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Research and Development of Niobium-Based Superalloys for Hot Components of Gas turbines

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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 ℃. Further studies toward an establishment of sufficient oxidation and corrosion resistance of the alloys at such high temperatures as 1500 ℃ is now under way based on the idea of diffusion barrier coatings.

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

1. INTRODUCTION

Recently, from a view point of a countermeasure of global environmental problems and of a sustainable development of the world, it is strongly required to reduce the carbon-dioxide(CO_2) emission in many industries. In Japan, an electricity from thermal power plays an important role, more than 50% of total. Therefore, the demands of increasing in thermal efficiency of the power plants are essential for the reducing the CO_2 emission. A combined cycle plant, which consists of steam and gas turbines, are very hopeful because of its higher thermal efficiency than that of the steam turbine alone.

The thermal efficiency is increased with the increase in the turbine inlet temperature(TIT) which results in reduction of the CO_2 emission. Accordingly, the tendency of increasing TIT will be continued to the future.

At present, Ni-based superalloys are excellent and most useful materials for many high temperature applications, especially in gas turbines (Harada and Yokokawa, 2003), and have been well developed particularly with the outstanding progress of jet engines. However, the increase of a temperature capability of the Ni-based superalloys will be limited because their melting points are lower than 1400℃.

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Although so-called ultra-high temperature materials (Tanaka, 1997), such as intermetallic compounds, refractory metals and alloys, ceramics and various composite materials are expected to surpass the temperature capability of the superalloys, these materials have such problems to be overcome as difficulty of processing, lack of ductility and toughness or the poor resistance to oxidation and hot-corrosion.

Table 1 shows physical properties of typical refractory metals compared with that of Ni and a Ni-based superalloy. Nb has a high melting point as 2468℃, a density (8.56 Mg/m^3) close to that of Ni(8.9 Mg/m^3), and sufficient ductility at room temperature. Although the melting point of Nb is the lowest among the refractory metals, it is more than 1000℃ higher than that of Ni. A coefficient of thermal expansion of Nb is about half compared with that of Ni, and Young's modulus of Nb is also half.

Considering these various advantages, Nb-based refractory alloys have been expected as a candidate material to be used at ultra-high temperature over the maximum operating temperature of the Ni-based superalloys.

Since 1960s, several studies were carried out to develop the Nb-based structural materials for high temperature applications mainly in US and Australia. However, no alloy was found to be able to replace the Ni-based superalloys. Jackson, et al. (1996) reported a Nb-based refractory metal-intermetallic composites (RMICs), and one of them has been named as " NbTiAl silicide DS composite", but the high temperature strength of this Nb-based composite is not far beyond the newest Ni-based single crystal superalloys (Harada and Yokokawa, 2003).

Therefore, the development of the new Nb-based superalloy with high specific strength at temperatures higher than 1000 ℃ have been challenged by us(Tanaka et al,2003). In this paper, an outline of the research and development is reported of the Nb-based superalloys, which will be applicable to hot components of the gas turbines for future power plants.

2. OBJECTIVE PROPERTIES AND FUNDAMENTAL APPROACH TO THEM

In due consideration of the applications for hot components of a gas turbine, following tentative objectives about properties were adopted.

Table 1 Physical properties of refractory metals compared with a Ni and Ni-based superalloy.*

Physical properties	Unit	Refractory metals					Ni and Ni-based superalloy	
		Nb	Ta	Mo	W	Re	Ni	MM-246**
Melting temperature	℃	2468	2996	2610	3410	3180	1455	1315-1345
Density ［25℃］	Mg/m^3	8.56	16.65	10.22	19.3	21.4	8.90	8.44
Coefficient of thermal expansion ［R.T.］	$10^{-6}k^{-1}$	7.3	6.5	4.9	4.6	6.7	13.3(0-100℃)	11.3(93℃)
Thermal conductivity ［20℃］	W/m・k	52.7	54.4	142	155	71	90.5	16.8(427℃)
Young's modulus ［R.T.］	GPa	103	185	324	400	469	204	205
Ductile-brittle transition temperature	℃	-140	-270	30	300	-	-	-

* Mainly from Rikagaku-Jiten(1998,Iwanami,Japan)
** INCO Catalog (High Strength Nickel Base Alloys (1977))

① Specific strength (proof stress/density) at 1500 ℃
: more than 50 $MPa/Mg/m^3$
② 1500℃-100 h creep rupture strength
: more than 150 MPa
③ Oxidation resistivity
(corrosion loss at 1500 ℃ 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 MPa・$m^{1/2}$.

