Precipitation and Growth of γ' and η Phases in 53Fe–26Ni–15Cr Alloy

Kiyoshi KUSABIRAKI, Yushin TAKASAWA¹⁾ and Takayuki OOKA²⁾

Faculty of Engineering, Toyama University, Gofuku, Toyama, Toyama-ken, 930 Japan.

1) Formerly Graduate Student, Toyama University. Now at Kokusai Electric Co., Ltd., Toranomon, Minato-ku, Tokyo, 105 Japan. 2) Formerly Faculty of Engineering, Toyama University, Gofuku, Toyama, Toyama-ken, 930 Japan.

(Received on November 30, 1994; accepted in final form on January 27, 1995)

The nucleation and growth behavior of γ' and η precipitates in A286 alloy was investigated by micro-Vickers hardness test and transmission electron microscopy. The morphology and the crystallography of them were also discussed. The hardness of A286 aged at 893–1 073 K for durations up to 720 ks was closely related to the mean size of γ' precipitates. The growth kinetics of the γ' precipitate in η -phase free region was explained by Lifshitz–Slyozov–Wagner's theory for diffusion controlled growth at 993–1 073 K. The activation energy for the growth of the γ' precipitates was estimated to be 283 kJ/mol.

KEY WORDS: iron base superalloy; precipitation; morphology; gamma prime; Ostwald ripening; cellular eta-phase; Widmanstätten eta-phase.

1. Introduction

Precipitation strengthened heat resistant alloy A286 has been used for rotor of jet engines and heat resistant bolts, because it is easily heat treatable and has got excellent high temperature strength and corrosion resistance up to about 920 K. The main precipitation strengthening phase of this alloy is $L1_2$ type γ' [$Ni_3(Al \cdot Ti)$: fcc] phase.^{1–3)} Because the growth velocity of precipitation particles is closely related to the strengthening mechanism of the alloy, it is extremely important to clarify the behavior of γ' phase in the alloy. In general, the growth of finely dispersed particles is often explained by the diffusion control growth process, called Ostwald ripening, and it is often attempted to analyze the growth rate of γ' phase by applying the Lifshitz–Slyozov⁴⁾–Wagner⁵⁾ theory (called LSW hereafter).

In this research, the age hardening of Fe–Ni based alloy containing a variety of alloying elements, A286, was investigated based on the measurement of hardness and transmission electron microscopy and the LSW theory was applied to the analysis of the growth of γ' precipitates.

2. Experimental Method

The test material is a heat resistant alloy equivalent

to A286. The alloy of 150 kg was melted in vacuum and cut into a fixed size and after surface grinding, cold-rolled to a strip of 0.4 mm in thickness. Chemical composition of the alloy is shown in **Table 1**. After cutting the strip into coupons of 15 × 15 × 0.4 mm the samples were solid solution heat treated in vacuum for 1.8 ks at 1 253 K, quenched into water, and aged in vacuum for up to 720 ks in a temperature range of 893 to 1 073 K. The aged samples were polished on one side by 0.1 mm with chemical polishing, mechanical polishing by water-proof polishing paper, and finished by buff polishing and the micro-Vickers hardness was measured at room temperature.

Transmission electron microscope (TEM) with an acceleration voltage of 200 kV was used to take photographs of electron microscopic structure and to identify the precipitates. After chemical polishing to about 80 μ m in thickness in a mixture of water (20) + hydrogen peroxide water (20) + nitric acid (5) + hydrochloric acid (7) + hydrofluoric acid (6) solutions, the sample was thinned below 50 μ m with water-proof polishing paper. The sample was electrolytically polished (55 V, 400 A/m²) with a twin jet electro-polishing device and was made into a thin film specimen. A mixture of acetic acid (90) + perchloric acid (10) solutions was used as the electrolyte.

The diameter of γ' phase particles was determined from

Table 1. Chemical composition of specimen. (mass%)

Fe	Cr	Ni	V	Ti	Al	Mo	Si	Mn	C	B	P	S	N	O
53.34	15.06	26.05	0.28	2.10	0.20	1.30	0.31	1.30	0.050	0.0112	0.003	0.0006	0.0020	0.0032

the mean value of a minimum of 400 particles measured using bright field micrographs of specimens for each aging temperature and time.

