Effect of Ta/W Ratio in γ' Phase on Creep Strength of Nickel-base Single Crystal Superalloys*

By Toshihiro YAMAGATA,** Hiroshi HARADA,** Shizuo NAKAZAWA** and Michio YAMAZAKI**

I. Introduction

Development of nickel-base single crystal (SC) superalloys in which grain boundary strengthening elements, C, B, Zr, and Hf, were excluded intentionally have resulted in a significant improvement in temperature capability of superalloys.¹⁻¹⁰⁾

It was shown that alloy design method developed for conventional cast (CC) superalloys could be successfully applied to the development of single crystal superalloys with excellent high temperature strength.⁹⁾ According to this alloy design method, creep rupture life is strongly correlated to γ' volume fraction and contents of Cr, W, Ta, etc., in γ' phase. The recent study by Nathal and Evert¹¹⁾ revealed that the contents of W and Ta controlled mechanical properties of SC superalloy. However, effects of the ratio of Ta to W in γ' phase on high temperature strength of superalloys have not been explored in detail.

The purpose of the present investigation is to examine the effect of Ta/W ratio on creep rupture life of SC superalloys and to obtain a guide for development of new SC superalloys with superior performance.

II. Alloy Design

Five SC superalloys were selected for the present investigation. Nominal chemical compositions of the alloys were determined on the basis of the computer-aided alloy design method developed for CC nickel-base superalloys.¹²⁾ The following four factors were particularly considered during the process of the alloy design.

(1) Precipitation hardening: volume fraction of γ' was fixed at 65 vol %.

(2) Phase stability: Solubility Index (SI) defined by Eq. (1) was fixed at 1.32 or 1.37 which was near the maximum value to yield stable γ - γ' two phase structure.

$$SI = \sum_i (C_i/C_{Li}) = \text{Cr (at\% in } \gamma')/14 + \text{W (at\% in } \gamma')/5.8 + \text{Ta (at\% in } \gamma')/8 + \dots \dots \dots (1)$$

where, C_i : atomic percent of i 'th element in γ'
 C_{Li} : solubility limits of i 'th element in γ'
 i : Cr, W, Ta, etc.

(3) Solid solution hardening of γ' : proportion of solutioning elements was optimized by using the regression equation (Eq. (2)) made for CC alloys.

Equation(2) predicts rupture life [τ (h)] at 1 000 °C and in stress level of 117.6 MPa.

$$\begin{aligned} \text{Log } (\tau) = & \text{const.} - 0.110 \text{ Cr (at\% in } \gamma') \\ & + 0.164 \text{ W (at\% in } \gamma') \\ & + 0.102 \text{ Ta (at\% in } \gamma') + \dots \dots \dots \\ & + 0.095 \gamma'(\text{vol\%}) - 0.00055 [\gamma'(\text{vol\%})]^2 \\ & \dots \dots \dots (2) \end{aligned}$$

(4) Hot corrosion resistance: Cr content was set in the range of 5 to 7 wt% which was the irreducible minimum level to keep hot corrosion resistance in commercial superalloys.

Five alloys (TMS-1, 2, 12, 17 and 19) having Ta (at% in γ')/W(at% in γ') ratio, hereafter shown as Ta/W ratio, in the range of 0.3 to 2.6 were designed in order to clarify the effect of Ta/W ratio on creep rupture life. Their chemical compositions are shown in Table 1. Designed compositions of γ' phase and Ta/W ratio of the alloys are presented in Table 2.

III. Experimental Procedure

Melting stocks of designed alloys, each of them being 20 kg, were cast. A piece of the stock was remelted at 1 570 °C and poured into an open bottom ceramics mold with right-angle selector which was placed on the copper chill plate and preheated at 1 500 °C. After casting, single crystals were directionally solidified into creep specimens with a 0.6 cm gage diameter and a 3.0 cm length, at a withdrawal rate of 20 cm/h.

Small pieces of as-cast single crystals were heat treated for 4 h at temperature between 1 300 °C and 1 372 °C to find out the temperature interval between complete γ' solutioning and the incipient melting point (heat treatment window). On the basis of this result, creep rupture specimens were solution treated

Table 1. Chemical compositions of designed alloys, and calculated γ' volume fraction and Solubility Index.

