Chapter 8

Summarising remarks, conclusions and future work

In this work the effects of the Hf, Ti and Nb additions individually on phase stability and microstructure, and oxidation behaviour at 800, 1000 and 1200 ^{o}C were studied in Cr-45Si-5Al and Cr-25Si-25Al based alloys with Al/Si 0.1 and 1, respectively. These alloys were studied because (i) it is likely that Cr-Si-Al based alloys might be used as components of a bond-coat system on Nb silicide based alloys and (ii) it is important to know what the effects of alloying with Hf, Nb and Ti (either as quaternary additions or from interdiffusion from the substrate) might be on phase stability and oxidation behaviour. Of course, in the real application there will more elements diffusing across the bond-coat/substrate interface, this would require the study of higher order systems and was outside the scope of the research presented in this thesis (see also section 8.3).

The Nb silicide based alloy substrates typically have between 15-20 at.% Ti, Cr and Al (each up to 5 at.%), Si up to 22 at.% (but in the range 16-22 at.%), less than 5 at.% Hf, and depending on other alloying additions (typically refractory metals and other simple metals and metalloids) the Nb concentration can be between 25-40 at.%. During oxidation of substrate alloys in the uncoated condition, the scale consists of Al, Cr and Ti niobates and Hf, Ti and Nb oxides. The Al, Cr and Si contents of un-coated substrate alloys cannot encourage formation of stable continuous alumina, silica or chromia scales. If the substrate were to be coated, depending on the bond coat composition, it is expected that there will be inward/outward diffusion (i.e., inter-diffusion) of elements across the interface, as shown schematically in Figure 8.1. What would be the effect of interdiffusion on the bond coat microstructure and oxidation?

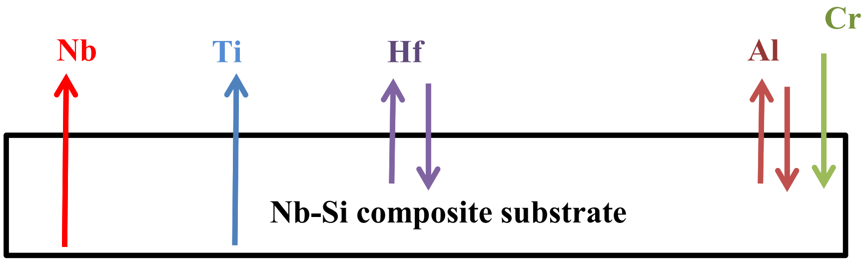

Figure 8.1 Schematic diagram showing inter-diffusion of elements across the substrate/bond coat interface for a coated typical Nb silicide based alloy.

Considering the composition of a typical substrate and the alloys of this study (which might be alloys in a bond coat system), it is expected that there would be no diffusion of Cr from the substrate to the bond-coat alloy as the Cr content in the former is lower compared with the latter. In contrast, Ti and Nb would be expected to diffuse across the interface, owing to their concentrations on either side of it. We do not know whether the behaviour of Hf, Ti and Nb individually would be the same if the substrate alloy was coated with the same Cr-Si-Al based bond coat. In this chapter we will discuss the effects of individual additions of Hf, Ti and Nb on phase stability and oxidation behaviour of the two Cr-Si-Al based alloys with different Al/Si ratios. Other members in the group study the synergetic effects of Hf, Ti and Nb on the phase equlibria and oxidation behaviour of Cr-Si-Al based alloys with the same Al/Si ratios.

8.1.Summarising remarks and discussion

8.1.1 Microstructure and phase equlibria

The addition of Hf, Ti and Nb destabilised the formation of CrSi in the alloys with Al/Si =0.1. In the alloys with Al/Si =1, the alloy with Hf addition formed Cr_3Si as the secondary phase whereas the alloy with Ti and Nb formed $(Cr,Ti)_5(Si,Al)_3$ and $(Nb,Cr)_{11}(Si,Al)_8$ as the secondary phase, respectively and the 6-5 silicide was stabilised in both alloys with different Al/Si ratio. The phases present in the alloys and their volume fractions are summarised in Figure 8.2. The T $(M,Cr)_6Si_5$ (M=Hf, Ti, Nb) phase was stabilised by the synergy of Cr and M with Al and Si. Aluminium controlled the stability of CrSi and $CrSi_2$ which were suppressed in favour of Cr_3Si particularly when its concentration in the alloy was high enough to lead to the formation of stable Cr aluminides(s). In the alloy with Al/Si=1, the Nb addition also stabilised the $Nb_{11}Si_8$ silicide which was not formed in any other alloys.

