High temperature strength, fracture toughness and oxidation resistance of Nb–Si–Al–Ti multiphase alloys

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Abstract

Nb–Si–Al–Ti quaternary phase diagram around three-phase region, which consists of niobium solid solution (Nbₙₙ), Nb₃Al and Nb₃Si₁, is constructed in this study. The three-phase region exists up to titanium content of about 20 mol%. Based on the quaternary phase diagram, three-phase alloys containing Nbₙₙ from about 50 to 75% in volume are prepared to improve high temperature strength, room temperature fracture toughness and oxidation resistance simultaneously.

When microstructure and composition are optimized (Nbₙₙ + Nb₃Al + Nb₃Si₁) three-phase alloy with the addition of titanium exhibits higher compressive strength than nickel-based superalloys at room temperature to 1573 K. Fracture toughness at room temperature of (Nbₙₙ + Nb₃Al + Nb₃Si₁) three-phase alloys is increased to over 12 MPa m¹/₂ by the addition of titanium without sacrificing high temperature strength. Oxidation resistance of (Nbₙₙ + Nb₃Al + Nb₃Si₁) three-phase alloys is improved by the addition of titanium. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Nb–Si–Al–Ti quaternary diagram; Niobium solid solution; Nb₃Al; Nb₃Si₁; High temperature strength; Fracture toughness; Oxidation resistance

1. Introduction

Recently, the development of high temperature structural material, whose operating temperature exceeds that of conventional nickel-based superalloy, is required in various fields. Refractory intermetallic compounds with high melting temperature, such as Nb₃Al [1,2], Nb₃Si [3], Irₙₙ [4], Crₙₙ [5] and MoSi₂ [6], have been extensively studied as candidate materials [7]. Among them niobium aluminide Nb₃Al is promising because of its high strength at elevated temperatures and low specific gravity, but it is very brittle at ambient temperature like most refractory intermetallic compounds.

It is widely accepted that fracture toughness of brittle material is improved by incorporating ductile reinforcement [8], which is named ductile phase toughening. This concept has been applied to Nb₃Al by incorporating pure Nb. Bloyer et al. [9] successfully improved the fracture toughness of Nb₃Al by laminating Nb₃Al and pure Nb. However, Nb₃Al/Nb laminates do not provide both high temperature strength and interfacial stability at elevated temperatures. Bencher et al. [10] and Gnanamoorthy et al. [11] have investigated mechanical properties of in situ composites consisting of Nb₃Al and niobium solid solution (Nbₙₙ) in equilibrium with Nb₃Al. Although it was found that fracture toughness is increased by incorporating the ductile phase and microstructures of these composites are stable at high temperatures, high temperature strength and room temperature toughness were not achieved simultaneously at a high level. Multiple functions such as stability of microstructure, fracture tolerance at room temperature, high temperature strength, oxidation resistance, and so on are required for practical uses of high temperature structural materials.

Recently, we have revealed that high temperature strength and fracture toughness at room temperature of three-phase alloy consisting of Nbₙₙ, Nb₃Al and Nb₃Si₁ in Nb–Si–Al–Ti system are higher than those of alloys in Nb–Al or Nb–Si binary system [12]. This implies that (Nbₙₙ + Nb₃Al + Nb₃Si₁) three-phase alloy may possess multi-functions, which are required for very high temperature structural materials. In this study, plane-strain fracture toughness, Kᵢₚ, and oxidation resistance of this three-phase alloy have been investigated to examine the further potential for very high temperature structural applications. It was reported that the addition of titanium in multiphase alloys in Nb–Cr [13] and Nb–Al [14] system, which consists of Nbₙₙ and intermetallic compound, improves remarkably fracture toughness. Moreover, titanium was reported to improve oxidation resistance of refractory alloys

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in Nb–Cr and Nb–Al system [15,16]. However, excess addition of titanium to the (Nb₅₅ + Nb₃₃ + Nb₂Si₃) three-phase alloy may decrease the high temperature strength, since the titanium addition lowers the melting point of (Nb₅₅ + Nb₃₃ + Nb₂Si₃) three-phase alloy.

