DEVELOPMENT OF LOW OR ZERO-RHENIUM HIGH-PERFORMANCE Ni-BASE SINGLE CRYSTAL SUPERALLOYS FOR JET ENGINE AND POWER GENERATION APPLICATIONS

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Abstract

Advanced superalloys with high levels of Re and Ru have difficulties with cost and having a stable supply for application in industry. Accordingly, 1.2 wt. % Re alloy TMS-286 and Re-free alloy TMS-1700 have been developed for aero engine and power generation applications. These alloys showed well-balanced hot corrosion resistance, creep strength, and thermo-mechanical fatigue (TMF) life. An optimized content of Re, Si and Mo improve the hot corrosion resistance, oxidation resistance and TMF life, respectively, without degrading creep properties.

Introduction

The 4th generation Ni-base superalloys, which contain Re and Ru, have achieved an average of more than 30 °C higher temperature capability [1,2] than those of the previous generation in terms of high-temperature creep strength, because Ru suppresses formation of topologically closed packed (TCP) phase precipitation [3]. The 6th generation superalloy TMS-238 [4] also contains Re and Ru, but Mo is reduced to optimize the microstructure stability, and so the oxidation resistance is improved and temperature capability of 1117 °C has been achieved. However, these advanced superalloys have high cost and unstable supply.

For recent jet engine applications, turbine blade materials with higher corrosion resistance, lower density and lower cost are required. Needless to say, degradation of mechanical properties is undesirable. In contrast, for power generation applications, thermo-

mechanical fatigue (TMF) properties are most important because of the frequent starting and stopping. Blades used in power generation gas turbines are much larger than that of aero engines, so the material cost is a significant concern.

In this study, lower or zero rhenium and zero ruthenium superalloys that have higher mechanical properties than 1st generation superalloys have been developed for the jet engine and power generation applications.

The 1st generation superalloy, TMS-6 [5], was used as the base material. This was the first alloy which was developed by using the Alloy Design Program (ADP) [6] in NIMS, in 1984. This alloy does not contain strengthening elements such as Mo and Re, but has excellent creep properties. Corrosion resistance and TMF properties of this alloy were improved without decreasing the creep properties.

Experimental Procedure

Two alloy series were developed in this study, using the ADP. One is designed to have better corrosion resistance and equivalent mechanical properties compared with the conventional 2nd generation superalloys for use in jet engine applications. TMS-286 [7] is the alloy, which contains only 1.2 wt. % of Re to improve corrosion resistance. Nb and Si are added to reduce the density and improve the oxidation resistance. TMS-277 and TMS-285 are alloys that were designed before TMS-286 to improve corrosion

Figure 1. Flow of Alloy Development.

resistance by adding Re and to reduce density by substituting Nb for Ta.

The other alloy series was designed to have better TMF properties and to be equivalent in other properties to the conventional 1st generation superalloys for use in power generation applications. TMS-278 and TMS-1700 were designed for this application. 1.2 wt. % of Mo was added to TMS-6 to become TMS-278, and was optimized at 0.6 wt. % to become TMS-1700.

A flow chart of the alloy development in this study is illustrated in Figure 1. Compositions of alloys developed in this study are shown in Table I with commercial superalloys as reference. Density, fraction of γ' , lattice misfit, Solubility Index (SI) [8], liquidus temperature, solidus temperature and temperature window of solution heat treatment calculated by the ADP are also shown in the

same table. The temperature used in the calculation was 900 °C. Temperature of the turbine blades in service varies wide range depends on the part of the blade and operating conditions. 900 °C is considered to be a typical operating temperature of a blade and NIMS uses this temperature as a standard for the alloy design. New alloys were designed to have similar fraction of γ' and similar or larger negative misfit to the base alloy, in order to avoid degradation of creep properties. SI value relates to phase stability. A larger value of SI means an increase in the possibility of topologically closed packed (TCP) phase formation. The temperature window of solution heat treatment is also an important factor for the production of castings. PWA1480 and René N4 are calculated to have a negative value of the solution heat treatment temperature window. This fact means that full solution heat treatment is difficult in these alloys. Alloys developed in this study were designed to have required mechanical and environmental

Table I. Nominal Compositions of Alloys (Ni bal.)