The solidification path of the alloys with Al/Si=0.1 was similar and is given below where M is transition metal Hf, Ti, Nb:

$$L \rightarrow L + M_6Si_5 \rightarrow L + M_6Si_5 + Cr_5Si_3 \rightarrow M_6Si_5 + Cr_5Si_3 + CrSi_2$$

The solidification path of the alloys with Al/Si=1 was as follows:

For the alloy Cr-25Si-25Al-5Hf

$L \rightarrow L + Hf_6Si_5 \rightarrow L + Hf_6Si_5 + Cr_3Si \rightarrow L + Hf_6Si_5 + Cr_3Si + Cr_5Si_3 \rightarrow Hf_6Si_5 + Cr_3Si + Cr_5Si_3 + Al_8Cr_5$

For the alloy Cr-25Si-25Al-5Ti

$L \rightarrow L + (Ti,Cr)_6Si_5 \rightarrow L + (Ti,Cr)_6Si_5 + (Cr,Ti)_5(Si,Al)_3 \rightarrow L + (Ti,Cr)_6Si_5 + (Cr,Ti)_5(Si,Al)_3 + Cr_5Al_8 \rightarrow (Ti,Cr)_6Si_5 + (Cr,Ti)_5(Si,Al)_3 + Cr_5Al_8 + Cr_4Al_9$

For the alloy Cr-25Si-25Al-5Nb

$L + (Nb,Cr)_6Si_5 \rightarrow (Nb,Cr)_{11}(Si,Al)_8 + \beta Nb_5Si_3 \rightarrow L + (Nb,Cr)_{11}(Si,Al)_8 + \beta Nb_5Si_3 + Cr_5(Si,Al)_8 \rightarrow (Nb,Cr)_{11}(Si,Al)_8 + \beta Nb_5Si_3 + Cr_5(Si,Al)_8 + Cr_4(Si,Al)_9$

In the alloys with Al/Si=0.1 the microstructure consisted of M_6Si_5, Cr_5Si_3 and $CrSi_2$ (M = Hf, Ti and Nb) with formation of CrSi observed in the heat treated microstructure of the alloy with Ti addition at 1300 ^{o}C. There was no solubility of Al in the 6-5 silicide. There was no solubility of

Hf in the Cr_5Si_3 silicide in cast and heat treated microstructures whereas the Ti and Nb solubility in the Cr_5Si_3 was low. The Al solubility in $CrSi_2$ was dependent on the addition of Hf, Ti and Nb. The solubility data is summarised in Figure 8.3.

In the alloys with Al/Si=1, unlike the alloys with Al/Si=0.1, the Al was soluble in the 6-5 silicide with the highest solubility in Ti_6Si_5. The 6-5 silicide was stable in all heat treated microstructures except in the alloy with Nb addition where after heat treatment it transformed to Nb rich Cr_5Si_3. In the alloys with addition of Ti, Nb the $Cr_5(Si,Al)_8$ and $Cr_4(Si,Al)_9$ aluminides were formed but the Hf addition did not stabilise the $Cr_4(Si,Al)_9$ aluminide. The solubility data is summarised in Figure 8.4.

