaviour up to about 1200 °C [130] compared with Al-Cr intermetallics which are expected to have good oxidation behaviour up to but not

exceeding 1000 °C and the densities of CrSi₂ and Cr₅Si₃ are desirable as they are about 5 and 6.5 g/cm³ respectively [131, 132]. (the density of Cr₃Si is 6.54 g/cm³ [131] and this phase formed in AN2 but was not stable at 1300 °C).