Effect of Alloy Chemistry on the High Temperature Strengths and Room Temperature Fracture Toughness of Advanced Nb-Based Alloys*¹

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High temperature strength and room temperature fracture toughness of Nb-based alloy system were investigated to explore a candidate material for gas turbine use at 1773 K as a function of chemical compositions. 0.2% proof stress at 1773 K and the fracture toughness were studied for the solid-solution hardening Nb-Mo-W alloys and the Nb₅Si₃-reinforcing Nb-Si-Mo-W-Hf alloys, and were found that the 0.2% proof stress linearly increases with increasing (Mo+1.5W) content and also increases with volume fraction of Nb₅Si₃, while the fracture toughness decreases with (Mo+1.5W) content in solid-solution. The critical content for a ductile-to-brittle transition to occur is at (Mo+1.5W) content of 33.5 mol% together with molybdenum content of 15 mol%. Nb-16Si-5Mo-15W-5Hf alloy with a microstructure consisting of 50 vol% solid-solution and 50 vol% Nb₅Si₃, obtained by optimizing the alloy chemistry without a significant loss of high temperature capability and ductility, and by modifying with 5Hf-5C addition, was found to demonstrate an unprecedentedly excellent creep resistance and also a creep rupture strength exceeding the target strength of 150 MPa and above at 1773 K for 100 h.

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1. Introduction

Future aerospace as well as gas turbine applications will require advanced materials with ever-increasing temperature-endurance and load-bearing capabilities for improved turbine performance, such as higher turbine inlet temperature (TIT), and higher thermal efficiency to reduce the emission of carbon dioxide. Currently employed Ni-based superalloys have reached their temperature limitation with operating temperature greater than 90% of their melting temperatures.¹⁾ Therefore, the developments of further advanced cooling and/or thermal barrier coating technologies are required, which cause some extent of thermal efficiency loss. So Ni-based superalloy will not be able to meet the higher temperature requirements of future advanced gas turbine systems.

Nb-based alloys have the potential for meeting the above requirements because of relatively low density, 1000 K higher melting temperature than those of Ni-based superalloys, and attractive high temperature strength properties combined with moderate room temperature ductilities. Niobium-alloy systems have been extensively explored for a number of applications such as space nuclear power systems, aerospace structures and aircraft gas turbine uses.²⁾ For developing further advanced turbine engine systems with much higher temperature capability, some Nb-based alloys composed of Nb-Ti-Al modified with chromium or hafnium and with silicon, chromium, aluminium, and hafnium have been studied, and are found to have attractive properties in toughness and strength.^{1,3)} However, the target temperatures of these alloys are only 1373–1473 K.

The purpose of this study is to investigate the strength and

toughness of niobium-based alloy systems as a function of chemical compositions, and to propose candidate alloys with the unprecedentedly high endurance temperature, 1773 K. This study is to obtain the following aimed high temperature strengths and room temperature fracture toughness including discussion on the strengthening and toughening mechanisms.

- strength at 1773 K: 450 MPa or above
- specific strength (density-normalized 0.2% proof stress) at 1773 K: 50 MPa/Mg/m³ or above, corresponding to 0.2% proof stress of 450 MPa for the density of being 9.0 Mg/m³.
- creep rupture strength at 1773 K for 100 h: 150 MPa or above
- fracture toughness at room temperature: 10 MPa·m^{1/2} (for reference)

As for oxidation-resistance, a newly developed concept for oxidation-resistant coating technology, which is applicable to Nb-based alloys at the temperature above 1473 K was explored and reported elsewhere,⁴⁾ is not included in this paper.

2. Experimental Procedure

2.1 Materials preparation

The materials studied in this investigation were ternary Nb-Mo-W solid solution (Nbss) alloys and quaternary Nb-Si-Mo-W Nbss/Nb₅Si₃ silicide alloys. Hafnium⁵⁾ and carbon⁶⁾ were selected as strengthening and toughening elements. On adding hafnium, the same amount (mol percent) of carbon was also added as NbC. The purities of starting raw materials were (in mass%) 99.9% Nb, 99.9% Mo, 99.9% W, 99.99% Si, 98% Hf and 99% NbC.

The Nb-based alloys were processed by arc-melting under an argon gas atmosphere in a water-cooled copper-hearth using a non-consumable tungsten electrode. The arc-melted ingots were reheated at least five times to ensure chemical

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homogeneity. The specimens were heat-treated at 1773 K for 48 h followed by furnace cooling to room temperature.

