Precipitation and Growth of Delta-phase (Ni_3Nb) in a Ni–15Cr–8Fe–6Nb Alloy

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The precipitation and growth behaviors of δ phase in Ni-base superalloy, modified Inconel X-750 type alloy (X-750M), were investigated mainly by optical and transmission electron microscopy. The strengthening phase in the aged X-750M was metastable γ'' phase. The γ'' phase changed gradually into the stable δ phase during aging. The orientation relationship between γ and δ phase in the cellular and the Widmanstätten precipitates was: $\{111\}_{\gamma} // (010)_{\delta}$, $\langle 1\bar{1}0 \rangle_{\gamma} // [100]_{\delta}$. The interlamellar spacing of the δ phase in each precipitation type was inversely proportional to the degree of undercooling below the equilibrium transformation temperature of γ phase to $\delta + \gamma$ phases. According to the theory of diffusion controlled eutectoidal growth, the equilibrium transformation temperatures of the cellular and the Widmanstätten precipitation were estimated to be 1 279 and 1 313 K, respectively. These temperatures were consistent with the experimental tendency.

KEY WORDS: nickel-base alloy; superalloy; Ni_3Nb ; δ phase; transformation; precipitation; cellular precipitation; discontinuous precipitation; Widmanstätten precipitation.

1. Introduction

Inconel X-750 is a precipitation strengthened alloy. The precipitation strengthening phase of the alloy is the γ' phase [$\text{Ni}_3(\text{Al}, \text{Ti})$] with a crystal structure of $\text{L}1_2$ type. In some Ni alloys,^{1–3)} such as Inconel 718, the γ'' phase [Ni_3Nb] with a DO_{22} type crystal structure has been applied as a precipitation strength phase. The present authors studied the possibility of precipitating the γ'' phase in a modified alloy (hereafter to be called as X-750M) substituting most of Al and Ti with Nb in Inconel X-750. Based on the results of measurement of hardness in the age hardening process with respect to formation and growth of the γ'' phase and transmission electron microscopy, the modified alloy was compared with the conventional Inconel X-750 type alloy.⁴⁾ Although the strengthening phase in the aged X-750M was found to be the metastable γ'' phase (bct), the γ'' tended to change gradually into the stable δ phase [Ni_3Nb : orthorhombic] during aging. Thus it is con-

sidered necessary to know the precipitation behavior of δ phase for the understanding of strengthening characteristics in aging of the alloy. On the basis of the study on precipitation hardening by optical and transmission electron microscopy, reports will be made on the two types of morphological variations of δ phase, the crystallographic orientation relationship between γ and δ phase, and the equilibrium transformation temperature in each type of δ phase.

2. Experimental Method

The test materials were a nickel base superalloy equivalent to Inconel X-750 (to be X-750) and its modification by substituting significant amounts of Al and Ti with Nb (to be X-750M). **Table 1** shows the chemical composition of each alloy. The materials were prepared by the processes of vacuum melting, two stage hot rolling and single stage cold rolling to a thickness of 0.5 mm. The samples were heated for 1.8 ks at 1 373 K,

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

	Ni	Cr	Fe	Nb	Ti	Al	Mo	Si	Mn	C	B	P	S	N	O
X-750	70.98	15.43	8.40	0.83	2.53	0.80	<0.01	0.11	0.11	0.041	<0.001	0.002	<0.001	0.0010	0.0019
X-750M	68.62	15.00	7.95	6.02	0.004	0.024	0.02	0.11	0.11	0.036	0.0001	0.005	<0.001	0.0010	0.0051

quenched into water, and aged in the temperature range between 893 and 1 123 K for a maximum of 2 880 ks. The results of hardness measurement of aged specimens at room and high temperatures, transmission electron microscopy, and identification of precipitates with x-ray diffraction were reported previously.⁴⁻⁶⁾

Optical microscopy was done in the following way. The aged samples were polished with emery papers and buffs, and etched chemically with a mixture of 42% hydrochloric acid + 42% glycerin + 16% nitric acid for the specimens aged less than 3.6 ks and electrolytically with 5% nital for the other specimens for microstructure observation.

3. Results and Discussion

3.1. Optical Microstructure

The samples, X-750 and X-750M, aged in a various combination of temperature and time were observed by an optical microscope. **Figure 1** compares the optical microstructures of X-750 and X-750M after aging for 3.6 (A, D) and 36 (B, E) and 360 ks (C, F) at 993 K. No appreciable change is found in the optical microstructures of X-750. However the transmission electron microscopy, as reported previously,⁵⁾ fine γ' was observed to precipitate and grow in grain interior during aging. The samples aged for 3.6 ks show no significance between X-750M (D) and X-750 (A). Cellular precipitation of δ phase is observed to start on grain boundaries in X-750M after 36 ks (E) and to grow extensively in the matrix after 360 ks (F). Transmission electron micrographs⁴⁾ showed the fine precipitation and rapid growth of γ'' in grain interior in the early stage of aging, 3.6 ks. A mixed microstructure of γ , γ'' and δ was formed after aging of 36 ks by precipitation of cellular δ phase in grain boundaries as identified with

transmission electron microscopy and x-ray diffractometry. Micro Vickers hardness measurement⁴⁾ showed the stages of significant hardening at 3.6 ks, overaging at 36 ks, and rapid softening in the subsequent aging at 993 K of X-750M.