In this paper, we aim to improve high temperature strength, fracture toughness at room temperature and oxidation resistance of (Nb₅₅ + Nb₃₃ + Nb₂Si₃) three-phase alloys in Nb–Si–Al–Ti system by optimizing the composition.

2. Experimental procedure

Alloy buttons with various compositions to be expected in the multiphase region were arc-melted in an argon atmosphere in order to investigate Nb–Si–Al–Ti quaternary phase diagram around (Nb₅₅ + Nb₃₃ + Nb₂Si₃) three-phase region. The button ingots were annealed in a vacuum under 1 × 10⁻³ Pa and at 1873 K for 360 ks for homogenization. The structures and compositions of heat-treated ingots were evaluated by optical microscopy (OM), scanning electron microscopy (SEM) and electron probe micro analysis (EPMA) to construct the partial quaternary phase diagram.

Specimens used for mechanical and oxidation tests, which contain Nb₅₅ from about 50 to 75% in volume, were prepared in the same process mentioned earlier, referring to Nb–Si–Al–Ti quaternary phase diagram in this experiment. Binary or ternary alloys were also prepared to compare with quaternary alloys. More detailed processing to prepare the binary or ternary alloys was described elsewhere [12].

High temperature strength was evaluated by compression tests using rectangular specimens with the dimension of 2 × 2 × 5 mm³. Compression tests were conducted in a vacuum under 2 × 10⁻³ Pa from room temperature to 1573 K and at an initial strain rate of 1.7 × 10⁻⁴ s⁻¹.

Fracture toughness was first evaluated by conventional SP (small punch) test [17,18], using specimens with the size of 10 × 10 × 0.5 mm³. The three-point bending tests in accordance with ASTM standard (E399) [19] were conducted for some specimens in order to measure plane-strain fracture toughness and compare with the fracture toughness obtained from SP test. The specimen size for bending test was 10 × 5 × 46 mm³. A notch with 0.1 mm in width and 3 mm in depth was introduced at the center of a specimen by electro-discharge machining. A fatigue crack of 2 mm in depth was introduced at a tip of the notch by four-point bending test. Finally, three-point bending tests were conducted under monotonic loading in vacuum to evaluate the plane-strain fracture toughness. Fractured surface after bending test was observed by SEM.

Oxidation tests were carried out at isothermal and heating conditions. Specimens with the size of 4 × 4 × 10 mm³ were mechanically polished by emery paper #1200 before oxidation test. Weight change was measured after isothermal oxidation test in air at 1273 and 1473 K for 3.6, 7.2, 14.4, 86.4, 180 and 360 ks, respectively. Isothermal and heating oxidation tests were conducted also in a mixture of argon and oxygen (argon:oxygen = 4:1), using thermogravimetric-differential thermal analysis (TG-DTA). Polished specimens with the size of 2 × 2 × 5 mm³ were used in this test. Isothermal tests were conducted at temperatures of 1273, 1473 and 1573 K. Heating rate in heating oxidation tests is 0.17 K s⁻¹. After oxidation tests, compositions and structures of oxide and reaction zone were examined using X-ray diffraction and SEM–EPMA.

3. Results and discussion

3.1. Microstructures

Fig. 1 shows a Nb–Si–Al–Ti quaternary phase diagram around (Nb₅₅ + Nb₃₃ + Nb₂Si₃) three-phase region at 1873 K, which is determined in this study. Evidently, the three-phase region becomes narrow with increasing titanium content, and it exists up to about 20 mol% Ti. The microstructure of in situ composite in three-phase region is stable above 1873 K. The compositions of constituent phases in the three-phase region at 1873 K are summarized in Table 1. The compositions of constituent phases in the three-phase alloys that contain the same contents of titanium were almost same, even if the contents of silicon and aluminum are different.

