

QUANTITATIVE ANALYSIS OF CREEP STRENGTHENING FACTORS IN NI-BASE SINGLE CRYSTAL SUPER ALLOYS

Tadaharu Yokokawa¹, Hiroshi Harada¹, Kyoko Kawagishi², Yutaka Koizumi¹, Toshiharu Kobayashi¹

¹Environment and Energy Materials Division

²High Temperature Materials Unit, Environment and Energy Materials Division

National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki, 305-0047, Japan

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Abstract

Ni-base single-crystal (SC) superalloys with superior mechanical properties are being developed to improve the thermal efficiency of jet engines and land-based gas turbines. In this study, we investigate the relationships among alloy compositional factors, structural factors, and the creep-rupture life of Ni-base SC superalloys by multi-regression analysis with creep-tested data for 75 alloys. We also obtain three equations to predict creep-rupture lives at 900 °C/392 MPa, 1000 °C/245 MPa, and 1100 °C/137 MPa with excellent multi-correlation coefficients from 0.94 to 0.98. The γ' phase composition, γ' volume fraction, and lattice misfit were used as explanatory variables. The regression coefficients of the refractory elements including W, Ta, and Re were comparatively large at 900 °C/392 MPa and they decreased with an increase in temperature and decrease in stress. The coefficient for negative lattice misfit increased at higher temperatures and lower stresses, especially at 1100 °C/137 MPa. The coefficient of Ru showed a small value for all the conditions in this study. Consequently, it is clear that solution strengthening is effective in the lower-temperature and higher-stress regions, and that a larger negative misfit leads to a quicker formation of the rafted γ/γ' structure with a finer interfacial dislocation network. The finer dislocation network assures superior creep resistance by preventing glide dislocation from cutting the rafted γ/γ' structure. The addition of Ru in alloys is effective in suppressing topologically close packed (TCP) phases formation by expanding the solubility limit. The lattice misfit shifts toward a slightly negative value with the addition of Ru, but this effect was small with respect to the enhancement of creep strength.

Introduction

Ni-base single-crystal (SC) superalloys with superior mechanical properties are being developed to improve the thermal efficiency of jet engines and land-based gas turbines. A series of such superalloys with excellent mechanical properties has been developed using the alloy design program (ADP) at the National Institute for Materials Science (NIMS) [1-5]. The ADP is available for Ni-base superalloys with arbitrary compositions, including those with platinum group metal (PGM) elements, under various temperatures and stresses.

Figure 1 shows the flowchart of the ADP used in this study. When the alloy composition and the applied temperature and stress are input, the structural properties, such as the chemical

compositions of the γ and γ' phases, the volume fraction of the γ' phase, and the lattice misfit between the γ and γ' phases, are calculated from the given alloy composition and temperature. Then, the mechanical properties, such as creep-rupture life, are predicted by regression equations that consider not only the alloy composition but also the structural parameters such as the γ/γ' lattice misfit and the volume fraction of the γ' phase.

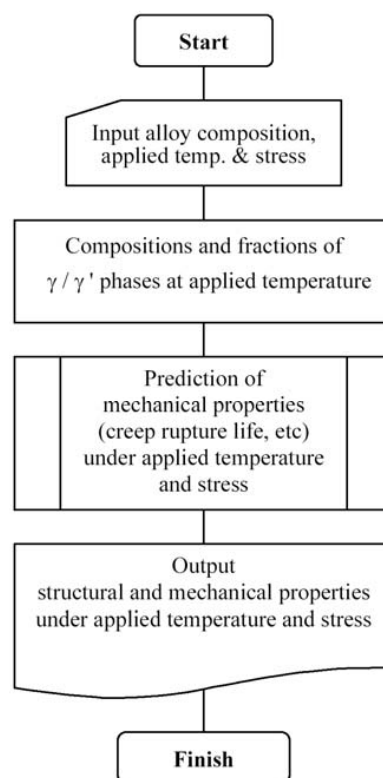


Fig. 1 Calculation flowchart for our alloy design program (ADP).

We previously reported that a negative lattice misfit ($a_\gamma > a_{\gamma'}$) promotes the formation of a rafted structure of the γ/γ' phases and that a finer interfacial dislocation network stimulated by a larger negative lattice misfit prevents dislocation glide, thereby increasing the creep resistance at higher temperatures under lower stresses [6, 7]. In this manner, we developed an alloy having the world's highest-temperature capability beyond 1100 °C [8].

From the viewpoint of alloy design for Ni-base SC superalloys, Sato et al investigated quantitatively the relationship among compositional factors, structural factors, and creep-rupture life at 1,000 °C/245 MPa [9]. However, in actual alloy development, it is necessary to consider a wide range of temperature and stress conditions.