Figure 2 shows the optical microstructure of X-750M aged at 1 073 K. No δ precipitate is detected after aging of the X-750M alloy for 0.36 ks (A), but after 3.6 ks (B) cellular δ phase appears as colonies in the vicinity of some grain boundaries. In the grain interior δ phase appears in a Widmanstätten like morphology. Both types of δ precipitates grow gradually with aging. In the aging at lower temperatures below 1 073 K, the cellular type shows a higher growth rate than the Widmanstätten type. **Figure 3** shows the optical microstructure of X-750M aged at 1 123 K; no δ phase is observed after 0.36 ks (A). Cellular δ phase starts to precipitate in the vicinity of grain boundaries in the sample aged for 1.8 ks (B) and subsequently the Widmanstätten type δ phase grows rapidly and preferentially.

With optical microscopy on δ phase was found in the X-750 alloy for every conditions of time and temperature in the present experiment. In the X-750M alloy the δ phase tended to precipitate as the cellular type in the temperature range of 943 to 1 073 K and as the Widmanstätten type above 1 123 K.

3.2. Transmission Electron Micrography

Figure 4 shows the transmission electron micrographs of X-750M aged for 540 ks at 943 K. The micrograph shows cellular colonies of δ and γ lamellas in the upper left part and a large amount of γ'' in the γ matrix in the other part; the blackish plate-like phase is δ and the grayish white matrix is γ . With aging while the γ'' phase gradually grew, the δ phase precipitated in grain boundaries grew extensively by reducing the region of

Fig. 1. Optical micrographs of X-750 aged at 993 K for 3.6: A, 36: B and 360 ks: C and X-750M aged at 993 K for 3.6: D, 36: E and 360 ks: F.

Fig. 2. Optical micrographs of X-750M aged at 1073 K for 0.36: A, 3.6: B, 18: C and 36 ks: D.

Fig. 3. Optical micrographs of X-750M aged at 1123 K for 0.36: A, 1.8: B, 3.6: C and 36 ks: D.

$\gamma + \gamma''$.⁴⁾ Transmission electron micrographs also proved the presence of both types of cellular and Widmanstätten morphology of δ phase.

Figure 5 shows the transmission electron micrograph and selected area electron diffraction pattern of cellular precipitates in X-750M precipitated at 1033 K for 180 ks. Precipitation of a blackish phase is noticed at a regular interval. Selected area diffraction from the encircled region proves that the dark precipitates are of the δ

phase; the diffraction pattern shows the spots of (001) and (011) from the δ phase besides the fundamental spots from the γ phase. These cellular δ precipitates are in a shape plate and have a crystallographic relation with γ phase: $\{111\}_{\gamma} // (010)_{\delta}$ and $\langle \bar{1}10 \rangle_{\gamma} // [100]_{\delta}$. This is in good agreement with the relation in available reports^{7,8)} on the δ precipitates in Ni base alloys.

Figure 6 shows the transmission electron micrograph and selected area electron diffraction pattern of

Fig. 4. Transmission electron micrograph of X-750M aged at 943 K for 540 ks.

Fig. 5. Transmission electron micrograph and its selected-area electron diffraction pattern obtained from the framed area of X-750M aged at 1033 K for 180 ks. Beam along $[\bar{1}10]_{\gamma}$ and $[100]_{\delta}$.
A: Bright field image.
B: Selected-area electron diffraction pattern.

Widmanstätten type phase precipitated in aging at 1123 K for 180 ks. The precipitates are dispersed in a regular spacing. Selected area diffraction from the encircled region shows that the Widmanstätten type dark grayish precipitates are also of the δ phase and have a crystallographic relation of $\{111\}_{\gamma} // (010)_{\delta}$ and $\langle \bar{1}10 \rangle_{\gamma} // [100]_{\delta}$ to the γ phase. These relations held for the precipitates formed in every conditions and were consistent with the available reports^{7,8)} on the δ phase.

Figure 7 shows a reflective electron image of EPMA on the section of the X-750M aged for 540 ks at 1023 K. The grayish white images in the gray matrix are pre-

Fig. 6. Transmission electron micrograph and its selected-area electron diffraction pattern obtained from the framed area of X-750M aged at 1123 K for 180 ks. Beam along $[\bar{1}10]_{\gamma}$ and $[100]_{\delta}$.
A: Bright field image.
B: Selected-area electron diffraction pattern.