Volume fraction of each phase, (Si + Al) content in Nb₅₅ and processing condition are listed in Table 2. The results of binary Nb–Si and Nb–Al alloys and single-phase Nb–Si–Al ternary Nb₅₅ alloys are also included in Table 2 for comparison. (Si + Al) content in Nb₅₅ equilibrating with intermetallic compounds in Nb–Si–Al ternary system decreases with decreasing aluminum content. Fig. 2 shows the microstructures of specimens annealed at 1873 K in Nb–Si–Al ternary system. As seen in Fig. 2(a), Nb–4.9Si–8.5Al consists of three phases, Nb₅₅, Nb₃Al and

![Fig. 1. Three-phase region in Nb–Si–Al–Ti phase diagram at 1873 K as a function of titanium content.](image-url)
Table 1
Compositions of constituent phases in the three-phase region at 1873 K

| Region                      | Phase         | Nb (mol%) | Si | Al | Ti |
|-----------------------------|---------------|-----------|----|----|----|
|                            | Nb3 (mol%)    | NbAl (mol%) | NbSi3 (mol%) |
| Three-phase (T = 0%)        | 93.4          | 80.3      | 61.3 |
| Three-phase (T = 5%)        | 87.1          | 76.3      | 55.8 |
| Three-phase (T = 10%)       | 78.7          | 70.9      | 51.3 |
| Three-phase (T = 15%)       | 70.7          | 67.7      | 48.4 |
| Nb-Al two-phase             | 89.5          | 79.8      | 62.2 |
| Nb-Si two-phase             | 99.1          | 0         |     |

Table 2
Volume fraction of each phase and (Si + Al) content in Nb3 (Sol.: Solution treatment, Iso.: Isothermal forging, Rec.: Recrystallization annealing, Rol.: Cold rolling)

| Sample name | Volume fraction of each phase (%) | (Si + Al) content in Nb3 (mol%) | Processing condition after arc melting |
|-------------|----------------------------------|---------------------------------|---------------------------------------|
|             | Nb3                             | NbAl                            | Si in Nb3 | Al in Nb3 | Si + Al |                                |
| Nb–5Si–9Al  | 50                              | 48                              | 2        | 1.1       | 5.5     | 6.1 | 1873 K, 100 h | Sol. 2073 K, 3 h + Iso. 1573 K, 70% + Rec. 1873 K, 48 h |
| Nb–7Si–9Al  | 40                              | 52                              | 8        | 1.1       | 5.5     | 6.6 | 1873 K, 100 h |
| Nb–8Si–9Al–10Ti | 62                          | 19                              | 19       | 1.3       | 8.5     | 9.8 | 1873 K, 100 h |
| Nb–10Si–9Al–10Ti | 36                          | 42                              | 22       | 1.3       | 8.5     | 9.8 | 1873 K, 100 h |
| Nb–6Si–11Al–15Ti | 65                          | 21                              | 14       | 1.3       | 11      | 12.3| 1873 K, 100 h |
| Nb–8Si–11Al–15Ti | 58                          | 18                              | 24       | 1.3       | 11      | 12.3| 1873 K, 100 h |
| Nb–4.9Si–8.5Al | 74                              | 19                              | 7        | 0.9       | 5.2     | 6.1 | 1873 K, 100 h |
|Nb–17.3Al     | 62                              | 38                              | 0        | 0        | 11.2    | 11.2| Sol. 2073 K, 3 h + Iso. 1573 K, 70% + Rec. 1873 K, 48 h |
| Nb–10.1Si a  | 61                              | 0                               | 5        | 0.9       | 0       | 0.9 | Sol. 2073 K, 3 h + Iso. 1573 K, 70% + Rec. 1873 K, 48 h |
| Nb–12.7Al    | 100                             | 0                               | 0        | 0        | 8.8     | 8.8 | Sol. 2073 K, 3 h + Iso. 1423 K, 70% + Rec. 1873 K, 4 h |
| Nb–0.5Si–9.5Al | 100                          | 0                               | 0        | 0.5       | 6.2     | 6.7 | Sol. 2073 K, 1 h + Hom. 1873 K, 48 h + Iso. 1423 K, 70% + Rec. 1873 K, 1 h |
| Nb–1Si–6Al   | 100                             | 0                               | 0        | 0.9       | 3.5     | 4.4 | Sol. 2073 K, 1 h + Hom. 1873 K, 48 h + Iso. 1573 K, 70% + Rec. 1873 K, 1 h |
| Nb–0.7Si–3Al | 100                             | 0                               | 0        | 0.7       | 1.7     | 2.4 | Sol. 2073 K, 3 h + Rol. 80% + Rec. 1773 K, 3 h |
| Nb–0.5Si     | 100                             | 0                               | 0        | 0.47      | 0       | 0.47| Sol. 2073 K, 3 h + Rol. 80% + Rec. 1773 K, 3 h |