In order to achieve these objectives, the microstructure of the Nb alloys was extensively controlled mainly by addition of alloying elements and heat treatment. The processes for development of the alloys are summarized roughly as Fig.1.

3. EXPERIMENTAL PROCEDURE

Raw materials used in this study were 99.9 mass%Nb, 99.9 mass%W, 99.999 mass%Si and 99 mass%Hf. C was added in a form of NbC with 99 mass% purity. Alloy buttons were prepared by arc-melting in an argon atmosphere on a water-cooled copper hearth using a non-consumable tungsten electrode. The button ingots were remelted several times to remove segregation and to enhance the chemical homogeneity. Heat treatment was carried out at 1800 ℃ for 24 h in an argon atmosphere followed by rapid furnace cooling. Samples for metallographic observations, chemical composition analysis, phase identification and mechanical testing were prepared by electro-discharge machining (EDM) of the heat treated ingots. Microstructural observations were carried out using back scattered electron images (BEI) in a scanning electron microscopy (SEM) to identify constituent phases by contrast difference. X-ray diffraction (XRD) was performed on the heat treated samples to examine the crystal structure of constituent phases. Compression test specimens with 3×3 mm cross-section and 6 mm in height and fracture toughness specimens with 3×6 mm cross-section and 24 mm span in three-point bending were prepared by EDM. Tensile creep rupture test specimens with 3×3 mm cross-section and 10 mm length in gauge portion were also prepared by EDM. Specimens were then mechanically polished with SiC paper and fine alumina particles with water. Compressive tests and tensile creep rupture tests were conducted mainly at 1500 ℃ in an argon atmosphere. Fracture toughness tests were carried out in three-point bending according to ASTM E399-1987 testing method without insertion of a fatigue pre-crack. An equation form

$$K_Q = (P_q S/BW^{3/2}) f (a/W) \qquad (1)$$

was used to calculate the fracture toughness value. In Eq. (1), a/W is 0.45-0.55, P is load, B is thickness, W is height, S is applied load span and a is notch depth. Fracture toughness tests were performed in air at room temperature and a cross-head speed of 0.5 mm/min.

4. IMPROVEMENT OF STRENGTH AND TOUGHNESS BY SOLID SOLUTION WITH ALLOYING ELEMENTS AND GRAIN REFINEMENT

The pure Nb has very hopeful properties as mentioned above. A drastic decrease of high temperature strength, however, is one of the subjects to be improved for practical applications of these bcc (body-centered cubic)-based materials. In the present study, the alloys were designed to have a good balance of the high temperature strength and the room temperature fracture toughness by alloying and modifications of the microstructure. Mo, W, Ta and V were chosen as solid solution strengthening elements, and it has been clarified that the additions of W and Mo increase effectively the high temperature strength of the Nb.

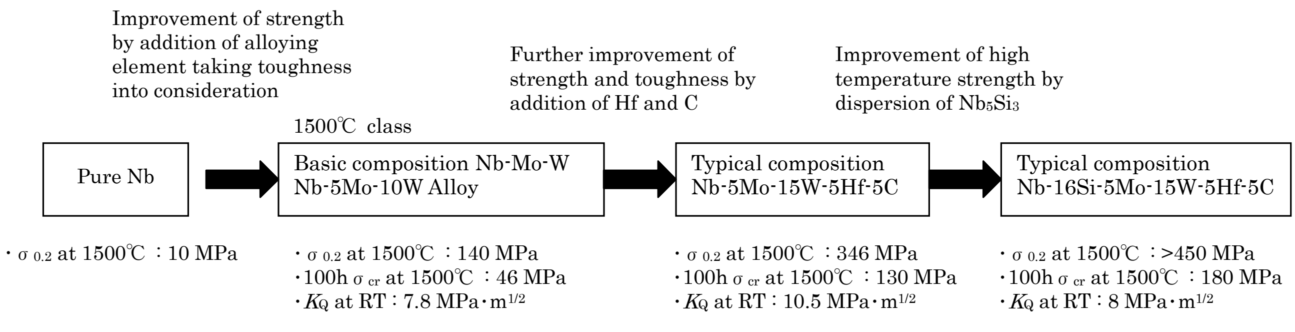


Fig.1 Process of development of the Nb-based superalloys.