In this study, by multi-regression analysis, we attempted to obtain equations in order to predict creep-rupture life under conditions ranging from 900 °C/392 MPa to 1100 °C/137 MPa. In addition, we developed a quantitative understanding of creep-strengthening factors in the middle-higher temperatures and middle-lower stress regions.

Experimental Procedures

In this study, 75 Ni-base SC superalloys, including first-generation to fifth-generation alloys, were used. Table 1 shows the alloy compositions, lattice misfit, and heat-treatment conditions. To avoid any influence of the differences in the manufacturing processes on the creep properties, all the SC samples used in this study were cast using NIMS's directional solidification casting furnace. Cylindrical bars having 10 mm diameter were supplied as materials with orientations within 8° of the [001] orientation. The samples were solution heat treated and aged with no residual eutectics and visible topologically close packed (TCP) phases in their microstructures. Creep-test specimens of 4 mm in diameter and 22 mm in gauge length were machined from the heat-treated samples.

Initially, creep tests were performed using NIMS's creep-test machines under conditions of 900 °C/392 MPa, 1000 °C/245 MPa, and 1100 °C/137 MPa. After creep testing, TCP phase formation was investigated using scanning electron microscopy. If a TCP phase was found in a crept specimen, its creep data were not used in the regression analysis. In this study, creep-test data for 75

alloys at 900 °C/392 MPa, 54 alloys at 1000 °C/245 MPa, and 55 alloys at 1100 °C/137 MPa were selected and used in the regression analysis.

Next, the γ' phase composition, the volume fraction of the γ' phase, and the lattice misfit of each alloy at 900 °C, 1000 °C, and 1100 °C were calculated using the ADP; these calculated values were in good agreement with the observed values [10-14]. For example, Fig. 2(a) shows the relationship between the observed and calculated concentrations of alloying elements in the γ' phase at 1100 °C for a third-generation superalloy TMS-75 containing 5 wt% Re [15]. Figure 2(b) shows the calculated volume fractions of the γ' phase for TMS-75 with the volume fractions measured by the X-ray diffraction method (open circles).

Figure 3 shows the relationship between the observed and calculated lattice misfits in a temperature range from room temperature to 1100 °C for 13 alloys, including first-generation to fifth-generation alloys. In this figure, the misfits associated with TMS-75 are shown as open circles. Here, owing to the changes in phase compositions and differences in thermal expansion coefficients for the γ and γ' phases, the lattice misfit changes with temperature. From this, several misfits have been plotted for an alloy in Fig. 3.

Results and Discussions

Regression analysis was performed for all alloying elements and lattice misfit. The regression model for creep-rupture life is defined by Eq. (1):

$$\log(\tau) = C_0 + \sum C_i X_i + C_\delta \delta + C_k (V_f - V_{opt})^2, \quad (1)$$

where τ is the creep-rupture life; X_i is the concentration of each alloying element in the γ' phase at temperature T ; δ is the lattice misfit at temperature T ; V_f is the volume fraction of the γ' phase at temperature T ; and C_0 , C_i , C_δ , and C_k are regression coefficients. $(V_f - V_{opt})^2$ is a term that corresponds to the optimal value of V_f , which is the value reported by Murakumo et al [16]. They found that creep-rupture lives are the longest at around 0.7 and 0.55 of the measured γ' volume fraction at 900 °C/392 MPa and 1100 °C/137 MPa, respectively, using TMS-75 and its γ/γ' tie-line alloys. In this study, V_{opt} is set to 0.7 for 900 °C/392 MPa, 0.55

Table 1 Compositional range, lattice misfit and heat treatment condition for all of alloys used in this study.

	Compositional range (at%; Ni: balance)											Misfit (%)
	Co	Cr	Mo	W	Al	Ti	Nb	Ta	Hf	Re	Ru	
min	0.0	0.0	0.0	0.0	11.4	0.0	0.0	0.0	0.0	0.0	0.0	-0.41 at 1100 °C
max	15.4	10.8	2.2	4.0	18.9	2.5	2.2	3.5	0.05	2.4	3.2	0.30 at 900 °C
Heat treatment				Solution treatment + 1100°C/5h,AC + 870°C/20h,AC								