Alloy	Co	Cr	W	Al	Ta	Ni	γ' (%)	SI
TMS-2	7.3	5.5	18.6	5.3	3.4	bal.	65	1.37
TMS-1	7.5	5.5	16.6	5.2	5.1	bal.	65	1.37
TMS-12	—	6.6	12.8	5.2	7.7	bal.	65	1.32
TMS-17	—	6.5	9.8	4.8	11.0	bal.	65	1.37
TMS-19	—	6.5	7.8	4.7	12.7	bal.	65	1.37

* Presented to the 109th ISIJ Meeting, April 1985, S629, at Tokyo Institute of Technology in Tokyo. Manuscript Received on November 19, 1985; accepted in the final form on March 4, 1986. © 1986 ISIJ

** National Research Institute for Metals, Nakameguro, Meguro-ku, Tokyo 153.

at 1 348 °C for 4 h followed by air quenching and aged in the two stages at 982 °C for 5 h and at 870 °C for 20 h (full heat treatment). Creep rupture tests were performed in two conditions of temperature and stress level: 800 °C, 735 MPa and 1 040 °C, 137.2 MPa. The test load was applied after the specimens were held for 20 h at test temperatures.

IV. Results and Discussion

Microstructures of the solution treated specimens were observed by optical microscopy to examine the variation of solution temperature as a function of Ta/W ratio in γ' phase and the result is shown in Fig. 1. The increase in Ta/W ratio raises the γ' solvus temperature from 1 300 to 1 348 °C. On the other hand, the increase in Ta/W ratio reduced the incipient melting temperature from above 1 372 to 1 360 °C. Complete solutioning of as-cast structure was obtained in a wide temperature range from 1 300 to 1 372 °C in alloys TMS-1 and 2 which had Ta/W ratio less than 0.5, and between 1 324 °C and 1 360 °C in the alloy TMS-12 having Ta/W=0.95. The heat treatment window was narrow in the alloys TMS-17 and 19 which had Ta/W ratio above 1.8. Consequently, the increase in Ta/W ratio tends to suppress complete solutioning of as-cast structure in the present series of alloys. A wide heat treatment window is an important factor in order to obtain excellent rupture strength in SC superalloys.⁴⁾

Typical creep curves at 1 040 °C and 137.2 MPa are shown in Fig. 2. Creep rupture lives of the alloys strongly depended on the Ta/W ratio in the γ' phase. The alloys having Ta/W ratio less than 1.0 showed longer rupture lives which were between 1 700 h and 1 910 h. However, rupture lives abruptly decreased as the Ta/W ratio increased over 1.0. The alloys having Ta/W ratio of 1.8 and 2.6 showed rupture lives of 1 224 h and 477 h, respectively. It is therefore confirmed that the alloys having a wide heat treatment window had long rupture life. Rupture elongation of the alloys except TMS-19 was about 10 %. The results of creep rupture tests are shown in Table 3. At 800 °C and 735 MPa, three alloys except TMS-19 exhibited almost the same rupture lives of 200 h. Rupture life of the alloy TMS-19 was one fifth times as short as that of the alloys TMS-1, 12 and 17. It can be concluded from these results that increase in Ta/W ratio over 2.0 reduces abruptly the creep rupture life at both low and high temperatures.

It is reported that creep strength of SC superalloys strongly depends on the γ' particle size. In two

superalloys, NASAIR 100⁵⁾ and MMT-143,^{13,14)} the rupture strength of a specimen containing fine γ' particle was stronger than that of a specimen containing coarse γ' particle. On the other hand, it was observed in an alloy CMSX-2 that rupture strength of a specimen containing coarse γ' particle was higher than that of a specimen containing fine γ' particles.¹⁵⁾

The microstructures in the present series of alloys after full heat treatment are shown in Photos. 1 (a)~(e), and the structures in alloys aged additionally at

Fig. 1. Heat treatment windows of the present series of alloys.

Fig. 2. Typical creep curves for the present series of alloys at 1 040 °C and 137.2 MPa.

Table 3. Creep rupture data of the present series of alloys tested at 800 °C, 735 MPa and 1 040 °C, 137.2 MPa.

Alloy	800 °C, 735 MPa			1 040 °C, 137.2 MPa		
	Life (h)	El. (%)	R.A. (%)	Life (h)	El. (%)	R.A. (%)
TMS-2	—	—	—	1 707	12	48
TMS-1	199	30	31	1 913	11	35
TMS-12	158	30	—	1 902	9	40
TMS-17	202	24	28	1 224	12	44
TMS-19	41	33	39	447	26	48

Table 2. Designed composition of the γ' phase, Ta/W ratio in γ' phase and lattice mismatch δ .

