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ARTICLE

Effect of Ti and Al Interaction on Microstructures and Mechanical Properties of the Nb-Ti-Si-Al Alloys

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Abstract: Nb-Si based alloys show great promise to surpass currently advanced Ni-base superalloys due to their low densities and high melting points. Both Ti and Al are beneficial alloying elements for Nb-Si based alloys. In literatures, a small amount (≤ 3 at%) of Al can be frequently examined, while Nb aluminides are usually not formed in this case. Since Nb_3Al and Nb_2Al have good strength and creep properties, $NbAl_3$ is also a candidate hot-section material; however the study of Nb-Si alloys with these possible Nb aluminides is lacking, so we focus our efforts on whether Nb aluminide is formed or not by adding more Al in the as-cast Nb-Ti-Si alloys. The microstructures and the mechanical properties of two Nb-Ti-Si-Al alloys (A2: Nb-18Ti-14Si-9Al, A4: Nb-21Ti-14Si-9Al) with higher Al content were studied in the present work. A4 alloy was designed to examine the alloying effect of more Ti. Results show that A2 alloy consists of (Nb), Nb_5Si_3 and Nb_3Al, while the A4 alloy is composed of (Nb) and Nb_5Si_3. The room temperature fracture toughnesses of A2 alloy and A4 alloy are 11.1 and 10.9 MPa·$m^{1/2}$, respectively. Moreover, the microindention tests were conducted to characterize the micro scale mechanical properties of these Nb-Ti-Si-Al alloys.

Key words: Nb-Si based alloy; Al addition; microstructure; fracture toughness; microindention test

For jet engines to run faster, alternative airfoils materials will have to surpass currently advanced Ni-base superalloys in performance. The Nb-Si alloys consisting of Nb solid solution and their silicides, occasionally with a small amount of $NbCr_2$, show great promise due to their low densities and high melting points[1,2]. Elements such as Ti, Hf, Cr, Al, B, Y, Zr, Ga, Ge and Sn are added into the alloys to obtain balanced mechanical properties and oxidation resistances[3-9]. The addition of Ti promotes the decomposition kinetics of $Nb_3Si \rightarrow (Nb)+\alpha\text{-}Nb_5Si_3$, and improves both room temperature toughness and oxidation resistance, but it will decrease melting points and weaken creep resistances, so the additions of Ti are usually less than 25at%[5]. Among the non-transition alloying elements such as Al, Ga, Ge and Sn, Al is most attractive from the point of view of enhancing the oxidation resistance and room temperature ductility[6]. The addition of Al is usually less than 3at% in the most studied Nb-Ti-Si-Hf-Cr-Al alloy system[7-9]. In this case, Al is partitioned preferentially into (Nb) and no Nb aluminide phase is found. In K. Zelenitsas's work[10], the microstructures of heat-treated (1500 K/100 h) Nb-24Ti-18Si-5Al alloy were still reported as (Nb) and Nb_5Si_3 two phases. S. Kashyap published a detailed study of Nb-Si alloy with only Al addition, and the Nb-12.7Si-9Al alloy also yielded (Nb)+Nb_5Si_3 eutectic structure[6]. Since Nb-rich aluminides, Nb_3Al and Nb_2Al have good strength and creep properties, $NbAl_3$ is also a candidate hot-section material[11]. However there is a lack of the study of Nb-Si alloys with Nb aluminides. In the present work, we focused our efforts primarily on whether Nb aluminide is formed or not by adding more Al in the as-cast Nb-Ti-Si alloys. The Nb-18Ti-14Si-9Al (A2) alloy and the Nb-21Ti-14Si-9Al (A4) alloy were designed by changing the content of Ti. The interaction effect of Al and Ti on the constitutional phases of two Nb-Si alloys was studied firstly, and then the

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mechanical properties including fracture toughness and microhardness were systematically investigated.

1 Experimental Procedures

Two alloys of Nb-18Ti-14Si-9Al(A2) and Nb-21Ti-14Si-9Al (A4) (all in at%) were selected in the present study. All of the starting materials used were high purity elements: 99.95% Nb slugs, 99.995% Ti slugs, 99.9999% Si lumps and 99.6% Al slugs. Button ingots with each weight of about 190 g were prepared by non-consumable tungsten electrode arc melting in a water-cooled copper crucible in an ultrahigh purity argon atmosphere (99.998% Ar). Each alloy ingot was melted and flipped five times to promote complete mixing and melting.

