DEVELOPMENT OF NI-BASED DS SUPERALLOY WITH EXCELLENT OXIDATION RESISTANCE AND LCF PROPERTIES FOR POWER-GENERATION GAS TURBINES

Akira Yoshinari[1], Osam Tamura[2], Yoshinori Murata[3], Masahiko Morinaga[3]

[1]Hitachi Research Laboratory, Hitachi Co. Ltd., 7-1-1 Ohmika-cho, Hitachi, Ibaraki 319-1292, JAPAN,
[2]Power Engineering R&D Center ,The Kansai Electric Power Company Inc., 11-20 Nakoji 3-chome, Amagasaki 661- 0974, JAPAN;
[3]Department of Materials Science and Engineering, Graduate School of Engineering, Nagoya University,
Furo-cho, Chikusa, Nagoya 464-8603, JAPAN

Abstract

In advanced industrial gas-turbine systems, there is a great demand for a new, excellent superalloy which can be used for large gas-turbine blades. Because it is very difficult to produce a large-scale Ni-based Single Crystal (SC) blade, we have developed new Directionally Solidified (DS) superalloys with an excellent combination of high-temperature creep strength, low-cycle-fatigue strength, good oxidation resistance, castability and hot-corrosion resistance. In this study, three kinds of Ni-based DS superalloys were designed with the aid of the d-electrons concept. The chemical compositions of these alloys were in the range of 1.4%Ti, 8.2%Cr, 11%Co, (0-1.0)%Ru, 3.6%Ta, 9.2%W, 1.0%Re, 5.2%Al, 1.40%Hf and balanced Ni in weight percent (wt%). Creep rupture tests, hot-corrosion burner-rig tests, low-cycle-fatigue tests and oxidation tests were conducted with heat-treated DS specimens of these alloys. Two of the designed alloys showed the same level of creep rupture life as those of the 2nd generation DS superalloys currently in wide use. Oxidation tests at 1313K proved that the oxidation resistance of all the designed alloys was superior to that of all the reference alloys. The results of the hot-corrosion burner-rig tests showed that all the designed alloys had better corrosion resistance than the 2nd generation DS superalloys. As for Low-Cycle-Fatigue (LCF) strength, it was found that even 0.6%Ru addition greatly improved LCF strength, and the 0.6%Ru containing Alloy-B showed better LCF strength than any commercially used reference DS superalloys. A casting test was accomplished in a model bucket of a first stage blade of a 25MW-class gas turbine.

Alloy-B is potentially a suitable alloy for making gas turbine blades with prolonged lifetimes and low maintenance costs in recent 1500 °C-class or even higher class gas turbines for power generation.

Introduction

In recent years, combined power-generation systems have been operating at very high fuel efficiencies, but still every effort must be made to raise the efficiency further and to reduce CO_2 emissions from the system by raising the turbine-inlet temperature. Therefore, new superalloys with excellent high-temperature properties are in high demand. We have succeeded in developing excellent Ni-based SC superalloys for power generation gas turbines. However, there are still many issues in applying SC superalloys to large-scale gas turbine blades due to issues of low productivity and high cost [1]. Up to now, 3rd generation SC superalloys have not been used commercially, despite their excellent creep strength at high temperatures. The metallurgical reasons can be summarized as follows:
1) It is difficult to produce large-scale SC blades with no grain defects;
2) The oxidation resistance at high temperatures is worse than that of 2nd generation SC superalloys;
3) The phase stability is poor at high temperatures, so that topologically closed-packed (TCP) phases tend to form. These TCP phases can cause the degradation of long-term properties, which are critical for power generation gas turbines.

In order to solve the issues listed above, and provide gas turbine blades which have longer service times and lower maintenance costs, we have developed nickel-based DS superalloys, which have high creep strength comparable to that of 2nd generation DS superalloys, as well as an excellent combination of hot corrosion resistance, oxidation resistance and LCF behavior.

In this study, three superalloys with different compositions were designed using the d-electrons concept. The creep strength, hot-corrosion resistance and oxidation resistance of these superalloys were evaluated through a series of experiments. We had previously succeeded in finding SC-alloys with high creep strength, good hot-corrosion resistance and good oxidation resistance [2, 3, 4, 5]. According to the results of those experiments, we successfully developed DS superalloys which possess excellent heat resistant characteristics and high industrial applicability that can be practically used for higher inlet temperature gas turbines for power generation. In particular, the Re was limited to 1.0wt% to suppress the raw material cost of the alloys, and the amounts of Ti, Cr, Mo, W and Ta were optimized to keep high heat resistance. On the other hand, some of the designed alloys did not contain Mo, because Mo is known to deteriorate oxidation resistance. As a result, the designed DS alloy, Alloy-B, has an excellent combination of high creep strength, LCF strength, hot corrosion resistance, extremely good oxidation resistance, and good castability.

Table 1. Chemical compositions and alloying parameters of experimental alloys (wt %).

	Ti	Cr	Co	Ni	Ru	Mo	Ta	W	Re	Al	Hf	Nb	C	B	Zr	$\overline{Md}$	$\overline{Bo}$
A	1.4	8.2	11.0	Bal.	-	-	3.6	9.2	1.0	5.2	1.4	-	0.07	0.015	0.015	0.9889	0.6793
B	1.4	8.2	11.0	Bal.	0.6	-	3.6	9.2	1.0	5.2	1.4	-	0.07	0.015	0.015	0.9907	0.6826
C	1.4	8.2	11.0	Bal.	1.0	-	3.6	9.2	1.0	5.2	1.4	-	0.07	0.015	0.015	0.9919	0.6849
SR	0.7	8.3	9.2	Bal.	-	0.5	3.2	9.5	-	5.5	1.5	-	0.08	0.015	0.01	0.9811	0.6703
LR	0.7	6.2	9.3	Bal.	-	0.5	3.5	8.5	2.9	5.7	1.4	-	0.07	0.015	0.005	0.9828	0.6621
HR	2.7	14.0	10.0	Bal.	-	1.5	4.7	4.3	-	4.0	-	-	0.07	0.015	-	0.9869	0.7175
IR	4.9	14.0	9.5	Bal.	-	1.5	2.8	3.8	-	3.0	-	-	0.10	0.010	-	0.9894	0.7209
JR	1.4	14.0	11.0	Bal.	-	-	4.0	5.0	1.0	5.4	1.4	-	0.07	0.015	0.015	1.0015	0.7085
NR	1.4	6.5	11.0	Bal.	1.4	-	6.8	6.0	4.8	5.4	1.4	-	0.07	0.015	0.015	1.0108	0.6909