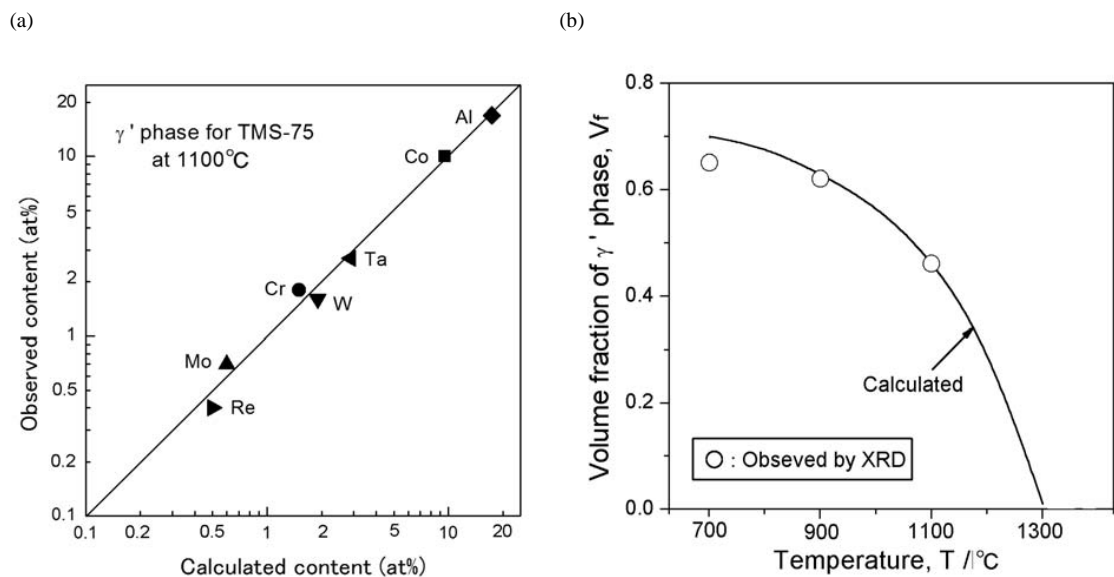


Fig. 2 Observed and calculated values of (a) concentration of alloying elements in γ' phase and (b) volume fractions of γ' phase in TMS-75.

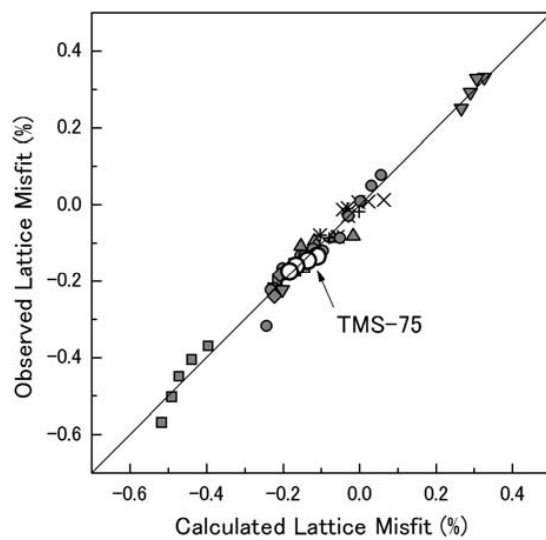


Fig. 3 Observed and calculated lattice misfits for several alloys, lattice misfits of TMS-75 are shown by open circles.