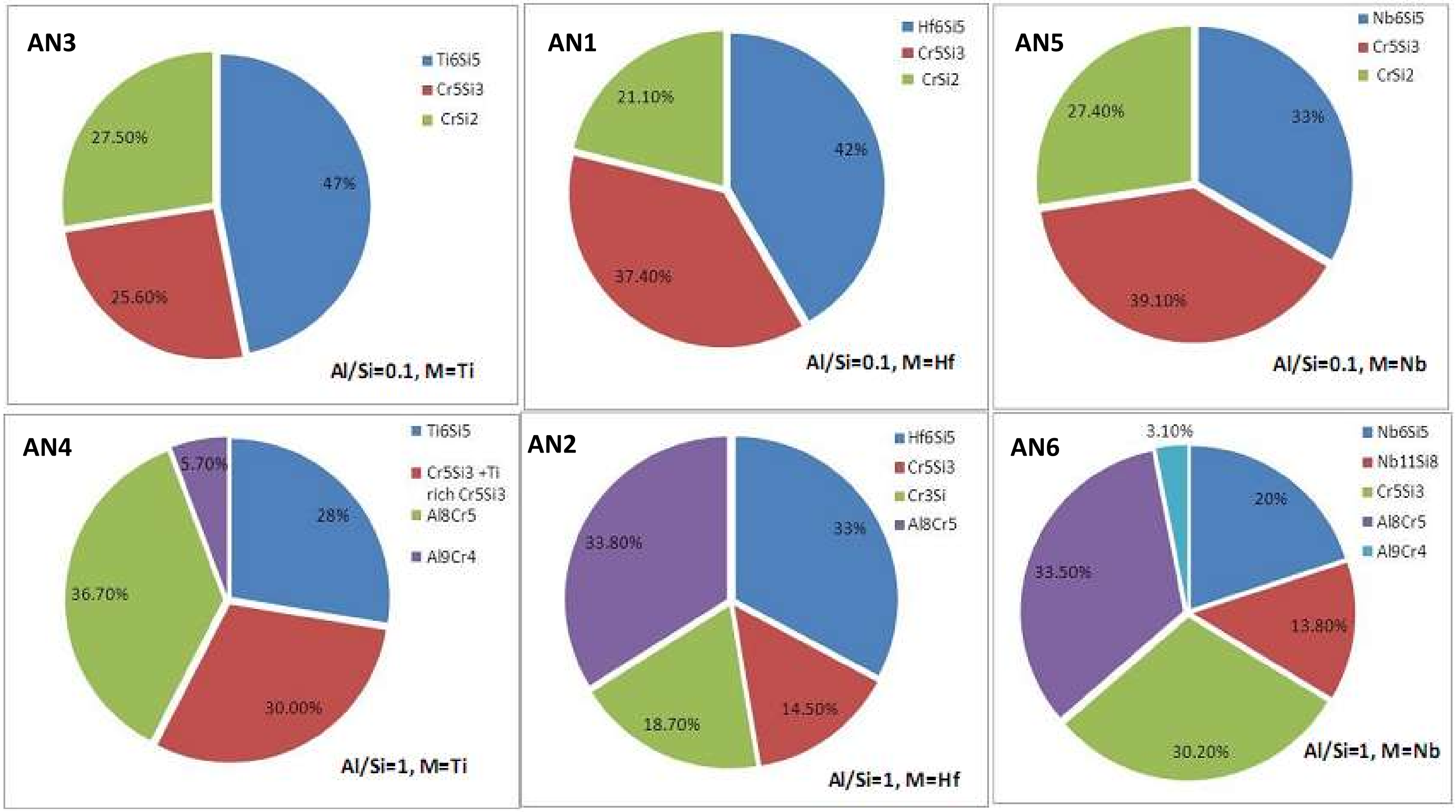

Figure 8.2 The vol. % of phases in the cast Cr-Si-Al-M alloys of this study.

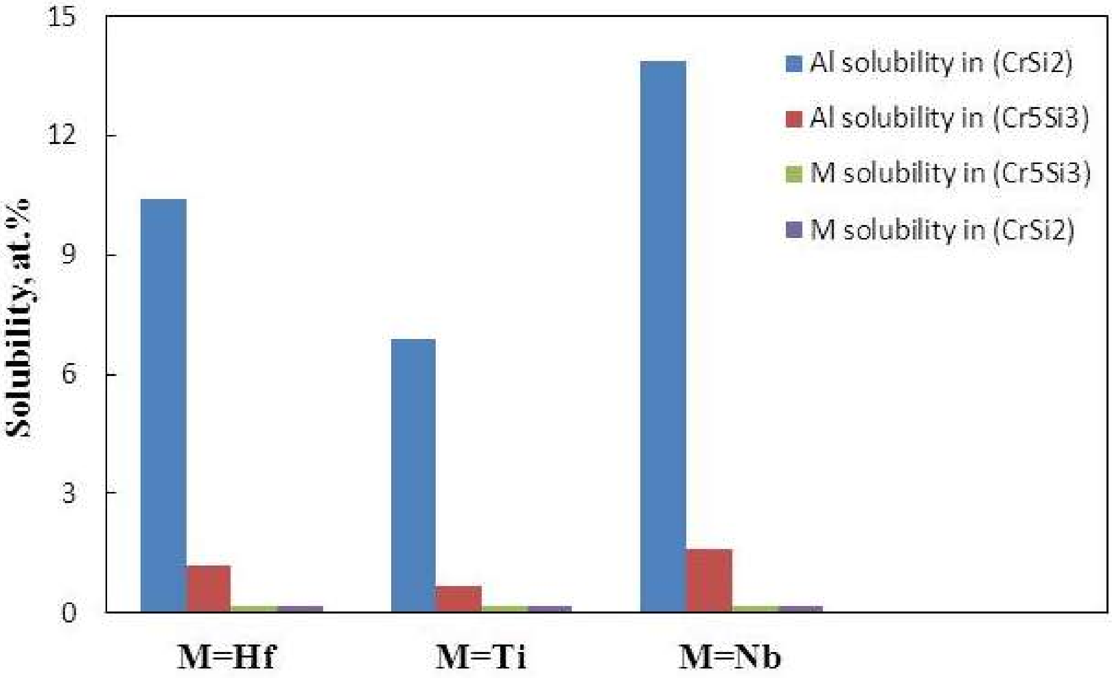

Figure 8.3 Solubilities of alloying additions in the phases in Cr-Si-Al-M alloys with Al/Si=0.1.

