Effect of Cr Addition on the Phase Equilibria and Oxidation Behavior of NbSi₂

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Effect of Cr addition on the phase equilibria and oxidation behavior of NbSi₂ was investigated. Although the crystal structures of NbSi₂ and CrSi₂ are both C40, they form separated ranges of homogeneities in the Nb–Cr–Si ternary system. The vertical section passing through the NbSi₂ and CrSi₂ binary edges were experimentally determined. A binary NbSi₂ alloy exhibited poor oxidation resistance, showing pest-like behavior upon cyclic oxidation at temperatures from 800 to 1200°C. On the other hand, Cr addition significantly improved the oxidation resistance of NbSi₂. The oxide layers that developed on the Nb–Cr–Si ternary alloys consisted of NbCrO₄, Cr₂O₃, and SiO₂, and the formation of Cr₂O₃ and NbCrO₄ suppresses the Nb₂O₅ formation, and thereby suppresses the pest-like behavior of the binary NbSi₂ alloy. However large Cr additions that exceed the solubility limit of NbSi₂ should not be suitable, because NbSi₂/CrSi₂ alloys were susceptible to spalling and disintegration of the oxide scales upon cyclic oxidation. [doi:10.2320/matertrans.MB201809]

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1. Introduction

Last decades, Nb–Si alloys have been considered as candidate materials for alternative high temperature structural materials with superior properties to Ni based superalloys.^{1,2)} The Nb–Si alloys have been shown to exhibit a good combination of high temperature strength and room temperature toughness through a suitable microstructure control.^{3,4)} However, one of the biggest challenges faced by Nb–Si alloys is low oxidation resistance.^{5,6)} Therefore, application of coating on Nb–Si alloys would be inevitable, coupled with significant improvement in the oxidation resistance of the Nb–Si alloy substrates.

Some refractory metal disilicides, such as MoSi₂ and WSi₂, are known to exhibit outstanding oxidation resistance at high temperatures, and thus disilicides would be promising for coating application. At the same time, selection of coating materials that are chemically compatible to the substrates is beneficial, because reactions between coating and substrate can be suppressed. From these perspectives, NbSi₂ based multiphase coatings are worth pursuing, since they have potential opportunity to be in equilibrium with Nb–Si alloy substrates. However, contrary to MoSi₂, NbSi₂ exhibits poor oxidation resistance at temperature above 800°C.⁷⁾ Previous studies have demonstrated that Cr is one of the effective alloying elements for improving the oxidation resistance of Nb silicides and Nb based alloys.^{8,9)} Therefore in this study, the focus was placed on the effect of Cr addition on the oxidation behavior of NbSi₂ and the phase equilibria in the Nb–Cr–Si ternary system.

2. Experimental Procedures

Alloys were prepared by an arc-melting furnace using high purity raw materials (Nb: 3N, Cr: 4N, Si: 5N) under an Ar atmosphere. The base alloy composition was Nb–66.7 mol%Si, and Cr addition was made to substitute the Nb

atoms under the fixed Si content. Hereafter all the alloy compositions are given in mole percent. Seven alloys were prepared in this study: Nb–66.7Si, Nb–3.3Cr–66.7Si, Nb–8.3Cr–66.7Si, Nb–16.7Cr–66.6Si, Nb–25Cr–66.7Si, Nb–30Cr–66.7Si, and Cr–66.7Si. These alloys are denoted by their atomic fraction with the subscripts to the right of each atom; e.g., “Nb₂₅Cr_{8.3}Si_{66.7}” for the Nb–8.3 mol%Cr–66.7 mol%Si alloy. Since the arc-melted ingots contained significant amounts of cracks and cavities, they were milled into powders, sieved under 25 μm, and consolidated again by spark plasma sintering (SPS) at 1200°C for 5 minutes under the applied pressure of 50 MPa. The SPS’ed samples were annealed at 1300°C for 50 h under vacuum. Microstructures were characterized by scanning electron microscopy (SEM). Phase identification was done by X-ray diffractometry (XRD) and energy dispersive X-ray spectrometry (EDS). Rietveld refinement was performed with the RIETAN software.¹⁰⁾ The melting temperatures of the alloys were determined by differential thermal analysis (DTA) using alumina crucibles in an Ar-flowing atmosphere. Oxidation behavior was examined by cyclic oxidation tests in air at 800, 1000, 1100 and 1200°C. The dimensions of the oxidation test specimens are 3 × 3 × 3 mm³. The specimens were placed in alumina crucibles during cyclic oxidation tests, and the weight change by each cycle was measured as the samples being stayed in the crucibles.