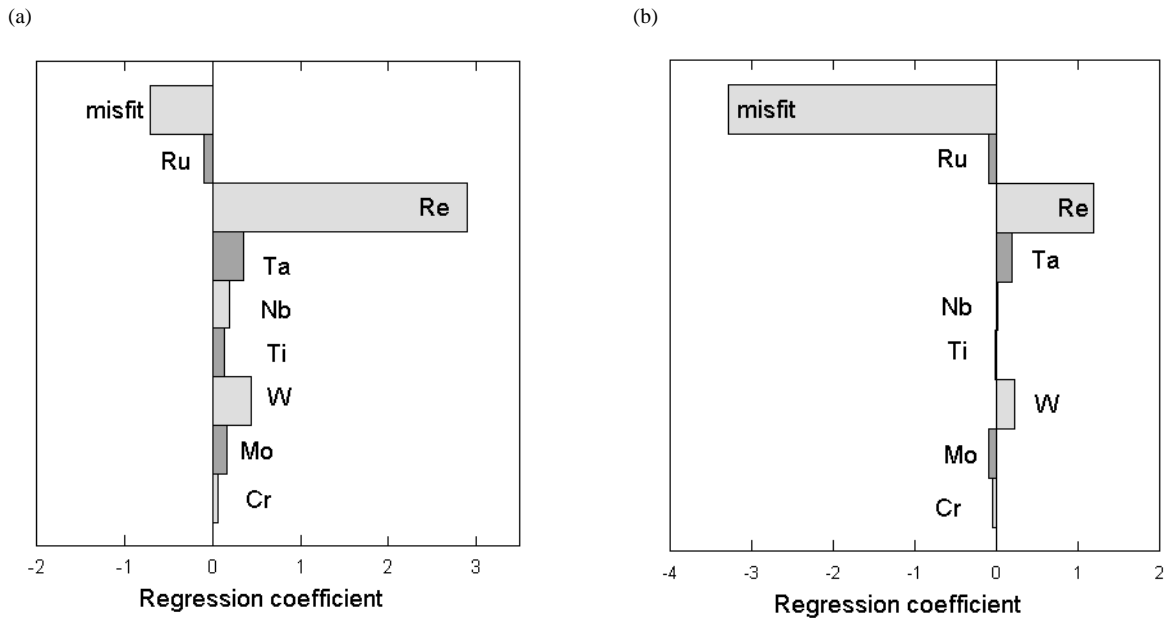


Fig. 4 Regression coefficients of alloying elements and lattice misfit in creep-rupture life-prediction equations at (a) 900 °C/392 MPa and (b) 1100 °C/137 MPa.

for 1100 °C/137 MPa, and 0.63 (an average value) for 1000 °C/245 MPa.

Regression coefficients in creep-rupture life-prediction equations

Three equations to predict creep-rupture lives at 900 °C/392 MPa, 1000 °C/245 MPa, and 1100 °C/137 MPa were obtained from regression analysis. These equations have excellent multi-correlation coefficients from 0.94 to 0.98. Figures 4 (a) and (b) show that the regression coefficients correspond to the alloying elements and lattice misfit in the equations for 900 °C/392 MPa and 1100 °C/137 MPa.

At 900 °C/392 MPa, the regression coefficients of alloying elements Mo, W, Ti, Nb, Ta, and Re were positive from 0.14 to 2.98, and the order of coefficients was $Ti < Mo < Nb < Ta < W \ll Re$. The coefficient of Re was about 10 times larger than that of Ta and W. This means that the effect of solution strengthening is large by the addition of refractory elements such as Ta, W, and especially Re; this increases the creep-rupture life at 900 °C/392 MPa. The coefficient of lattice misfit was a negative value of -0.64. The lattice misfit of Ni-base superalloys is usually negative ($a_\gamma > a_{\gamma'}$); therefore, a lattice misfit with a negative value is effective to increase creep-rupture life at 900 °C/392 MPa.

At 1100 °C/137 MPa, the coefficients of Ti, Ta, W, and Re ranged from 0.01 to 0.91, which were smaller than the values at 900 °C/392 MPa. In contrast, the coefficient of lattice misfit was an even larger negative value of -3.3, which was five times larger than that at 900 °C/392 MPa. This means that the effect of solution strengthening by the addition of refractory elements decreases, and the contribution of a negative lattice misfit

increases at 1100 °C/137 MPa. The coefficient of Mo was a negative value of -0.11, and solution strengthening by the addition of Mo is not expected in this condition. However, the lattice parameter of the γ phase is expanded by the addition of Mo, because Mo is preferably partitioned in the γ phase [10, 17]; therefore, the lattice misfit tends to be a negative value, and we can expect an increase in creep-rupture life. However, if excess of Mo is added to the alloy, creep-rupture life shortens owing to the collapse of the γ/γ' coherency, because the interfacial stress at the γ/γ' phase interface increases too much.

The coefficient of Cr is very small and that of Ru has a negative value of -0.1 under both low- and high-temperature conditions. These observations indicate that the contributions of Cr and Ru in solution strengthening are very small, although Cr and Ru are respectively effective elements in improving oxidation resistance and in suppressing TCP formation by expanding the solubility limit [10,15]. Ru also makes a small contribution to increasing creep-rupture life by changing the lattice misfit toward a negative value by the partitioning of Ru in the γ phase.

To clarify the changes in regression coefficients according to creep conditions, the regression coefficients of the major alloying elements and the lattice misfit are shown in Fig. 5. The regression coefficients of refractory elements such as W, Ta, and Re are comparatively large at 900 °C/392 MPa, and these coefficients decrease with increasing temperature and decreasing stress. On the other hand, the coefficient of lattice misfit is a negative under all creep-test conditions. At higher temperatures with lower stresses, especially at 1100 °C/137 MPa, the coefficient for lattice misfit becomes a relatively large value of -3.3. These results suggest that solution strengthening by the addition of refractory