Alloy	Composition (wt%)											Density (g/cm ³)	Fract. Gp (-)	Misfit (%)	SI (-)	Liq. Temp. (° C)	Sol. Temp. (° C)	SHT Window (° C)
	Co	Cr	Mo	W	Al	Ti	Nb	Ta	Hf	Re	Si							
TMS-6	-	9.2	-	8.7	5.3	-	-	10.4	-	-	-	8.9	0.66	-0.082	1.217	1395.3	1336.4	10.2
TMS-277	-	9.0	-	8.0	5.4	-	-	10.0	-	1.2	-	8.92	0.66	-0.090	1.221	1394.5	1332.9	9.9
TMS-285	-	9.0	-	8.0	5.4	-	2.3	5.8	-	1.2	-	8.74	0.66	-0.178	1.193	1389.5	1318.8	18.2
TMS-286	-	9.0	-	8.0	5.4	-	2.3	5.8	-	1.2	0.15	8.73	0.68	-0.221	1.218	1389.6	1319.1	19.0
TMS-278	-	9.0	1.2	8.0	5.4	-	-	10.0	-	-	-	8.88	0.70	-0.208	1.319	1393.0	1334.5	11.1
TMS-1700	-	9.0	0.6	7.6	5.4	-	-	10.0	-	-	-	8.84	0.66	-0.115	1.202	1393.4	1336.7	17.8
SRR99	5.0	8.5	-	9.5	5.5	2.2	-	2.8	-	-	-	8.51	0.64	-0.074	1.074	1398.1	1310.0	29.1
PWA1480	5.0	10.0	-	4.0	5.0	1.5	-	12.0	-	-	-	8.7	0.68	-0.053	1.266	1377.7	1288.9	-37.0
RenéN4	8.0	9.0	2.0	6.0	3.7	4.2	0.5	4.0	-	-	-	8.53	0.57	-0.234	1.380	1376.6	1250.1	-16.5
RenéN500	7.5	6.0	2.0	6.0	6.2	-	-	6.5	0.6	-	-	8.61	0.69	-0.265	1.082	1408.4	1351.6	66.5
CMSX-4	9.6	6.4	0.6	6.4	5.6	1.0	-	6.5	0.1	3.0	-	8.75	0.65	-0.100	1.184	1405.8	1317.8	30.9

Figure 2. Metal losses in hot corrosion crucible test at 900 °C.

properties while considering density, possibility of TCP formation and temperature window.

Single crystal samples were produced using vacuum induction melting and fabricated using a standard directional solidification casting furnace. Samples were 10 mm diameter cylindrical bars with orientations within 10 degrees of the [001] orientation. Solution and age heat treatments were applied; residual eutectic and TCP phases were not observed in the microstructures. Creep-test specimens of 4 mm in diameter and 22 mm in gauge length were machined in the [001] direction from the heat-treated samples, and creep rupture tests were conducted to rupture under the following conditions: 800 °C/735 MPa, 900 °C/392 MPa, 1000 °C/245 MPa and 1100 °C/137 MPa. Specimens with their longitudinal directions within 5 degrees of <001> orientation were machined for the TMF test. The gauge section of the specimens was 5 mm in diameter and

15 mm in length. TMF testing was carried out under the out-of-phase condition, with compression at 900 °C for 1 h dwell time/tension at 400 °C, and strain range was $\pm 0.64\%$. High temperature cyclic oxidation tests were conducted at 950 °C and 1100 °C in air, with 1 hour per cycle. Specimens were machined to 9 mm in diameter and 5 mm in thickness, and the surfaces were finished with 600-grade SiC paper polishing followed by cleaning with ethanol. Specimen weight change was measured at the end of each cycle. Hot corrosion properties were investigated. Specimens measuring 9 mm in diameter by 5 mm in thickness were soaked into 75 % Na₂SO₄+25 % NaCl molten salt at 900 °C for 20 hours. Metal losses in thickness were calculated from weight losses after a 20 hour soak.

Results and Discussion

Figure 3. Cross sectional SEM images of (a) TMS-285, (b) TMS-286 and (c) CMSX-4 after 1100 °C for 250 cycles.

Figure 4. Cyclic oxidation test at 1100 °C.

Low rhenium alloy for jet engine applications

Figure 2 shows the result of a hot corrosion crucible test. Smaller metal losses were seen in the Re modified alloys TMS-277, 285 and 286, while TMS-6 experienced much larger metal loss by orders of magnitude. It is clear that the addition of 1.2 wt. % Re is extremely effective at improving the hot corrosion resistance and the addition of Si does not degrade hot corrosion resistance. Moreover, cyclic oxidation tests at 1100 °C showed that the oxidation resistance was improved by Si additions. Cross-sections of the oxide scale after 250 cycles of 1100 °C cyclic oxidation test are displayed in Figure 3. Thin and adhesive Al_2O_3 protective oxide is formed in TMS-286 while CMSX-4 forms a thick spinel layer at the surface. Figure 4 shows the oxidation resistance at 1100 °C. Oxidation behavior of TMS-285 is poorer than that of TMS-277 due to Nb substitution for Ta, but an addition of 0.15 wt. % Si recovered the behaviour of TMS-286.