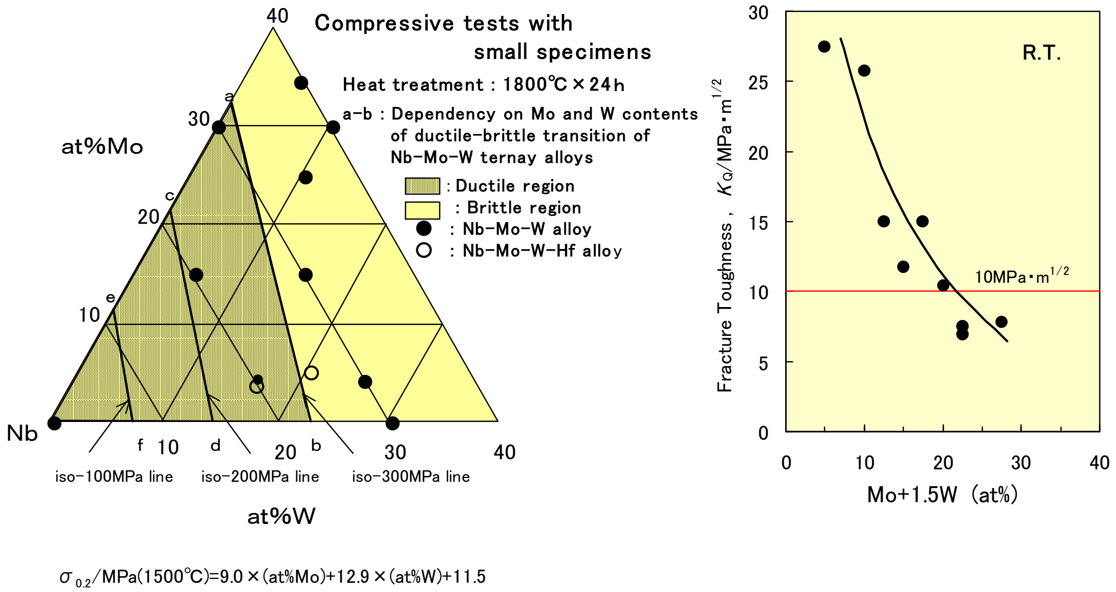


Fig.2 Compressive strength of Nb-Mo-W ternary alloys and fracture toughness.

In addition, the mechanical properties of the Nb alloys containing both of Mo and W have been investigated. In Fig.2 (a), iso-strength lines of 100, 200 and 300 MPa of proof stress according to the compressive test results at the temperature of 1500℃, showed in Nb-Mo-W ternary compositional triangle, and the proof stress by compression tests($\sigma_{0.2}$) at 1500℃ for the ternary alloys has been expressed approximately as following equation;

$$\sigma_{0.2}/\text{MPa(at 1500 ℃)} = 9.0\times(\text{at\%Mo}) + 12.9\times(\text{at\%W}) + 11.5 \qquad (2)$$

In the Fig.2 (a), ductile region (shaded) and brittle regions (bright) are separated by a-b line based on observations of the fracture surfaces after compression tests. On the other hand, the fracture toughness of a series of these ternary alloys is shown in Fig.2 (b) as a function of Mo and W content, in which coefficients of Mo and W in Eq. (2) have been simplified as Mo:W = 1:1.5. In this figure, fracture toughness at room temperature of the alloys decreases drastically with increasing of Mo and W contents, and the value of the fracture toughness is roughly expressed as a function of (Mo+1.5W), where contents of Mo and W are expressed by at%, respectively, and coefficient of W is simplified to 1.5 as mentioned above. As can be seen, if the (Mo+1.5W) exceeds about 20, the fracture toughness values become lower than 10 MPa・m$^{1/2}$.

Therefore, in order to keep the toughness of the alloys, both of Mo and W contents will be limited as less than about 10%, respectively.

To further improve the mechanical properties of alloys to be consistent with the strength and toughness, Hf and C were added to the Nb-Mo-W alloys in expectation of the formation of carbide (Nb,Hf,Mo)C. Additions of these two elements bring about fine carbide distributions especially on grain boundaries, reducing the tendency of brittle fracture at grain boundaries, and increasing the rupture elongation in tensile tests. It has been found that both of the strength at high temperature and the fracture toughness at room temperature have been improved (Kim, 2002) shown in the middle part of Fig.1.

5. STRENGTHENING BY SILICIDE DISPERSION

Dispersion of intermatallic compound in alloys has frequently been utilized as one of the useful means for improvement of the strength at high temperature under compatibility with toughness. In this study, as a result from several examinations, an addition of silicon has been chosen to make forming a composite structure consists of Nb solid solution (Nb_{ss}) and silicide Nb_5Si_3,same as so-called *in-situ* composite. A typical microstructure of the Nb-Mo-W alloys added 16 at%Si is shown in Fig.3, in which large bright grains are primary crystal Nb_{ss} and fine particles embedded in matrix are Nb_{ss} and Nb_5Si_3 eutectic. Excellent mechanical properties have been obtained in these alloys as shown in right hand of the Fig.1. Although the fracture toughness is a little less than 10 MPa・m$^{1/2}$, 450 MPa of the proof stress, $\sigma_{0.2}$, has been achieved and specific strength (proof stress/density) corresponds to 50 MPa/Mg/m^3, because the density of the alloy is about 9 Mg/m^3.