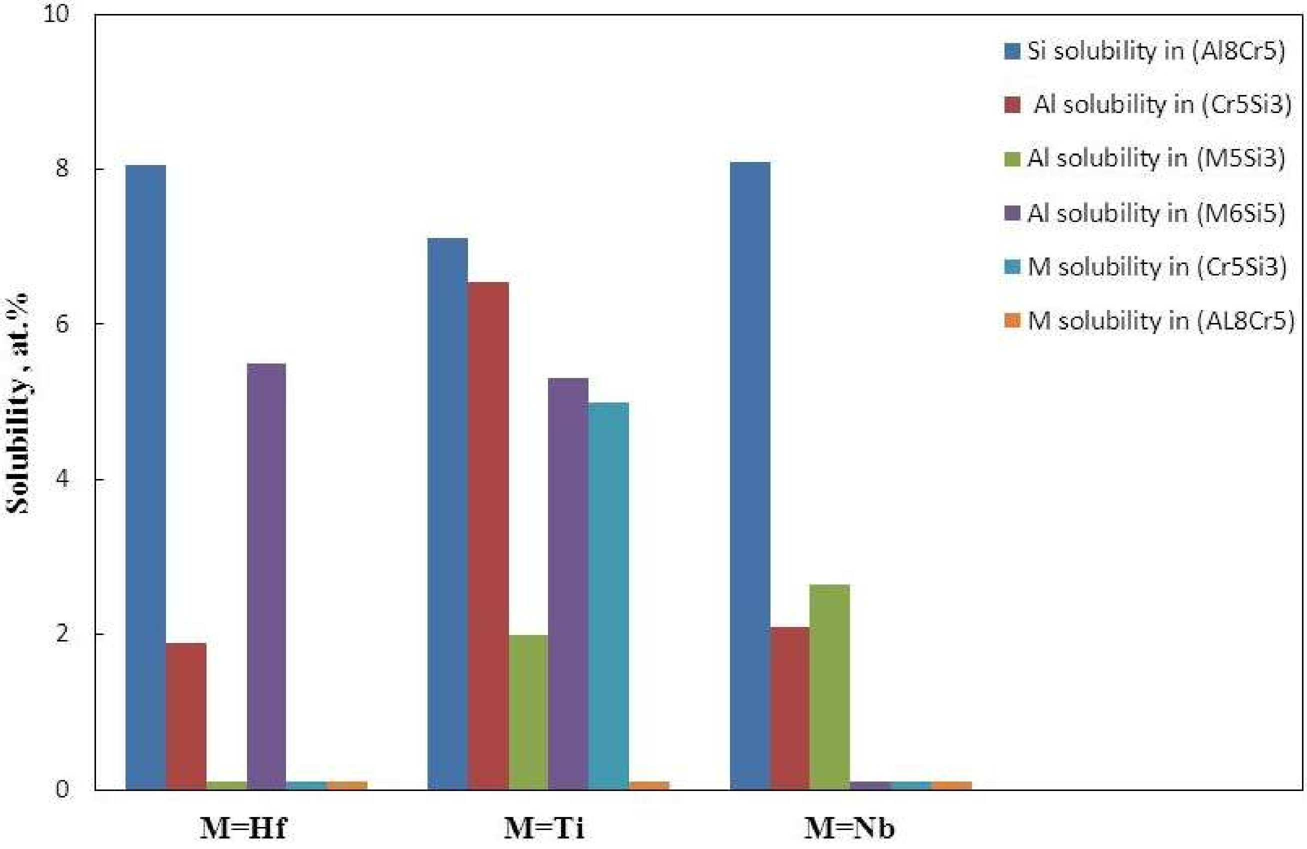

Figure 8.4 Solubilities of alloying additions in the phases in Cr-Si-Al-M alloys with Al/Si=1.

8.1.2 Isothermal oxidation

800 ^{o}C: The alloys with Hf, Ti and Nb addition and with Al/Si= 0.1 and Al/Si=1 exhibited parabolic oxidation and did not pest at 800 ^{o}C. The alloys with Ti and Hf addition and with Al/Si=0.1 and Al/Si=1 had the lowest weight gain and the alloys with Nb addition had the highest, see Figure 8.5.

For the alloy with Al/Si=0.1, the Ti addition had the most beneficial effect on the oxidation of the alloy compared with Hf and Nb, and the Nb addition was the least beneficial. For the alloy with Al/Si=1, the Hf addition had the most beneficial effect on the oxidation of the alloy and the Ti addition was the least beneficial for the oxidation but still better compared with Nb addition, see Figure 8.5.

