Niobium for High Temperature Applications
Edited by Young-Won Kim and Tadeu Carneiro
TMS (The Minerals, Metals & Materials Society), 2004

NEWLY DEVELOPED NIOBIUM-BASED SUPERALLOYS FOR ELEVATED TEMPERATURE APPLICATION

[1]Ryohei Tanaka, [1,2]Akio Kasama, [3]Masakuni Fujikura, [1]Isao Iwanaga,
[1]Hisao Tanaka and [1]Yoshikazu Matsumura

[1]Japan Ultra-high Temperature Materials Research Institute (JUTEMI)
573-3 Okiube, Ube,Yamaguchi, Japan
Phone:+81-836-51-7007, Fax:+81-836-51-7011, E-mail:tryohei@jutem.co.jp
[2]Present Address:Kurume Technical Colledge
[3]Gifu Institute, JUTEMI

Keywords: gas turbine, refractory metals, niobium-based superalloy,
high temperature strength, diffusion-barrier coating

Abstract

Niobium(Nb)-based alloy is one of the candidate materials for ultra-high temperature applications, because of its high melting point, a good ductility at room temperature and a moderate density. Making a best use of these merits in Nb, a series of Nb-based superalloys have been developed for hot components of gas turbines. During the development, a solid-solution and a dispersion strengthening mechanisms were fully utilized through the additions of such alloying elements as Mo, W, Si, Hf and C. Typical composition of the strongest Nb-based alloy developed from this study is as follows: Nb-16Si-5Mo-15W-5Hf-5C(at%) with creep rupture life over 100 h under 150 MPa at 1500 °C. Further studies toward an establishment of sufficient oxidation and corrosion resistance of the alloys at such high temperatures as 1500 °C is now under way based on the idea of diffusion barrier coatings.

Introduction

Recently, from the viewpoint of climate change and the global warming, much emphasis has been placed on improvement of thermal efficiency in electric power plants firing up fossil fuels, especially in Japan. Because carbon dioxide emission from the generation of electricity takes up about one thirds of the total carbon dioxide emission in Japan, and more than 98 percent of the emission has been resulted from the thermal power plants.

As well known, the thermal efficiency of the thermal power plants is increased with increasing operating temperature. At present, the thermal power plant with the highest efficiency is that of so-called combined cycle system with steam- and gas-turbines. In this system, the total thermal efficiency is controlled mainly by turbine-inlet-temperature (TIT) of the gas-turbine. For the increasing of the TIT, there are strong demands on increasing of temperature capability of a series of high temperature materials. The most useful high temperature materials, at present, is superalloys based on nickel, and research and development of these alloys brought about an excellent temperature capability by the progress of alloy designs and process technologies. The newest single crystal superalloy produced by unidirectional solidification, designed TMS-162, has been reported with temperature capability of 1100°C under a criterion of 137 MPa-1000 h creep rupture life[1,2].However, it can be easily understood that, the practically available temperature of the Ni-based alloys must be limited because melting point of the alloys are lower than 1400 °C. So the cooling system of such gas-turbine components as combustors, blades and vanes made by the Ni-based superalloys are indispensable for the recent tendency of the increasing TIT of the gas-turbines, which is reaching to 1500°C. And reinforcing the cooling will restrain the increase of the thermal efficiency.

From these reasons, advanced structural materials have been strongly demanded for the applications at temperature above the maximum operating temperature of the conventional Ni-based superalloys. Under such situations, developmental studies on various Nb-based refractory alloys and materials have been reported [3-14]. Because the Nb-based alloys have a high melting point and a relatively low density, these alloys have been expected as candidate materials to be used at ultra-high temperature over the maximum operating temperature of Ni-based superalloys. Drastic decreases of strength and poor oxidation resistance at high temperature, however, are serious problems to be overcome for practical applications of these materials.

In JUTEMI (Japan Ultra-high Temperature Materials Research Institute) started the research and development of Nb-based superalloys for hot-components of gas-turbines from 1996. In consideration of the applications for hot components of the gas-turbine, following tentative objectives about properties were adopted.

Specific strength (proof stress/density) at 1500 °C: more than 50 MPa/g/cm3

1. Supposing the density of developed alloy as 9.0 g/cm2, specific strength of 50 MPa/g/cm3 corresponds to net proof stress of 450 MPa.
2. 1500 °C -100 h creep rupture strength: more than 150 MPa
3. Oxidation resistivity (corrosion loss at 1500°C for 10,000 h): less than 250 μm Subsidiary objective of fracture toughness at room temperature is also adopted as not far less than 10 Mpam$^{1/2}$.

At first, the most studies for the developing new Nb-based alloys have focused on the improvement in high temperature strength on the basis of the concepts of solid solution strengthening and dispersion strengthening [15-24]. Further improvement in the high temperature strength of the alloys have been continued with a concept of so-called *in-situ* composites [20,25-39], and finally, the above mentioned target of higher temperature capability as 1500 °C have been cleared [39, 42].