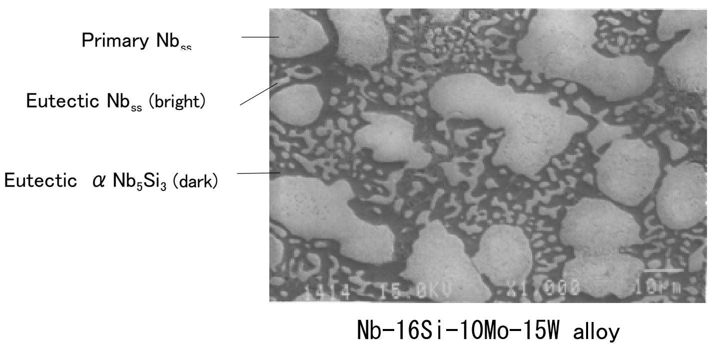
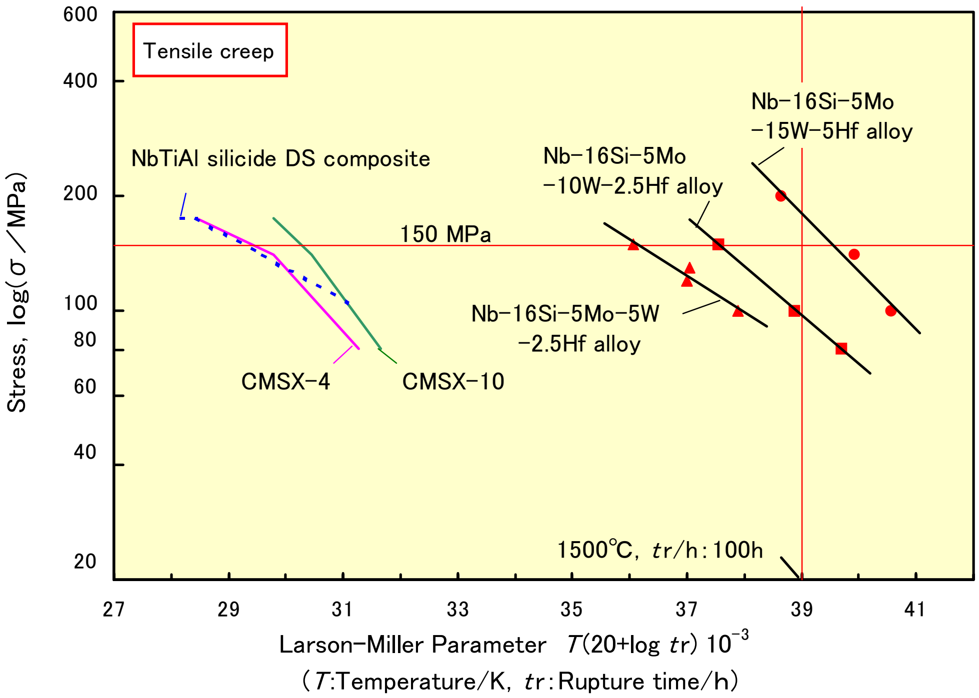


Fig.3 Typical microstructure of a Nb-16%Si-10%Mo-15%W alloy.



·NbTiAl silicide DS composite : Nb−Ti−Al−Cr−Si alloy,1100℃/Ar

·Ni−base single crystal superalloy : 1100℃/Air

CMSX−4(6.5Cr−9Co−0.6Mo−6W−6.5Ta−3Re−5.6Al−1.0Ti−0.1Hf−Bal.Ni), 2nd gene.alloy

CMSX−10(2Cr−3Co−0.4Mo−5W−8Ta−6Re−5.7Al−0.2Ti−0.3Hf−0.1Nb−Bal.Ni), 3rd gene.alloy

Fig.4 Creep rupture strength of the developed Nb-based alloys compared with the Ni-based CMSX-4 and –10, and with NbTiAl silicide DS composite.

Creep rupture properties, expressed by Larson-Miller plots, of some developed alloys has been compared with single crystal Ni-based superalloys CMSX-4 and -10, so-called as 2nd and 3rd generation alloys, respectively, and also compared with NbTiAl silicide DS composite (Jackson et al.1996) mentioned above. It can be seen that the objective of this study (more than 150 MPa in 100 h creep rupture strength at 1500 ℃) is clearly exceeded in Nb-16Si-5Mo-15W-5Hf alloy (with 5 at% C).