Experimental Procedure

Alloy Chemistry

Three Ni-based DS superalloys containing 1.4Ti - 8.2Cr -11Co - 1.4Hf - 3.6Ta - 9.2W - 1.0Re - (0-1.0) Ru - 5.2Al - Ni were designed with the aid of the d-electrons concept. Their chemical compositions are listed in Table 1. The d-electrons concept has been devised on the basis of molecular orbital calculations of electronic structures [6]. Two parameters used in this concept are Md and. Bo. Md is the d-orbital energy level of the alloying element, and Bo is the bond order between the alloying element and the Ni atoms. One of the advantages of this concept is its ability to precisely predict the alloying limits of refractory elements in view of the phase stability, even in superalloys containing high levels of Re [7]. This prediction method is well known as New PHACOMP [8-11]. Furthermore, the volume fraction of the γ' phase in the alloy is predictable through these parameters [12].

Both the $\overline{Md}$ and the $\overline{Bo}$ values for the designed alloys are shown in Table 1. They were obtained from the compositional average of the d-electron parameters, Md and Bo. The compositions of the refractory elements such as Cr, Mo, W and Ta in the alloys were adjusted so that the $\overline{Md}$ and $\overline{Bo}$ values lay in the range of $\overline{Md}$ = 0.98-0.995, and $\overline{Bo}$ = 0.67-0.69, since our previous research indicated that the target region for alloy design is located in this range [7]. As shown in the $\overline{Md}$ - $\overline{Bo}$ map (Fig. 1), the three designed alloys are nearer to the 2nd generation SC superalloys than the 14%Cr DS superalloys. In Table 1, alloys A through C are free of Mo in order to raise the oxidation resistance. Alloy-SR through Alloy-NR are the reference alloys. Alloy-SR has the same composition as MM247LC. Alloy-LR is the 2nd generation DS alloy with the same composition as CM186LC. Alloy-HR corresponds to the 14%Cr DS alloy developed in Japan, Alloy IR corresponds to the 14%Cr DS alloy developed in the US, and both alloys are now commercially used in industrial gas turbines. Alloy-JR and Alloy-NR are specially designed alloys. Alloy-JR, contenting 14%Cr, 1.4%Ti and no Mo is expected to have excellent corrosion and oxidation resistance. Alloy-NR is a kind of transition state alloy from SC to DS alloy with 1.4%Ru and 4.8%Re. Alloy-NR is expected to have high creep strength.

Alloy Preparation and Heat Treatments

First, the master ingots of these alloys were prepared in a vacuum induction furnace by carefully limiting the contents of gas elements to be as low as possible. Then, using those ingots, DS alloy ingots 100mm in width, 14mm in thickness, and 230mm in length were grown using the directionally solidified method. The conditions of the solution heat treatment and aging heat treatment are listed in Table 2. Every specimen was first heat-treated following the conditions shown in Table 2, and then used in a series of experiments.

Table 2. Heat treatment conditions

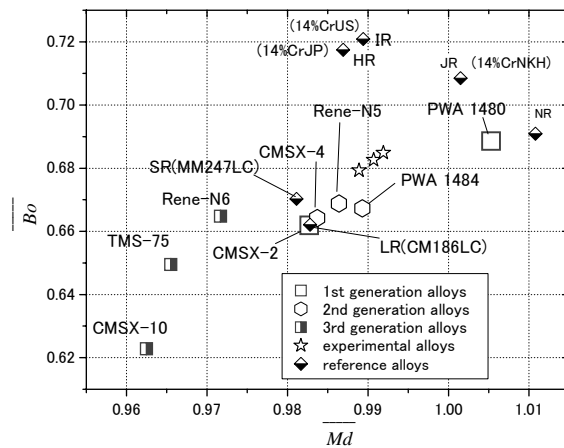| Alloy	Solution	1st Step aging	2nd Step aging
A	1513K/4h	1393K/4h,AC	1144K/20h,AC
B			
C			
SR	1503K/2h + 1523K/2h	1353K/4h,AC	1144K/20h,AC
LR	non	1353K/4h,AC	
HR	1473K/4h	1394K/2h,AC	1123K/24hr, AC
IR	non	1394K/4h,AC	1116K/24hr, AC
JR	1473K/4h	1393K/4h,AC	1144K/20h,AC

Fig. 1. $\overline{Md}$ - $\overline{Bo}$ map: the points of the designed alloys, the 2nd generation SC superalloys , the 3rd generation SC superalloys and reference DS alloys.

Microstructural Observation

The microstructures in the DS alloys were observed with SEM before and after the creep rupture tests. The cross sections of the specimens after a hot corrosion test and oxidation tests were also observed using a SEM equipped with an EDX analyzer. For these observations, the specimen surface was first mechanically polished with emery papers and then with a buff dripping water containing Al_2O_3 powders. Finally, the surface was etched chemically in a HCl-HNO$_3$ solution.

Creep Rupture and Tensile Test

The heat-treated DS alloys were mechanically machined into the specimens for the creep rupture test and the tensile test. The specimens were machined with a 30-mm gauge length and 6-mm gauge diameter. These tests were performed in accordance with the ASTM-E139 standard. The tensile tests were carried out at room temperature and 973K with a strain rate of 5.56×10^{-5}/s. The creep rupture tests were performed under the temperature/stress conditions of 1313 K/137 MPa, 1255 K/206 MPa, 1193 K/314 MPa, and 1123 K/441 MPa.