2.2 Microstructure observations

Scanning electron microscopic (SEM) studies were performed on the polished and the etched cross section by secondary or backscattered electron image (BEI) using a Hitachi S-800 scanning electron microscope operating at 15 kV. After fracture testing, the fracture surface was characterized using SEM fractography. Thin foils for transmission electron microscopic (TEM) studies were prepared by grinding to 60 μm thick with emery paper, followed by dimpling to 40 μm thick, and then were thinned by ion-milling to electron transparency. TEM observations were performed using a Hitachi H-800 electron microscope at an accelerating voltage of 200 kV. The constituent phases and their compositions were determined by using an energy-dispersive spectroscopy (EDS) (Kvex 8000 in the SEM and a Horiba EMAX 3000 in the TEM).

2.3 Mechanical testing

The dimensions of tensile and compressive test specimens were 10 mm gage length with 3 mm $\times$ 3 mm cross section, and 6 mm height with 3 mm $\times$ 3 mm cross section, respectively. These specimens were sectioned by electric discharge machining (EDM) and mechanically polished using SiC paper and Al_2O_3 particles with water. Tensile and compressive tests were carried out using a MTS 808 and an Instron 8500 testing machine in an argon atmosphere at temperatures up to 1773 K and a strain rate of $3 \times 10^{-4} \text{ s}^{-1}$. The fracture toughness, K_Q , was determined by three-point bend testing utilizing single-edge notch specimen at a crosshead speed of 0.5 mm/min following ASTM-E399-1987 standard except for fatigue-precracking. The bend bar dimensions for K_Q tests were 30 mm long $\times$ 3 mm wide $\times$ 6 mm thick, and the EDM notch dimensions were 3 mm deep $\times$ 0.05 mm root radius. K_Q was obtained by the following equation:

$$K_Q = (P_Q S / BW^{3/2}) \times f(a/W)$$

where P_Q is load, S is applied load span, B is thickness, W is height, a is notch depth, and a/W is 0.45 $\sim$ 0.55.

High temperature creep tests were carried out on five ultra-high temperature creep testing machines, Toshin HCTT-3000, at temperatures between 1473 K and 1773 K under nominal stresses from 10.5 to 200 MPa in an argon atmosphere. The purity of argon gas used was 99.999%. The tungsten heating elements and SiC hot jigs to transmit the applied stress to test piece were adopted. The dimensions of tensile creep specimens were 10 mm gage length with 3 mm $\times$ 3 mm cross section and four integral flags (upper and lower flags at the both side of the test piece) were mechanically processed for continuous monitoring of creep displacement between upper and lower flags. The compressive creep specimen was the same in size as that of the previously mentioned compression test.

The creep strain measurement at elevated temperatures up to 1773 K was one of the most challenging problems, because the usual contact-type extensometer can not be used, and any alternative device was not commercially available. A new optical-type methodology for accurate creep strain measure-

Fig. 1 Schematic diagram of optical-type Thermal-Image-Processing-Displacement-Analyzer extensometry system.

ment up to 2273 K has been developed in our laboratory (JUTEMI) which includes CCD (charge coupled device) cameras with 481 $\times$ 512 pixels resolution and also includes a controlling function to compensate for strain fluctuation with the change in room temperature. This optical extensometry system, in which strain was continuously measured from change in the distance between the gravity centers of upper and lower flags, was found to work well for the present investigation. Figure 1 shows the schematic diagram of the optical extensometry system.

3. Results and Discussion

3.1 Nb-Mo-W solid-solution alloys

The high temperature strength properties especially at target temperature of 1773 K are examined for Nb-based Nb-Mo-W alloys and Nb-Mo-W-5 mol% Hf alloys (henceforth denoted as Nb-Mo-W-5Hf alloys). Figure 2 shows 0.2% proof stresses, $\sigma_{0.2}$, in compression tests against (Mo+1.5W) content in mol%. A linear relationship between the $\sigma_{0.2}$ and (Mo+1.5W) content in the range of 5 $\sim$ 15% Mo and 5 $\sim$ 30% W could be found, which can be expressed as the following equation:

Fig. 2 Plots of compressive 0.2% proof stress, $\sigma_{0.2}$, for Nb-Mo-W alloys and Nb-Mo-W-5Hf alloys at 1773 K as a function of (Mo+1.5W) content.

$$\sigma_{0.2}/\text{MPa} = 8.3(\text{Mo} + 1.5\text{W}) + 16.7, \quad R^2 = 0.997 \quad (1)$$