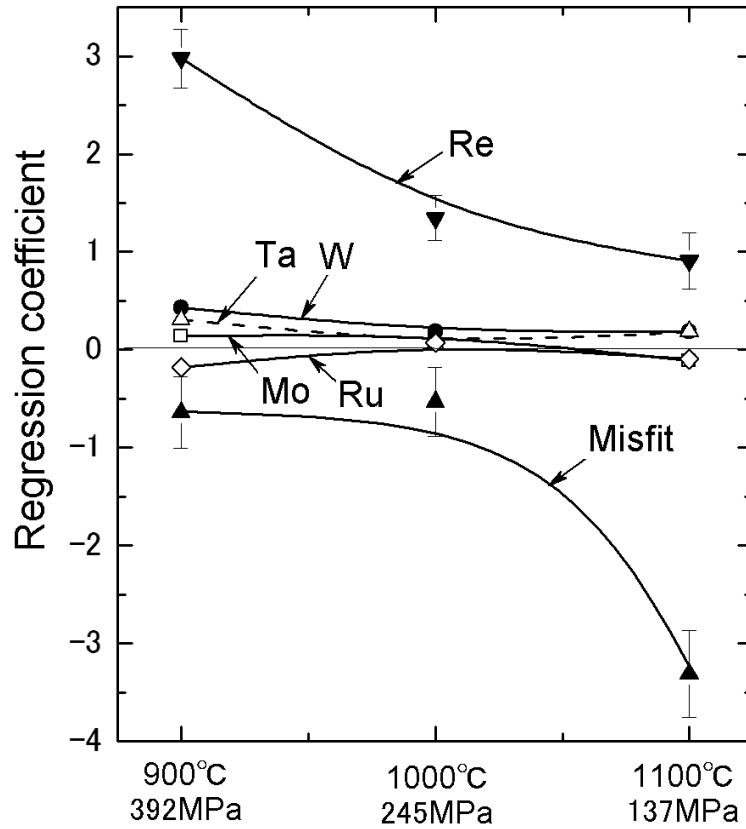


Fig.5 Regression coefficients of Mo, W, Ta, Re, Ru and lattice misfit under various creep test conditions.

elements such as Ta, W, and especially Re is dominant at lower temperatures, and that the formation of a rafted structure of the γ/γ' phases promoted by the negative lattice misfit plays an important role in preventing dislocation glide [7], thereby increasing creep resistance at higher temperatures and lower stresses.

These tendencies show good agreement with our previous understanding of creep-strengthening mechanisms [6, 18, 19].

Because an optimal value was introduced into the term regarding the γ' volume fraction, it is difficult to discuss the contribution of the γ' volume fraction itself to creep strength. Although the coefficient for the γ' volume fraction is about 0.5 under low- and high-temperature conditions, because this value is larger than that of W and Ta, we suppose that the creep-rupture life is sensitive to deviation from the optimum value of γ' volume fraction compared with the alloying element addition.

Prediction accuracy of the equation for creep-rupture life

Figures 6(a) and (b) show excellent agreement between the predicted and observed creep-rupture lives at 900 °C/392 MPa and 1100 °C/137 MPa, respectively. The dotted lines in these figures show a limitation of 95% significance.

To further examine the prediction accuracy of the equation for creep-rupture life, the creep-rupture lives of the first-generation alloy ReneN4 [20], third-generation alloy ReneN5 [21], and fourth-generation alloy TMS-138 [7, 8, 22], which were not used for the regression analysis, were calculated by these equations.

Table 2 shows the compositions of these alloys. Table 3 shows the predicted creep-rupture lives, the volume fractions of γ' phase, and the lattice misfits between the γ/γ' phases for these alloys at 900 °C/392 MPa, 1000 °C/245 MPa, and 1100 °C/137 MPa.