Alloy	Co	Cr	W	Al	Ta	Ni	Ta/W	δ (%)
TMS-2	6.75	3.08	5.51	17.54	1.60	bal.	0.29	0.17
TMS-1	6.75	3.08	4.93	17.38	2.40	bal.	0.49	0.32
TMS-12	—	3.08	3.77	17.48	3.60	bal.	0.95	0.49
TMS-17	—	3.08	2.90	16.82	5.20	bal.	1.79	0.78
TMS-19	—	3.08	2.32	16.66	6.00	bal.	2.59	0.93

Photo. 1. Scanning electron micrographs of fully heat treated specimens (a) TMS-2, (b) TMS-1, (c) TMS-12, (d) TMS-17, (e) TMS-19 and specimens aged additionally at 1 040 °C for 20 h after full heat treatment, (f) TMS-2, (g) TMS-1, (h) TMS-12, (i) TMS-17, (j) TMS-19.

1 040 °C for 20 h after full heat treatment are shown in Photos. 1(f)~(j). The former structures give the initial γ' morphology of the specimens tested at 800 °C. The latter gives the γ' morphology at 1 040 °C just before the test load was applied. The minimum size of γ' particle was observed at 0.49 in Ta/W ratio and the deviation of Ta/W ratio from 0.49 caused very rapid coarsening. In Ta/W ratio over 1.0, the coarsening rate decreased. The shape of γ' particles was cuboidal in the alloys having Ta/W ratio less than 1.8 and spherical in the alloy having Ta/W ratio of 2.6. These results indicate that cuboidal particles are beneficial for the increase in rupture life compared with the spherical particles in the present series of alloys.

It has been observed in SC superalloys that the γ' particles directionally coarsened from the initial cubic morphology to lamellar array (rafted structure) perpendicular to the applied stress during tensile creep test beyond 900 °C and that well developed lamellar array yielded long creep rupture life.¹³⁻¹⁶⁾ In the MMT-143 alloy, rupture life of a specimen containing fine cuboidal γ' particles ($\sim 0.1 \mu\text{m}$ in size) array was longer than that of a specimen containing coarse odd-shaped γ' ($0.3 \mu\text{m}$). In the latter specimen, less perfect rafted structure developed as the results of misfit dislocation formed in γ/γ' interface in order to relieve the interfacial strains which arise from the lattice mismatch between γ' and γ . Lattice mismatch δ is defined by Eq. (3).

$$\delta = 2(a_{\gamma'} - a_{\gamma}) / (a_{\gamma'} + a_{\gamma}) \dots\dots\dots(3)$$

where, $a_{\gamma'}$ and a_{γ} : the lattice parameter of the γ' and γ phases, respectively.
The δ of MMT-143 is -0.7% .¹³⁾ In the CMSX-2 alloy ($\delta=0.14 \%$), specimens containing large cuboidal γ' ($0.45 \mu\text{m}$) showed longer rupture life than that of specimens containing odd-shaped γ' ($\sim 0.3 \mu\text{m}$). However, no misfit dislocations were observed in the both specimens.

Fig. 3. Effects of Ta/W ratio in γ' phase on heat treatment window, rupture life at 1 040 °C and 137.2 MPa, γ' particle size, and calculated lattice mismatch δ .

The δ values of the TMS-alloys, calculated by the alloy design method, were 0.17 % in alloy with Ta/W ratio of 0.3 and 0.93 % in alloy with Ta/W=2.6 (Table 2). Thermal expansion coefficient of γ phase is larger than that of γ' phase, so that lattice mismatch of the present series of alloys at 1 040 °C may be smaller than the calculated values. The δ value of CMSX-2, calculated by this alloy design method, was 0.39 %, therefore the TMS-alloys can be regarded a similar type of superalloys to CMSX-2 rather than NASAIR 100. All the results obtained in the present study are plotted against Ta/W ratio in Fig. 3.
At 1 040 °C, creep rupture lives longer than 1 700 h observed in the alloys TMS-1, 2 and 12 indicat that cuboidal γ' particles directionally coarsened and formed well developed rafted structures. In the alloy TMS-17, rupture life may be decreased to 1 224 h because of coarse γ' particles make up coarse rafted structure. The shortest rupture life obtained in the alloy TMS-19 among the present alloys, 447 h, means that coarse and odd-shaped γ' particles formed

less perfect rafted structure, as observed in CMSX-2. At 800 °C, alloys containing cuboidal γ' particle array, TMS-1, 12 and 17, showed longer rupture life than that of the alloy TMS-19 containing odd-shaped γ' particles. This result shows that rupture life at 800 °C strongly depends on the γ' particle shape than the particle size. In the present study, γ' particle size and shape were the function of alloy composition, however the effect of γ' particle morphology on rupture properties of the present alloys agreed with the results observed in CMSX-2, in which γ' morphology was the function of aging temperature. The results observed in CMSX-2 and the present alloys indicate that if TMS-19 is aged at higher temperature, γ' particles shape become cuboidal and rupture life increases. It can be concluded from these results that the most important key factor to develop advanced single crystal superalloys is a selection of alloy composition forming cuboidal particles and a wider heat treatment window over 40 °C above 1300 °C.