At the last symposium on "Tantalum and Niobium" held at 2000, A. Kasama et al.[21] made a interim report on the microstructure and mechanical properties, including a few creep data, of Nb-based innovative superalloys. In this presentation, the further studies after the previous report [21] on high temperature strength with good balancing to room temperature fracture toughness have been summarized. And a newly proposed oxidation-resisting coating system of the Nb-based superalloys will be introduced by Professor Toshio Narita, Hokkaido University, Japan, in this symposium.

Experimental

Raw materials used in this study were 99.9 mass% Nb, 99.9 mass% Mo, 99.9 mass% W,99.999 mass% Si and 98 mass% Hf. Carbon was added in a form of carbide NbC with 99 mass% purity. Alloy buttons were prepared by arc-melting furnace under reduced pressure atmosphere of high purity argon gas on a water-cooled copper hearth using a tungsten electrode. Prior to sample melting, pure titanium located in the furnace was melted for at least 2 minutes in order to remove mainly oxygen remaining in the argon atmosphere. To ensure compositional homogeneity, all the samples were remelted several times to remove segregation and to enhance the chemical homogeneity. The mass loss before and after melting were less than 0.1 mass%, which implies that the alloy compositions are fairly close to the nominal compositions. Heat treatment was carried out at the temperature of 1500 °C to 1850°C for 12 to 48 hours in the atmosphere of high purity argon gas followed by rapid furnace cooling. Some of the samples were also heat treated at 2000 °C to observe the microstructural change, particularly for carbide. Samples were prepared by electric-discharge machining (EDM) for metallographic observation, chemical composition analysis, phase identification and mechanical testing. Microstructural observation was carried out using back scattered electron images (BEI) in a scanning electron microscope (SEM) to identify constituent phases by contrast difference. Electron probe microanalysis(EPMA) equipped with a wave length dispersive spectroscope (WDS) was used in determining the chemical composition of the constituent phases. X-ray diffraction (XRD) was performed on the heat-treated samples to examine the crystal structure of constituent phases.

The dimensions of test piece is 3 mm x 3 mm x 6 mm for compressive test, and 3 mm in thickness with 10 mm gage length for tensile test as shown in Figure 1. These specimens were sectioned by EDM and mechanically polished using SiC paper and alumina particles with water. Tensile and compressive tests were carried out at an initial strain rate of 3 x 10-4 s-1 in laboratory air at room temperature, and in the case of elevated temperature were carried out in high purity argon atmosphere after keeping at the testing temperature for at least 15 minutes, using an Instron-type testing machine.

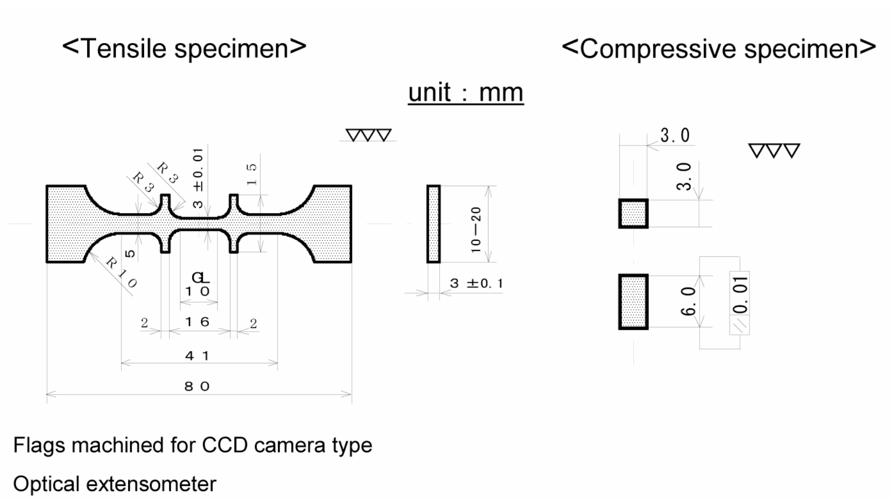


Figure 1. Dimensions of specimens for compressive and tensile tests.

High temperature creep tests were carried out on ultra-high temperature creep testing machines, Toshin HCTT-3000, at temperature between 1200 °C and 1500 °C under nominal stresses from 10.5 to 200 MPa in an argon atmosphere with the purity of 99.999 %. The tungsten heating elements were used and SiC hot jigs were adopted to transmit the applied stress to test piece. The dimensions of tensile creep specimens were 10 mm gage length with 3 mm x 3 mm cross section and four integral flags. These flags of upper and lower portion at the both side of the test piece, were prepared for continuous monitoring of creep displacement between upper and lower flags. The geometry of compressive creep specimen were same as that for the compressive test above mentioned. For accurate creep strain measurement, a new optical extensometry system were successfully utilized, which is established in JUTEMI [42].