a Nb–10.1Si contains Nb3Si of 34% in volume.
3.2. Mechanical properties

High temperature strength and toughness at room temperature of Nb–Si–Al three-phase alloys are compared with those of binary alloys in Fig. 4. The comparison was conducted among multiphase alloys that have similar volume fraction of Nb<sub>ss</sub>, because mechanical properties are influenced by the volume fraction of ductile phase. Fracture toughness is evaluated by SP test. Fracture toughness, \( K_{\text{IC}} \), is obtained by the fracture stress in SP tests, using an experiential relation between fracture stress in SP test and plane-strain fracture toughness, \( K_{\text{IC}} \) [12, 17, 18]. SP energy, \( E_{\text{SP}} \), is obtained from the area under load–deflection record in SP test. Saito et al. [17, 18] and Mao et al. [20] indicated that the SP energy, \( E_{\text{SP}} \), corresponds empirically to

![Fig. 2. Backscattered electron images of multiphase alloys of (a) Nb–4.9Si–8.5Al, (c) Nb–17.3Al and (d) Nb–10.1Si, and an optical micrograph of Nb<sub>ss</sub> alloy of (b) Nb–0.7Si–3Al.](image)

![Fig. 3. Backscattered electron images of three-phase alloys, (a) Nb–5Si–9Al, (b) Nb–7Si–9Al, (c) Nb–8Si–9Al–10Ti, (d) Nb–10Si–9Al–10Ti, (e) Nb–6Si–11Al–15Ti and (f) Nb–8Si–11Al–15Ti.](image)

![Fig. 4. Compressive yield stress at 1273 K, SP energy and fracture toughness estimated by SP test at room temperature as a function of (Si + Al) content in Nb<sub>ss</sub> of multiphase alloys having similar volume fraction of Nb<sub>ss</sub>.](image)
elastic–plastic fracture toughness, $J_{IC}$. The 0.2% proof stress at 1273 K is obtained from compression tests. The horizontal axis of Fig. 4 indicates (Si + Al) content in Nb$_{5}$, equilibrating with intermetallic compounds in multiphase alloys. The proof stress at 1273 K and $K_{IC\text{SP}}$ of Nb–Si–Al three-phase alloy are higher than that of Nb–Si and Nb–Al binary alloys. SP energy decreases with increasing (Si + Al) content in Nb$_{5}$. This means that elastic–plastic fracture toughness, $J_{IC}$, decreases with increasing (Si + Al) content in Nb$_{5}$, that is, with decreasing ductility of Nb$_{5}$. However, high temperature strength and fracture toughness have no linear relationship with the ductility of Nb$_{5}$.