Oxidation and Hot Corrosion Test

The plate specimens 10x25x1.5 mm were cut from the DS alloys using an electro-spark machine. Two kinds of oxidation tests were employed in this study. One was the cyclic oxidation test, in which the specimens were held in air at 1373 K for 20 hours and then for 60 hours followed by air-cooling after each cycle. This cycle was repeated 12 times for each step, so the total exposure time at 1373 K was 1000 hours. Second was the continuous oxidation test at 1313 K for 3000 or 6000 hours and at 1255 K for 3,000 or 6,000 hours.

In order to examine the hot corrosion resistance of the DS alloys, a hot-corrosion burner-rig test was carried out at 1173 K for 25 hours with specimens 8 mm in diameter and 30 mm in length. The burning gas was a fuel containing 0.06% sulfur and an atomized brine of 68.4 ppm NaCl.

DS-alloy Casting of a Model Bucket

The casting test was carried out with a model bucket for the first stage of a 25MW-class gas turbine. The model bucket was 170 mm long with a return-flow type cooling structure inside it.

Low Cycle Fatigue Test

LCF tests were conducted at 1173 K in air under strain control with a constant strain rate of 0.4%/sec and two kinds of total strain (1.0% and 0.8%) were selected. The loading mode was a triangle of tensile and compression.

Experimental Results

Microstructure

It is found that the designed DS alloys were easily directionally solidified, and had no reaction with the mold. Therefore, these designed DS alloys have good castability. The solution temperature of three of the designed alloys was rather high compared to Alloy-SR. The designed alloys have no problem in the solution heat-treatment. The rates of volume fraction in solution part are 60, 70, 70% for alloys A, B, C, respectively. All of the designed alloys showed no partial solution areas. The microstructures of Alloy-A and Alloy-B after the second aging step are shown in Fig. 2. The two alloys have similar uniform γ/γ' phase microstructures, but the sizes of the γ' phases are different compared to those of the reference alloys. The size of the γ' phase is about 0.3 μm in Alloy-A and Alloy-B, and about 0.3-0.5 μm in reference alloys NR through HR, with the exception of Alloy-IR. Alloy-NR and Alloy-LR with high Re content have rather angular γ' phase microstructures.
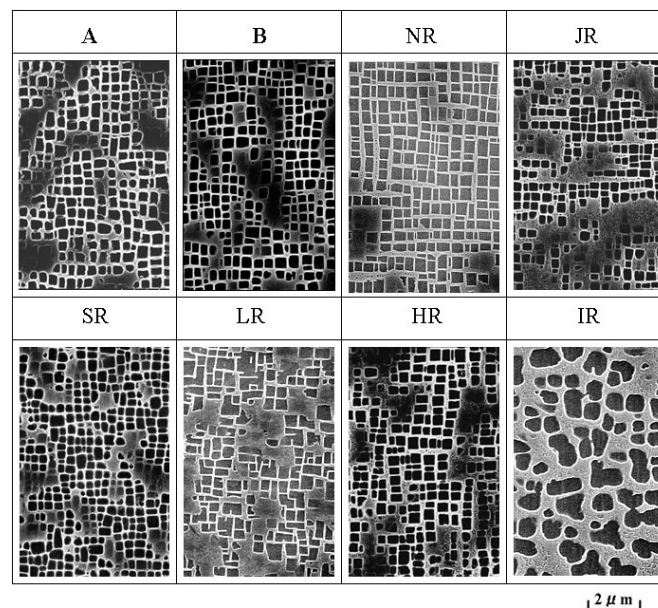

Fig. 2. SEM micrographs of round bar specimens after aging heat treatment.

Tensile Strength

The results of the tensile tests at room temperature and 973K are shown in Fig. 3 and Fig. 4, respectively. The tensile strengths at room temperature are in the range of 1000 to 1130 MPa for the designed alloys, A, B, C and the reference alloys, SR through NR, which are sufficient for the turbine blade. On the other hand, for the designed alloys, the 0.2% proof strength and the tensile strength at 973 K are in the range of 920 to 980 MPa and 1130 to 1200 MPa, respectively. The strength is higher at 973 K than at room temperature. The designed alloys are considered to possess the same level of strength as those of the reference alloys. The designed alloys also have sufficient elongation and reduction except for the elongation of alloy-A at room temperature.
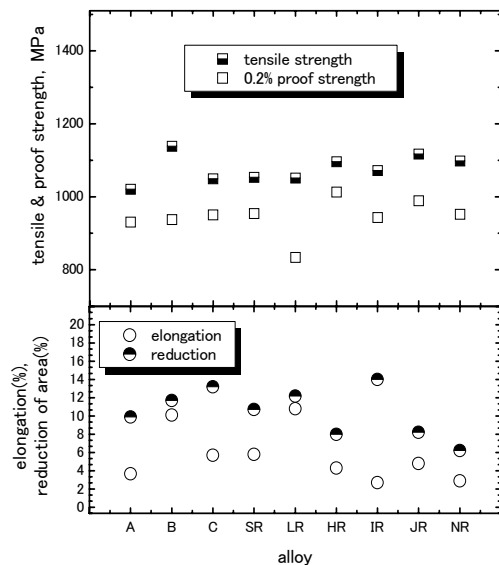
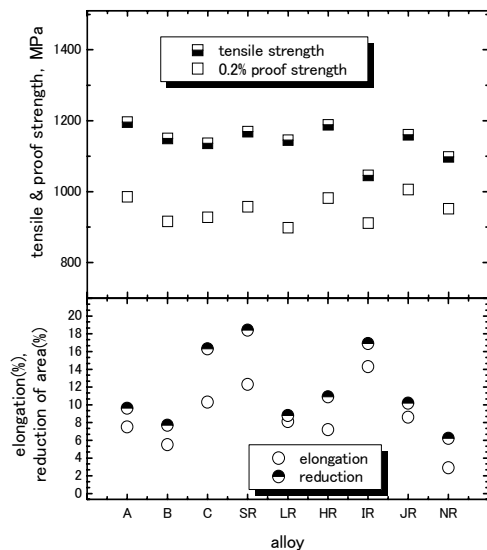Fig. 3. Results of tensile tests at room temperature.

Fig. 4. Results of the tensile tests at 973K.