Figure 2 also indicates that 0.2% proof stresses of Nb-Mo-W alloys containing 25 ~ 35% Mo and 5 ~ 15% W, together with (Mo+1.5W) content over 32.5% are lower comparing to those of alloys with Mo content of 15% and less at the same (Mo+1.5W) content. Moreover, SEM observations on the Nb-25~35Mo-5~15W alloys with (Mo+1.5W) content over 32.5% after compression test at 1773 K exhibited remarkable intergranular fracture behaviors, while Nb-5~15Mo-5~30W alloy group and Nb-25Mo-5W alloy with (Mo+1.5W) content of 32.5% exhibited predominant transgranular fracture mode. A previous study on Nb-0~35Mo-5W alloys with a constant tungsten content⁶⁾ exhibits that 0.2% proof stress increases with increasing molybdenum content up to 15% both in tension and in compression. With further molybdenum addition, the 0.2% proof stress in compression still reveals an increasing tendency, whereas molybdenum addition more than 15% causes the decrease in the strength in tension, and also the change in the fracture behavior from transgranular mode to intergranular mode accompanying pre-yield fracture is observed. In the present study, the oxygen contents of the Nb-Mo-W alloys in the range of 10 ~ 35% Mo and 5 ~ 15% W were measured as 71 ~ 128 mass ppm and those for all Nb-0~35Mo-5W alloys were reported to be about 200 mass ppm. Therefore the lowering of increasing degree of 0.2% proof stress in compression (Fig. 2), and the notable effect of molybdenum addition, from positive to negative contributions to the strength in tension, on Nb-0~35Mo-5W alloys at 1773 K⁶⁾ can not be explained by oxygen relating fracture characteristics. Instead, the 0.2% proof stress for ternary Nb-Mo-W alloys could be interpreted in term of a competitive relationship between solid-solution hardening and the cohesive strength weakening at grain boundary due to molybdenum and tungsten additions. So some explanation is necessary for the results that the decrease in increasing rate of 0.2% proof stress in compression (Fig. 2) and a significant loss of the strength in tension⁶⁾ occur at 1773 K over a certain critical amount of alloy additions, accompanying the change in dominant fracture mode from transgranular type to intergranular type. One possible interpretation for the grain boundary fracture to be promoted would be that the strength of grain boundary decreases with increasing alloy content, whereas the strength of grain interior increases due to solid-solution hardening, resulting in the much lower strength of grain boundary than that of grain interior. The formation of molybdenum oxide at grain boundary especially with low melting temperature,⁷⁾ and the strong anisotropy of grain boundary bonding are enumerated as factors lowering the grain boundary strength. Accordingly, more detailed studies are necessary to understand sufficiently the effect of metallurgical factors such as alloy additions, test temperature and manufacturing procedures on the strength characteristics at high temperature on the basis of grain boundary structure and chemistry.

The addition of 5Hf-5C are effective to raise the 0.2% proof stress for Nb-5Mo-5W and -15W alloys at 1773 K as shown in Fig. 3. The increments in 0.2% proof stress due to 5Hf-5C addition are 44 MPa for Nb-5Mo-5W alloy and 73 MPa for Nb-5Mo-15W alloy, approaching a saturated

Fig. 3 Effect of hafnium addition on the 0.2% proof stress for Nb-5Mo-5W and -15W alloys at 1773 K. (On adding hafnium, the same mol% of carbon was also added).

Fig. 4 The TEM micrograph (a) and diffraction pattern of Nb₂C carbide with [2 5 16] zone axis (b) at the center of (a) through 0.5 μm selected area aperture for Nb-5Mo-15W-5Hf alloy annealed at 2073 K for 48 h followed by furnace cooling to room temperature.

value by 5Hf addition. TEM and EDS observations on Nb-5Mo-15W-5Hf alloy, as shown in Fig. 4, revealed that Nb₂C carbide appears in the granular type (~0.65 μm) and coarse rod-like forms. However, neither detectable hafnium substitution for some of niobium in Nb₂C nor visible formation of hafnium carbide, HfC, were found. To evaluate which is more dominant as the strengthening mechanism between solid-solution hardening and Nb₂C dispersion strengthening, Orowan stress, σ_{or}, was estimated according to eq. 2;

$$\sigma_{or} = 0.8 \text{ MGb} / \lambda \quad (2)$$

where M is the Taylor factor (=3), G is the shear modulus (G at 1773 K is 108.4 GPa), b is Burgers vector (=0.28 nm) and

Fig. 5 Fracture toughness, K_Q , plotted against (Mo+1.5W) content at room temperature for the solid-solution alloys.

λ is the average spacing of the Nb_2C obstacles ($=581 \text{ nm}$). The obtained Orowan stress, σ_{or} , for Nb-5Mo-10W-5Hf alloy is 45 MPa, which is at most 16% of the 0.2% proof stress. This result indicates that the solid-solution hardening, which is advantageous from the viewpoint of long-term stability, substantially supports the high temperature strength of the Nb-based alloys at 1773 K.

