ALLOY DESIGN FOR HIGH STRENGTH NICKEL-BASE SINGLE CRYSTAL ALLOYS

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Summary

The purpose of this study is to develop high strength nickel-base single crystal alloys for gas turbine blades. A computer-aided alloy design system previously developed in NRIM is applied for this purpose.

Five alloys were designed; chemical compositions of the alloys were calculated with respect to following four factors, 1) precipitation hardening: volume fraction of γ' was fixed at 65 or 75 vol%, 2) solid solution hardening: proportions of solutioning elements were optimized by a regression equation, 3) phase stability: solubility index was fixed at its maximum(1.32 or 1.37) for alloys to be composed of stable γ and γ' , 4) hot corrosion resistance: Cr content was set in the range of 5-10 wt%. Other important factors such as lattice mismatch, density, melting point, etc. were also calculated by the alloy design program.

Five alloys thus designed, TMS-1, etc. contained 5-10Cr, 8-19W, 5-6Al, 3-12Ta, 0 or 7Co(in wt%), and no other elements except for Ni. Test pieces were prepared by single crystal solidification techniques. All alloys except one could be solutioned perfectly without incipient melting. Creep rupture tests were carried out after the solution heat treatments followed by two-step aging treatment.

Creep rupture strengths of designed alloys were superior to those of existing alloys such as ALLOY 454 and NASAIR 100. For instance, at a condition of 1040°C-14kgf/mm², rupture lives of designed alloys were about 1000-2000 hrs whereas those of existing ones were estimated to be about 500 hrs or less. Designed alloys were found to have excellent specific creep rupture strength(corrected by density) as well. The creep deformation behavior is discussed. It has been found that accelerated creep deformation occurs by a double slip system whose glide planes are (111) and ($\bar{1}11$).

Introduction

An alloy design system was previously established in NRIM for γ' precipitation hardening nickel-base superalloys[1,2]. By this calculating system, several successful alloys have been produced. The alloys have superior temperature capabilities as well as other properties required for conventionally cast(CC) or directionally solidified(DS) gas turbine blades. These alloys are under investigations for their practical use in the LNG-driven advanced gas turbine to be constructed in the "Moonlight" national project of Japan[3].

In the present paper, the alloy design system is now applied to research and developing for high strength nickel-base single crystal(SC) alloys. Some promising alloys are designed and evaluated in term of creep rupture strength. Structural study is also carried out with the help of X-ray Laue analysis. The lattice rotation is discussed in connection with morphological change of γ' precipitate.

Alloy Design

There are several alloys designed for use as single crystal gas turbine blades. Representatives of them are ALLOY 454[4,5], NASAIR 100[6], CMSX-2 [7,8], etc. Because of absence of grain boundary strengthening elements, C, B, Zr, and Hf, the alloys can be solutioned perfectly at high temperatures, and this brings about their excellent high temperature strengths. Our alloy design for SC alloys basically stands on the above principle.

There are two fundamental strengthening mechanisms for γ' precipitation hardening nickel-base superalloys, precipitation hardening and solid solution hardening. Effects of the two mechanisms were evaluated separately in our previous study on CC alloys[2], and it has been clear that both two mechanisms are highly effective to obtain alloys with superior creep rupture strength. For instance, it was found that creep rupture life of the CC alloy at 1000°C-12kgf/mm² could be expressed as a function of γ' chemical composition(solid solution hardening) and γ' volume fraction(precipitation hardening), as eq.1. The equation predicts superior rupture strength for alloys containing low Cr, high W, and high Ta, and containing large amount (up to 86 vol%) of γ' .

$$\begin{aligned} \text{Log[Rupture life(hr) at 1000°C-12kgf/mm}^2, \text{ CC alloys]} \\ = \text{Const. } -0.110\text{Cr(at\% in } \gamma') + 0.164\text{W(at\% in } \gamma') \\ + 0.102\text{Ta(at\% in } \gamma') + \dots\dots\dots \\ + 0.095\gamma'(\text{vol\%}) - 0.00055[\gamma'(\text{vol\%})]^2 \end{aligned} \quad \text{-----(1)}$$

Based on the above consideration, our single crystal alloy design was carried out with intention to have alloys of extremely solid solution hardened γ and γ' , at their fractions optimum for both solution treatment and strengthening of the alloys. Five alloys were designed using our alloy design system; chemical compositions of the alloys were calculated with respect to following four factors.