3. Results and Discussion

3.1 Microstructure and phase equilibria

Figure 1 shows SEM micrographs of as-cast alloys: (a) Nb₂₅Cr_{8.3}Si_{66.7}, (b) Nb_{16.7}Cr_{16.7}Si_{66.6}, and (c) Nb_{8.3}Cr₂₅Si_{66.7} alloys. In accordance with the previous reports,^{11,12)} NbSi₂ and CrSi₂ exhibit separate ranges of homogeneities in the Nb–Cr–Si ternary system, although they both possess the same crystal structure of C40 (*hP9*, *P6₃/22*).¹³⁾ The primary solidification phase of the alloys shown in Fig. 1 is NbSi₂ with brighter contrast, and CrSi₂ forms subsequently to enclose the primary phase. This indicates that a peritectic type reaction is present in the NbSi₂–CrSi₂ pseudo-binary.

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Fig. 1 SEM-BSE micrographs of as-cast alloys: (a) Nb₂₅Cr_{8.3}Si_{66.7}, (b) Nb_{16.7}Cr_{16.7}Si_{66.6}, and (c) Nb_{8.3}Cr₂₅Si_{66.7} alloys.

Fig. 2 SEM-BSE micrographs of the alloys SPS'ed and annealed at 1300°C for 50 h: (a) Nb₂₅Cr_{8.3}Si_{66.7}, (b) Nb_{16.7}Cr_{16.7}Si_{66.6}, and (c) Nb_{8.3}Cr₂₅Si_{66.7} alloys.

Since the as-cast ingots contained a significant amount of shrinkage cavities and microcracks as shown in Fig. 1, they were milled into powder and consolidated again by SPS, which is followed by annealing at 1300°C for 50 h. Figure 2 shows SEM micrographs of the alloys after the annealing. Although some small cavities are visible on the micrographs, sound specimens without any microcracks have been obtained after SPS and annealing. These alloys exhibit two-phase microstructures comprised of NbSi₂ and CrSi₂, and the volume fraction of CrSi₂ increases with increasing Cr content. Image analysis on the SEM micrographs has revealed that the volume fraction of CrSi₂ is 3% in the Nb₂₅Cr_{8.3}Si_{66.7} alloy, while 75% in the Nb_{8.3}Cr₂₅Si_{66.7} alloy. The compositions of NbSi₂ and CrSi₂ phases were analyzed

Table 1 Summary of EDS results analyzed in the Nb_{16.7}Cr_{16.7}Si_{66.6} alloy annealed at 1300°C.

Phase	Composition (mol%)		
	Nb	Cr	Si
NbSi ₂	23.3 ± 0.9	10.0 ± 1.6	66.7 ± 1.9
CrSi ₂	3.5 ± 0.7	30.9 ± 2.9	65.6 ± 2.8

by EDS, of which results are summarized in Table 1. The range of homogeneity for NbSi₂ is comparatively larger than that for CrSi₂ in the ternary system.

Figure 3 shows a result of Rietveld refinement on the annealed Nb_{16.7}Cr_{16.7}Si_{66.6} alloy. Upon Rietveld refinement,

Fig. 3 A result of Rietveld refinement on the annealed Nb_{16.7}Cr_{16.7}Si_{66.6} alloy. The refined structure parameters are summarized in Table 2.

Table 2 The structure parameters NbSi₂ and CrSi₂ refined the Rietveld method.