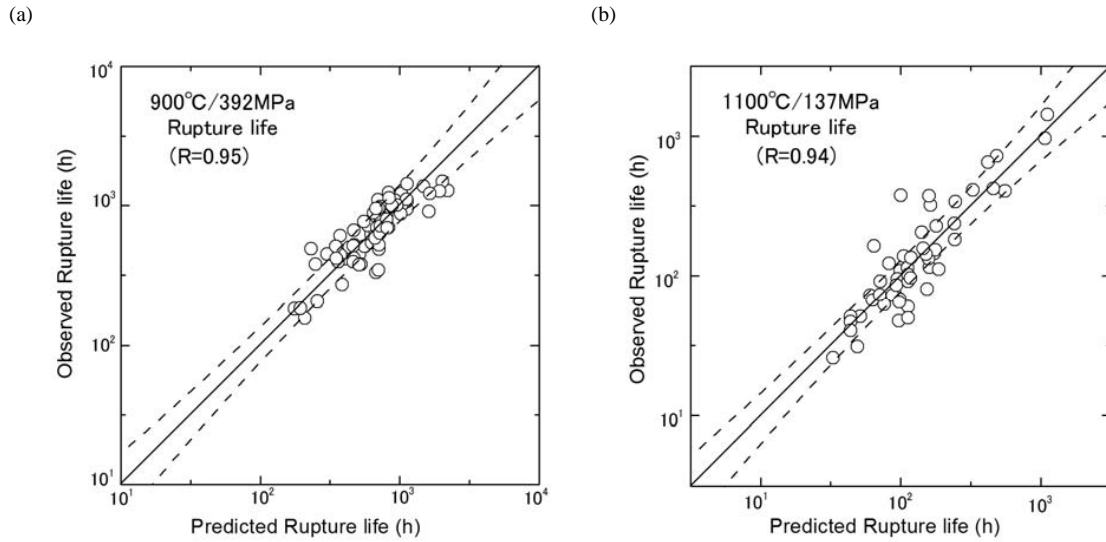


Fig.6 Relationship between observed and predicted creep-rupture lives at (a) 900 °C/392 MPa and (b) 1100 °C/137 MPa.

Table 2 Chemical composition of ReneN4, ReneN5, and TMS-138.

Alloy	Composition (wt%, Ni;bal.)										
	Co	Cr	Mo	W	Al	Ti	Ta	Nb	Hf	Re	Ru
ReneN4	8.0	9.0	2.0	6.0	3.7	4.2	4.0	0.5	-	-	-
ReneN5	8.0	7.0	2.0	5.0	6.2	-	7.0	-	0.2	3.0	-
TMS-138	5.8	2.9	2.9	5.9	5.9	-	5.9	-	0.1	4.9	2.0

Table 3 Volume fractions of γ' phase, lattice misfits and creep rupture lives of ReneN4, ReneN5, and TMS-138.

Alloy	900°C / 392MPa				1000°C / 245MPa				1100°C / 137MPa			
	Vf (%)	Misfit (%)	Creep rupture life(h)		Vf (%)	Misfit (%)	Creep rupture life(h)		Vf (%)	Misfit (%)	Creep rupture life(h)	
			Obs.	Calc.			Obs.	Calc.			Obs.	Calc.
ReneN4	57	-0.23	223	298	51	-0.25	52	92	42	-0.27	31	51
ReneN5	74	-0.29	340	598	71	-0.34	96	305	65	-0.38	89	270
TMS-138	64	-0.21	987	840	62	-0.30	381	366	55	-0.34	412	360

These predicted creep-rupture lives at 900 °C/392 MPa and 1100 °C/137 MPa are also plotted in Figs. 7(a) and (b). As shown in Fig. 7(a), the predicted creep-rupture lives of these alloys at 900 °C/392 MPa were in excellent agreement with the observed values. On the other hand, at 1100 °C/137 MPa, although the predicted values of ReneN4 and TMS-138 also have fairly good agreement with the observed values, the predicted values of ReneN5 far exceeded the observed values. Because relatively large amount of refractory elements (such as Re and Ta) are

included in ReneN5, harmful TCP phases are formed more easily at higher temperatures (Fig. 8), resulting in shorter creep life. This is the reason for the large difference between the observed and predicted creep-rupture lives of ReneN5.

Consequently, it has been clarified that the creep life can be predicted with sufficient accuracy using the prediction equations obtained in this study, except for the case when harmful TCP phases are formed.