Creep Strength

The results of the creep rupture tests are shown in Fig. 5. The two important creep strengths in the longitudinal direction along the grain boundary and its transverse direction are marked by L and T in Fig. 5. Unlike the tensile strength, creep strength varied according to chemical composition. The measured creep strength of Alloy-A is the best of the three designed alloys, and the creep strength decreases with increasing Ru content. Under the creep conditions of 1313 K and 137 MPa, the creep rupture life (L) of Alloy-A is about 175 hours, which is similar to the rupture life of Alloy-LR: 193 hours.

Under the creep conditions of 1255 K and 206 MPa, the creep rupture lives of alloys A, B and C are 210, 187 and 178 hours, respectively .

All of them are longer than that of Alloy-LR, 177hours. It can be clearly seen that the creep rupture strength of alloys A and B are very high in spite of the low Re content of 1.0%. As for creep strength in the T direction, all the designed alloys have about 60% of the creep rupture lives in the L direction. All the designed alloys have longer rupture lives than Alloy-SR and the three kinds of 14%Cr reference alloys: Alloy-HR, Alloy-IR and Alloy-JR. Reference alloy NR had the longest rupture life among all alloys, which seems simply to come from its rich Re content, 4.8%. Reference Alloy-HR is commercially used as a material for first stage blades in 1300 °C and 1500 °C-class gas turbines. Therefore, it can be said Alloy-A, Alloy-B and Alloy-C have adequate creep strength for 1500 °C-class or even higher temperature class gas turbines.
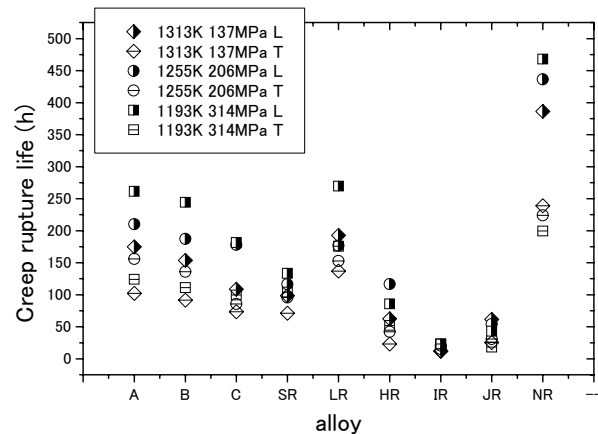

Fig. 5. Results of creep rupture tests.

Hot Corrosion Resistance

The results of mass changes in the hot corrosion test are shown in Fig. 6 for the designed alloys and the reference alloys. This hot corrosion burner rig test was performed at 1173 K for 25 hours. Every designed alloy exhibits good hot-corrosion resistance, and their mass changes are comparable to or even smaller than that of reference alloy-IR, which is the practically used 14%Cr alloy for the first stage blade of 1300 °C TRIT power generation gas turbines. For example, the mass changes of designed alloys A, B and C are very small (0.56, -0.064, and 0.66 mg/cm^2, respectively), whereas the mass changes of reference alloys SR, LR and NR are

rather large (-39.78, 2.46, and 1.66 mg/cm^2, respectively). For Alloy-HR and Alloy-IR (14% Cr alloys), materials used in the first stage blades of 1500°C and 1300°C-class TRIT power generation gas turbines, the mass changes are -0.38 mg/cm^2 and -0.92 mg/cm^2 because the corroded scale that formed on their surfaces flaked off.

The photos of the specimens after the burner rig test are shown in Fig. 7, including the three designed alloys, A, B, C and also the seven reference alloys. The corroded surfaces of these designed alloys appear smooth and the surfaces are covered with thin scales. In contrast to these designed alloys, the reference alloys (SR and LR) show very rough surfaces, which are covered by thick and ragged corroded scales. The results indicate that the hot-corrosion resistances of both of these alloys are poor. On the other hand, no such ragged corroded scale is found on the surface of the 14%Cr DS-alloys because of high corrosion resistance of these alloys. The scales on the surface probably flaked off during the test, as mentioned above.
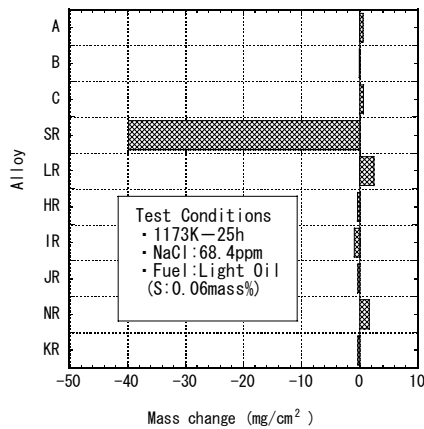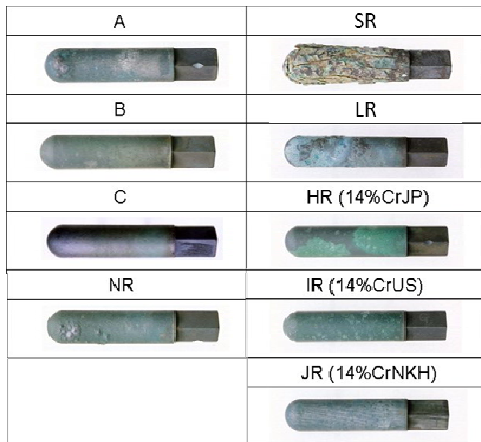

Fig.6. Results of hot corrosion burner rig tests.

Fig.7. Photos of specimens after hot corrosion burner rig tests.