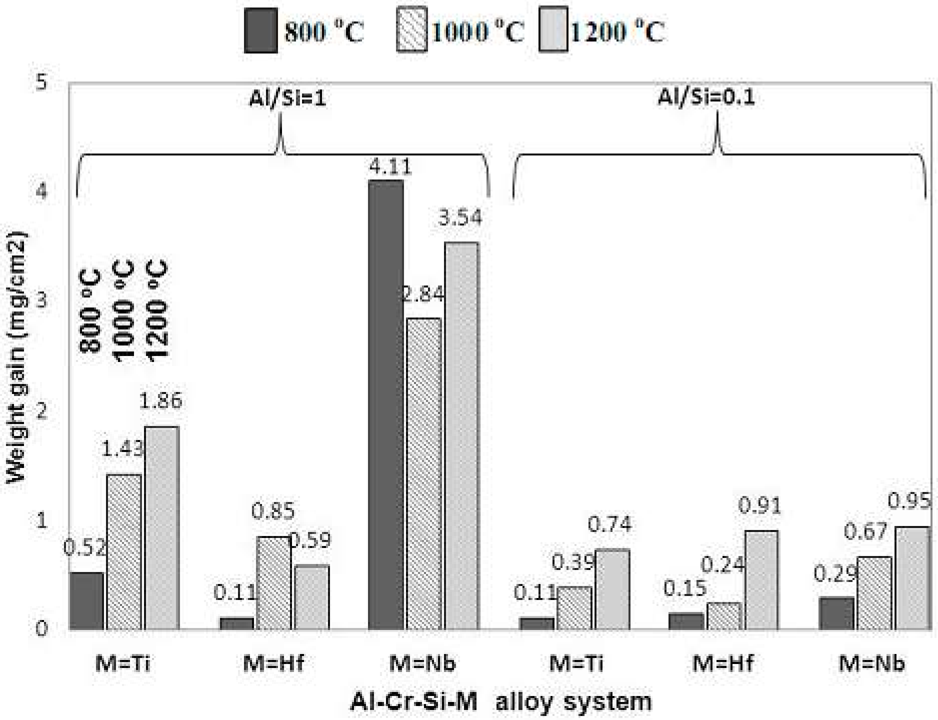

Figure 8.5 Comparison of weight gain in Cr-Si-Al-M alloys at 800, 1000 and 1200 ^{o}C.

For the alloys with Al/Si=0.1, there was no spallation of the scale formed on the alloys with Hf, Ti and Nb addition. The alloy with Ti addition had the smaller kp ($3.3\text{x}10^{-14}$ $g^2.cm^{-4}.s^{-1}$) than the alloys with Hf and Nb addition. By increasing the Al/Si ratio to 1, the scales formed on the alloys with Hf, Ti, Nb did not spall although the scale formed on the alloys was not uniform scale and the surface was not fully covered by the scale. The alloy with Hf addition had the smaller kp ($1.3\text{x}\ 10^{-13}$ $g^2.cm^{-4}.s^{-1}$) than the alloys with Ti and Nb.

At 800 ^oC, for the alloys with Al/Si=0.1 and M= Hf, Ti and Nb the scale consisted mainly of alumina, silica, mullite. HfO_2, TiO_2 and Nb_2O_5 also formed. Chromia was observed in the alloys with Ti and Nb. By increasing the Al/Si ratio to 1, the alloy with M=Hf formed continuous alumina scale with some silica islands. For the alloys with M=Ti and Nb, alumina, silica and mullite formed in the scale and chromia only formed in the alloy with the Ti addition. Transition metal oxide only formed in the alloy with the Nb addition. For both Al/Si ratios (0.1 and 1) the morphology of the scale (cell) on the alloy with Hf addition was different from the alloys with Ti and Nb (whisker morphology).

1000 ^oC: No pest oxidation was observed in the alloys at 1000 ^oC The alloy with Al/Si=0.1 and Hf addition exhibited parabolic oxidation for the first 35 hours followed by linear oxidation. By increasing the Al/Si ratio to 1, the alloy exhibited parabolic oxidation for the whole exposure time. The isothermal oxidation of the alloy with Ti addition and Al/Si=0.1 and 1 was parabolic for the whole exposure time. The isothermal oxidation of the alloy with Al/Si=0.1 and Nb addition was cubic for the first 16 hours and by increasing the Al/Si ratio to 1, it became parabolic for the whole exposure time, see Figure 8.6. Therefore it is concluded that in order to have parabolic oxidation for the whole exposure time in alloys with Hf and Nb addition the Al/Si ratio must be 1. The alloys with Hf addition had the lowest weight gains for the alloys with Al/Si = 0.1 and 1, see Figure 8.4. The alloy with Nb addition had the highest weight gains among the alloys with Al/Si=0.1 and Al/Si=1.

For the alloys with Al/Si=0.1, no spallation of the scale was observed for the alloys with Ti and Nb addition whereas the scale of the alloy with Hf addition was spalled. The alloy with Ti addition had the lowest kp ($6.7\text{x}10^{-13}$ $g^2.cm^{-4}.s^{-1}$) than the alloys with Hf and Nb addition for the longer exposure time (100 hours) although the alloy with Hf addition had better oxidation for the first 35 hours with lower kp ($3.3x10^{-13}$ $g^2.cm^{-4}.s^{-1}$) compared with the alloy with Ti and Nb addition.