3. Results and Discussion

3.1. Age Hardening

Figure 1 shows the relation between the hardness and the aging time of samples aged at 893–1073 K after the solid solution heat treatment. The age hardening progressed extremely slowly at 893 K and did not harden enough after 720 ks. The hardening velocity at 943 K was higher than that at 893 K and after about 720 ks, the maximum hardness of about HV320 was reached. The hardening velocity became much faster at 993 K and the maximum hardness was reached after about 360 ks, beyond which, however, softening started. Above 1033 K, hardness did not increase largely.

3.2. Microstructural Observation

TEM structures of the samples aged at 993 K for 0.36 ks: A, 3.6 ks: B, 36 ks: C and 360 ks: D are shown in Fig. 2. In the sample A aged for 0.36 ks, the pres-

ence of precipitation phase was not definite. With the progress of aging from B to D the precipitates become appreciable in the microstructure. The size of precipitates is not clear at this magnification. The selected area electron diffraction (SED) of every aged samples showed the precipitation of γ' phase, although the results were not shown in Fig. 2. The occurrence of precipitation with aging is in good correspondence to the age hardening curve in Fig. 1.

Figure 3 shows the TEM micrograph of the samples aged at 1073 K; γ' phase is shown to grow much faster than in the sample aged at 993 K. The structure of the samples aged for 36 ks: C or more corresponds to the structure of overaging when compared with the age hardening curve shown in Fig. 1. In the sample aged for 360 ks: D, the diameter of γ' phase particles has grown up to about 50 nm. As observed in the upper-left corner of the photograph of sample C aged for 36 ks, γ' phase gradually changed into cell-like or Widmanstätten-like planar precipitates with increasing aging time; the planar precipitation phase were observed in the optical microscope, and precipitated in a shorter time with increasing temperature from 970 to 1150 K but at temperature

Fig. 1. Variations in micro Vickers hardness with aging time.

Fig. 2. Transmission electron micrographs of A286 aged at 993 K for 0.36: A, 3.6: B, 36: C and 360 ks: D.

Fig. 3. Transmission electron micrographs of A286 aged at 1073 K for 0.36: A, 3.6: B, 36: C and 360 ks: D.

Fig. 4. Transmission electron micrograph and its selected-area electron diffraction pattern of A286 aged at 1033 K for 360 ks. Beam along $[0\bar{1}1]_{\gamma}$.

higher than 1150 K, it took a longer time to precipitate. At temperature higher than 1223 K, the occurrence of the planar precipitation phase was not observed even in the sample aged for 180 ks.

Figure 4 shows the TEM and SED micrographs of the sample aged at 1033 K for 360 ks. Figure 4 is a typical micrograph showing the spherical precipitation phase precipitated uniformly in grain interior. The superlattice diffraction patterns such as $(011)_{\gamma'}$ were detected in SED besides the spots of the matrix, suggesting precipitation of γ' phase.

Fig. 5. Transmission electron micrograph of cellular η precipitates in A286 aged at 1073 K for 720 ks. Beam along $[1\bar{1}0]_{\gamma}$ and $[\bar{1}00]_{\eta}$.

The volume fraction of γ' phase in the sample aged at 1033 K for 540 ks was measured to be 8.6%. This value is near the values obtained by Thompson *et al.*⁶⁾ for the aged material at 990 K for 7.2 ks and for 360 ks, which were 9.5 and 10.7%, respectively.

In the Ni-based heat resisting alloys, the growth of γ' phase differs variously in morphology: growth in spherical shape, change from spherical to cubic shape at an intermediate stage, and growth in cubic shape.⁷⁾ It is said that these morphologies of γ'/γ phases are closely related to the lattice misfit with the matrix, and γ'

Fig. 6. Variations in micro Vickers hardness of γ' precipitated area with aging time.

grows spherically in case the misfit is from 0 to 0.2%, cubically from 0.5 to 1.0%, and planar above 1.25%.⁸⁾ However, the lattice misfit between γ' phase and matrix in A286 was reported to be 0.45% when aged for a shorter time and 0.5% for a longer time.⁶⁾ In the samples used in this study, γ' phases were spherical as shown in Figs. 3 and 4, and did not transform to a cubic shape, when their diameters were less or equal to 70 nm. This was in good agreement with the published reports.^{6,9)}