Fracture toughness tests were carried out in three-point bending according to ASTM E399-1987 testing method, using the specimens with 3 mm x 6 mm cross section and 24 mm span, without insertion of a fatigue pre-crack, and a cross head speed of 0.5 mm/min.

Results and discussion

Effects of solid solution strengthening and carbide dispersion on the mechanical properties of Nb-based alloys

At first, the high temperature strength of the Nb-alloys with W, Mo, Ta, and V were examined from a view point of solid solution strengthening. It has been found that Mo and W are more effective elements than V and Ta for solid solution strengthening of niobium at high temperature. Then combined additions of Mo and W to Nb were examined, and it has been concluded[21] that Nb-based ternary alloys added Mo of 15 to 25 at% and W of 5 to 15 at% are the most promising base composition for applications at such high temperature as 1500 °C [21]. In the alloys with the contents ranged of 5~15 at% Mo and 5~30 at% W, a linear relationship between 0.2% proof stress, $\sigma_{0.2}$ and (Mo +1.5 W) at% were expressed as follows [42].

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

And the combined additions of 5 at% Hf-5 at% C are also effective to raise the 0.2 % proof stress at 1500°C and improve the fracture toughness at room temperature for Nb-Mo-W alloys.

However, further study [42] showed that a room temperature fracture toughness, K_Q , tends to decrease with increasing of 0.2 % proof stress both at room temperature and 1500°C as indicated in Figure 2. Accordingly, in order to improve the fracture toughness, introduction of carbide particles in the Nb-rich solid solution has been examined [23]. Because of the high thermal stability and strength of MC type carbide at elevated temperature, Hf and C have been added to the alloy in expectation of the formation of fine dispersion of carbide (Nb,Hf)C. The additions of Hf and C has been found to be effective to raise the proof stress of Nb-5Mo-5W and -15W alloys at 1500°C.

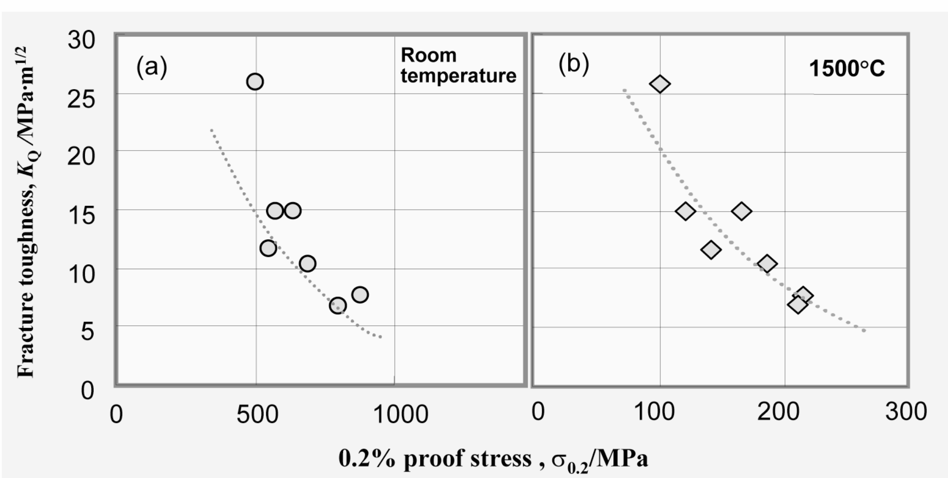


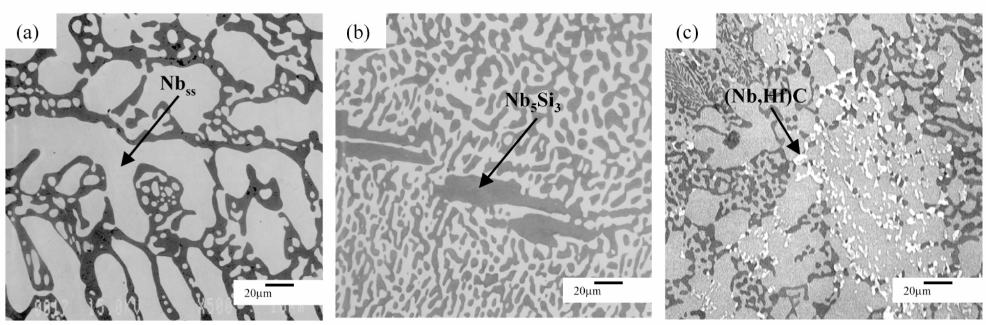
Figure 2. Relation between fracture toughness at room-temperature and proof stress at room- and high-temperature of Nb-based solid solution strengthened alloys.