Oxidation Resistance

The results of the mass changes during the continuous oxidation at 1255 K are shown in Fig. 8. There are no large differences among the designed alloys and reference alloys except for the reference alloy IR. The measured mass changes of the designed alloys are small, about +1mg/cm^2, even after the oxidation tests of 3000 and 6000 hours. On the other hand, the mass change of the reference alloy IR, namely 14%CrUS alloy, was as large as -48.6 mg/cm^2. As for the reference Alloy-HR, namely 14%CrJP alloy, the mass reduction began at 600 h and continued with exposure time. The mass change measured after 6000 hours is about -1.6 mg/cm^2. Other reference alloys' mass changes are within the range of ±1 mg/cm^2. They show good oxidation resistances at 1255 K.
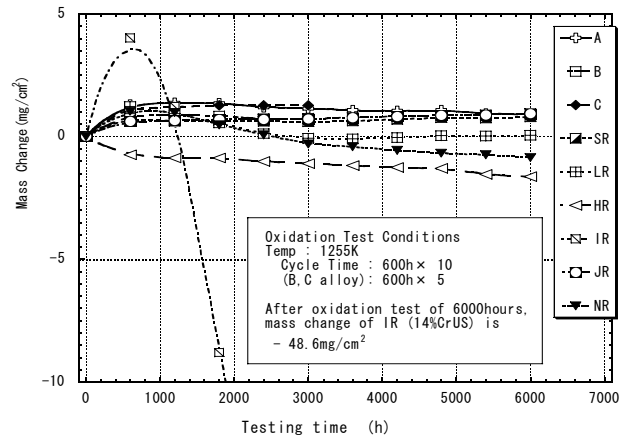

Fig. 8. Results of continuous oxidation tests at 1255K.

The results of the continuous tests at 1313 K and the cyclic tests at 1373 K are shown in Fig. 9 and Fig. 10, respectively. At 1313 K, weight reduction began more clearly in the reference alloys (SR, LR, and NR), but the degree of oxidation remains small, about -2.5 mg/cm^2, even after the 6000-hour tests. Alloy-HR shows more obvious weight reduction. Its mass change after 6000 hours is about -8 mg/cm^2. The mass change of alloy-IR is the largest, at -107 mg/cm^2. Alloys A, B, C and reference alloy JR show no weight reduction after 3000 and 6000 hours oxidation, proving to have excellent oxidation resistance at 1313 K.

At 1373 K, the trend of weight reduction in the tested alloys is markedly different from the results of 1255 K and 1313 K. The reference 14%Cr 1.4Ti DS-alloy JR has the best oxidation resistance; it shows the smallest mass change of -0.78 mg/cm^2 among the tested alloys after 1000 hours. Alloy-A and Alloy-C have the second best oxidation resistance, with weight reductions of about -2.2 mg/cm^2; this is almost the same as that of the reference alloys SR and LR. However, Alloy-B shows a fairly large weight reduction of -9.02 mg/cm^2 after 1,000 hours, which is similar to that of reference alloy HR, -12.29 mg/cm^2. The reason why only 0.6%Ru containing Alloy-B shows fairly large mass change, while 1.0%Ru containing Alloy-C has a small weight reduction of about -2.2 mg/cm^2 still remains unclear. It is supposed that Ru might have some detrimental effect on oxidation resistance under a certain condition. At 1373K, reference alloy NR suddenly shows a large weight reduction of -44.2 mg/cm^2, different from the trends of the oxidation test at 1255 K and 1313

K. On the other hand, only Alloy-NR has a rich Re content of 4.8%, which suggests that Re has severe detrimental effects on oxidation resistance especially at the high temperature of 1373 K. At any temperature, reference alloy IR shows the poorest oxidation resistance. By considering the difference of chemical compositions between Alloy-HR and Alloy-IR, it seems that the richest Ti contents of 4.9% shows the most severe detrimental effect on oxidation resistance, while it also has a highly beneficial effect on hot corrosion resistance.
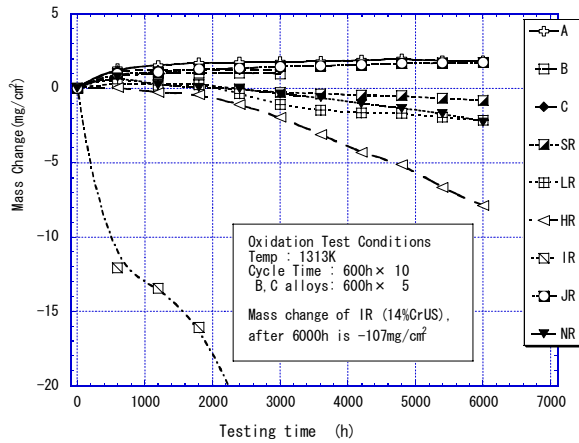

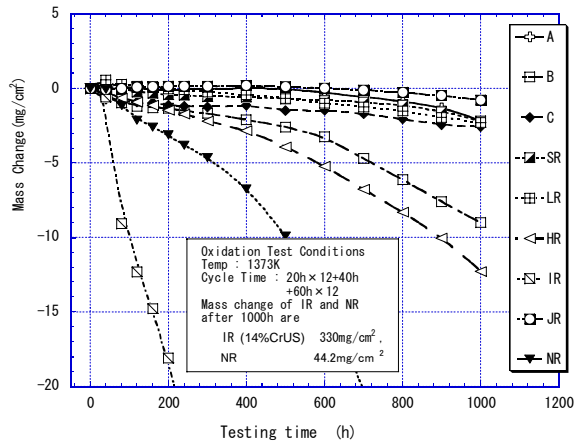Fig.9. Results of continuous oxidation tests at 1313 K.

Fig.10. Results of cyclic oxidation tests at 1373 K.

DS alloy Casting in a Model Bucket

In order to evaluate the castability of the designed DS alloy, a casting test of Alloy-A was carried out using a model bucket for the first stage blade of a 25MW-class gas turbine. We have successfully cast a DS model bucket (length: 170 mm). The blade is shown in Fig. 11. The model bucket was heat-treated following the aging condition of Alloy-A as shown in Table 2. There are no

grain boundary cracks in the blade, and no heavy reaction with the mold is confirmed. It can be seen that the typical parallel pillar-shaped DS microstructure from the wing point toward dovetail is formed.