- 1) Precipitation hardening: Volume fraction of γ' was fixed at 65 or 75vol%, the largest fractions expected to be solutioned perfectly.
- 2) Solid solution hardening: Proportions of solutioning elements were optimized by the regression equation(eq.1). Although the equation was established properly for conventionally cast(CC) alloys, rupture life calculated can be used as a criterion for high temperature strength of single crystals.
- 3) Phase stability: Solubility Index(SI) defined by eq.2 was fixed at its

Fig. 1. Pseudo-quaternary Phase Diagram showing the Composition Range in which Alloys Designed are lying. X and Y represent Solid Solution Elements, Cr, W, Ta, etc.

Table I. Nominal Chemical Compositions of Designed(TMS-) and Existing Alloys, with Structural Factors(as SC) and Creep Rupture Lives (as CC alloys) Predicted.

Alloy	Chemical Composition (wt%)							γ' (vol%)	SI	LM [*] (%)	D (g/cm ³)	Life ^{**} (hr)
	Co	Cr	Mo	W	Al	Ti	Ta					
TMS- 1	7.5	5.5	-	16.6	5.2	-	5.1	65	1.37	.32	9.16	1450
TMS- 2	7.3	5.5	-	18.6	5.3	-	3.4	65	1.37	.17	9.16	1470
TMS-12	-	6.6	-	12.8	5.2	-	7.7	65	1.32	.49	9.07	1190
TMS- 6	-	9.2	-	8.7	5.3	-	10.4	75	1.37	.28	8.90	820
TMS-13	-	5.4	-	9.4	5.5	-	12.1	75	1.37	.78	9.08	1870
NASAIR 100	-	9.0	1.0	10.5	5.75	1.2	3.3	69	1.15	-.04	8.59	550
CMSX-2	4.6	8.0	0.6	7.9	5.6	0.9	5.8	64	1.09	.39	8.61	460
ALLOY ^{***} 454	5.0	10.0	-	4.0	5.0	1.5	12.0	>80	>1.32	<.28	8.67	>430
RR SR99 ^{****}	5.0	8.5	-	9.5	5.5	2.2	2.8	68	1.10	.25	8.50	460

* Lattice mismatch(%) = $[(a_{\gamma'} - a_{\gamma}) / a_{\gamma}] \times 100$

** Predicted values by assuming CC structure from the given composition, at 1000°C-12kgf/mm²(118 MPa), by eq.1.

*** Exact solution can not be calculated for factors and life.

**** Chemical composition is from ref.[9]

maximum(1.32 or 1.37) for alloys to be composed of stable γ and γ' .

$$SI = \sum_i (C_i / CL_i) \quad \text{-----} \quad (2)$$

C_i : concentration(at%) of i'th element in γ' of alloy

CL_i : solubility limit(at%) of i'th element in γ' (Ni₃Al)

i : Cr, Mo, W, Ti, Nb, Ta, and Hf

4) Hot corrosion resistance: Cr contents of the alloys were set in the range of 5 to 10 wt% to attain minimum hot corrosion resistance required.

Other important factors such as lattice mismatch, density, melting point, and so on were also calculated in the alloy design program and were taken into consideration for alloy selection.

Chemical compositions of alloys thus designed are presented schematically in Fig. 1. Nominal chemical compositions of the alloys, TMS-1, TMS-2, TMS-6, TMS-12, and TMS-13, are shown in Table I, with those of representative existing alloys. Structural factors and creep rupture lives(as CC alloys) predicted are also shown in the table. Although the creep rupture lives predicted are not for the single crystal but for the conventionally cast structure, it is to be remarked that rupture lives for designed alloys are longer than those of existing alloys.