Such a beneficial effect of 5Hf-5C additions has been attributed to the restraint of intergranular fracture [23]. TEM and EDS observations on Nb-5Mo-15W-5(Hf+C) alloy revealed that Nb2C carbide appeared in the granular type (~0.65μm)and coarse rod-like forms, however hafnium substitution for some of niobium in Nb_2C, and any hafnium carbide, HfC, were not found. On the other hand, the maximum proof stress obtained by each 10 % of Hf and C has been ever lower than 450 MPa, which is one of the target values.

Effect of silicide by addition of Si on the mechanical properties of Nb-based alloys

The results in the previous section have suggested that the mechanical properties of the Nb-Mo-W solid solution alloys is not sufficient to meet the strength required to be 450 MPa at 1500°C. Nb-Si alloy system is our interest because of its wide two-phase region consisting of ductile Nb solid solution (hereafter denote as Nb_{ss}) and Nb_5Si_3 intermetallic phase, of which melting point is almost 2254°C [43]. So, high temperature strength can be anticipated by the coexisting of the intermetallic phase. It has also been demonstrated that the fracture toughness of Nb_{ss}/ Nb_5Si_3 *in-situ* composite is superior to the single Nb_5Si_3 intermetallic phase in the binary Nb-Si system due to ductile phase toughening[4].

Therefore, we have tried to explore alloys with higher strength than the Nb-Mo-W solid solution alloys by utilizing intermetallic compound Nb-silicide using addition of Si. BEI micrographs of three kinds of alloys [40] are shown in Figure 3. Combining with XRD and EPMA results, both the microstructure of Nb-16Si-5Mo-5W (Figure 3 (a)) and Nb-20Si-10Mo(Figure 3(b)) are composed of coarse primary Nbss particles and fine eutectic Nbss and α Nb_5Si_3 (hereafter denoted as Nb_5Si_3). The bright and dark contrasted regions in Figure 3(a) and (b), are identified to be Nbss and Nb_5Si_3 intermetallic phase, respectively. The two alloys with 16 at% Si have a hypo-eutectic microstructure composed of the primary Nb_{ss} and eutectic of Nb_{ss} and Nb_5Si_3, while the alloy with 20 at% Si has a hyper-eutectic ones contained primary Nb5Si3 instead of Nb_{ss} primary crystal. The microstructure of Nb-16Si-5Mo-15W-5Hf-5C alloy (Figure 3(c)) is composed of three phases, in which dark and middle contrasted regions are identified to be Nb_5Si_3 and Nb_{ss}, respectively, and bright one is carbide (Nb,Hf)C. The carbide particles are dispersed to grain boundaries and interfaces between Nb_{ss} and Nb_5Si_3



(a) Nb-16Si-5Mo-5W, aged at 1773K for 62h
(b) Nb-20Si-10Mo, aged at 1773K for 58h
(c) Nb-16Si-5Mo-15W-5Hf-5C, aged at 1773K for 477h

Figure 3. BEI images of three Nb-based alloys.

Figure 4 shows that the volume fraction of silicide, V_{Nb5Si3}, increases linearly with Si content as V_{Nb5Si3} = 3.085 x (Si %) [42]. The compressive proof stress at 1500°C and fracture toughness at room temperature of three series of alloys are shown in Figure 5 as a function of (Mo+1.5W)%. Although, generally in these studies on the Nb-based alloys, the values obtained by compressive tests are slightly higher than that by tensile tests, it is possible to say that the both values are in fair agreement, if considered their experimental error [21]. In all three series of alloys in Figure 5,the proof stresses increase linearly with (Mo+1.5W) contents, and a data plot of the alloy Nb-16Si-5Mo-15W-5(Hf+C) indicates the proof stress value more than 450 MPa at around of Mo+1.5W of 27.5 at% which corresponds to 5 at%Mo plus 15 at%W, maintaining the fracture toughness (Figure 5(b)) of nearly 10 MPam$^{1/2}$.

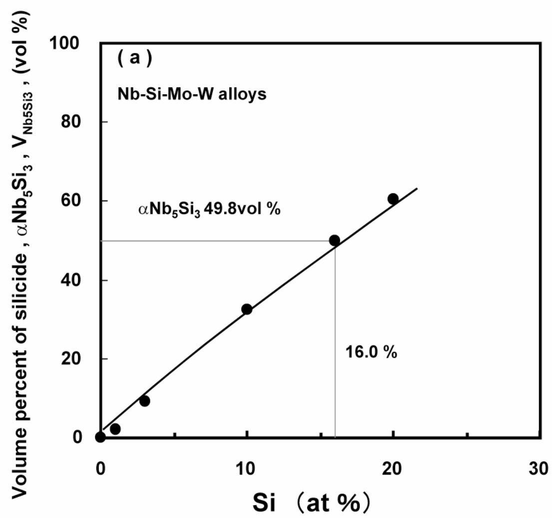


Figure 4. Si content dependency of volume fraction of silicide, Nb_5Si_3, in Nb-Si-Mo-W alloys.