V. Summary

The effect of Ta/W ratio in γ' phase on the creep rupture life of nickel-base single crystal superalloys designed was investigated at temperatures of 800 and 1040 °C.

(1) Heat treatment window showed the widest range at the Ta/W ratio in the range of 0.3 and 0.5, and became narrower in Ta/W ratio over 1.0.

(2) Creep rupture life at 1040 °C and in stress level of 137.2 MPa was maximum at the Ta/W ratio in the range of 0.3 and 1.0, and monotonically decreased down one third of the maximum value at Ta/W=2.6.

(3) Creep rupture life at 800 °C and 735 MPa did not change in the Ta/W ratio between 0.3 and 1.8, but it dropped into a quarter of the former value at 2.6 in Ta/W ratio.

(4) Size of γ' particles in fully heat treated specimens showed minimum value at the Ta/W ratio of 0.5 and became larger with the increase in this ratio over 0.5.

(5) Shape of γ' particles in fully heat treated specimens was cuboidal in the Ta/W ratio between

0.3 and 1.0, and it became spherical at Ta/W=2.6.

Acknowledgements

This work was performed as a part of the R & D project of Basic Technology for Future Industries sponsored by Agency of Industrial Science and Technology, Ministry of International Trade and Industry.

REFERENCES

- 1) U.S. Patent, No. 4116723, (1979).
- 2) U.S. Patent, No. 4209348, (1980).
- 3) U.S. Patent, No. 4222794, (1980).
- 4) M. Gell, D. N. Duhl and A. F. Giamei: Proc. of 4th Int'l Symp. on Superalloys, ed. by J. K. Tien *et al.*, ASM, Ohio, (1980), 205.
- 5) T. E. Strangman, G. S. Hoppins III, G. M. Phipps, K. Harris and R. E. Schwer: Proc. of 4th Int'l Symp. on Superalloys, ed. by J. K. Tien *et al.*, ASM, Ohio, (1980), 215.
- 6) Japan Patent, Published Unexamined Patent Application, No. 57-89451.
- 7) K. Harris, G. L. Erickson and R. E. Schwer: Proc. of 5th Int'l Symp. on Superalloys, ed. by M. Gell *et al.*, ASM, Ohio, (1984), 233.
- 8) T. Khan, P. Caron and C. Duret: Proc. of 5th Int'l Symp. on Superalloys, ed. by M. Gell *et al.*, ASM, Ohio, (1984), 147.
- 9) T. Yamagata, H. Harada, S. Nakazawa, M. Yamazaki and Y. G. Nakagawa: Proc. of 5th Int'l Symp. on Superalloys, ed. by M. Gell *et al.*, ASM, Ohio, (1984), 147.
- 10) D. A. Ford and R. P. Arthey: Proc. of 5th Int'l Symp. on Superalloys, ed. by M. Gell *et al.*, ASM, Ohio, (1984), 213.
- 11) M. V. Nathal and L. J. Ebert: Proc. of 5th Int'l Symp. on Superalloys, ed. by M. Gell *et al.*, ASM, Ohio, (1984), 125.
- 12) H. Harada, M. Yamazaki, Y. Koizumi, N. Sakuma, N. Furuya and H. Kamiya: Proc. of Conf. on High Temperature Alloys for Gas Turbines 1982, ed. by R. Brunetant *et al.*, D. Reidel Publishing Co., Dordrecht, (1982), 721.
- 13) D. D. Pearson, F. D. Lemkey and B. H. Kear: Proc. of 4th Int'l Symp. on Superalloys, ed. by J. K. Tien *et al.*, ASM, Ohio, (1980), 513.
- 14) R. A. Mackay and L. J. Ebert: Proc. of 5th Int'l Symp. on Superalloys, ed. by M. Gell *et al.*, ASM, Ohio, (1984), 135.
- 15) P. Caron and T. Khan: *Mat. Sci. Eng.*, **61** (1983), 173.
- 16) M. V. Nathal and L. J. Ebert: *Script. Met.*, **17** (1983), 1151.