Figure 5 shows the relationship between room temperature fracture toughness, K_Q , and (Mo+1.5W) content. The K_Q tend to decrease with increasing (Mo+1.5W) content. It is notable from Figs. 3 and 5 that by adding 5Hf-5C to Nb-5Mo-15W alloy the K_Q value increased from 7.3 to 10.1 $\text{MPa}\cdot\text{m}^{1/2}$, while the 0.2% proof stress increased from 239 to 308 MPa. Such the enhancement both in strength and ductility by 5Hf-5C addition is considered to be due to the restraint of intergranular fracture.^{6,8)}

From the above results, there were two types of ductile-to-brittle transition behavior in Nb-Mo-W alloys at 1773 K. One is observed in compression when (Mo+1.5W) content exceeds 32.5% (Fig. 2), and the other reported in tension when molybdenum content is above 15%.⁶⁾ Alloy additions over these critical contents cause a change in fracture behavior from transgranular type to intergranular type accompanying the decrease in increasing degree of 0.2% proof stress observed in compression on Nb-25~35Mo-5~15W alloys with (Mo+1.5W) content over 32.5% (Fig. 2), and a significant loss of the strength in tension with a pre-yield fracture for Nb-0~35Mo-5W alloys with above 15% Mo.⁶⁾ In Fig. 6, the pertinent compositional range is presented, where the two ductile-to-brittle transition boundaries are shown in the Nb-Mo-W ternary alloy diagram together with iso-strength lines of 100, 200 and 300 MPa levels at 1773 K. The transition boundary for Nb-25~35Mo-5~15W alloys is considered to exist between the two alloys with the (Mo+1.5W) contents of 32.5% and 40.0%. Because the value of 32.5% represents the maximum (Mo+1.5W) content where the predominant transgranular fracture mode was observed and the value 40.0% the minimum (Mo+1.5W) content where the predominant intergranular fracture mode was observed. So the compositional boundary here was assumed to be 33.5% which corresponds to the iso-strength

Fig. 6 Ductile-to-brittle transition boundaries (a-a') for compression and (c-c') for tension⁶⁾ of the Nb-Mo-W solid-solution alloys together with 0.2% proof strength levels of 100, 200 and 300 MPa at 1773 K.

$$\begin{aligned} & \text{a-a'} : \% \text{ Mo} + 1.5 \times \% \text{ W} = 33.5\% \\ & \text{c-c'} : 15\% \text{ Mo with (Nb+W) of 85\%} \end{aligned}$$

line of 300 MPa at 1773 K and is very close to the above alloy content. A good combination of strength and ductility is present within the compositional region surrounded by a-c'-c'-Nb corner.

3.2 Nb-Mo-W solid-solution/ Nb_5Si_3 silicide composite alloys

The results in the previous section show that the Nb-Mo-W solid-solution alloys do not meet the strength requirement ($\geq 450 \text{ MPa}$ at 1773 K). Therefore, we have tried to explore alloys with higher strength than Nb-Mo-W alloys by utilizing intermetallic compound Nb-silicide,⁹⁾ $\alpha \text{ Nb}_5\text{Si}_3$, which was reported to exhibit the compressive fracture strength of $\sim 670 \text{ MPa}$ at 1773 K, but without appreciable ductility at 1473–1673 K¹⁰⁾ before general yielding in tension.

Figure 7 shows the mechanical properties for Nb-0~20Si-xMo-xW quaternary alloys in compression as a function of

Fig. 7 Mechanical properties in compression for Nb-0~20Si-xMo-xW quaternary alloys as a function of silicon content, where the composition of Nb solid-solution are designed to be the same as Nb-15Mo-15W.

volume fraction of silicide. The volume fraction of silicide, V_f , was reported to linearly increase with silicon content as $V_f = 3.085 \times (\%Si)$.⁹⁾ In Fig. 7, chemical compositions of Nb solid-solution were designed to keep equal to Nb-15Mo-15W.⁹⁾ The results of Fig. 7 exhibit that 0.2% proof stress both at room temperature and 1773 K increased with increasing silicide volume fraction, whereas rupture strain rapidly decreased with silicide content up to 9 vol%, and then gradually decreased, to lesser extent, with further increase in silicide volume fraction. The target strength of 450 MPa at 1773 K is obtained with 48.6 vol% silicide *i.e.* 15.8% silicon addition, and the microstructures reveal two constituent phases consisting of 50 vol% α Nb₅Si₃ (hereafter denoted as Nb₅Si₃) and 50 vol% Nb solid-solution. As for Nb-Si binary alloy, previous work showed that the microstructures exhibit composite-like configurations¹¹⁾ of (Nb phase + Nb₅Si₃) two phases which are thermochemically and morphologically stable, at least, up to 1773 K for 100 h.¹²⁾ Furthermore, considering the eutectic reaction to occur at 18.7% Si in Nb-Si alloy, silicon addition should be limited below 18.7% because the primary and eutectic Nb phases are expected to act as a so-called plasticizer in order to hold ductility.