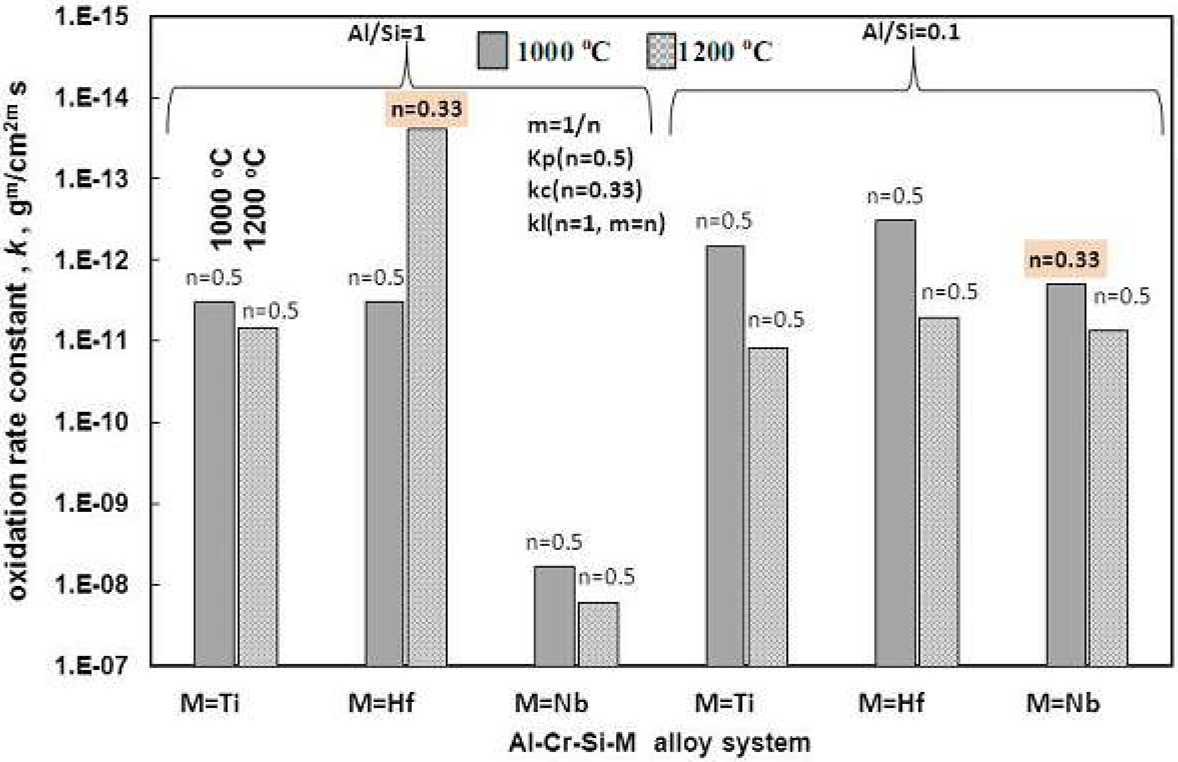

Figure 8.6 Oxidation rate constants of Cr-Si-Al-M alloys at 1000 and 1200 °C.

By increasing the Al/Si ratio to 1, the scales formed on the alloys with Hf, Ti and Nb were partially spalled, spalled and unspalled, respectively. The alloys with Hf and Ti addition had the same kp ($3.3x 10^{-12}$ $g^2.cm^{-4}.s^{-1}$) that was lower than that of the alloy with Nb addition, see Figure 8.6.

At 1000 °C, for the alloys with Al/Si=0.1, the scale formed on the alloy with M= Hf consisted of silica, mullite and $(Al,Cr)_2O_3$ solid solution and the alloys with M=Ti and Nb formed silica, mullite, alumina and chromia. It was concluded that the scale formed on the alloys with Ti and Nb addition lie in two phase region in the Al_2O_3-Cr_2O_3 phase diagram whereas the alloy with

M=Hf can only form solid solution corundum. Hafnia and titania formed in the scales of the alloys with M=Hf and Ti but there was no formation of Nb_2O_5 on the alloy with M=Nb. By increasing the Al/Si ratio to 1, the scale on the alloy with M=Hf was continuous alumina with dispersed mullite. The alloy with M=Ti formed only alumina scale and the alloy with M=Nb formed alumina, chromia and Nb_2O_5. In general, the morphologies of the scales on the alloys with M=Hf, Ti, Nb was cell/whisker and cell respectively for the alloys with Al/Si=0.1 and Al/Si=1.