Phase	Site	Wyck.	g	x	y	z	U (Å ²)
CrSi ₂	Si1	6i	1	0.1658	0.3316	0	0.0100
	Cr1	3c	0.97	1/2	0	0	0.0096
	Nb1	3c	$= 1 - g(\text{Cr1})$	$= x(\text{Cr1})$	$= y(\text{Cr1})$	$= z(\text{Cr1})$	$= U(\text{Cr1})$
NbSi ₂	Si2	6i	1	0.1658	0.3316	0	0.0076
	Nb2	3c	0.69	1/2	0	0	0.0039
	Cr2	3c	$= 1 - g(\text{Nb2})$	$= x(\text{Nb2})$	$= y(\text{Nb2})$	$= z(\text{Nb2})$	$= U(\text{Nb2})$

Fig. 4 Variation in the unit cell volume against Cr concentration.

no substitutional defects were assumed to occur on the Si sites of both NbSi₂ and CrSi₂, and the atom positions were fixed to the reported coordinates of the binary compounds.¹³⁾ Table 2 summarizes the structure parameters for NbSi₂ and CrSi₂ that have been refined in this study. The occupancy of Cr at the Cr1 site of CrSi₂ is 0.97, while that of Nb at the Nb2 site of NbSi₂ is 0.69. This means that the expected composition of the CrSi₂ phase is $C_{\text{Nb}} = 1.0$, $C_{\text{Cr}} = 32.3$, $C_{\text{Si}} = 66.7$ in the mole percent, and that of the NbSi₂ phase is $C_{\text{Nb}} = 23.0$, $C_{\text{Cr}} = 10.3$, $C_{\text{Si}} = 66.7$. These values reasonably agree with those obtained by EDS summarized in Table 1.

Figure 4 represents a change in the unit cell volume against the Cr concentration. Here the unit cell volume, v , is defined by the following equation,

$$v = a^2 c \sin \frac{2\pi}{3}, \quad (1)$$

where a and c are the lattice parameters of NbSi₂ and CrSi₂ determined by the Rietveld refinements. The unit cell volume decreases with Cr content, and it becomes constant within the range of compositions, where two phases of NbSi₂ and CrSi₂ are in equilibrium. The phase boundaries were defined by the intersections between the straight line by the Vegard's law and the line within the two phase region, as shown in Fig. 4. The determined phase boundary concentrations of Cr are 7.8 and 29.5. These values reasonably agree with those determined by EDS.

The melting temperatures of the alloys were determined by DTA. Figure 5 shows DTA profiles for (a) Nb_{16.7}Cr_{16.7}Si_{66.6},

Fig. 5 Experimental DTA profiles for (a) Nb_{16.7}Cr_{16.7}Si_{66.6}, (b) Nb_{8.3}Cr₂₅Si_{66.7} and (c) Cr_{33.3}Si_{66.7} alloys.

(b) Nb_{8.3}Cr₂₅Si_{66.7} and (c) Cr_{33.3}Si_{66.7} alloys. Cr_{33.3}Si_{66.7} alloys is a binary CrSi₂ single-phase alloy that exhibits congruent melting,¹⁴⁾ and therefore the profile exhibits pure-metal like behavior as in Fig. 5(c). By averaging the onset temperatures of melting and freezing, the melting temperature of CrSi₂ is determined to be 1428°C, which is slightly lower than the reported temperature of 1439°C.¹⁴⁾ On the other hand, Nb_{16.7}Cr_{16.7}Si_{66.6} and Nb_{8.3}Cr₂₅Si_{66.7} alloys exhibit a solid-solution like freezing behavior, showing less-distinct onsets upon freezing. In such cases, it has been pointed out that good results are often obtained by defining the deviation point from the base line to be the onset of freezing.¹⁵⁾ Therefore in this study, the onset of freezing is defined from the point, at which the signals start to deviate from the base lines, as in Fig. 5(a) and (b).