Metallographic specimens were prepared from each ingot using standard techniques and examined in a HITACHI S-4800 scanning electron microscope. X-ray diffraction (XRD) was performed on a Panalytical X0 Pert PRO. The phase search and match were conducted based on the JCPDS (Joint Committee on Powder Diffraction Standard) files. The fracture toughness of the alloy was measured using single-edge notched specimen loaded in 3-point bending at room temperature. The bend tests were performed in Instron 3382 mechanical testing machine at a crosshead speed of 0.2 mm/min. The fracture surfaces were examined and photographed by a scanning electron microscope (SEM) in second electron (SE) imaging mode. Micro-indentation mechanical properties were measured using a Shimadzu micro-compression-tester with type W501 (MCT) equipped with a Berkovich diamond indenter. During the tests, specimens for indentation investigation were tested at the load of 50×10^{-3} N, and the loading speed of 9.6841×10^{-3} N/s for the constitutional phase. The indentation load-displacement data obtained during one cycle of loading and unloading were recorded simultaneously. The hardness corresponding to the measuring point was then analyzed from the load-displacement curve.

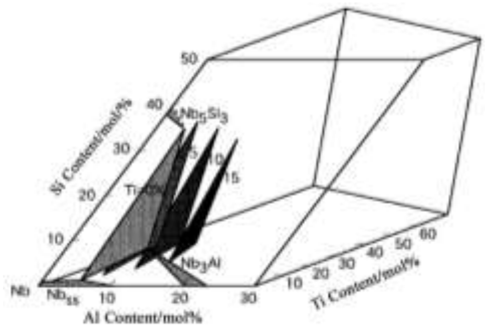

Fig.1 Three-phase region of (Nb)+Nb_3Al+Nb_5Si_3 in Nb-Ti-Si-Al phase diagram at 1873 K[12]

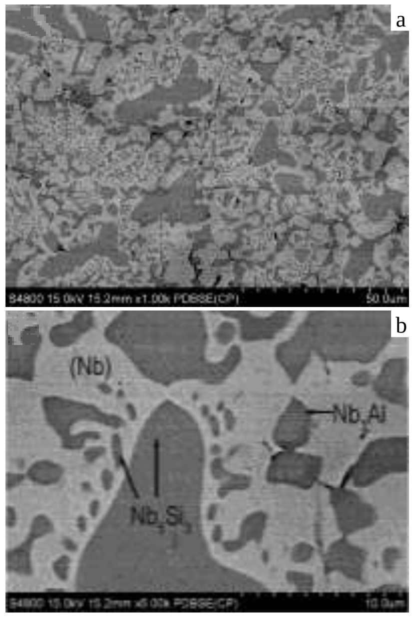

Fig.2 Low magnification (a) and high magnification (b) SEM-BSE images of A2 alloy

2 Results and Discussion

2.1 Microstructures of the Nb-Ti-Si-Al alloys

Fig.1 shows the 1873 K isothermal tetrahedron of the Nb-Ti-Si-Al quaternary system conducted by Yonosuke Murayama[12]. There is a preliminary (Nb)+Nb_3Al+Nb_5Si_3 phase region proposed in the Nb-rich corner, and this three-phase region becomes narrow with increasing of Ti content. When the composition is optimized, the (Nb)+Nb_3Al+Nb_5Si_3 alloys could exhibit higher strength than nickel-based superalloys, and have more balanced room temperature toughness and oxidation resistance than Nb-Si or Nb-Al binary alloys[12,13]. This suggests that the (Nb)+Nb_3Al+Nb_5Si_3 heterogeneous phase equilibria could provide new opportunities for Nb-Si based alloy design.

Fig.2a and 2b show the SEM-BSE images of A2 (Nb-18Ti-14Si-9Al) alloy. Fig.3 shows the XRD patterns of two alloys, and the constituent phases in each sample were identified based on the JCPDS (Joint Committee on Powder Diffraction Standard) files. Table 1 lists the phases and the EDS measured phase constituents of these alloys. Based on the XRD, SEM and EDS results, the microstructure of A2 alloy consists of (Nb), Nb_5Si_3 and Nb_3Al. Bright matrix with the composition of Nb-18.07Ti-9.97Al-2.69Si is (Nb). In bcc-(Nb) phase, both Ti and Al substitute Nb, while Si occupies interstitial sites. The constituent of large scale gray phase is Nb-10.01Ti-5.67Al-30.17Si, the ratio of Nb+Ti content to Al+Si content is close to 5:3, and it is identified as Nb_5Si_3 according to XRD pattern. By the similar way, very small gray phase is also determined as Nb_5Si_3. As listed in Table 1, some medium scale gray phase is detected with the constituent range of Nb-(17.26-23.66)Ti-(8.62-10.50)Al-(5.11-12.74)Si, which is determined as Nb_3Al by the aid of XRD identification.