Fracture toughness estimated by SP test, $K_{IC\text{SP}}$, may be less reliable, although SP test is very convenient. We conducted three-point bending tests of single-phase Nb$_{5}$ and three-phase alloy. The plane-strain fracture toughness obtained from SP test, $K_{IC\text{SP}}$, and three-point bending test, $K_{IC\text{ASTM}}$, are summarized in Table 3. SP energy and high temperature strength at 1573 K are also included. Table 3 indicates that the fracture toughness estimated by SP test, $K_{IC\text{SP}}$, corresponds to that by three-point bending test, $K_{IC\text{ASTM}}$. Therefore, it is most likely that the fracture toughness of three-phase alloys is higher than that of binary alloys as shown in Fig. 4. The plane-strain fracture toughness of three-phase alloy is estimated to be about 10 MPa m$^{1/2}$. This value is acceptably high, since 6.5 MPa m$^{1/2}$ has been reported as fracture toughness of multiphase alloy in Nb–Al binary system [21,22]. High temperature strength at 1573 K of three-phase alloy in Nb–Si–Al system is extremely higher than that of single-phase Nb$_{5}$ alloy. It is noteworthy that fracture toughness of single-phase Nb$_{5}$ alloy is lower than that of three-phase alloy, though the SP energy of single-phase Nb$_{5}$ alloy is much higher. Thus, it is evident that (Nb$_{5}$ + Nb$_{2}$Al + Nb$_{5}$Si$_{3}$) three-phase alloy in Nb–Si–Al system has better balance of high temperature strength and fracture toughness than binary alloys.

Fig. 5 shows true stress–true strain curves in tensile tests of single-phase Nb$_{5}$ alloys at room temperature. Nb–0.7Si–3Al and Nb–0.5Si deform plastically to a large strain, while Nb–1Si–6Al, having the composition close to that of Nb$_{5}$ equilibrating with intermetallic compounds in the three-phase region, exhibits fracture before plastic yielding. Thus, the ductility of Nb$_{5}$ reinforcement does not seem to be directly related to the improvement of fracture toughness of (Nb$_{5}$ + Nb$_{2}$Al + Nb$_{5}$Si$_{3}$) three-phase alloy.

Nb$_{5}$ equilibrating with Nb$_{5}$Si$_{3}$ in Nb–Si binary alloy may be the most ductile, since Nb–0.5Si shows the largest elongation in Fig. 5. Thus, a maximum increase in toughness by the ductile reinforcement is expected in Nb–10.1Si among alloys in Fig. 4. However, Nb–10.1Si has low fracture toughness compared to Nb–4.9Si–8.5Al in spite of high SP energy. Similarly, fracture toughness of single-phase Nb$_{5}$ alloy, Nb–0.7Si–3Al, is not so high, compared to three-phase alloy as shown in Table 3, though Nb–0.7Si–3Al shows large elongation (Fig. 5) and the high SP energy (Table 3). Thus, ductility of the reinforcement is effective to increase the elastic–plastic fracture toughness, $J_{IC}$, but not to increase the plane-strain fracture toughness, $K_{IC}$.

Fig. 6 shows the stress–strain curves of single-phase Nb$_{5}$ alloys at 1573 K. All the specimens tensile-tested at 1573 K deform plastically to a large strain. It should be noted that Nb–1Si–6Al, having the composition close to that of Nb$_{5}$ equilibrating with intermetallic compounds in the three-phase alloy, shows the highest strength by solid solution hardening. That is, the strength at 1573 K of Nb$_{5}$ is higher in the ternary alloy than in the binary alloys when Nb$_{5}$ has the composition in equilibrium with intermetallic compounds. Therefore, the high strength of Nb$_{5}$ results in the high temperature strength of the three-phase ternary

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Table 3

| Sample name | Toughness by bending test $K_{IC\text{ASTM}}$ (MPa m$^{1/2}$) | Toughness by SP test $K_{IC\text{SP}}$ (MPa m$^{1/2}$) | SP energy $E_{SP}$ (J) | 0.2% Proof stress at 1573 K $a_{0.2}$ (MPa) |
|-------------|-------------------------------------------------------------|------------------------------------------------------|-------------------------|-----------------------------------------------|
| Nb–0.7Si–3Al | 7.8                                                         | 9.3                                                  | 1.19                    | 46.9                                          |
| Nb–5Si–9Al  | 10.35                                                       | 10.7                                                 | 0.04                    | 209.6                                         |

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Fig. 5. True stress–true strain curves of Nb$_{5}$ single-phase alloys in tensile tests at room temperature.
Fig. 6. True stress–true strain curves of Nb₃₆ single-phase alloys in tensile tests at 1573 K.