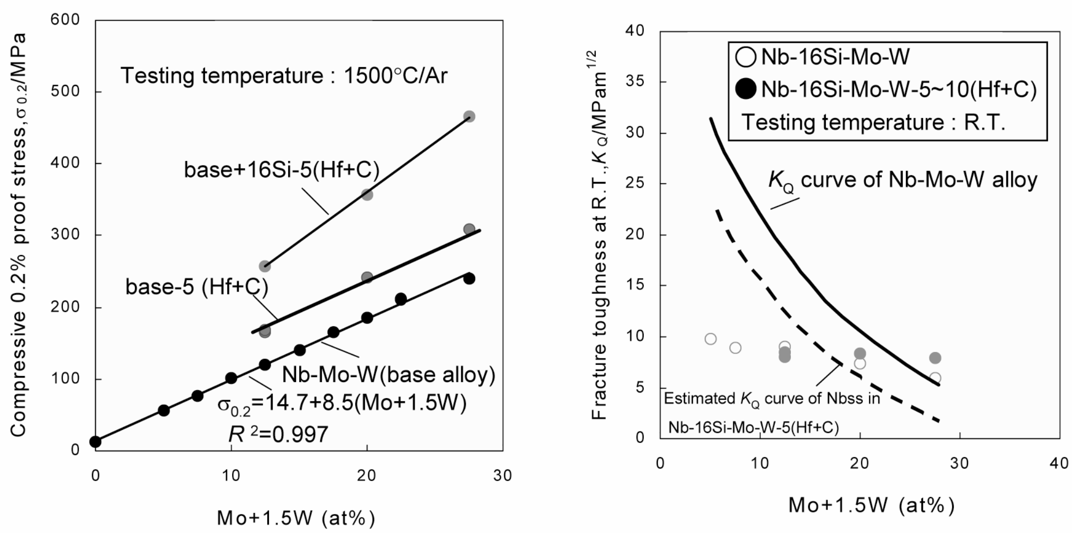


Figure 5. Mo and W contents dependency of proof stress and fracture toughness in Nb-Mo-W alloys with and without (Hf+C) and Si.

The typical creep curves of silicide-reinforced Nb-alloys at 1500°C are shown in Figure 6. In Figure 7, the Larson-Miller parameter plots for three Nb-based alloys, Nb-16Si-5Mo with variable W and Hf (C), in comparison with those for directionally solidified (DS) NbTiAl silicide composite [8] and for the single crystal Ni-based superalloys of second and third generations [44]. The stress rupture performance of the above mentioned DS composite is similar to those of advanced single crystal Ni-based superalloys. The Nb_5Si_3-reinforced Nb-16Si-5Mo-15W-5(Hf+C) alloy demonstrates an extremely high creep rupture strength, and it is clearly found that the strength value satisfies the target of 150 MPa at 1500 °C for 100 h.

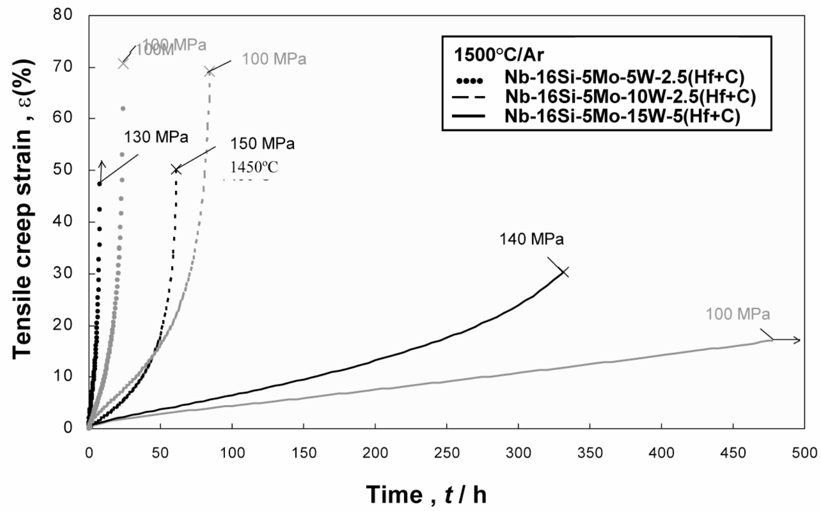
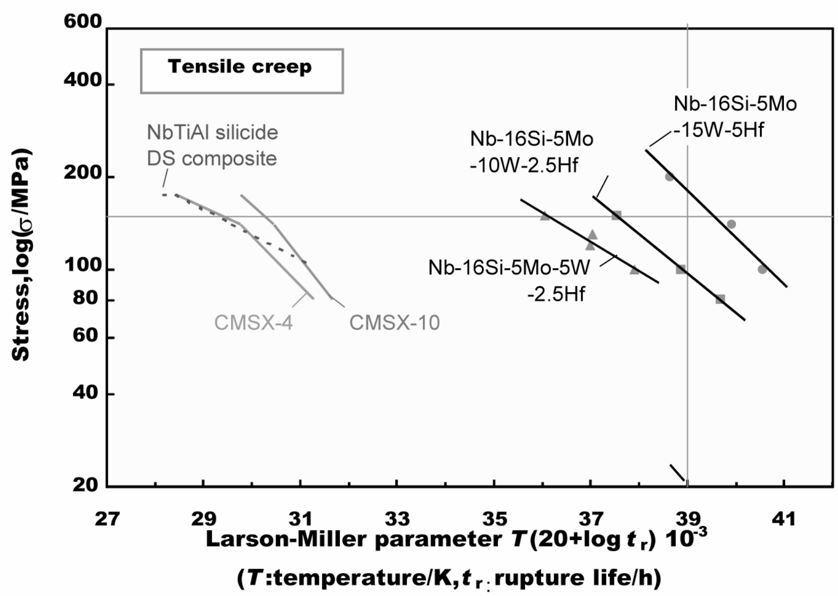