Based on the results of EDS, XRD and DTA, coupled with microstructural observations, the vertical section that connects between the NbSi₂ and CrSi₂ binary edges was determined as shown in Fig. 6. The melting temperature of NbSi₂ was adopted from the literature.¹⁶⁾ It is found that the

Fig. 6 The vertical section between NbSi₂ and CrSi₂ in the Nb–Cr–Si ternary system.

range of homogeneity for NbSi₂ at 1300°C is larger than at 1000°C previously reported.^{11,12)} On the other hand, Nb substitutional defects that can develop at the Cr site of CrSi₂ are smaller than those reported by Goldschmidt *et al.*,¹¹⁾ but comparable to those by Zhao *et al.*¹²⁾

3.2 Oxidation behavior

Oxidation behavior of the alloys was studied by cyclic oxidation tests in air at 800, 1000, 1100, and 1200°C. For

oxidation tests, the specimens were put in a furnace heated to the test temperatures, kept for a set time, and removed from the furnace, which was followed by weight change measurements by measuring the weight of crucibles as the samples being stayed. Therefore in this study, small disintegration or spalling of oxide products will not result in weight loss. Series of these procedures were repeated with the keeping duration of 10 h up to the cumulative time of 100 h, and the keeping duration of 20 h up to the cumulative time of 500 h.

Figures 7 and 8 summarize the appearances of the specimens tested at 1000°C and 1200°C for the representative cumulative oxidation times. The Nb_{33.3}Si_{66.7} alloy (i.e., binary NbSi₂ alloy) exhibited pest-like behavior both at 1000 and 1200°C, where oxidized products had disintegrated and swelled inside the crucibles. Figure 9 shows an XRD profile obtained from the disintegrated powder of the Nb_{33.3}Si_{66.7} alloy oxidized at 1000°C. The oxide products are mainly composed of two niobium pentoxides, γ -Nb₂O₅ (T-Nb₂O₅, JCPDS #27-1312) and β -Nb₂O₅ (JCPDS #26-0885). This is consistent with the previous reports, where the formation of Nb₂O₅ is responsible for pest-like behavior due to its porous and non-protective character.^{7,17)}

Although the binary NbSi₂ compound did not show any protective oxidation behavior, Cr addition to NbSi₂ was found to improve the oxidation resistance drastically. At 1000°C, all the Cr-containing alloys exhibited no spalling or disintegration after oxidation up to 500 h. The surfaces of the samples have tarnished into a greenish color, implying that Cr₂O₃ could have formed on the surface. On the other hand, after cyclic oxidation at 1200°C for 500 h, the Nb_{16.7}Cr_{16.7}Si_{66.6} and Nb_{8.3}Cr₂₅Si_{66.7} alloys exhibited dis-

Fig. 7 Change of the appearances of oxidation test specimens tested at 1000°C for various cumulative oxidation durations. Cubic specimens were placed in alumina crucibles.

Fig. 8 Change of the appearances of oxidation test specimens tested at 1200°C for various cumulative oxidation durations. Cubic specimens were placed in alumina crucibles.

Fig. 9 An XRD profile of the disintegrated powder of the Nb_{33.3}Si_{66.7} alloy oxidized at 1000°C.

integrations at the edges of the specimens, as shown in Fig. 8. The detailed mechanism of the disintegration is unclear, but speculated that a NbSi₂/CrSi₂ two-phase microstructure is susceptible to spalling of the oxide scales due to the difference in the oxidation characteristics of the two. Note that the Cr_{33.3}Si_{66.7} alloy is a CrSi₂ single-phase alloy, and the Nb₂₅Cr_{8.3}Si_{66.7} alloy is nearly single-phase of NbSi₂, of which the volume fraction is 97%.

Figure 10 shows the weight change per unit surface area at (a) 800°C, (b) 1000°C, (c) 1100°C, and (d) 1200°C upon cyclic oxidation. Note that the results of the Nb_{33.3}Si_{66.7} alloy (i.e., binary NbSi₂ alloy) were not included in Fig. 10, because it exhibited severe pesting behavior so that the weight change could not be measured accurately. As shown in Fig. 10(a), all the alloys exhibited gradual weight gains with elapsed oxidation time at 800°C. At 1000°C