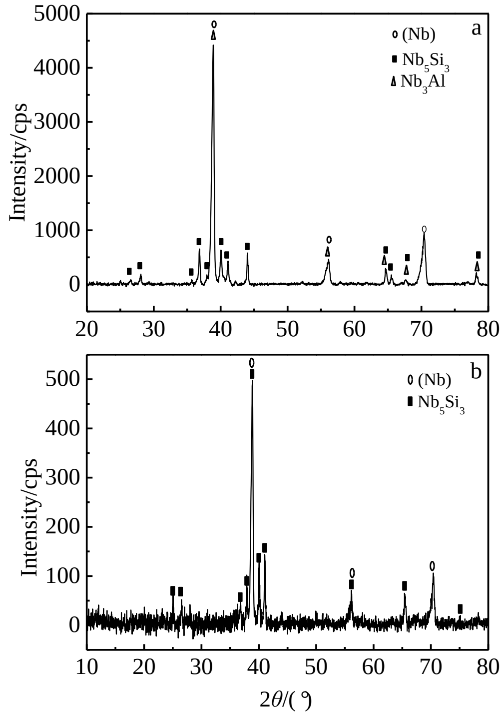

Fig.3 XRD patterns of the A2 alloy (a) and the A4 alloy (b)

Table 1 EDS measured phase constituents in alloys A2 and A4 in Fig.3

No.	Phases	Phase constituent
A2	(Nb)	Nb-18.07Ti-9.97Al-2.69Si
	Nb_5Si_3	Nb-10.01Ti-5.67Al-30.17Si
	Nb_3Al	Nb-(17.26-23.66)Ti-(8.62-10.50)Al-(5.11-12.74)Si
A4	(Nb)	Nb-27.22 Ti-9.83Al-1.98Si
	Nb_5Si_3	Nb-15.28Ti-5.49Al-30.73Si

In the Nb-Al binary system, Nb_3Al is formed by the liquid+(Nb)→Nb_3Al peritectic reaction at 2324 K, and the content of Al in Nb_3Al is from 18at% to 25 at%[14]. In the Nb-Ti-Al ternary system, Nb_3Al appears in the liquidus projection, and it has a large homogenous range in the isothermal sections from 1923 to 873 K. At 1923 K, Nb_3Al is of large homogeneity range of Nb-(0-17.8)Ti-(20.0-23.5)Al, which has been thermodynamically modeled as $(Nb, Ti, Al)_{0.75}(Al, Nb, Ti)_{0.25}$ to describe the solubility and site occupancy[14]. In this quaternary alloy, the solubility of Al decreases in the Nb_3Al phase, while a certain amount of Si is detected. The deviations of Nb_3Al from stoichiometry enables its alloying to improve the properties. This founding also could provide valuable information for further phase equilibria study of the Nb-Ti-Si-Al quaternary system. Moreover, since the molecular weight of alloying Nb_5Si_3 and Nb_3Al are close to each other, their contrasts are quite similar in the microstructure. It is actually difficult to differentiate them only by contrast and morphology.

Fig.4 shows the SEM-BSE image of A4 (Nb-21Ti-14Si-9Al) alloy. The microstructure consists of non-faceted bright matrix,

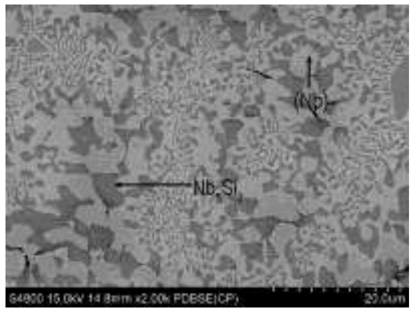

Fig.4 SEM-BSE image of A4 alloy

faceted gray blocks, and a fine lamellar eutectic structure composed of gray phase and bright phase. Based on EDS measurements, the constituents of faceted gray blocks and bright matrix are Nb-15.28Ti-5.49Al-30.73Si and Nb-27.22Ti-9.83Al-1.98Si, respectively. The bright matrix is (Nb). By the similar way with that of the alloy A2, the gray phase can be attributed to Nb_5Si_3 with considering XRD analysis. Moreover, Nb_5Si_3 simultaneously solidified with the (Nb) phase forms the fine eutectic lamellar eutectic at the last solidification stage. Comparing A2 and A4 alloys, A4 is designed with 3 at% more Ti, and Nb_3Al does not appear in A4 alloy. This demonstrates that the alloying elements will sensitively affect the constitutional phases in the Nb-Si alloys and constitutional phases of as-cast alloy; directionally solidified alloys and annealed alloys could be well predicted based reliable thermodynamic descriptions. Keeping this in mind, the phase equilibria information of the Nb-Ti-Si-Al system is required to tune the alloy compositions and microstructures.