1200 ^{o}C: No pest oxidation was observed in the alloys. The alloy with Al/Si=0.1 and Hf addition exhibited parabolic oxidation for the first 25 hours followed by linear oxidation. By increasing the Al/Si ratio to 1, the alloy obeyed cubic oxidation for the whole exposure time, see Figure 8.6. The alloy with Ti addition and Al/Si=0.1 exhibited parabolic oxidation for the first 16 hours followed by paralinear oxidation and by increasing the Al/Si ratio to 1, the alloy obeyed parabolic oxidation for the whole exposure time. The alloy with Nb addition and Al/Si=0.1 obeyed parabolic oxidation for the first 16 hours and by increasing the Al/Si ratio to 1, the alloy exhibited parabolic oxidation for the whole exposure time, see Figure 8.6. The alloys with Ti and Hf addition respectively with Al/Si=0.1 and Al/Si=1 had the lowest weight gain among the other alloys and the alloy with Nb addition had the highest weight gains among the alloys with Al/Si=0.1 and Al/Si=1, see Figure 8.5.

For the alloys with Al/Si=0.1, the Hf addition had the most beneficial effect on oxidation for the early stage of the oxidation (t<25 hours) compared with Nb and Ti. For the alloys with Al/Si=1, the Hf addition was the most beneficial compared with Ti and Nb. The Nb addition had the least beneficial effect on oxidation compared with Hf, Ti for the alloys with Al/Si=0.1 and 1.

For the alloys with Al/Si=0.1, the scale formed on the alloys with Hf and Nb addition was partially spalled whereas the scale of the alloy with Ti addition was completely spalled. The alloy with Hf addition had the lowest kp ($5x10^{-12}$ $g^{2}.cm^{-4}.s^{-1}$) than the alloys with Ti and Nb addition. By increasing the Al/Si ratio to 1, the corrugated scales formed on the alloys with Hf, Ti and Nb addition were partially spalled along the ridges. The alloy with Hf addition had different oxidation kinetics (cubic) compared with the alloys with Ti and Nb addition that had parabolic oxidation. The scale formed on the alloy with Hf addition was more protective than on the alloy with Ti and Nb addition.

At 1200 ^{o}C, for the alloys with Al/Si=0.1, the scale formed on the alloy with M=Ti consisted of alumina whereas the scale on the alloys with M= Hf and Nb were $(Al,Cr)_2O_3$ solid solution. Mullite also formed on the alloy with M=Nb. Alumina and chromia were also stable in the scale of the alloy with M=Nb. For the alloys with Al/Si=1, the alloys with M=Hf, Ti and Nb formed $(Al,Cr)_2O_3$ and mullite. There was no formation of transition metal oxides (HfO_2, TiO_2 and Nb_2O_5) in the alloys with Al/Si=0.1 and 1 at 1200 ^{o}C.

The activation energies for the oxidation of the alloys indicated that in the range 800-1000 ^{o}C the alloy with Hf addition and Al/Si=0.1 had the lowest activation energy and best oxidation behaviour. In the range 1000-1200 ^{o}C the alloy with Ti addition and Al/Si=0.1 had the lowest activation energy and best oxidation behaviour.

8.2. Conclusions

8.2.1 Cr-45 Si-5Al-X (X=Hf, Ti, Nb)

It is shown for the first time that the quaternary addition X at 5 at.% has an effect on the $CrSi_2$, CrSi and Cr_5Si_3 phase equlibria mainly via destabilization of the CrSi silicide with Hf and Nb being the most effective. All quaternary additions stabilise the 6-5 silicide and Ti has the strongest effect on the Al content of $CrSi_2$ which decreases compared with Hf and Nb and the ternary Cr-Si-Al equlibria. Thus, with Hf and Nb the TM_6Si_5, TM_5Si_3 and $CrSi_2$ intermetallics are stabilised in the microstructure at different volume fractions, as indicated in Figure 8.2.

None of the quaternary additions individually caused pest oxidation. It was possible to form alumina in the scale up to 1200 ^{o}C with each quaternary addition, however with the addition of Nb, mullite also formed in the scale. Chromia had some solubility in the alumina scale with the addition of Hf or Nb whereas it was not soluble in alumina in the presence of Ti. The alloys with Ti and Nb could form smooth scale regardless of spallation whereas the alloy with Hf formed a corrugated scale due to having improved oxide scale adhesion via the formation of hafnia oxide pegs. Thus, it is suggested that (i) the residual stresses induced due to differential contraction/expansion effects between the scale/substrate interface and (ii) the high adhesion of scale to substrate could cause the rumpling of the scale. Therefore, the scales of the alloys with Nb or Ti addition were more susceptible to spallation up to 1200 ^oC. The Hf containing alloy showed better oxidation behaviour having the smaller kp (parabolic oxidation rate constant) value and weight gain compared with the alloys with Nb or Ti addition but for a limited exposure time, instead the Ti containing alloy had rather comparable oxidation kinetics for longer exposure time at lower temperature (1000 ^oC). Therefore, long term oxidation resistance of these three alloys appears to be limited to different temperatures depending on the quaternary alloying addition. Thus, the isothermal oxidation study of these three alloys would suggest that the Ti containing alloy exhibits better long term oxidation resistance at 1000 ^oC compared with Hf and Nb and none of the alloys possess long term oxidation resistance at 1200 ^oC as their parabolic oxidation kinetics were only stable for a limited period (16-25 hours), however the Hf containing alloy offered better oxidation compared with the two other alloys. The spalling issue appears to have been accelerated in the Ti and Nb containing alloys compared with the Hf containing alloy under isothermal oxidation. Despite not having a long term oxidation resistance at 1200 ^oC in these alloys with 5 at.% Al, the alloys exhibited oxidation rate constants that are comparable to those of Ni and Pt based intermetallic alloys for limited exposure time (t = 16-25 hours).