Fig.11. Overview of the DS model bucket
(length: 170 mm)

In order to evaluate the actual strength of the cast blade, test pieces were cut from a dovetail of the DS alloy bucket. The results of the tensile tests are shown in Fig. 12, and Fig. 13, and the results of the creep tests are shown in Fig. 14.
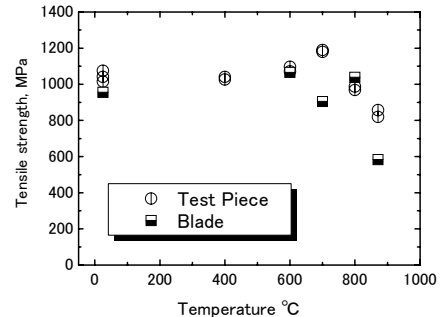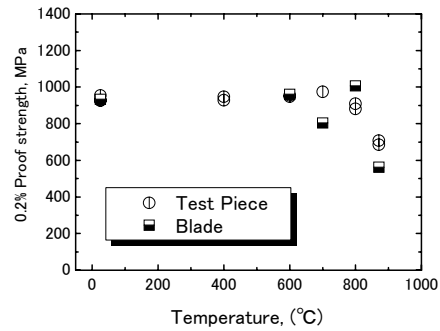

Fig. 12 and Fig.13. Results of the tensile tests of cast blade and test piece from a cast board specimen.
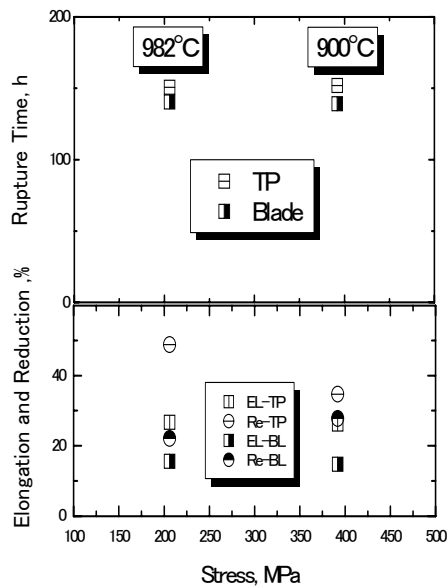
Fig.14. Results of creep tests: test piece from cast blade and cast board specimen.

Generally, there is no difference in tensile strength. At 700 °C and 900 °C, the tensile strengths of the cast blade decrease about 15-20%. On the other hand, it becomes about 10% higher than that of a test piece cut from a cast board specimen at 800 °C. As for creep strength, at test temperatures of 900 °C and 982 °C, the rupture times of the cast blade are about 6-7% shorter than those of a test piece cut from a cast board specimen. It can be seen that the cast blade had almost the same creep strength as that of the cast board specimen. However, the elongation and reduction of area of the blade decrease relative to those of the cast board specimen. It proves that the cast blade has adequate casting characteristics.

Low Cycle Fatigue Teat

The LCF tests results of experimental alloys A, and B, reference alloys SR, HR, IR, and NR, and SC alloy CMSX-4 are shown in Fig.15.
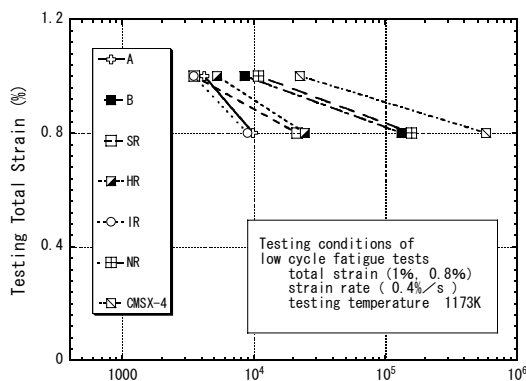

Fig. 15. Results of LCF tests of alloys A, B, and reference alloys (including CMSX-4).

Alloy-A has a fatigue strength similar to that of reference alloy IR, but unexpectedly 0.6%Ru containing Alloy-B has an excellent fatigue strength that is similar to that of reference alloy NR and even comparable with the 2nd generation SC superalloy. It is found that a small amount of Ru, even as little as 0.6%, has a greatly beneficial effect on improved LCF strength.

Discussion

Creep Strength

Great efforts have been made to enhance the creep strength of superalloys by controlling the volume fraction of the γ' phase and by increasing the contents of refractory elements such as Mo, W, Re and Ta. In fact, the total wt% of (Mo+W+Re) in 3rd generation superalloys is typically more than 10%. In addition, the lattice misfit between the γ and γ' phases is controlled to a proper value [13]. Through this approach, several SC superalloys have been developed [14].

In this study, to determine the chemical composition of DS alloys, the content of Re was first adjusted to 1.0wt%, considering the balance of its cost and effect on heat resistance characteristics, and then the chemical compositions of the designed alloys were optimized by the d-electron theory. Alloy-A is found to have the highest creep strength of all alloys with 1.0%Re and 0% Ru. Alloy-B and Alloy-C were designed with 0.6% and 1.0%Ru, respectively, to investigate the effect of Ru on all the heat resistant characteristics. As shown in Fig. 5, the addition of Ru decreases the creep strength. The addition of 0.6%Ru reduces creep strength by about 10%, and the addition of 1.0%Ru reduces it about 15%-38% in the L direction. It seems that the Ru content must be lower than 1.0% in DS alloys because of its creep strength lowering effect. The reason for this effect has not been investigated yet. In the case of SC-alloys, according to our experience, the addition of 0.6% or 1.4% Ru has no significant effect on decreasing of creep strength, both lowering and in some condition raising it, with a deviation of about 10%. The addition of 3% Ru surely enhances creep strength at any temperature [4].
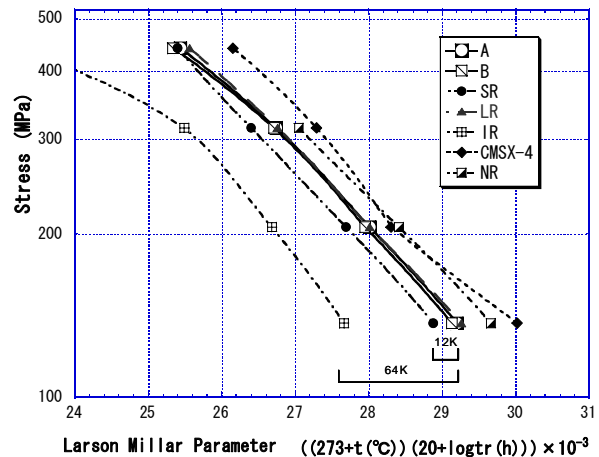

Fig. 16. Creep rupture strength of Alloy-A, Alloy-B and reference alloys (including CMSX-4).