Figure 5 shows the TEM and SED photographs from the $[1\bar{1}0]$ orientation of γ phase containing cellular precipitates in the specimen aged at 1073 K for 720 ks. The precipitates occur at almost regular intervals. As shown in the SED, in addition to the spots from the matrix γ phase, precipitates spots were also observed. These precipitates spots correspond to the η phase $[\text{Ni}_3\text{Ti}:\text{hcp}, \text{DO}_{24} \text{ type}]$. Thus, it was concluded that the precipitation phase is the η phase. The η phase has the crystal habit plane of the $\{111\}_{\gamma}$ and the following crystalline orientation relationship with the matrix: $\{111\}_{\gamma}/\{001\}_{\eta}$ and $\langle 110 \rangle_{\gamma}/\langle 010 \rangle_{\eta}$. Such relations did not contradict the published reports.^{3,9,10)} Cellular η phase nucleated at the vicinity of γ grain boundary by cellular reaction and grew up in clusters. Widmanstätten-like η phase nucleated in the matrix grain. Besides it often intersected in different orientations, it is nearly straight and the degree of parallelism is quite high.

3.3. Relation between Average Particle Diameter of γ' Phase and Increase in Hardness

The age hardening behavior shown in Fig. 1 is a combined effect of hardening by the precipitation of γ' phase, softening by subsequent coarsening of precipitates, and precipitation of η phase. Then, to separate the hardening behavior solely due to the precipitation and growth of γ' phase, the hardness curve of the area without precipitation of η phase was obtained. Figure 6 shows the result. It was shown that no great difference was obtained in the sample aged at 993 K compared with Fig. 1 and the level of hardening was larger in the samples aged at 1033 and 1073 K compared with Fig. 1. At these temperatures, both reached the maximum hardness and then softened by coarsening of γ' phase. Correlation of the amount of increase in hardness with aging and the average particle diameter of γ' phase was examined from the result of Fig. 6, and Fig. 7 was obtained. In Fig. 7, curves corresponding to the smaller mean particle di-

Fig. 7. Relations between increased hardness and mean diameter of γ' precipitates.

ameter are drawn based on the particle diameter obtained from the extrapolated values from Fig. 8. Contribution to the hardening by γ' phase was small in the range where the particle diameter is small, but became larger with the increase in diameter and the hardness reached its maximum at about 25 nm. Then, the hardening decreased with coarsening of γ' phase. This result is in good agreement with the general tendency in the precipitation hardening type alloys. The fact that the increase in hardness was smaller for aging at higher temperatures compared with aging at lower temperatures was thought to arise because, during aging at higher temperatures, precipitation density was low because of the low nucleation frequency of γ' phase, and the amount of precipitation was small, even if the particle diameters were the same because of the increase of amount of solid solution in the matrix.

It was reported by Silcock¹⁾ and Thompson⁶⁾ that the maximum hardening of A286 was obtained when the particle diameter of γ' phase is 10–18 nm. The difference might be due to the method of measurement in that the bright field image was used to read γ' phase in this research while the dark field images were used in the published reports.

3.4. Growth Rate of γ' Phase

By aging the supersaturated solid solution obtained by solid solution heat treatment, precipitation occurred and the concentration in the matrix reached that of

Fig. 8. Variation in mean diameter of γ' precipitates with (aging time) $^{1/3}$.

Table 2. Activation energies for the growth of γ' precipitates in Fe and Ni base alloys. (kJ/mol)

Precipitates	Alloy						
	This work A 286	Inconel X-750	Inconel 718	Ni–Al	Ni–Ti	Ni–Si	Co–Ni–Cr–Ti
γ'	283	281 ⁷⁾ , 290 ¹³⁾	245 ¹¹⁾ , 271 ¹²⁾	269 ¹⁵⁾	282 ¹⁶⁾	262 ¹⁷⁾	298.9 ± 28.9 ¹⁸⁾

equilibrium. The decrease in interfacial energy between the precipitated phase and the matrix acts as the driving force for the growth of precipitates after the equilibrium concentration is reached.

Equation (1) holds to the growth of a dispersion particle when the LSW theory^{4,5)} based on volume diffusion control is applied to the growth of the spherical precipitation phase.

$$d^3 - d_0^3 = 64\sigma DC_e V_m^2 / 9RT = K't \quad \text{.....(1)}$$

where d_0 and d denote the average diameters of the precipitated phase at the initiation of growth and at time t after the initiation, respectively, σ is the interfacial energy of boundary between the precipitated phase and the matrix, D the diffusion coefficient of the solute atom in the matrix, C_e the concentration of solute atoms in the matrix in equilibrium with the particle which has an infinite size, V_m the molar volume of the precipitation phase, R the gas constant, T the absolute temperature, and K' is the growth rate constant. The diffusion coefficient is represented as $D = D_0 \exp(-E/RT)$, where D_0 is the pre-exponential factor and E the activation energy of diffusion. Therefore, K' in Eq. (1) is represented by Eq. (2).

$$K' = 64\sigma D_0 C_e V_m^2 \exp(-E/RT) / 9RT \quad \text{.....(2)}$$

The activation energy E for the growth of particles can be obtained from the slope of Arrhenius plot of Eq. (2) by assuming that the temperature dependency of σ , C_e and V_m in Eq. (2) is small and that they are almost constant in the range of 993–1073 K.