Figure 8 shows a typical microstructure of Nb-16Si-10Mo-15W alloy annealed at 1973 K for 48 h. The micrograph indicates that the overall equilibrium microstructure could be viewed as large dendritically formed primary and small eutectically formed Nb solid-solutions particles distributed in the continuous Nb₅Si₃ silicide matrix. The chemical compositions of constituent phases are presented in Table 1.⁹⁾ The XRD examinations revealed that the lattice parameters of Nb₅Si₃ were almost constant with the change in molybdenum and tungsten content, implying very little alloying potential of these elements into Nb₅Si₃. Whereas, molybdenum and

tungsten are enriched in the Nb solid-solutions, and the ratios of these alloying contents in the Nb solid-solution to those in nominal alloy composition are 1.4~1.5 for molybdenum and 1.5~1.7 for tungsten. The silicon content is only 0.4~0.6% in the solid-solution, while it is 37.4~38.5% in Nb₅Si₃.

The relationship between 0.2% proof stress at 1773 K and (Mo+1.5W) contents for Nb-16Si-Mo-W alloys is shown in Fig. 9, where a linear relationship is clearly observed. The increasing rate of 0.2% proof stress with respect to alloy content for Nb-16Si-Mo-W alloys was almost 2.5 times higher than that of Nb-Mo-W alloys probably due to the segregation of molybdenum and tungsten in Nb solid-solution phase. Figure 9 also shows that the target strength of 450 MPa at 1773 K is achieved by the addition of (Mo+1.5W) content above 16%.

If the rule of mixtures,¹³⁾ which is generally known as to the strength of fiber reinforced ceramic matrix composite material, is valid in the present Nbss/Nb₅Si₃ composite alloy, the strength, σ_{comp} , may be expressed as

$$\sigma_{comp} = V_f \sigma_{silicide} + (1 - V_f) \sigma_{ss} \quad (3)$$

where V_f is the volume fraction of Nb₅Si₃, $\sigma_{silicide}$ is the strength of Nb₅Si₃ at 1773 K, which has been reported to be ~670 MPa¹⁴⁾ as the compressive fracture strength, and σ_{ss} is the strength of Nb solid-solution phase at 1773 K which is obtained as the 0.2% proof stress corresponding to 1.5 times nominal (Mo+1.5W) content in Nb-Mo-W solid-solution

Fig. 8 SEM micrograph of Nb-16Si-10Mo-15W alloy annealed at 1973 K for 48 h. Large dendritic primary Nb solid-solutions (A) and small eutectic Nb solid-solutions (B) embedded in dark eutectic α Nb₅Si₃ matrix (C).

Fig. 9 Plots of compressive 0.2% proof stress, $\sigma_{0.2}$, as a function of (Mo+1.5W) content at 1773 K for Nb-16Si-Mo-W alloys together with those of Nb-Mo-W alloys for reference. Schematic representation of strengthening mechanism is also shown, where σ_{ss} is the assumed 0.2% proof stress for Nb solid-solution, Nbss, as a constituent phase and σ_{comp} is that for Nbss/Nb₅Si₃ composite alloy.

Table 1 Chemical compositions of the constituent phases in Nb-16Si-Mo-W alloys annealed at 1973 K for 48 h.

Alloys	Constituent phases	Phase compositions	
		α Nb ₅ Si ₃	Nbss
Nb-16Si-10Mo-5W	Nbss + α Nb ₅ Si ₃	Nb-1Mo-0.4W-37.4Si	Nb-14.8Mo-7.4W-0.6Si
Nb-16Si-10Mo-10W	Nbss + α Nb ₅ Si ₃	Nb-1.2Mo-0.5W-38.5Si	Nb-14.4Mo-15.5W-0.6Si
Nb-16Si-10Mo-15W	Nbss + α Nb ₅ Si ₃	Nb-1.5Mo-0.8W-37.5Si	Nb-14.8Mo-25.3W-0.5Si
Nb-16Si-5Mo-15W	Nbss + α Nb ₅ Si ₃	Nb-0.6Mo-0.9W-37.8Si	Nb-6.7Mo-25.7W-0.4Si

Nbss: Nb solid-solution

alloy as in Fig. 9. The coefficient, 1.5, is the mean ratio of the molybdenum and tungsten contents in Nb solid-solution phase to those as nominal contents (Table 1). In case of C_x equal to 17%, for example, where the measured σ_{comp} for Nb-16Si-Mo-W alloy is 455 MPa, using $V_f = 0.5$, $\sigma_{\text{silicide}} \sim 670$ MPa, and σ_{ss} for Nbss phase (at point C) is 235 MPa which corresponds to σ_{ss} for Nb-Mo-W alloys at 1.5 C_x , eq. (3) yields σ_{comp} for a Nb-16Si-Mo-W alloy with nominal (Mo+1.5W) content of 17% to be ~ 453 MPa which is regarded to be comparable with the actual value for σ_{comp} being 455 MPa. Such an agreement is observed only in the C_x range from 15% to 20%. The measured 0.2% proof stress, σ_{comp} , is fairly smaller than the predicted value from eq. (3) when C_x is below 15%, and however the measured value is larger than the predicted value when C_x is above 20%. These results indicate that the rule of mixtures is not valid in the wide range of C_x value for the present Nb solid-solution/Nb₅Si₃-reinforced composite alloys, wherein the strength and ductility levels are greatly different between the two constituent phases unlike the SiC fiber reinforced SiC matrix SiC/SiC composites consisting of the same constituent material (SiC). The 0.2% proof stress, σ_{comp} , for Nb-16Si-Mo-W alloys is then given by a linear regression analysis as