Figure 6. Typical tensile creep curves of silicide-reinforced Nb-alloys.



·NbTiAl Silicide DS composite : Nb-Ti-Al-Cr-Si alloy,1100°C /Ar
·Ni Ni-based single crystal superalloys : 1100°C /Air
CMSX-4(6.5Cr-9Co-0.6Mo-6W-6.5Ta- .6Al-1.0Ti-0.1Hf-Bal.Ni), 2nd.gen.alloy
CMSX-10(2Cr-3Co-0.4Mo-5W-8Ta .7Al-0.2Ti-0.3Hf-0.1Nb-Bal.Ni),3rd.gen.alloy

Figure 7. Larson-Miller parameter plots for three Nb-based alloys compared with those for directionally solidified (DS) NbTiAl silicide composite [8] and for the Ni-based single crystal superalloys with second- and third-generations[44].

It has been concluded that, based on above mentioned many data, including 0.2 %proof stress at room temperature, 100 h creep rupture strength at 1500°C, and also fracture toughness at room temperature, the Nb-16Si-5Mo-15W-5Hf-5C alloy has a sufficient mechanical properties which satisfy the tentative targets. Because the alloy has a poor resistance to oxidation, a diffusion barrier coating system for preventing the oxidation has newly been developed, and details of the system will be introduced in this symposium by Professor Toshio Narita, Hokkaido University, Japan.

It is needless to say, however, that the further many works will be indispensable for the practical applications of the alloy to such hot-components as blades and vanes in gas-turbine.

Summary

A new Nb-based superalloy has been explored, which far exceeds recently developed Ni-based single crystal superalloys in high temperature strength, for hot-components of gas-turbines. The proposed alloy has such nominal compositions as Nb-16Si-5Mo-15W-5Hf-5C(at%). The microstructure of the alloy consists mainly of a Nb solid solution (Nb_{ss}) with Mo and W, a silicide of Nb_5Si_3, and a few amount of carbide (Nb,Hf)C distributing in grain boundaries of Nb_{ss} and interfaces between Nb_{ss} and silicide grains. The alloy has exhibited a 0.2 % proof stress more than 450 MPa at 1500°C, which corresponds to a specific strength of 50 MPa/g/cm^3, assuming the density as 9.0 g/cm^3, and a creep rupture strength exceeds 150 MPa at 1500°C for 100 h. However, the further many works will be indispensable for the practical applications of the alloy, including the improvement of coating system against oxidation and innovating manufacturing processes for hot-components of gas-turbine, which is suitable for the Nb-based superalloys.

Acknowledgements

This work was carried out by the project "Research and Development of Innovating Processes for the Components Materials made from Refractory Metals" supported by The New Energy and Industrial Technology Development Organization (NEDO) of Japan. The authors would like to express our hearty thanks to NEDO for the financial support. The authors would also like to thank to professor S.Hanada of Tohoku University and Professor Y.Mishima of Tokyo Institute of Technology for their kind advices. The authors would also like to express many thanks their colleagues in Japan Ultra-high Temperature Materials Research Institute (JUTEMI) for technical assistance and valuable discussions.