Equation (1) was applied to the analysis of the growth rate of γ' phase in A286. Figure 8 shows the relation between the average particle diameter and 1/3rd power of aging time. A linear relation was approved between the 1/3rd power of aging time and $\bar{d}_{\gamma'}$ in each case when aging was performed between 993 and 1073 K. This result did not contradict the results obtained at a temperature

Fig. 9. Arrhenius plots for determination of the activation energy for growth of γ' precipitates in Fe and Ni base alloys. K' : Rate constant, T : Temperature.

range of 973 and 1123 K by Silcock *et al.*,¹⁾ Thompson *et al.*⁶⁾ and Clark *et al.*⁹⁾ It indicated that the γ' phase in A286 grew by the volume diffusion controlled process in which the driving force was given by the Ostwald ripening mechanism by the decrease in boundary energy between γ and γ' phase. However, the cause of d_0 indicating a larger value at higher temperatures was not clear whether it was due to the difference in growth rate in the initial stage of precipitation or to the error in the analysis.

The growth rate constant of γ' phase at each aging temperature was obtained from the slope of straight lines in Fig. 8 and the Arrhenius plot is shown in Fig. 9. For comparison, the published results in other Ni-based alloys which generated γ' phase in the matrix are shown in Fig. 9. The growth rate constant K' of A286 seemed to have a somewhat small value compared with other alloys. Apparent E for the growth of γ' phase obtained from the slope of straight line and the value obtained

for other alloys are shown in Table 2. The value of E for the growth of γ' phase in A286 was 283 kJ/mol.

In general, the main composition of γ' phase is $\text{Ni}_3(\text{Al} \cdot \text{Ti})$, but the elements like Fe, Cr and Mo can also take part in the formation of γ' .¹⁹⁾ Although the activation energy of diffusion of each element in A286 could not be certain because there is no relevant report, the activation energy for the diffusion of Al, Ti, Ni, Fe, Cr and Mo in γ -Fe was reported to be 234, 251 (1 433–1 593 K), 313 (1 403–1 633 K), 275 (1 273–1 622 K), 292 (1 223–1 673 K) and 323 kJ/mol (1 223–1 573 K).²⁰⁾ According to this data, it can be judged that E of the growth of γ' phase is almost in coincidence with those of the diffusion of the element in γ -Fe which can take part in the growth. However, because the activation energy of diffusion of each element was close to each other, it was difficult to determine definitely the diffusion element which controlled the growth of γ' , based only on E obtained in the analysis. There was some difference in E among the alloying elements shown in Table 2. But this also could not be judged exactly if it was based on the difference among diffusion elements. However, the value of E obtained for A286 did not contradict the previous analysis which showed that the growth of γ' phase was controlled by the Ostwald ripening by diffusion controlled process of solution atoms.

It was clarified that the growth rate of γ' phase in multi-component A286 could be explained by the theory of LSW as well as in Ni-based binary alloys which had been confirmed until now. Doi *et al.*²¹⁾ had observed many examples in which γ' phase precipitated in a cubic shape was divided into two, eight, or more particles after growing to some size (for instance larger or equal to 0.25 μm in Ni–Al alloy). However, in A286, this kind of phenomenon was not confirmed in all the samples treated in each condition. This was thought to arise from the large influence of the boundary energy on the growth rate in the case of A286, where the size of γ' phase was small and the shape was almost spherical, so that the influence of elastic strain energy and elastic interaction energy mentioned by Doi *et al.* was small. In fact, in their results γ' phase precipitated in a spherical or a small cubic shape was not divided into smaller size. Therefore, it is thought that a big problem did not occur in this research in the analysis of the growth rate of γ' phase by the use of the theory of LSW based on the Ostwald ripening mechanism.