Fig. 7. Temperature dependence of 0.2% proof stress of Nb–Si–Al–Ti three-phase alloys with volume fractions of Nb₃₆ denoted in brackets.

Fig. 8. Comparison of yield strengths for Nb–Si–Al–Ti three-phase alloy, Nb–10Si in situ composite [3] and nickel-base super alloys [23,24].

Fig. 9. Plane strain fracture toughness, Kᶜ, evaluated by three-point bending tests and high temperature strength of three-phase alloys. (a) Nb–7Si–9Al, (b) Nb–5Si–9Al, (c) Nb–8Si–9Al–10Ti, (d) Nb–6Si–11Al–15Ti.
strength at all the temperatures. The compressive strength of Nb–8Si–9Al–10Ti three-phase alloy containing 62 vol% Nb₃ is compared to conventional nickel-based superalloys in Fig. 8. The temperature dependence of yield strength was evaluated by compression test for Nimowal [23] and Mar–200 [24] and by tension and bending tests for Inconel 718 [24] and Nb–10Si [3]. The strength of Nb–8Si–9Al–10Ti exceeds that of superalloys in the temperature range investigated, even though the different initial strain rate is taken into consideration. The high temperature strength of Nb–6Si–11Al–15Ti containing 15 mol% Ti was also comparable to Nimowal.

The results on fracture toughness and high temperature strength are summarized in Fig. 9. Clearly the fracture toughness of three-phase alloy exceeds 12 MPa m^{1/2} in Nb–8Si–9Al–10Ti. A slight decrease in fracture toughness by the addition of 15 mol% Ti may be caused by the micro-structural effect. Fig. 10 shows SEM micrographs on a crack propagation path in three-point bending test. The cleavage fracture surface of alloy without titanium looks smooth, while river patterns can be seen in the alloy containing titanium. Therefore, it is suggested that titanium addition enhances the mobility of dislocation in Nb₃s and then improves the fracture toughness at room temperature.

The fatigue-crack growth rates in cyclic four-point bending test under stress ratio of 0.1 are summarized in Fig. 11. The growth rates of pure Nb, Nb₃Al and (Nb₃s + Nb₃Al) composite, which are obtained by Murugesh et al. [21], are also included in the Fig. 11 for comparison. The addition of titanium improves the crack growth behavior. The growth rate of alloy containing 15 mol% Ti is comparable with that of pure niobium. High temperature strength of three-phase alloy is superior to that of nickel-based superalloy. Furthermore, the addition of titanium improves remarkably fracture toughness of three-phase alloy. Thus, it is concluded that the addition of titanium to (Nb₃s + Nb₃Al + Nb₃Si) three-phase alloy improves the fracture toughness and high temperature strength simultaneously.

3.3. Oxidation resistance

It is well known that niobium has poor oxidation resistance, which is caused basically by both high solubility limit and high diffusion coefficient of oxygen in niobium. Furthermore, diffusion coefficient of aluminum in niobium is low, though aluminum is expected to form rigid proof-oxidation film [25]. Although a large amount of titanium, silicon or aluminum addition has been found to improve the oxidation resistance of niobium alloys [15,16], it often makes sacrifices of high temperature strength and fracture tolerance at room temperature.

Fig. 12 shows weight gains in isothermal oxidation test of three-phase alloys in Nb–Si–Al system and binary alloys in
Fig. 12. Isothermal oxidation tests of Nb–Si–Al multiphase alloys at 1273 K in air.