References

1. H.Harada and T.Yokokawa, "Superalloys for Next Generation Jet Engine and Advanced Gas Turbine Applications", *Materia Japan* ,42(9)(2003),621-625 in Japanese.
2. Y.Koizumi et al., "Development of Next Generation Ni-base Single Crystal Superalloys Containing Ruthenium", *J.Japan Inst.Metals*,67(9)(2003),468-471 (in Japanese).
3. H.Inouye, "Niobium in High Temperature Applications", *Niobium, Proc.Intl.Symposium*, ed.H.Stuart (Warrendale,PA:The Metallurigical Society of AIME,1984),615-636.
4. M.G.Mendiratta, J.J.Lewandowski, and D.M.Dimiduk, "Strength and Ductile Phase Toughening in the Two-Phase Nb/Nb5Si3Alloys", *Metall.Transactions A* ,22A (7) (1991), 1573-1583.
5. D.M.Shah et al.,"In-situ Refractory Intermetallic Based Composites", *Materials Science and Engineering* ,A192/193(1995),658-672.
6. P.R.Subramanian and J.A.Shields,Jr.,"Refractory Metals and Materials : Joining and Applications", *JOM* ,48(1)(1996),32.
7. P.R.Subramanian,M.G.Mendiratta and D.M.Dimiduk, "The Development of Nb-Based Advanced Intermetallic Alloys for Structural Applications", *JOM* ,46(1)(1996),33-38.
8. M.R.Jackson et al.,"High Temeprature Refractory Metal-Intermetallic Composites", *JOM* ,48(1)(1996),39-44.
9. D.M.Farkas and A.K.Mukherjee, "Creep Behavior and Microstructural Correlationof a Particle-Strengthend Nb-1Zr-0.1C alloy."*J.Materials Research*,11(9)(1996), 2198-2205.
10. B.P.Bewlay,M.R.Jackson and H.A.Lipsitt, "The Balance of Mechanical and Environment

Properties of a Multielement Niobium-Niobium Silicide-Based *In-Situ* Composite" *Met.and Mat.Trans.A*. 27A(12)(1996),3801-
11. B.P.Bewlay,J.J.Lewandowski and M.R.Jackson, "Refractory Metal-Intermetallic In-situ Composites for Aircraft Engines", *JOM* ,49(8)(1997),44-45,67.
12. R.Tanaka, "Research and Development of Ultra-High Temperature Materials in Japan", *Materials at High Temperature*, 17(4)(2000),457-464.
13. J.Sha et al., "Microstructure and Mechanical Properties of Nb-Mo-Ti-Si-C *in-situ* Composites Prepared by Arc Melting and Directional Solidification", *J.Japan Inst.of Metals*, 64(5)(2000),331-334(in Japanese).
14. H.Hirai et al., "Microstructure and Mechanical Properties of Directionally Solidified Nb-xMo-22Ti-18Si *in-situ* Composites", *J.Japan Inst.of Metals*, 64(6) (2000),474-480(in Japanese).
15. J.Sha et al., "Mechanical Properties of As-Cast and Directionally Solidified Nb-Mo-W-Ti-Si *in-situ* Composites at High Temperature", *Metallurgical and Materials Transactions A*, 34A(1)(2003),85-94.
16. Y.Tan et al., "Microstructure and High Temprerature Compressive Strength of Nb-Ir Alloys", *J.Japan Inst.of Metals*, 63(5)(1999),605-608(in Japanese).
17. H.Tanaka et al., "Solid Solution Strengthening of Nb-based Refractory Materials", *Intl.Conf.on Advanced Technology in Experimental Mechanics*, *(ATEM '99)*, ASME-MMD (1999), 539-542.
18. C.L.Ma et al., "Synthesis of Nb/Nb5Si3 in-situ Composites by Mechanical Milling and Reactive Spark Plasma Sintering", *Materials Transactions,JIM*, 41(6) (2000),719-726.
19. Y.Tan et al., "Solid Solition Strengthening and High-Temperature Compressive Strength of Nb-X(X=Ta,V,Mo and W)", *J.Japan Inst.of Metals*, 64(7)(2000),559-565 (in Japanese).
20. Y.Tan et al., "Solid Solition Strengthening and High-Temperature Compressive Ductility of Nb-Mo-W Ternary Alloy", *J.Japan Inst.of Metals*, 64(7)(2000),566 - 570(in Japanese).
21. A.Kasama et al., "Microstructure and Mechanical Properties of Niobium-Based Refractory Metals,"*Intl.Symposium on Tantalum and Niobium* (2000),213-217.
22. Y.Tan et al., "Influence of Boron Addition on High Temperature Mechanical Properties of Nb•Ir Intermetallic Compound", *Materials Transactions,JIM*, 41(12) (2000),1605-1611.
23. W-Y.Kim et al., "Effect of Carbon on Tensile Properties of Nb-Mo-W Alloys", *J.Alloys and Compounds*, No.333(2002),170-178 .
24. W-Y.Kim et al., "High Temperature Strength at 1773 K and Room Temperature Fracture Toughness of Nb-Mo-W Refractory Alloys with and without Carbide Dispersoids", *Materials Science & Engineering* ,A346(2003),65-74.
25. Y.Tan et al., "Effect of Alloy Composition on Microstructure and High Temperature Properties of Nb-Zr-C Ternary Alloys", *Materials Science & Engineering* , A341(2003),282-288 .
26. C.L.Ma et al., "Microstructure and Mechanical Properties of Nb/Nb-Silicide in-situ Composites Synthesized by Reactive Hot Pressing of Ball Milled Powder", *Materials Transactions,JIM*, 41(3)(2000),444-451.
27. C.L.Ma et al., "Phase Equilibria in Nb- Mo-Rich Zone of the Nb-Si-Mo Ternary System", *Materials Transactions,,JIM*, 41(10)(2000),1329-1336.
28. C.L.Ma et al., "Microstructure and Mechanical Properties of Nb/Nb5Si3 *in-situ* Composites in Nb-Mo-Si and Nb-W-Si Systems" *Report of the 123rd Committee on Heat-Resisting Materials and Alloys,JSPS*•40(3)(1999),335-347
29. C.L.Ma et al., "Microstructure and Mechanical Properties of Nb/Nb5Si3 *in-situ* Composites in Nb-Mo-W-Si Quaternary System", *Report of the 123rd Committee on Heat-Resisting Materials and Alloys,JSPS*•40(3)(1999),349-360
30. W-Y.Kim, et al., "Microstructure and Room Temperature Deformation of Nbss/Nb5Si3 *in-situ* Composites Alloyed with Mo", *Intermetallics*, 9(2001),521-527.