$$\sigma_{\text{comp}}/\text{MPa} = 22.42(\text{Mo} + 1.5\text{W}) + 37.4, \quad R^2 = 0.973 \quad (4)$$

Figure 10 shows the room temperature fracture toughness, K_Q , plotted against (Mo+1.5W) content for Nb-16Si-Mo-W and Nb-16Si-Mo-W-5~10 Hf alloys. The K_Q values for Nb-Mo-W alloys are also shown for comparison. The K_Q values for Nb-16Si-Mo-W alloys, including alloys modified with 5Hf-5C addition, tended to decrease rather slowly with increasing (Mo+1.5W) content comparing to those for Nb-Mo-W alloys. The K_Q values for Nb-16Si-5Mo-5~15W-5Hf alloys with the (Mo+1.5W) content of 12.5 ~ 27.5% slightly decreased with tungsten content from 8.5 MPa·m^{1/2} to 7.9 MPa·m^{1/2}, while 0.2% proof stresses at 1773 K greatly increased from 257 MPa to 465 MPa, satisfying the target strength. Furthermore, the addition of 5Hf-5C to Nb-16Si-

5Mo-10W and -15W alloys results in the increase in K_Q value of 1.0 and 1.9 MPa·m^{1/2}, respectively. Kim *et al.*,⁵⁾ have reported that the beneficial effect of 5Hf-5C addition could result from the existence of Nb carbide dispersoids as well as Nb₅Si₃ phases, which causes the crack deflection and branching through the interphase-debonding between Nb solid-solution and Nb carbide dispersoids or Nb₅Si₃ and Nb solid-solution.⁵⁾ It is also noted that the Nb carbide, which some of niobium was replaced by hafnium and confirmed by TEM and EDS to be (Nb, Hf)₂C, became smaller in size by the addition of 5Hf-5C.^{5,8)}

3.3 High temperature creep strength

0.2% proof stress at 1773 K for the silicide-reinforced Nb-16Si-5Mo-5~15W-5Hf alloys, especially for the alloys with 15% tungsten exceeds the target strength. Accordingly, the high temperature creep and creep rupture tests have been carried out mainly on the silicide-reinforced alloys to clarify the effects of chemical compositions, and to select the most possible candidate alloy.

The typical creep curves at 1773 K are shown in Fig. 11 along with some of the solid-solution hardened alloys for comparison. The applied stresses are 100 MPa for the silicide-reinforced alloys and the half of that for the solid-solution alloys depending on the strength levels of the alloys. Figure 11 shows that better creep resistance was observed at Nb-16Si-5Mo-15W-5Hf alloy.

Figure 12 represents plots of the normalized minimum creep rate against the normalized stress for several Nb-Mo-W solid-solution alloys, Nb-16Si-Mo-W silicide-reinforced alloys and intermetallic Nb₅Si₃, where the values of activation energy for minimum creep rate, Q_c , were 655 kJ/mol for Nb-Mo-W alloys,¹⁵⁾ 675 kJ/mol for Nb-16Si-Mo-W alloys,¹⁶⁾ and 234 kJ/mol for Nb₅Si₃,¹⁰⁾ respectively. Figure 12 indicates that the creep resistances are improved by increasing molybdenum and tungsten content *i.e.* (Mo+1.5W) content for the solid-solution alloys, and also the silicide-reinforced alloy with 15% W exhibits a higher creep resistance than the solid-solution alloys. Nb₅Si₃ shows the lowest creep rate, but it is not applicable to structural uses because of its poor

Fig. 10 Fracture toughness, K_Q , at room temperature for Nb-16Si-Mo-W and Nb-16Si-Mo-W-5~10Hf alloys. The K_Q values for Nb-Mo-W alloys are also plotted for comparison.

Fig. 11 Typical tensile creep curves at 1773 K for Nb-Mo-W solid-solution hardened alloys and Nb-16Si-Mo-W silicide-reinforced alloys.

Fig. 12 Normalized minimum creep rate of several Nb alloys as a function of stress/Young's modulus. The creep rate is converted into that at 1773 K using apparent activation energy, Q_c , for minimum creep rate.

toughness and ductility.