4. Conclusion

The age hardening and change in micro structures of Fe–Ni base heat resistant alloy A286 were investigated and the growth kinetics of γ' precipitates was analyzed by applying the Lifshitz–Slyozov–Wagner theory based on the Ostwald ripening mechanism. The results are summarized in the following:

(1) In the case of aging at about 943 K after solution heat treatment, the maximum micro-Vickers hardness of about 320 was obtained after about 720 ks. Further aging at this temperature did not induce overaging. Aging at

temperatures above 973 K produced precipitated of η phase and aging at temperatures above 1 033 K produces a large number of η precipitates resulting in no appreciable increase in hardness.

(2) The precipitation strengthening phase by aging was γ' phase, whose volume fraction was 8.6% after aging for 540 ks at 1 033 K. The γ' phase particle grew almost in a spherical shape from the initial stage of precipitation and the hardening was maximum at the average particle diameter in the vicinity of 25 nm.

(3) The LSW theory was applied to the growth of γ' phase and the results were obtained in good agreement with the Ostwald ripening mechanism that was based on the diffusion controlled process. The apparent activation energy for growth was obtained to be 283 kJ/mol. This value was very close to the activation energy for diffusion of solute elements in γ -Fe which are considered to contribute to the growth of γ' phase.

(4) The η phase, which had two types of precipitate shapes, cellular and Widmanstätten, precipitated in a shorter time at high temperature range between 970 and 1 150 K and needed a longer time at temperatures above 1 150 K.

Acknowledgements

The authors would like to thank their deep gratitude to the research laboratories of Hikari works, Nippon Steel Corporation, for the cooperation in melting and fabrication of the test samples. One of the authors (KK) acknowledges financial support from the Saneyoshi Scholarship Foundation.

REFERENCES

- 1) J. M. Silcock and N. T. Williams: *J. Iron Steel Inst.*, **204** (1966), 1100.
- 2) D. Raynor and J. M. Silcock: *Met. Sci.*, **4** (1970), 121.
- 3) C. T. Sims, N. S. Stoloff and W. C. Hagel: *Superalloys II, High-Temperature Materials for Aerospace and Industrial Power*, John Wiley & Sons, New York, (1987), 165.
- 4) M. Lifshitz and V. V. Slyozov: *J. Phys. Chem. Solids*, **19** (1961), 35.
- 5) C. Wagner: *Z. Electrochem.*, **65** (1961), 581.
- 6) A. W. Thompson and J. A. Brooks: *Acta Metall.*, **30** (1982), 2197.
- 7) K. Kusabiraki, H. Nagahama, L. Wang and T. Ooka: *Tetsu-to-Hagané*, **75** (1989), 1354.
- 8) W. C. Hagel and H. J. Beattie: *Iron and Steel Inst., Special Report*, London, **64** (1959), 98.
- 9) B. R. Clark and F. B. Pickering: *J. Iron Steel Inst.*, **205** (1967), 70.
- 10) G. R. Speich: *Trans. Metall. Soc. AIME*, **227** (1963), 754.
- 11) K. Kusabiraki, L. Wang, T. Ooka and K. Yamada: *Tetsu-to-Hagané*, **76** (1990), 1341.
- 12) Y. Han, P. Deb and M. C. Chaturvedi: *Met. Sci.*, **16** (1982), 555.
- 13) C. Castani and V. Lupine: *Metall. Ital.*, **7/8** (1977), 306.
- 14) A. J. Ardell and R. B. Nicholson: *Acta Metall.*, **14** (1966), 1295.
- 15) A. J. Ardell and R. B. Nicholson: *J. Phys. Chem. Solids*, **27** (1966), 1793.
- 16) A. J. Ardell: *Metall. Trans.*, **1** (1970), 525.
- 17) P. K. Rastogi and A. J. Ardell: *Acta Metall.*, **19** (1971), 321.
- 18) M. Chaturvedi and D. W. Chung: *J. Inst. Met.*, **101** (1973), 253.
- 19) O. H. Kriege and J. M. Baris: *Trans. ASM*, **62** (1969), 195.
- 20) Tekkou-Binran I Kiso, 3rd ed., ed. by the Iron and Steel Inst. of Japan, Maruzen, Tokyo, (1981), 287.
- 21) M. Doi and T. Miyazaki: *Bull. Jpn. Inst. Met.*, **28** (1989), 467.

(Originally published in *Tetsu-to-Hagané*, **78** (1992), 1854, in Japanese)