8.2.2 Cr-25Si-25Al-X (X=Hf, Ti, Nb)

It is shown for the first time that each quaternary addition did not destabilise the Al-Cr intermetallic(s) the presence of which would lead to liquation in the microstructure at high temperature. Hf stabilised only the Al_8Cr_5 intermetallic but Ti and Nb stabilised this intermetallic together with the $Al_{11}Cr_4$ and Al_9Cr_4 intermetallics, respectively. Furthermore, Hf and Ti stabilised the Si poor Cr_3Si silicide in which the Al solubility is very low. Each quaternary addition also stabilised the TM_6Si_5 and TM_5Si_3 silicides.

None of the quaternary additions individually caused pest oxidation. Alumina and mullite formed in the scale up to 1200 ^oC with each quaternary addition. Chromia had some solubility in the alumina scale in these alloys. The alloys formed uneven scale on the substrate that was partially spalled in the ridges. The Hf containing alloy showed better oxidation behaviour having the smaller oxidation rate constant and weight gain compared with Nb or Ti. The Hf or Ti containing alloys had identical oxidation rates for longer exposure time at lower temperature (1000 ^{o}C). The isothermal oxidation of these three alloys would suggest that the Hf containing alloy exhibits better oxidation resistance at 1200 ^{o}C compared with the Ti and Nb containing alloys. The Hf and Ti containing alloys showed better oxidation resistance at 1000 ^{o}C, however the Hf containing alloy had smaller weight gain compared with the two other alloys. The scale adhesion appeared to have been improved in these alloys compared with the alloys with Al/Si=0.1. The alloys exhibited parabolic oxidation kinetics up to 1200 ^{o}C.

The Al-Cr intermetallic(s) formed in these alloy are not desirable constituent phase for achieving good oxidation resistance although they contain high amount of Al, their low melting point temperature can deteriorate the oxidation resistance of the alloys above 1000 ^{o}C as well as their mechanical properties. Despite having parabolic oxidation kinetics in theses alloys with rather high Al concentration, they could not achieve oxidation rate constants that are comparable to those of Ni and Pt based intermetallic alloys for the long term oxidation resistance.

8.3.Suggestion for future work

1- For the reason discussed in the section 8.1 it is essential that a future study should consider the synergistic effects of the two or more transition metal additions (M=Hf, Ti, Nb, Ta) on the phase equlibria and oxidation behaviour of the alloys based on Cr-45Si-5Al and Cr-25Si-25Al with Al/Si=0.1 and 1, respectively. It will be interesting to find out which synergies (if any) of transition metal additions can destabilise the Al-Cr intermetallic in the alloys with Al/Si =1.0

2- Study the thermal expansion anisotropy of selected Cr-Si based alloys because of importance of CTE on the integrity of the substrate bond-coat interfaces.

3- Study isothermal oxidation at the intermediate temperatures of 900 and 1100 ^{o}C and at 700 ^{o}C to obtain more information about the oxidation of this type of alloys in wider temperature range of interest and extend oxidation studies above 1200 ^{o}C for alloys where there is no danger of liquation.

4- Study cyclic oxidation of selected alloys using cycles of industrial interest (e.g. 1, 5 or 10 hours at operating temperature before cooling to room temperature)

5- The Al/Si ratio was found to be a key factor to precursor phase formation in the alloys of this study. Thus, it will be interesting to study alloys with different Al/Si ratios in order to find out below which Al/Si ratio the Al-Cr intermetallic(s) become unstable. This would enable (i) optimisation of bond-coat alloy components based on multi component Cr-Si-Al-X alloys and (ii) understanding of the behaviour of the bond-coat alloy in service.

6- As the processes by which a selected bond coat alloy of studied composition could be deposited on a typical substrate, such as plasma spray, are non-equilibrium processes, it is essential to study phase formation and stability and oxidation behaviour in alloy deposited on a selected substrate using a typical method, for example vacuum plasma spray.