2.2 Fracture toughness of Nb-Ti-Si-Al alloys

Fig.5a and 5b show the fracture surfaces of A2 alloy and A4 alloy, respectively. For A2 alloy, flat cleavage surface is exposed for intermetallic phases, either Nb_5Si_3 or Nb_3Al, as indicated in the oval regions. While ductile (Nb) phase exhibits ductile failure with the feature of pull-out on the fracture surface, as indicated in the quadrangle region. Fracture toughness of 11.1 MPa $m^{1/2}$ is obtained for A2 alloy, as listed in Table 2. The fracture toughness of 7.85 MPa $m^{1/2}$ has been reported for the as-cast Nb-18Ti-14Si[15]. The addition of 9 at%Al significantly improves fracture toughness to 11.1 MPa $m^{1/2}$, which is partly cooperated by the substitution of Si by metallic Al, as listed for the composition of Nb_5Si_3 in Table 1. This value is close to those tested from the as-cast Nb-18Ti-14Si-4.5B alloy and the directionally solidified Nb-10Mo-17Si-0.1Ga alloy[15,16]. Obviously these values are not satisfactory for aerospace applications. The fracture behavior of these Nb-Si based alloys would be dominatingly reflected by the fatigue behavior of intermetallic compound. In intermetallic compounds, different elements are substituted into different sites in the ordered structure, and they have few slip systems activated under deformation process. But hard intermetallics such as Nb_5Si_3 and Nb_3Al have low creep rates,

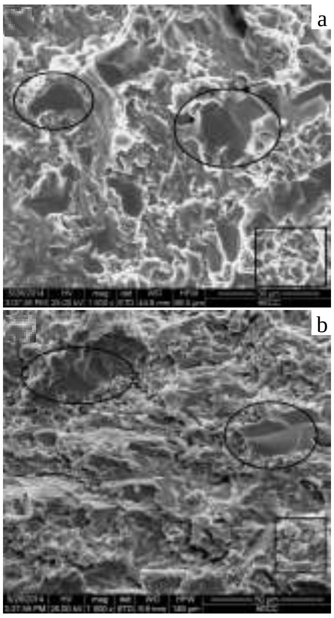

Fig.5 Fracture surfaces of A2 alloy (a) and A4 alloy (b)

Table 2 Comparison of the fracture toughness of alloys (MPa m$^{1/2}$)

Alloy	Test 1	Test 2	Test 3	Average
A2	11.2	11.3	10.8	11.1
A4	10.5	11.6	10.5	10.9

which can retain high-temperature strengths[12], so the various intermetallics combined with ductile metallic solution phase can supply balanced room temperature and high temperature mechanical properties for turbine blade applications. In addition, it is worth exploring that heat treatment and directionally solidification are promising to improve fracture toughness to an acceptable value[17-19].

For A4 alloy, intermetallics Nb_5Si_3 fractures in a brittle manner completely, and flat cleavage surface is exposed, as indicated in the oval regions. While ductile (Nb) matrix shows plastic deformation, as indicated in the quadrangle. The fracture toughness of A4 alloy is 10.9 MPa m$^{1/2}$, which is slightly lower than That of A2 alloy. This is due to Nb_3Al formed in A2 alloy, and Nb_3Al has primary metallic bonding while Nb_5Si_3 presents covalent bonding, so silicides are more brittle than aluminide in common. It may account for that even more 3 at% Ti in A4 alloy does not improve the fracture toughness.

2.3 Hardness

Under the load of 5×10^{-2} N, the micro-indentation experiments were conducted at the loading speed of 9.6841×10^{-3} N/s for A2 alloy and A4 alloy. Fig.6 shows the curves of the load versus the penetration depth for (Nb) and intermetallic phase (Nb_5Si_3 or Nb_3Al). Again, Nb_5Si_3 or Nb_3Al is not differentiated in A2 due to their similar morphology. In general, indenter displacement of ductile (Nb) is larger than that of intermetallic phase. Moreover, these curves are sharp in the initial stage and gentle in the subsequent stage in all phases. The micro-scale materials to macro-scale materials possess non-linear mechanical properties; such scale effect could impact the curves in the initial stage. When indenter displacement is small enough, the scale effect is very sensitive, but when indenter displacement is large, the scale effect is not sensitive, and traditional elastic-plastic theory can explain the deformation behavior[20].