Nb–Si and Nb–Al system. Specimens were exposed to air and the weight change was measured at 3.6, 7.2 and 14.4 ks. The weight gain of Nb–17.3Al is smaller than that of Nb–10.1Si probably because of a large difference of substitutional content in Nb∞ between Nb–17.3Al and Nb–10.1Si, as shown in Table 2. The effect of simultaneous addition of Si and Al on weight gain cannot be seen, as far as

Fig. 13. Effect of titanium on the oxidation resistance of Nb–Si–Al–Ti three-phase alloys in isothermal oxidation tests at 1273 K in air. Nb–6Si–11Al–15Ti is also exposed at 1473 K.

Nb–5Si–9Al and Nb–10.1Si are concerned. Fig. 13 shows the effect of titanium addition on the oxidation resistance of Nb–Si–Al–Ti three-phase alloys, where the isothermal oxidation tests were conducted in air at 1273 K for 360 ks. The addition of titanium is found to retard the weight gain of three-phase alloys. The weight gain of Nb–10Si–9Al–10Ti with 36 vol% Nb∞ is smaller than that of Nb–8Si–9Al–10Ti with 62 vol% Nb∞. This result strongly suggests that oxidation resistance is sensitive to volume fraction of Nb∞, since both the alloys consist of three phases with quite

Fig. 14. Isothermal oxidation tests of Nb–6Si–11Al–15Ti three-phase alloy in a mixture of Ar and O₂ (Ar: O₂ = 4:1).

Fig. 15. DTA curves of Nb–Si–Al–Ti three-phase alloys at a heating rate of 0.17 K s⁻¹.
similar compositions. Nb–6Si–11Al–15Ti is exposed to air at 1473 K to compare with the oxidation behavior at 1273 K. The weight gain of specimens exposed at 1473 K increases rapidly at an early stage of oxidation, but it is reversed in exposure for longer times. This oxidation resistance of Nb–6Si–11Al–15Ti is extremely better than that of commercial niobium alloys, but the metal loss of Nb–6Si–11Al–15Ti after exposure at 1473 K for 360 ks is about as much as 10 times of nickel-based superalloys. Fig. 14 shows the results of the isothermal oxidation tests of Nb–6Si–11Al–15Ti three-phase alloy in a mixture of argon and oxygen. Results of oxidation tests in air are also shown for comparison. The weight gain in the mixture is larger than that in air, although a similar tendency is seen. The weight gain curve in air is nearly linear at 1273 K, while it is parabolic at 1473 K. As a result, the weight gain curves at 1273 and 1473 K are reversed, as shown in Fig. 14. Fig. 15 shows the DTA curves of Nb–Si–Al–Ti three-phase alloys at a heating rate of 0.17 K s⁻¹. A strong endothermic reaction at about 1100 K can be seen in Nb–5Si–9Al and another reaction peak is observed around 1300 K. The first peak at 1100 K shifts to higher temperature with increasing titanium content. A drastic decrease in weight gain was accompanied by an increase in titanium content. The second peak around 1300 K of Nb–6Si–11Al–15Ti shifts to 1500 K, which corresponds to large weight gain at 1573 K as shown in Fig. 14. Thus, it is obvious that the oxidation resistance of Nb–Si–Al three-phase alloys is improved remarkably by the addition of titanium.

Fig. 16 shows backscattered electron micrographs of a section near the oxide scale of various alloys exposed to air. Titanium-containing alloys form a grayish reaction zone arising from an increased oxygen concentration, as shown in Fig. 16(b)–(d), while no obvious difference in contrast can be seen in titanium-free alloy in Fig. 16(a). The structure of this reaction zone and a base metal zone adjacent to the reaction zone was examined by micro X-ray diffraction. Fig. 17 shows the diffraction profiles of Nb–6Si–11Al–15Ti after isothermal oxidation at 1273 K in air for 360 ks. Diffraction peaks from both the zones correspond to Nb₃S₃, Nb₃Al and Nb₅Si₃, and there was no apparent difference in the peaks before and after the oxidation test. Fig. 18 shows the backscattered electron micrograph of Nb–6Si–11Al–15Ti and corresponding X-ray composition maps of oxygen, titanium, silicon, niobium and aluminum after isothermal oxidation test at 1273 K in air for 360 ks.
Fig. 18. Backscattered electron micrograph and corresponding X-ray maps of O, Ti, Si, Nb, Al for Nb–6Si–11Al–15Ti after isothermal oxidation test at 1273 K in air for 360 ks.