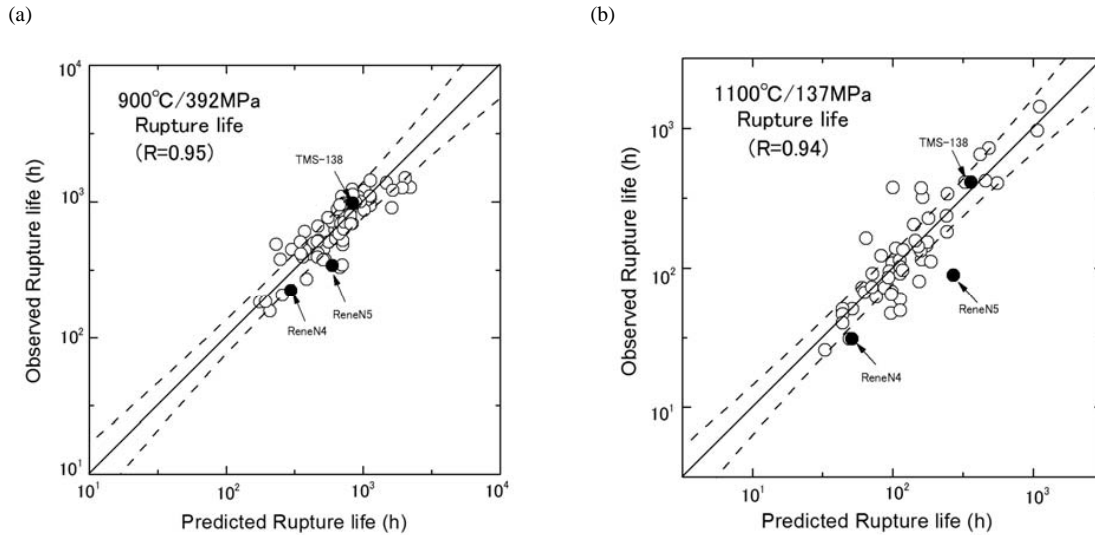


Fig.7 Relationship between experimental and predicted creep-rupture lives at (a) 900 °C/392 MPa and (b) 1100 °C/137 MPa. Open circles show predicted values of alloys used for regression analysis, solid circles show predicted values of ReneN4, ReneN5, and TMS-138 that were not used for regression analysis.

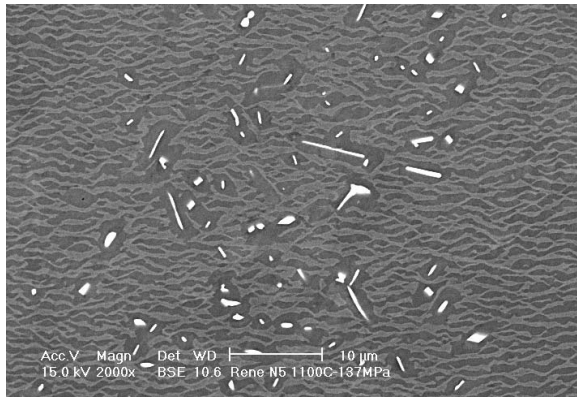


Fig.8 Microstructure showing ReneN5 crept at 1100 °C/137 MPa.

Conclusions

By multi-regression analysis using the creep data for 75 Ni-base SC superalloys, the creep-strengthening factors from 900 °C/392 MPa to 1100 °C/137 MPa were investigated. The following results were obtained.

1. Three equations to predict creep-rupture lives at 900 °C/392 MPa, 1000 °C/245 MPa, and 1100 °C/137 MPa were obtained with excellent multi-correlation coefficients from 0.94 to 0.98. From analysis of the coefficients of these prediction equations, we were able to quantitatively understand creep-strengthening factors at 900–1100 °C/137–392 MPa.
2. From the values of the regression coefficients, it was shown that solution strengthening is affected by the addition of Re, W, and Ta at 900 °C/392 MPa.
3. The regression coefficients suggests that the formation of a rafted structure of the γ/γ' phases with a finer interfacial dislocation network stimulated by a larger negative lattice misfit ($a_{\gamma} > a_{\gamma'}$) enhances creep resistance at 1100 °C/137 MPa.
4. The addition of Ru to alloys is effective in suppressing TCP formation, and shifts the lattice misfit toward slightly negative values. This lattice misfit shift is not very effective in enhancing the creep strength at 900–1100 °C/137–392 MPa.
5. Creep life can be predicted with sufficient accuracy using the prediction equations obtained in this study, except for cases when harmful TCP phases are formed during high-temperature exposure.