It is noted here that alloys A and B possess high creep strength similar to that of the 2nd generation DS superalloy, Alloy-LR, as shown in Fig. 16. It has about 12K higher temperature capability than reference alloy SR and 64K higher than reference alloy IR, and also shows excellent hot corrosion resistance and oxidation resistance (Figs. 6, 7, 8 and 9).

Oxidation Resistance

According to our previous study [15], the adherent Al_2O_3 layer tends to be formed predominantly on the alloy surface in the first stage of oxidation compared to TiN, TiO_2, AlN. From this it can be inferred that the difference in the free energy of formation between TiO_2 and Al_2O_3 is not large enough. When the Ti content is higher; TiO_2 and Al_2O_3 oxides are formed competitively. Therefore, it is important to control the Ti/Al compositional ratio in order to keep good oxidation resistance.

In this study, alloys A, B, and C have the same Ti/Al compositional ratio and almost the same chemical composition. The only difference of these alloys was the Ru content, 0%, 0.6%, 1.0%, respectively. It is supposed that the oxidation resistance of these alloys is similar. According to the results of oxidation tests (1255 K and 1313 K), these three designed alloys and reference alloy JR show no weight reduction. However, at a very high temperature, 1373 K, Alloy-B with 0.6%Ru shows about 4 times the weight reduction of Alloy-A (0%Ru), and Alloy-C (1.0%Ru). The reason that only Alloy-B shows such a large weight reduction is not known yet. The oxidation test of Alloy-B was done in 2009, that of Alloy-A was done twice, in 2008 (shown in Fig. 10), and 2010, and that of Alloy-C was done in 2010. The difference in tested year might be one reason for the different results. Another possible reason is that Ru might have some detrimental effect on oxidation resistance under some conditions. Repeated oxidation testing is needed to investigate this phenomenon. As for the three reference 14%CrDS alloys, the results of oxidation tests clearly indicate that oxidation resistance is truly in inverse proportion to the Ti/Al compositional ratio. A rich Cr content has no detrimental effect on oxidation resistance. Reference alloys SR, and LR have small Ti/Al compositional ratios and generally have good oxidation resistance. Reference Alloy NR had the same Ti/Al ratio as designed alloys A, B, and C. Below 1313K it showed fairly good oxidation resistance, similar to that of Alloy LR. However, because it had rich 4.8%Re and 1.4%Ru contents, at a high temperature of 1373K, the oxidation resistance decreased next to the worst oxidation resistance Alloy-IR, because Re is an element that can deteriorate oxidation resistance [16]. Therefore, for high temperature applications, it is necessary to decide the chemical composition carefully when considering high-temperature oxidation with rich Re and Ru contents.

Hot Corrosion Resistance

All the designed alloys exhibit excellent hot-corrosion resistance. In this respect, the designed alloys are comparable to the 14%Cr reference alloys, and the hot-corrosion resistance does not decline with the addition of Ru. In our previous study [15], it is shown that sulfuration occurs prior to oxidation, and then sulfides are oxidized. It is well known that such sulfuration and subsequent oxidation reactions take place alternately and repeatedly. The surface layers penetrate deeply into the base alloy [15, 17]. Therefore, the hot-corrosion resistance will be improved if the sulfuration reaction is suppressed in some way. For example, when the Ti content of an alloy reaches a certain level, an adherent TiO_2-rich layer forms quickly on the specimen surface owing to the better thermal stability of TiO_2 relative to Cr_2O_3. In such a case, Cr is never oxidized because of the higher dissociation pressure of Cr_2O_3 compared to TiO_2. Instead, Cr interacts with sulfur to form a sulfide under the oxide layer. As a result, sulfuration does not proceed further into the base alloy, resulting in the maintenance of good hot-corrosion resistance [15]. From the EDX analyses of the designed SC-alloys in our previous study, the Cr concentration became very high in the region where sulfur was detected in the corrosive area. Although in this study EDX analyses were not conducted, the Cr content (8.2%) in the designed alloys is so high that the CrS layer is supposed to be formed in Cr-rich superalloys.

Low Cycle Fatigue Strength

Of all of the seven tested alloys, the SC-alloy CMSX-4 exhibits the best LCF strength. The second highest alloy was reference alloy NR, which contains 1.4%Ru and 4.8%Re. These results are not surprising considering the chemical compositions of these alloys. Alloy-A shows high creep strength similar to alloy-LR, but its LCF strength is the second worst, exceeded only by Alloy-IR. To improve the LCF strength of the alloy, several methods of changing chemical composition were conducted. The addition of a small amount of 0.6%Ru was considered one reasonable proposal. The result was startling, and the LCF strength is improved greatly. Alloy-B shows similar LCF strength to that of Alloy-NR. In our previous study, the LCF strength of a SC alloy can be improved by adding 3%Ru [6]. It is reported that the LCF strength is improved in the compression side cycle strength by adding Ru [18]. Although the merit of using Ru should be considered on the basis of operational conditions and the usable lifespan of the practical gas turbine blade, it is clearly seen that the method can surely improve LCF strength without decreasing the other heat resistant characteristics.

Conclusions

Ni-based DS superalloys were designed in order to develop DS alloys which are usable for the first stage blades in high-efficiency 1500°C or higher class industrial gas turbines. A series of experiments were conducted on the tensile strength, creep strength, hot corrosion resistance, hot oxidation resistance and castability. The results are summarized as follows:

1. 1.4Ti-8.2Cr-11.0Co-1.4Hf-3.6Ta-9.2W-1.0Re-5.2Al-Ni: Alloy-A has high tensile strength and excellent creep strength. It has 12K higher temperature capability than reference alloy SR and 62 K higher than reference alloy IR (14%CrUS-alloy). Alloy-B with 0.6%Ru addition has 9K higher temperature capability than reference Alloy-SR and 59K higher than reference Alloy-IR.