Fig. 19. Backscattered electron micrograph and corresponding X-ray maps of O, Ti, Si, Nb, Al for Nb–6Si–11Al–15Ti after isothermal oxidation test at 1473 K in air for 7.2 ks.
is found from the backscattered electron micrograph and titanium and oxygen maps that fine titanium oxide particles are produced in Nb₆₀ and the density of the oxide particles is higher in the reaction zone than in the base metal zone. This result implies that the increase in oxidation resistance by titanium addition is attributed to the oxide formation in Nb₆₀. Furthermore, the oxygen content indicated in the oxygen map appears to be higher in the reaction zone than that in the base metal zone, suggesting that the distributed intermetallics interrupt the oxygen diffusion. Fig. 19 shows the backscattered electron micrograph of Nb–6Si–11Al–15Ti and corresponding X-ray composition maps of oxygen, titanium, silicon, niobium and aluminum after isothermal oxidation test at 1473 K in air for 7.2 ks. Obviously, a high density of fine titanium oxide particles is formed in Nb₆₀. In addition, the titanium and oxygen maps show that titanium and oxygen are concentrated along phase boundaries between Nb₆₀ and intermetallics in the reaction zone, especially as the oxide scale is approached. SEM–EPMA analysis indicated that titanium content in Nb₂Al and Nb₂Si₃ decreases after the oxidation test at 1473 K. It is suggested from these results that oxygen that diffuses in Nb₆₀ reacts with titanium in the intermetallics to form titanium oxide at the interface, although a mechanism of the reaction is not known at present. These two types of preferential internal oxidation, that is, the distribution of fine titanium oxide particles in Nb₆₀ and the formation of titanium oxide films at phase boundaries, will contribute to the increase in the oxidation resistance of titanium-containing alloy at 1473 K.

Thus, the improvements of toughness and high temperature strength are harmonically attained in (Nb₆₀ + Nb₂Al + Nb₂Si₃) three-phase alloys in the Nb–Si–Al–Ti quaternary system. Oxidation resistance of (Nb₆₀ + Nb₂Al + Nb₂Si₃) three-phase alloys is also improved by the addition of titanium. However, the oxidation resistance of the alloy is inferior to nickel-based superalloys. Further studies are needed to improve oxidation resistance for practical uses at very high temperatures.

4. Conclusions

1. (Nb₆₀ + Nb₂Al + Nb₂Si₃) three-phase alloy in Nb–Si–Al ternary shows high fracture toughness and high temperature strength, compared to Nb–Si and Nb–Al binary alloys when the composition is optimized.

2. (Nb₆₀ + Nb₂Al + Nb₂Si₃) three phase alloy can contain titanium up to about 20 mol% in Nb–Si–Al–Ti binary system.

3. High temperature strength of titanium-containing (Nb₆₀ + Nb₂Al + Nb₂Si₃) three-phase alloy exhibits higher strength than nickel-based superalloys in the temperature range between room temperature and 1573 K when the composition is optimized.

4. Fracture toughness at room temperature of (Nb₆₀ + Nb₂Al + Nb₂Si₃) three-phase alloys in Nb–Si–Al–Ti quaternary system is improved by the addition of titanium. Plane-strain fracture toughness, K₁C, over 12 MPa m⁰.⁵ is obtained without sacrificing high temperature strength.

5. Oxidation resistance of (Nb₆₀ + Nb₂Al + Nb₂Si₃) three-phase alloys in Nb–Si–Al–Ti quaternary system is improved by the addition of titanium.

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