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Reference

1. H. Harada, M. Yamazaki, Y. Koizumi, N. Sakuma, N. Furuya, H. Kamiya: "Alloy Design for Nickelbase Superalloys", Proc. High Temperature Alloys for Gas Turbines 1982, Liege, Belgium (1982) 721-735.
2. T. Yamagata, H. Harada, S. Nakazawa, M. Yamazaki: "Alloy Design for High Strength Nickel-base Single Crystal Alloys", Superalloys, 1984 (TMS, 1984), 157-166.
3. H. Harada, K. Ohno, T. Yamagata, T. Yokokawa, M. Yamazaki: "Phase Calculation and Its Use in Alloy Design Program for Nickel-base Superalloys", *Superalloys 1988*, (TMS, 1988) 733-742.
4. H. Harada, et al. "Calculation of Gamma-Prime/Gamma Equilibrium in Multi-Component Nickel-base Superalloys", Proc. High-Temperature Materials for Power Engineering 1990 (European Commission, 1990) 1319.
5. H. Harada, H. Murakami: "Design of Ni-base Superalloys", Springer Series in Materials Science, 34 (1999) 39-70.
6. J. X. Zhang, T. Murakumo, Y. koizumi, T. Kobayashi, H. Harada and S. Masaki Jr: "Interfacial Dislocation Networks Strengthening a Fourth-Generation Single-Crystal TMS-138 Superalloy", Metall. and Mater. Trans. A 33A(12) (2002) 3741-3746.
7. J. X. Zhang, J. C. Wang, H. Harada and Y. Koizumi: "The effect of lattice misfit on the dislocation motion in superalloys during high-temperature low-stress creep", Acta Materialia, 53 (2005) 4623-4633.
8. Y. koizumi, T. Kobayashi, T. Yokokawa, J. X. Zhang, M. Osawa, H. Harada, Y. Aoki and M. Arai: "Develop of Next Generation Ni-base Single Crystal Superalloys", Superalloys 2004, (TMS, 2004) 35-43.
9. A. Sato, T. Yokokawa, Y. Koizumi, T. Kobayashi and H. Harada: "A Factor Analysis of Creep Rupture Properties of Ni-Base Superalloys", J. Japan Inst. Metals 69 (2005) 691-694.
10. T. Yokokawa, M. Osawa, K. Nishida, T. Kobayashi, Y. Koizumi, H. Harada: "Partitioning behavior of platinum group metals on the γ and γ' phases of Ni-base superalloys at high temperatures", Scripta Materialia 49, (2003) 1041-1046.
11. T. Yokokawa, M. Osawa, Y. Koizumi, T. Kobayashi and H. Harada: " Estimation of γ/γ' Phase Equilibrium in Ru-bearing Ni-base Superalloys ", J. Japan Inst. Metals 69 (2004) 577-580.
12. T. Yokokawa, M. Osawa, K. Nishida, Y. Koizumi, T. Kobayashi and H. Harada: " Effect of Ru Addition to Partitioning Behavior of Alloying Elements into γ and γ' phases of Ni-base Superalloys ", J. Japan Inst. Metals 68 (2004) 138-141.
13. T. Yokokawa, M. Osawa, T. Kobayashi, Y. Koizumi T. Yamagata and H. Harada: " High Temperature Measurement of γ/γ' Lattice Misfit in Third Generation Ni-base Superalloy", Materials for Advanced Power Engineering 1998, (The Institute of Materials) (1998) 1121-1128.
14. T. Yokokawa, K. Ohno, H. Murakami, T. Kobayashi, T. Yamagata and H. Harada: "Accurate Measurement of Lattice Misfit between γ and γ' Phase in Ni-base Superalloys", Advances in X-ray Analysis, 39 (1997) 449-456.
15. T. Kobayashi, Y. Koizumi, H. Harada and T. Yamagata: "Design of high Re containing single crystal superalloys with balanced intermediate and high temperature creep strengths", Proc. 4th int'l Charles Parsons turbine conference, (The Institute of Materials, 1997), 766-773.
16. T. Murakumo, T. Kobayashi, Y. Koizumi and H. Harada: "Creep Behaviour of Ni-base Single Crystal Superalloys with Various γ' Volume Fraction", Acta Metall., 52(12) (2004) 3737-3744.
17. A. C. Yeh, K. Kawagishi, H. Harada, T. Yokokawa, Y. Koizumi, T. Kobayashi, D. H. Ping, J. Fujioka and T. Suzuki: "Development of Si-bearing 4th Generation Ni-base Single Crystal Superalloys", Superalloys 2008, (TMS, 2008) 619-628.
18. Y. koizumi, T. Kobayashi, T. Yokokawa, M. Osawa, H. Harada, Y. Aoki and M. Arai: "Effects of Alloying Additions on the Creep Strength of a Fourth Generation Single-Crystal Superalloy", J. Japan Inst. Metals 68 (2004) 206-209.
19. H. Harada: "High Temperature Materials for Gas Turbines: The Present and Future", Proc. Int'l Gas Turbine Congress 2003 Tokyo, (IGas Turbine Society of Japan, 2003) 1-9.
20. T. Khan and P. Caron: "Single Crystal Superalloys for Turbine Blades in Advanced Aircraft Engines", Proc. ICAS 1986 (Int'l Council of the Aeronautical Science, 1986), 944-950.
21. W. S. Walston, K. S. O'Hara, E. W. Ross, T. M. Pollock and W. H. Murpy: "Rene N6 Third Generation Single Crystal Superalloy", Superalloys 1996, (TMS, 1996) 27-34.
22. Y. Koizumi, J. X. Zhang, T. Kobayashi, T. Yokokawa, H. Harada, Y. Aoki and M. Arai: "Development of Next Generation Ni-base Single Crystal Superalloys Containing Ruthenium", J. Japan Inst. Metals 67 (2003) 468-471.