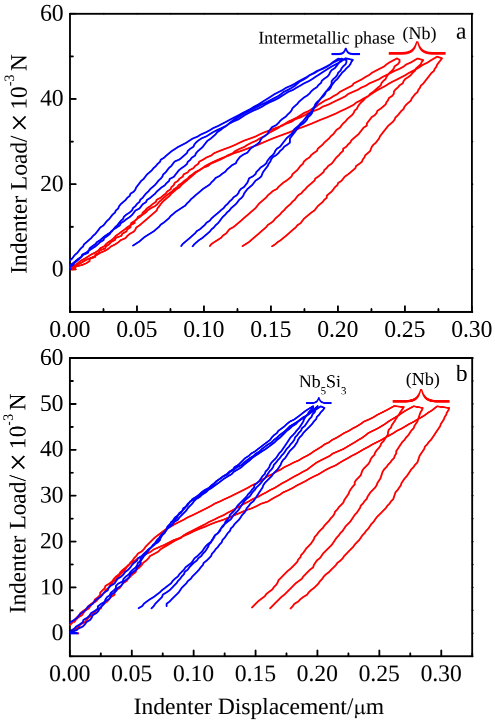

Fig.6 Indenter load-indenter displacement curves of the constitutional phases in A2 alloy (a) and A4 alloy (b)

Using the approach described in Ref. [21], the harnesses of the individual phases were calculated simultaneously with the curves in Fig.6. For each phase, at least three data were used to obtain the average value, while the scattered data were not considered. The mean hardness for (Nb) and intermetallic phase is 30.33 and 48.93 GPa, respectively in A2 alloy. The mean hardness for (Nb) and Nb_5Si_3 is 26.09 and 50.41 GPa, respectively in A4 alloy. The difference value of the same phase should be caused by the alloying effects and multi-element interaction. In general, fracture toughness testing combined with the indention experiments give a globe view in macro and micro scale properties of the Nb-Ti-Si-Al alloys.

3 Conclusions

1) A2 alloy consists of (Nb), Nb_5Si_3 and Nb_3Al. Nb_3Al is detected with a large homogeneity range of Nb-(17.26-23.66)Ti-(8.62-10.50)Al-(5.11-12.74)Si. With the content of more

3at% Ti, the A4 alloy is composed of (Nb) and Nb_5Si_3. The constitutional phases are sensitively affected by the interaction of alloying Ti and Al, so the accurate phase equilibria information is required for compositional design in the future.

2) The fracture toughness of Nb-18Ti-14Si[15], Nb-18Ti-14Si-9Al (A2) and Nb-21Ti-14Si-9Al (A4) is 7.85, 11.1 and 10.9 MPa $m^{1/2}$, respectively. The addition of 9at%Al significantly improves the fracture toughness of Nb-Si alloys. This improvement of fracture toughness is cooperated by the substitution of Si by metallic Al in Nb_5Si_3 and by the formation of Nb_3Al with metallic Nb-Al bonding.

3) According to the micro-indentation experiments of the constitutional phases of A2 alloy and A4 alloy, the indenter displacement of ductile (Nb) is larger than that of intermetallic phase, and the sensitive scale effect is found at the initial stage of all indenter load-Indenter displacement curves.

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Ti 和 Al 的交互作用对 Nb-Ti-Si-Al 合金微观组织和力学性能的影响

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摘　要：研究高 Al 含量对合金中 Nb-Al 金属间化合物形成的影响及 2 个高 Al 含量的 Nb-Ti-Si-Al 合金(A2: Nb-18Ti-14Si-9Al、A4: Nb-21Ti-14Si-9Al)的微观组织和力学性能，其中设计 A4 合金是为了分析 Ti 含量变化的影响。结果表明：A2 合金由(Nb)、Nb_5Si_3 和 Nb_3Al 3 相组成，而 A4 合金由(Nb)和 Nb_5Si_3 2 相组成。A2 和 A4 合金的室温断裂韧性分别为 11.1 和 10.9 MPa $m^{1/2}$。同时对 2 个合金进行微压痕测试，以表征合金在微观尺度的力学性能。

关键词：Nb-Si 基合金；Al 合金化；微观组织；断裂韧性；微压痕测试

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