(Fig. 10(b)), the Cr_{33.3}Si_{66.7} alloy showed a relatively large weight gain, however the other ternary alloys, Nb₂₅Cr_{8.3}Si_{66.7}, Nb_{16.7}Cr_{16.7}Si_{66.6} and Nb_{8.3}Cr₂₅Si_{66.7}, exhibited less-significant weight changes at this temperature. If diffusion of oxygen through a growing oxide scale were the rate determining process for the weight gains, the parabolic rate constant, k_p , for Nb₂₅Cr_{8.3}Si_{66.7} at 1000°C can be evaluated to be: $k_p = 5.8 \times 10^{-8} \text{ (mg}^2\text{/cm}^4\text{/s)}$, which is three orders of magnitude smaller than that for some commercial Ni-based superalloys at the same temperature.¹⁸⁾ At 1100°C (Fig. 10(c)), the Cr_{33.3}Si_{66.7} alloy exhibited more pronounced weight gains, while the other alloys exhibited small weight change during oxidation up to 500 h. On the contrary, the weight gain of the Cr_{33.3}Si_{66.7} alloy at 1200°C appears to be lower than that at 1100°C. It is reported that Cr₂O₃ sublimates at temperatures above 1000°C through the following reaction:^{19,20)} $\text{Cr}_2\text{O}_3(\text{s}) + 3/2\text{O}_2 \rightarrow 2\text{CrO}_3(\text{g})$. Therefore, this was caused by sublimation of Cr₂O₃ that became more significant at 1200°C than at 1100°C. At the same time, the Nb_{16.7}Cr_{16.7}Si_{66.6} and Nb_{8.3}Cr₂₅Si_{66.7} alloys showed considerable fluctuation in the weight change. This behavior would be associated with the disintegrations of the specimens upon cyclic oxidation, as depicted in Fig. 8. In this context, the Nb₂₅Cr_{8.3}Si_{66.7} alloy showed the highest oxidation resistance up to 1200°C, because the amount of weight change is the smallest, and the disintegration of the specimen is minimal.

To identify the oxides that form on the surface during oxidation tests, the samples were milled into rough powder, and oxidized in air at 1200°C for 50 h. Figures 11 and 12 show XRD profiles obtained from the oxidized powders of Nb₂₅Cr_{8.3}Si_{66.7} and Cr_{33.3}Si_{66.7}, respectively. For the Nb₂₅Cr_{8.3}Si_{66.7} alloy shown in Fig. 11, NbCrO₄, Cr₂O₃, and

Fig. 10 Weight change by cyclic oxidation tested at (a) 800°C, (b) 1000°C, (c) 1100°C, and (d) 1200°C.

Fig. 11 An XRD profile of the Nb₂₅Cr_{8.3}Si_{66.7} alloy oxidized in air at 1200°C for 50 h.

Si are indicated to have formed after oxidation at 1200°C, while formation of Nb₂O₅ is not confirmed. It has been pointed out that formation of NbCrO₄ instead of Nb₂O₅ is

beneficial for suppressing the pest-like behavior and thereby enhancing the oxidation resistance of Nb silicides.^{17,21)} Therefore, the significant improvement in the oxidation

Fig. 12 An XRD profile of the $\text{Cr}_{33.3}\text{Si}_{66.7}$ alloy oxidized in air at 1200°C for 50 h.

Fig. 13 SEM micrographs of the surfaces (a–c) and the cross sections (d–f) of the specimens oxidized at 1200°C for 50 h. (a, d) $\text{Nb}_{25}\text{Cr}_{8.3}\text{Si}_{66.7}$ (b, e) $\text{Nb}_{16.7}\text{Cr}_{16.7}\text{Si}_{66.6}$, and (c, f) $\text{Nb}_{8.3}\text{Cr}_{25}\text{Si}_{66.7}$.

resistance of NbSi_2 by Cr additions would be attributed to the formation of NbCrO_4 , in addition to Cr_2O_3 formation. At the same time, formation of Cr_2O_3 and Si were indicated in $\text{Cr}_{33.3}\text{Si}_{66.7}$ from XRD profile as shown in Fig. 12. It should be noted that, for both $\text{Nb}_{25}\text{Cr}_{8.3}\text{Si}_{66.7}$ and $\text{Cr}_{33.3}\text{Si}_{66.7}$ alloys, formation of crystalline SiO_2 (α -cristobalite) during oxidation at 1200°C for 50 h was indicated in this study. It is well known that, for many silicides, amorphous SiO_2 usually forms at the early stage of its formation, and crystallization of SiO_2 gradually proceeds during exposure at temperatures higher than 1100°C .⁷⁾ In fact, the formation of α -cristobalite together with Cr_2O_3 has been confirmed in Cr–Mo–Si alloys for oxidation in the temperature range of 1000 – 1200°C .²²⁾ It is therefore suggested that SiO_2 also forms on the surfaces of the alloys, which contributes increased oxidation resistance.