Very little has been reported on the creep behavior of monolithic Nb_5Si_3 . Nb_5Si_3 has the ordered tetragonal structure with 32 atoms/cell both in α Nb_5Si_3 and β Nb_5Si_3 ,¹⁷⁾ and has been considered that the dislocation creep is unlikely to occur, because large Burgers vector and complex dislocation core structure are expected in this monolithic intermetallic. Instead, based on a stress exponent n of ~ 1 , and the activation energy for creep, Q_c , it, has been suggested that creep of Nb_5Si_3 probably occurs by the Nabarro-Herring mechanism.

The normalized minimum creep rate, $\dot{\epsilon}_m$, for Nb-16Si-5Mo-15W-5Hf silicide-reinforced alloy as the most possible candidate material can be described in the form of power relation by

$$\dot{\epsilon}_m = 1.922 \times 10^{23} \times (\sigma/E)^{2.4} \exp(-8.11 \times 10^4/T) \quad (5)$$

where E is the Young's modulus in MPa, σ is the applied stress in MPa, and T is the test temperature in K. The stress exponent, n ($=2.4$), and the activation energy, Q_c ($=675$ kJ/mol)¹⁶⁾ are used in calculating eq. (5). Considering the Q_c value of this alloy and the reported values of activation energy for diffusion of molybdenum and tungsten in niobium, 511 kJ/mol and 653 kJ/mol, respectively,¹⁸⁾ it seems that the creep process in this alloy is rate-controlled by the diffusion of tungsten in the Nb solid-solution.

Figure 13 shows plots of time-to-rupture, t_r , against stress, σ , at 1773 K. It is evidently shown that the rupture time, t_r , is simply given by $t_r = k\sigma^m$, where k is the constant and m is the stress exponent for rupture, and also t_r becomes longer with increasing tungsten and hafnium content for Nb-16Si-5Mo-W-Hf alloys, and also the substitution of silicon or molybdenum for tungsten is not valid to improve the creep rupture strengths as observed in Nb-20Si-Mo alloys. These results lead to conclude that the tungsten addition is significantly effective to enhance the high temperature creep strength, but the addition should be controlled below the critical (Mo+1.5W) content with respect to the ductile-to-

Fig. 13 Time-to-rupture as a function of stress for several silicide-reinforced alloys at 1773 K (solid symbols denote alloys with 2.5 or 5.0% Hf added).

Fig. 14 10% creep strength σ_{10} at 1573 K for 100 h in compressive creep tests plotted against silicon, molybdenum and tungsten contents for silicide-reinforcing alloys.

brittle transition, and to be optimized to a proper amount without deteriorating the fracture toughness and the ingot soundness.

The quantitative strengthening effects of silicon, molybdenum, and tungsten on the 10% creep strength in compressive creep tests for silicide-reinforced Nb-16Si-Mo-W alloys has been studied as a function of the alloy composition in the range of 5 ~ 15% Mo, 0 ~ 20% W, and 16 ~ 25% Si. Figure 14 shows 10% creep strength plotted against the alloy content, and indicates that the relative ratios of strengthening effect of molybdenum, silicon, and tungsten were 1: 0.65: 1.6. The strengthening effects of these alloying elements mainly result from solid-solution hardening as to both molybdenum and tungsten, and silicide-reinforcing effect as to silicon as discussed in the previous section. These results reveal that the strengthening effect of tungsten is much greater than those of molybdenum and silicon, which was similarly observed in the tensile and compressive tests of this work.

Fig. 15 SEM micrograph for Nb-16Si-5Mo-15W-5Hf alloy crept at 1773 K and 140 MPa to 332 h with creep rupture strain of 21.3%.

Fractographic observations have been conducted to examine the fracture behavior of the most possible candidate alloy, Nb-16Si-5Mo-15W-5Hf, crept at 1773 K and 140 MPa to 332 h with an elongation after creep rupture of 21.3%. Figure 15 shows a SEM micrograph of fracture surface exhibiting a number of different fracture modes which include brittle fracture of Nb_5Si_3 (A), transgranular fracture with some dimples of Nb solid-solution (B), Nb solid-solution/ Nb_5Si_3 interface decohesion (C), and the crack evolving from the silicide to the adjacent Nb solid-solution (D). EDS analysis revealed the microstructural constituents are Nb solid-solution and Nb_5Si_3 phase. A large number of cracks in the Nb_5Si_3 matrix were observed to initiate at the interface. These cracks evolved into the inner part of Nb_5Si_3 phase and eventually collided with the other solid-solutions particles, resulting in the interface decohesion in some case or the solid-solution cracking as marked by C in Fig. 16. TEM examinations clearly reveal that a microcrack

Fig. 16 BEI micrograph of longitudinal cross-section for Nb-16Si-5Mo-15W-5Hf alloy crept at 1773 K and 140 MPa to 332 h with an elongation after creep rupture of 21.3%. A: crack evolving into the inner part of Nb_5Si_3 , B: interface decohesion, C: crack penetrating through Nb solid-solution, D: crack-bridging.