Solidification and Heat Treatment

Test pieces of alloys designed were prepared by single crystal solidification techniques; each melting stock of the alloys was remelted and then directionally solidified in a mold with a narrow path called selector between the starter part and test piece. Solidification rate was 200mm/hr for all alloys.

Fig. 2. Solution Heat Treatment Ranges, "Windows", of Alloys Designed.

Fig. 3. Creep Rupture Lives of Existing and Developed Alloys.

Solution heat treatment ranges, "windows", of alloys designed were examined. The specimens were heated for 4 hrs at various temperatures between 1300°C and 1372°C. From microstructural observation of the heated specimens, width of the "windows" were measured and are shown in Fig.2. It is clear that all alloys except one have sufficient "windows". The exceptional alloy, TMS-13, contains relatively high amount of Ta and low amount of Cr, and also contains high amount of γ' ; all these are considered to result in formation of significant amount of eutectic γ - γ' which can not be solutioned up to 1360°C, and at this temperature the incipient melt occurs. It is to be remarked that "windows" of alloys TMS-1 and TMS-2 are very wide (more than 72°C) in comparison with those of existing alloys, ALLOY 454 and CMSX-2, whose "windows" are reported to be about 28°C in width [4,7].

Based on the above examination, alloys TMS-1, TMS-2, TMS-12, and TMS-13 were solutioned for 4 hrs at 1348°C, although TMS-13 was solutioned imperfectly. TMS-6 was solutioned for 4 hrs at 1324°C. All solution treatments were followed by the current two step aging treatment (982°C x 5hrs, AC. and 870°C x 20hrs, AC.) [6].

On the structural stability, small amount of plate like precipitate was observed in heat treated alloy TMS-2 which has highest W concentration (18.6 wt% W). Alloy TMS-1 (16.6 wt% W) had a same trend, but, if any, the amount was quite small.

Creep Rupture Strength

Creep rupture tests were carried out at conditions of 1040°C-14kgf/mm² (137 MPa) and 900°C-40kgf/mm² (392 MPa). Fig.3 shows creep rupture lives of alloys designed, in comparison with those of existing alloys, at 1040°C. It is clear that alloys designed in this study have excellent creep rupture strengths when solutioned perfectly. Alloy TMS-13, which could not be solu-

Fig. 4. 1000 hr Specific Creep Rupture Strength of Existing and Developed Alloys.

tioned perfectly, has poor strength. Alloy TMS-6 showed extremely poor strength when tested without heat treatment, the rupture life being 91 hrs at the same condition. From the facts, it is confirmed that the heat treatment has serious effect on the high temperature strength of single crystal alloys. At the condition of 900°C-40kgf/mm²(392 MPa), alloys TMS-1, TMS-2, TMS-6, and TMS-12 had also creep rupture lives longer than those of existing alloys.

The advantage of alloys designed in creep rupture strength over existing alloys is attributed to the solid solution hardening effects of W and Ta on both γ and γ' . W and Ta are, however, the heaviest(in atomic weight) elements used in nickel-base superalloys, and they increase alloy density. This is a demerit for alloys used as turbine blades operated under the centrifugal stress. Therefore, it is most reasonable for the alloys to be evaluated by specific creep rupture strength corrected by density.

In Fig. 4, a comparison is made among alloys TMS-1, a representative of designed alloys, and ALLOY 454[5], NASAIR 100[6], and Mar-M247(containing C, B, Zr, and Hf)[6], using the specific rupture strength. It is well indicated that alloy TMS-1 has an excellent property at least in intermediate and higher temperature ranges. Although it is not shown in the figure, alloy CMSX-2 with special heat treatment(1315°C x 0.5hr, AC. + 1050°C x 16 hrs, AC. + 850°C x 48 hrs) is reported to have an excellent creep rupture strength[7,8]. Its specific rupture strength is almost the same as that of NASAIR 100 at higher temperature range and that ALLOY454 at intermediate and lower temperature ranges. ALLOY 203E(Ni-5Cr-1.1Ti-2Mo-5W-3Re-6.5Ta-5.5Al-0.4V, in wt%)[5] is an alloy given a high strength by replacement of a part of W content by Re. Although its density is not reported, the specific rup-

ture strength is estimated to be almost the same as that of TMS-1 at around 900°C. However, the strength falls behind TMS-1 and also NASAIR 100 at temperatures higher than 1000°C.