Figure 13 shows SEM micrographs of the surfaces and the cross sections of the specimens oxidized at 1200°C for

50 h: (a, d) $\text{Nb}_{25}\text{Cr}_{8.3}\text{Si}_{66.7}$ (b, e) $\text{Nb}_{16.7}\text{Cr}_{16.7}\text{Si}_{66.6}$, and (c, f) $\text{Nb}_{8.3}\text{Cr}_{25}\text{Si}_{66.7}$. The oxides on the surfaces showing thin-disk morphology are Cr_2O_3 , which was confirmed by EDS. This suggests that Cr was preferentially oxidized to form Cr_2O_3 on the surface, which at the same time contributes to improve the oxidation resistance of Nb–Cr–Si ternary alloys, particularly at lower temperatures. The surface oxide layers are comprised of plural oxides, which is in agreement with the empirical knowledge: oxide scales comprised of SiO_2 and metal-oxides tend to form in NbSi_2 , TaSi_2 and CrSi_2 , of which oxygen affinity of the metallic element is close to that of Si.²³⁾ Cross sectional observations have clearly depicted the development of reaction layers beneath the surface oxide layers. The region with dark contrast in the reaction layer was identified to be the Si phase by EDS. This is consistent with the XRD results shown in Fig. 11, where the formation of Si was observed in the oxidized powder. The white phase adjacent to Si in the reaction layer is the NbSi_2 phase, of

which Cr content is lower than that inside. It is indicated that the formation of the Si phase occurs because outward diffusion of Cr occurs significantly due to Cr₂O₃ formation on the surface. At the same time, it is speculated that inward diffusion of oxygen leads to stabilization of the Si phase, since the three phase equilibrium of NbSi₂/SiO₂/Si is attained in the Nb–Si–O system,^{24,25)} and CrSi₂/SiO₂/Si in the Cr–Si–O ternary system.²⁶⁾

In this study, Cr addition to binary NbSi₂ compounds was found to be effective to enhance the oxidation resistance drastically. This is primarily caused by the preferential formation of NbCrO₄ and Cr₂O₃, by which the oxygen potential at the interface between the oxide scale and substrate is lowered to the dissociation pressure of Nb₂O₅ and thereby the formation of deleterious Nb₂O₅ is suppressed. However the amount of Cr addition should be limited within the homogeneity range of NbSi₂, because NbSi₂/CrSi₂ two-phase alloys are susceptible to spalling and disintegration of the oxide scales upon cyclic oxidation. In addition, Cr₂O₃ can sublime at 1100°C or higher, which results in degradation of the oxide scales developed on the substrates. In this context, the Nb₂₅Cr_{8.3}Si_{66.7} alloy, which has nearly a NbSi₂ single-phase microstructure, showed the highest oxidation resistance at temperatures up to 1200°C.

4. Conclusions

NbSi₂ and CrSi₂ are found to form separated ranges of homogeneities in the Nb–Cr–Si ternary system. The vertical section passing through the NbSi₂ and CrSi₂ binary edges (i.e., the isopleth at 66.67 mol% Si) was experimentally determined in this study. The range of homogeneity of NbSi₂ is found to be larger than that previously reported. A binary NbSi₂ alloy exhibits poor oxidation resistance, showing pest-like behavior during oxidation at temperature between 800 and 1200°C due to the formation of Nb₂O₅. In contrast, Nb–Cr–Si ternary alloys show better oxidation resistance by forming NbCrO₄, Cr₂O₃ and SiO₂, which then suppresses the formation of a detrimental oxidation product of Nb₂O₅. However large Cr additions that exceed the solubility limit of NbSi₂ should be avoided, because the alloys with NbSi₂/CrSi₂ two-phase microstructure were susceptible to spalling and disintegration of the oxide scales upon cyclic oxidation.

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