2. The three designed alloys exhibit excellent oxidation resistance similar to that of reference alloys SR and LR. It is possible to improve oxidation resistance greatly even in 14%CrDS alloys with the addition of 1.0% Re by optimizing the Ti/Al compositional ratio.

3. The three designed alloys have higher hot corrosion resistance than reference alloy LR. Although it has rather lower hot corrosion resistance than the 14Cr DS alloys, it is considered to be enough for almost all LNG fuel GAS turbines applications in Japan.

4. There is no inherent problem of castability in the designed DS alloys. A model bucket 170 mm in length was successfully grown using Alloy-A for the first stage blade of a 25MW-class industrial gas turbine.

5. It is found that the addition of 0.6%Ru has a dramatic effect in improving LCF strength. Alloy-B has the third best LCF strength next to Alloy-NR and SC alloy CMSX-4.

The designed alloy B is considered a potential candidate for gas turbine blades with excellent prolonged life times and low maintenance costs for recent 1500°C-class or higher class gas turbines for power generation.

Acknowledgments

References

[1] Y. Yoshioka, "Feramu ", *The monthly journal of The Iron and Steel Institute of Japan*, 11(2006) 8-14.

[2] A. Yoshinari, R. Hashizume, Y. Murata and M. Morinaga, "Development of the third generation single crystal superalloy for power generation gas turbines" (Proceeding of 8th Int. Gas Turbine. Conf. 2003 Tokyo (IGTC2003), edited by T. Watanabe, Gas Turbine Society of Japan, Tokyo).

[3] R. Hashizume, A. Yoshinari, T. Kiyono, Y. Murata, M. Morinaga, "Development of Ni-based Single Crystal Superalloys for Power-generation Gas Turbines" (Proceedings of the Tenth International Symposium on Superalloys 2004, edited by Kenneth A. Green, Tresa M. Pollock, and the TMS Seven Springs International Symposium Committee).

[4] R. Hashizume, A. Yoshinari, T. Kiyono, Y. Murata, M. Morinaga, "Development of Ni-based Single Crystal Superalloys for Power-generation Gas Turbine Blades", *Materials for Advanced Power engineering 2006*, (2006), 273-286.

[5] R. Hashizume, A. Yoshinari, T. Kiyono, Y. Murata, M. Morinaga, "Development of Ni-based Single Crystal Superalloys for Power-generation Gas Turbine Blades", (Proceeding of 9th Int. Gas Turbine. Conf. 2007 Tokyo, edited by T. Watanabe).

[6] M. Morinaga, N. Yukawa and H. Adachi, "Alloying Effect on the Electronic Structure of Ni_3Al (γ')," *J. Phys. Soc. Japan*, 53 (1984), 653-663.

[7] Md. Moniruzzaman, Y. Murata, M. Morinaga, R. Hashizume, A. Yoshinari and Y. Fukui, "Alloy Design of Ni-Based Single Crystal Superalloys for the Combination of Strength and Surface Stability at Elevated Temperatures," *ISIJ International*, 43 (2003), 1244-1252.

[8] M. Morinaga, N. Yukawa, H. Ezaki and H. Adachi, "Solid Solubilities in Transition-Metal Based FCC Alloys", *Phil. Mag.*, A51 (1985), 223-246.

[9] M. Morinaga, N. Yukawa, H. Ezaki and H. Adachi, "Solid Solubilities in Nickel-Based FCC Alloys", *Phil. Mag.*, A51 (1985), 247-252.

[10] M. Morinaga, Y. Murata and H. Yukawa, "Recent Progress in the New PHACOMP Approach", *Materials Design Approaches and Experiences*, edited by J.-C. Zhao, M. Fahrmann and T.M. Pollock, TMS (The Minerals, Metals & Materials Society), (2001), 15-27.

[11] M. Morinaga, N. Yukawa and H. Adachi, "New PHACOMP and Its Application to Alloy Design", *Superalloys* 1984, edited by M. Gell, MC.S. Kortovich, R.H. Bricknell, W. B. Kent and J.F. Radavich, The Metallurgical Society of AIME , 1984, pp.523-532.

[12] Y. Murata, S. Miyazaki, M. Morinaga and R. Hashizume, "Hot Corrosion Resistant and High Strength Nickel-Based Single Crystal and Directionally-Solidified Superalloys Developed by the d-Electrons Concept", *Superalloys*1996, edited by R. D. Kissinger et al., The TMS, (1996),.61-70.

[13] H. Harada, "Materials Design" (Report of the 123 Committee on Heat-Resisting Metals and Alloys), *Japan Society for the Promotion of Science*, 28 (1997), 185-196.

[14] T. Hino, Y. Yoshioka, Y. Koizumi, T. Kobayashi and H. Harada, "TMS-82+: A High Strength Ni-Base Single Crystal Superalloy", *Materials for Advanced Power engineering* 2002, ed. By J. Lecomte-Beckers et al., Forchungszentrum, Julich GmbH, (2002), 303-312.

[15] Y. Murata, R. Hashizume, A. Yoshinari, N. Aoki, M. Morinaga and Y. Fukui, "Alloying Effect on Surface Stability and Creep Strength of Nickel Based Single Crystal Superalloys containing 12mass%Cr", *Superalloys* 2000, edited by T.M. Pollock et al., The TMS, (2000) 285-294.

[16] Md. Moniruzzaman, M. Maeda, Y. Murata and M. Morinaga, "Degradation of High-Temperature Oxidation Resistance for Ni-Based Alloys by Re Addition and the Optimization of Re/Al Content", *ISIJ International*, 43(2003), 386-393.

[17] F.S. Pettit and G.H. Meier, "Oxidation and Hot Corrosion of Superalloys," *Superalloys1984,* edited by M. Gell et al., *The Metallurgical Society of AIME*, (1984), 651-687.

[18] N. Tsuno, K. Kakehi, CMF.RAE, and R. Hashizume, "Effect of Ruthenium on Creep Strength of Ni-Base Single-Crystal Superalloys at 750 °C and 750 MPa," *Metallurgical and Materials Transactions A,* 40A (2009), 269-272.