Fig. 17 Crack advancement from Nb_5Si_3 to Nb solid-solution through the interface observed in Nb-16Si-5Mo-15W-5Hf alloy crept at 1773 K and 140 MPa to 332 h with an elongation after creep rupture of 21.3%, (a) TEM micrograph, (b) TEM pattern of cracked Nb solid-solution with [001] zone axis.

formed in the Nb solid-solution through $\text{Nbss}/\text{Nb}_5\text{Si}_3$ interfaces, which does not notice in BEI micrograph, was observed at the position where an advancing crack in the Nb_5Si_3 collides with the Nb solid-solution, as shown in Fig. 17.

Figure 18 shows the Larson-Miller plots for the Nb solid-solution alloys and the Nb_5Si_3 -reinforced alloys studied in the present investigation in comparison with those for

Fig. 18 Comparison of creep rupture strength of newly developed Nb-based alloys with those of NbTiAl silicide DS composite, and second- & third-generation Ni-based single-crystal superalloys.

directionally-solidified(DS) NbTiAl silicide composite,³⁾ and second- and third-generation single crystal Ni-based superalloys.¹⁹⁾ The stress-rupture performance of the DS composite is similar to those of advanced single-crystal Ni-based superalloy. The Nb-Mo-W solid-solution alloys modified with Hf show significantly higher temperature capabilities than those of the referred alloys. Especially the Nb₅Si₃-reinforced Nb-16Si-5Mo-15W-5Hf alloy as a most possible candidate material demonstrates an extremely high creep rupture strength, and satisfies the target strength of 150 MPa or above at 1773 K for 100 h. When Larson-Miller parameter, $L - MP = T(20 + \log t_r)$, is related to stress, σ , in the form of

$$L - MP \times 10^{-3} = k \log \sigma + \sigma_0 \quad (6)$$

where T is the temperature in K, t_r is the creep rupture time in h, and k and σ_0 are constants, Nb-16Si-5Mo-15W-5Hf alloy shows a creep rupture strength of 180 MPa at 1773 K for 100 h, and an endurance temperature of 1800 K at 150 MPa for 100 h. It should be noticeable that materials having such unprecedentedly high strength at such high temperature have not been reported before.

4. Conclusions

A Nb-based alloy system expecting the use for gas turbine materials at 1773 K was explored, focusing on the ultra-high temperature strength and room temperature fracture toughness as a function of chemical composition. The main results obtained are summarized as follows.

(1) 0.2% proof stresses of both Nb-Mo-W solid-solution alloys and Nb₅Si₃-reinforced Nb-Si-Mo-W alloys with a microstructure consisting of Nb solid-solution and Nb₅Si₃ at 1773 K were found to increase linearly with (Mo+1.5W) content, and that of the latter alloys also increased with the volume fraction of Nb₅Si₃.

(2) Room temperature fracture toughness, K_Q , of both alloy systems decreased with (Mo+1.5W) content, while K_Q of Nb₅Si₃-reinforced alloys decreased to lesser extent than that of Nb-Mo-W alloys. The critical (Mo+1.5W) content was 33.5 mol% together with molybdenum content of 15 mol% in Nb solid-solution phase for a ductile-to-brittle transition to occur, accompanying change in fracture mode and pre-yield fracture.

(3) The addition of 5Hf-5C to strengthen Nb-5Mo-15W alloy and Nb-16Si-5Mo-15W alloy yields 2.8 and 1.9 MPa·m^{1/2} higher room temperature fracture toughness than those of alloys without 5Hf-5C addition, respectively.

(4) 10% creep strength of Nb-Si-Mo-W alloys is enhanced by the additions of Mo, Si, and W, where the relative ratios of the strengthening effect are to be Mo:Si:W = 1:0.65:1.6.

(5) Excellent creep resistances and higher creep rupture strengths exhibited for Nb-16Si-5Mo-15W-5Hf alloy among the Nb-based alloys studied, where the greater tungsten content gave the higher creep strength.

(6) Several fracture modes including extensive fracture of

brittle Nb₅Si₃ and the resultant Nbss/Nb₅Si₃ interface decohesion and cracking in Nbss were observed in creep ruptured Nb₅Si₃-reinforced Nb-16Si-Mo-W alloys.

(7) Nb-16Si-5Mo-15W-5Hf alloy as the most possible candidate alloy exhibits a 0.2% proof stress of 465 MPa, a specific strength of 52 MPa/Mg·m⁻³ at 1773 K, and a creep rupture strength of 180 MPa at 1773 K for 100 h satisfying the target strengths.

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