Figure 5 illustrates the creep curves at 800 °C/735 MPa, 900 °C/392 MPa, 1000 °C/245 MPa and 1100 °C/137 MPa. Creep rupture life of TMS-286 is inferior to TMS-6 and slightly superior to CMSX-4 in the 1100 °C/137 MPa test condition. SEM observation of fractured specimens is shown in Figure 6. The fracture of alloy

TMS-286 was initiated by TCP phase precipitation during high temperature creep. More TCP phase was found and creep rupture lives were deteriorated in TMS-286 + 0.1 wt. % Si compared to TMS-286. Additions of Si are effective at improving the oxidation resistance further, but it seems to enhance TCP formation during high temperature creep, thus it is necessary to find the optimal amount of Si for obtaining both excellent oxidation and mechanical properties.

Figure 7 displays the relationship between hot corrosion resistance and creep properties. TMS-286 has well-balanced corrosion resistance and mechanical strength compared with CMSX-4 and SRR99, despite having lower Re content than that of CMSX-4.

Zero rhenium alloy for power generation applications

Creep properties of TMS-1700 are shown in Figure 8. Creep rupture lives of TMS-1700 are inferior to those of TMS-6, but similar or superior to TMS-286 and René N500, and superior to CMSX-4 at 800 °C/735 MPa and 1100 °C/137 MPa conditions.

Figure 5. Rupture life of TMS-286 in (a) 800 °C/735 MPa, (b) 900 °C/372 MPa, (c) 1000 °C/245 MPa, and (d) 1100 °C/137 MPa conditions.

(a) 1000 °C/245 MPa

(b) 1100 °C/137 MPa

Figure 6. Microstructure of the fracture specimens in which brighter phases are TCP.

Figure 7. Relationship between hot corrosion resistance and creep properties at 1100 °C.

Figure 8. Rupture life of TMS-1700 in (a) 800 °C / 735 MPa, (b) 900 °C / 372 MPa, (c) 1000 °C / 245 MPa, and (d) 1100 °C / 137 MPa conditions.

Figure 9. Cyclic oxidation properties of TMS-1700 at (a) 950 and (b) 1100 °C.

Oxidation behavior at 950 °C and 1100 °C is shown in Figure 9. Cyclic oxidation resistance of TMS-1700 is superior to that of PWA1480 at 950 °C. At 1100 °C, it is slightly poorer than TMS-6 and CMSX-4, but is clearly better than René N4 and PWA1480.

Figure 10 shows the relationship between TMF and creep properties. Mo was added to TMS-6 in order to improve TMF. TMS-278 contains 1.2 wt. % of Mo, but this value was too high as creep and TMF properties were deteriorated from TMS-6. The relatively larger SI value of TMS-278 shown in Table 1 encourages

TCP formation. The Mo and W content of TMS-1700 were modified to optimize the microstructural stability and γ/γ' lattice misfit. Creep rupture life at 1100 °C/137 MPa and TMF life were improved from TMS-278, and showed greater balance in these properties than CMSX-4 and conventional 1st generation superalloys, PWA1480 and René N4.

A large-scale single-crystal imitation blade of 300 mm in length was cast to confirm the castability of TMS-1700 for power generation applications. In order to improve the crystal integrity of the large-scale single-crystal growth in the casting process, a high

Figure 10. Relationship between TMF property and creep property at 1100 °C.

Figure 11. Microstructure of large-scale imitation blade.

thermal gradient casting furnace was used. Casting conditions such as casting temperature, casting speed and so on were optimized to enhance crystal growth in the [001] direction. Microstructure observation of the large-scale blades in the trial castings was carried out and the SEM images are displayed in Figure 11. Uniform and fine dendrite formation and γ/γ' coherent structure with minimized defects were observed. Orientation of the crystal growth was within 10 degrees of the [001] orientation. Surfaces of etched blades were inspected and it was confirmed that the blades did not exhibit grain anomalies, such as freckles or bicrystals. These results give the promise of high performance of TMS-1700 in gas turbine blade applications for high-efficiency power generation.

Conclusions

1.2 wt. %-Re alloy TMS-286 and Re-free alloy TMS-1700 have been developed. Hot corrosion resistance and oxidation resistance of TMS-286 were improved by additions of Re and Si, for aero engine applications. TMS-1700 was designed to have well-balanced TMF and creep properties by optimizing Mo content, for power generation applications. This study confirmed that alloy design of Ni-base single crystal superalloys with various criteria, such as improved oxidation/corrosion resistance, reduced density, improved TMF, mechanical property and composition constraints, is possible.

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