Providing the temperature capability as 100 h creep rupture strength under stress of 150 MPa, the capability of NbTiAl silicide DS composite is nearly the same as Ni-base CMSX-4 and is a little less than CMSX-10. This figure obviously shows that, the developed Nb-based alloys has about 400 ℃ higher temperature capability.

6. PRINCIPLE OF DEVELOPING OXIDATION PROTECTION COATINGS

The pure Nb oxidizes easily at such low temperature as 600-700 ℃ under the air and oxidizing atmosphere producing powdered oxide Nb_2O_5. Accordingly, the Nb should be said that the oxidation resistance is very poor. Unfortunately, alloying elements have not yet been found to improve radically the oxidation resistance of the Nb. Therefore, the development of coating systems has to strongly be required. Narita (2002) and Fukumoto et al. (2002) have proposed an idea of “Diffusion Barrier Coating”, which is illustrated schematically in Fig.5. In this figure, Renium (Re)-based alloy, prepared by electrochemical process, is designed as the diffusion barrier, through which inward diffusion of oxygen is perfectly suppressed and, at the same time, outward diffusion of the Nb and the other alloying elements contained in the alloys should also be prevented. On outside of the Re-based diffusion barrier, Al-rich alloy layer is prepared by cementation process, for giving a such stable protective oxide film as alumina(Al_2O_3). The Al-rich alloy layer is expected to have a self-healing property.

This idea have been applied to the coating of the developed Nb alloys. At present, the Nb alloys with this kind of Re-diffusion barrier coating have been found to have a good oxidation resistance until 1200℃, and Al-rich alloys layer, without Nb-based substrate, has given us strong expectation to be withstand to long term exposure at 1500 ℃.

7. CONCLUSIONS

The Nb-based superalloys expected to be able to apply to hot components of the gas turbine have been developed. Such strengthening mechanisms have fully been utilized as a solid solution hardening by additions of Mo and W, and a dispersion strengthening with Nb-silicide Nb_5Si_3 by addition of Si, and a carbide (Nb,Hf,Mo)C, by additions of Hf and C. Typical composition of the strongest alloy are as follows: Nb-16Si-5Mo-15W-5Hf-5C(at%) with the creep rupture life over 100 h under 150 MPa at 1500℃, and with specific strength (proof stress/density) at 1500 ℃ as 50 MPa/Mg/m^3, both of which have cleared the tentative objectives.

Further studies toward an establishment of sufficient oxidation and hot corrosion resistance of the Nb-based superalloys at such high temperature as 1500℃ is now under way based on an idea of diffusion barrier coatings.

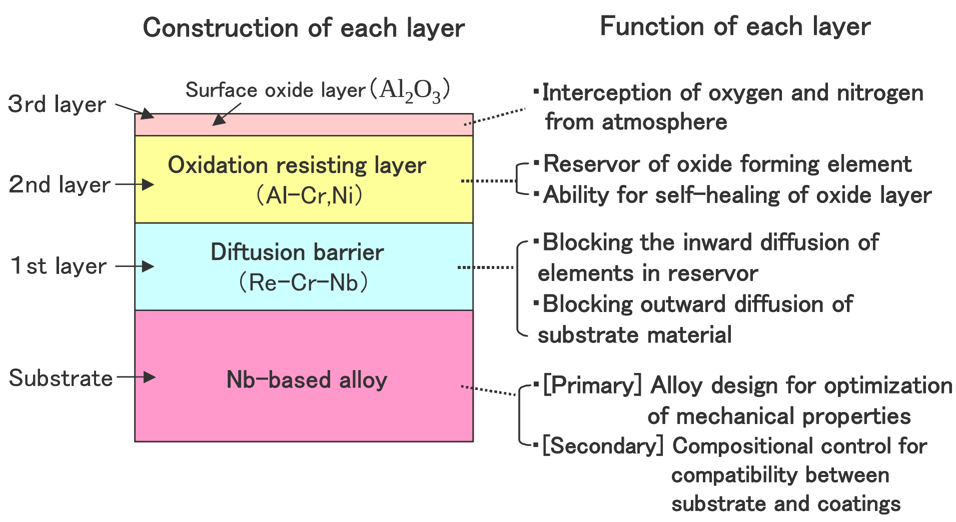


Fig.5 Principle of diffusion barrier coatings of Nb-based superalloys.

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