Another merit of alloys designed is their simplicity in chemical compositions; the alloys designed contain only 4 or 5 elements except for Ni. It is also remarked that the alloys have superior strength without any peculiar elements such as V and Re.

Creep Deformation and Structural Change

Lattice rotation of creep-ruptured specimens was examined by X-ray Laue analysis in connection with the structural change.

The structure of creep-ruptured specimens was observed after etching, as shown in Fig. 5. Under a suitable lighting condition (a kind of optical darkfield observation condition), it was found that the rafted structure[10] area looked bright, and deformed area, which was considered to have been deformed in accelerated creep, appeared dark. In this dark area, many lines appeared intersecting each other. The darkness of the lines means that the rafted structure is seriously broken along these lines, and so, the lines are considered as slip lines from which a double slip is strongly proposed

Results of X-ray Laue analysis are very consistent with above observations. Fig. 6. shows a lattice rotation observed in the same specimen that is shown in Fig. 5. The numbers beside the points correspond to those in Fig. 5. The rotation is small in the rafted structure area(2). The rotation starts suddenly in the dark area(3 - 6) in which "slip lines" appear and rafted structure is broken. It is also to be remarked that the rotation direction is quite different from that usually observed in the specimens deformed at high temperatures, rotations toward $[\bar{1}01]$ by single slip or toward $[\bar{1}12]$ by double slip[Ref.11].

From all the above observations, it was concluded that the accelerated creep deformation occurred by the operation of unusual double slip system. A couple of glide planes most reasonable for the "slip lines" was examined by two surface analysis. It was found by the analysis that (111) and $(\bar{1}11)$ were the most fit glide planes for observed "slip lines".

The lattice rotation was also examined with eight other specimens creep ruptured at 1040°C-14kgf/mm²(137 MPa) or 900°C-40kgf/mm²(392 MPa). The original longitudinal orientations of the specimens were within 20° of $\langle 001 \rangle$. Although there were some exceptions, the majority of the specimens showed almost the same lattice rotation direction as mentioned above. It was also indicated that lattice rotation direction was independent of the heat treated structure; specimens imperfectly solutioned(TMS-13) and without heat treatment(TMS-6) showed the same rotation direction as above.

On the rafted structure, it was found that the raft was formed in the specimens solutioned perfectly and creep rupture tested at 1040°C-14kgf/mm²(137 MPa). In the specimens tested at 900°C-40kgf/mm²(392 MPa), the raft was formed but it was loose. The rafted structure was not observed in the specimens of alloy TMS-13(imperfectly solutioned) and no heat treated TMS-6 whose creep rupture strengths were very poor. The effect of the lattice mismatch on the formation of rafted structure was not clear.

Fig. 5. Structures of Creep-ruptured Specimen(alloy TMS-12, at 1040°C-14kgf/mm²), observed in an optical darkfield condition(top) and in SEM(middle and bottom). The numbers correspond to each other.

Fig. 6. Lattice Rotation observed in the Creep-ruptured Specimen (Alloy TMS-12, ruptured at 1040°C - 14kgf/mm^2), the same Specimen that is shown in Fig. 5.

Conclusion

An alloy design system previously established in NRIM was applied for the research and development for high strength nickel-base single crystal alloys. Five promising alloys were designed and evaluated in term of creep rupture strength. The creep deformation behavior is also discussed. As the results,

1. All alloys except one showed superior creep rupture strength. For example, at a condition of 1040°C - 14kgf/mm^2 , rupture lives of designed alloys were about 1000-2000 hrs whereas those of existing alloys, ALLOY 454, NASAIR 100, were estimated to be about 500 hrs or less.
2. An unusual double slip system whose glide planes were $(1\bar{1}1)$ and $(\bar{1}11)$ was found in the area deformed by accelerated creep.

All the results obtained in this paper have been adopted back again to our alloy design. R&D has been started further to design next alloys with several superior properties required for single crystal gas turbine blades.

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