31. W-Y.Kim, et al., "Microstructure and Room Temperature Fracture Toughness of Nbss/ Nb/Nb5Si3 *in-situ* Composites", *Intermetallics*, 9(2001),827-834.
32. W-Y.Kim et al., "Microstructure and Mechanical Properties of Nbss/ Nb/Nb5Si3 *In-situ* Composites Alloyed with Mo", *The Fourth Pacific Rim Intl.Conf.on AdvancedMaterials and Processing(PRICM4)*, ed.S.Hanada, Z.Zhong, S.W.Nam and R.N.Wright (The Japan Inst.of Metals,2001),963-966.
33. H.Tanaka et al., "Microstructure and Mechanical Properties of Nbss/ Nb/Nb5Si3 *In-situ* Composites Alloyed with Mo and W", *J.Japan Inst.of Metals*, 66(3)(2002), 182-187(in Japanese).
34. W-Y.Kim,H.Tanaka and S.Hanada, "Microstructure and High Temperature Strength at 1773 K of Nbss/Nb5Si3 Composite Alloyed with Molybdenum",*Intermetallics*,10 (2002),625-634.
35. C.L.Ma et al., "Phase Equilibria in Nb-W Rich Zone of the Nb-W-Si Ternary System", *Materials Transactions,JIM*, 43(4)(2002),688-693.
36. H.Tanaka et al., "Room Temperature Strength and Fracture Toughness of Two Phase Nbss/Nb•Si• Alloyed with Mo,"*J.Japan Inst.of Metals*, 66(7)(2002),772-777 (in Japanese).
37. W-Y.Kim, H.Tanaka and S.Hanada, "High Temperature Strength at 1773 K and Room Temperature Fracture Toughness of Nbss/Nb5Si3 Composite Alloyed with Mo", *J.Materials Science*, 37(12)(2002), 2885-2891.
38. W-Y.Kim et al., "Effect of Cr Addition on Microstructure and Mechanical Properties in Nb-Si-Mo Base Multiphase Alloys", *Materials Transactions,JIM*, 43(12)(2002),3254-3261.
39. R.Tanaka et al., "Refractory Metals Focusing on Development of Niobium Base Superalloy", *J.of the Gas Turbine Soc.of Japan* ,31(2)(2003),81-86.
40. W-Y.Kim,H.Tanaka and S.Hanada, "Effect of W Alloying and NbC Dispersion on High Temperature Strength at 1773 K and Room Temperature Fracture Toughness in Nb5Si3/Nb i*n-situ* Composites", *Materials Transactions*, 44(6)(2003),1415-1418.
41. H.Tanaka et al., "Effect of Mo,W and (Nb,Hf)C on Creep Rupture Properties on Nb/Nb5Si3 *in-situ* Composites", *J.Japan Inst.of Metals*, 67(8)(2003), 385-390 (in Japanese).
42. M.Fujikura et al., "Effect of Alloy Chemistry on the High Temperature Strengths and Room Temperature Fracture Toughness of Advanced Nb-Based Alloys", *Materials Transactions,A* (Recieved,Sep.2003)
43. T,B.Massalski, ed., "*Binary Alloy Phase Diagrams*",Vol.2 (Metals Park,Ohio,ASM)(1991), 2767.
44. G.L.Erickson, "The Development and Applications of CMSX-10", *Superalloys 1996*, ed. R.D.Kissinnger et al.(Warrendale,Penn:The Metallurgical Society Inc.) (1996), 35-48.