Fig. 7. Reflective electron image and concentration profiles of Ni and Nb obtained by EPMA on the cross section of X-750M aged at 1023 K for 540 ks.

cipitates or inclusions. The dark regions are holes formed by drop out of precipitates and inclusions in polishing. The line analysis for Ni and Nb characteristic x-rays along the white line below the center in the figure suggests that the precipitates are of the δ phase, since the grayish white precipitates phase (which is mainly of Widmanstätten type in the figure) has a higher concentration of Nb and a nearly same concentration of Ni compared with the matrix. In Fig. 7, some grayish white particles show a lower Ni and higher Nb content than the matrix; these are thought to be NbC the presence of which is

identified with transmission electron microscopy and x-ray diffractometry of the electrolytic extracts. Thus from the observation with optical and transmission electron microscopy the δ precipitates in the X-750M alloy show two types of morphology, cellular and Widmanstätten type. These precipitates were identified as δ phase from the x-ray diffractometry of the electrolytic extracts.⁴⁾ The two types of morphological variations in δ phase precipitating in the X-750M alloy are consistent with the available reports¹⁾ on Ni base alloys.

As evident from the transmission micrographs in Figs. 5 and 6, both cellular and Widmanstätten types of the δ phase show tendency to precipitate at a regular interval. In estimation of the interlamellar spacing of δ precipitates, a method of observing the surface replica on specimen section⁹⁾ is not enough accurate. Thus the following method was used in the present study. In

general the δ phase has a tendency to precipitate in plate parallel to the $\{111\}$ of the γ matrix. **Figure 8** shows the orientational relationship between δ and γ in the case of electron beam incidence vertical to the $\{110\}$ plane of the γ phase. The figure shows three types of appearance for the δ phase. The true interlamellar spacing d of δ phase can be calculated from the equation in the figure.

Figure 9 shows the relation between the true interlamellar spacing of δ phase and aging time for each aging temperature. The interlamellar spacing is found to be mostly dependent on the aging temperature with little dependence on aging time. The spacing is smaller in aging at lower temperatures that represent higher degree of supersaturation. This tendency is similar to the case of η phase precipitation.⁹⁾

Figure 10 shows the results of the similar analysis on the Widmanstätten type δ phase. Also in this case, the

Fig. 8. Schematic representation of real (d) and apparent interplanar spacing (D) and interplanar angles in a cubic crystal.

Fig. 9. Interlamellar spacing d of cellular δ phase plotted as a function of aging time for X-750M aged at various temperatures.

Fig. 10. Interlamellar spacing d of Widmanstätten δ phase plotted as a function of aging time for X-750M aged at various temperatures.

interlamellar spacing is solely dependent on the aging temperature; It is narrower for the aging at lower temperatures.

3.3. Application of Diffusional Transformation Theory for Eutectoid Phase

A trial was made to analyze the growth of cellular δ phase by applying the diffusional transformation theory derived for the growth of eutectoid phase.¹⁰⁾ The growth behavior of the cellular δ phase is schematically shown in Fig. 11. The extension of Zener's method¹¹⁾ results in Eq. (1) for the free energy of interface formation in $\gamma \rightarrow \gamma + \delta$ transformation per unit volume, ΔG_s .

$$\Delta G_s = 2\sigma/d \quad (1)$$

where σ is the free energy of interface per unit area and d the interlamellar spacing. A net change in free energy in $\gamma \rightarrow \gamma + \delta$ transformation per unit volume, ΔG , is given by Eq. (2).

$$\Delta G = \Delta G_0 - 2\sigma/d \quad (2)$$

where ΔG_0 represents the change in free energy of the formation of γ plus δ without a interface. Since the smallest possible interlamellar spacing, d_M , can be derived in a condition of $\Delta G = 0$, Eq. (3) is obtained.

$$d_M = 2\sigma/\Delta G_0 \quad (3)$$

Thus Eq. (2) is written as Eq. (4).

$$\Delta G = \Delta G_0(1 - d_M/d) \quad (4)$$

Equation (5) is obtained by assuming that the growth velocity, $\dot{R}$, depends solely on the velocity of diffusion necessary for redistribution of the solutes in phase transformation.

$$\dot{R} = K D \Delta G_0(1 - d_M/d)/d \quad (5)$$

where K is a constant. The value of R is maximum at $d\dot{R}/dd=0$ and Eq. (6) is derived from Eq. (3).

Fig. 11. Schematic illustration of growth of cellular δ phase.

$$d = 4\sigma/\Delta G_0 \quad (6)$$

By approximating that ΔG_0 is linearly proportional to the degree of supercooling, Eq. (7) is derived.

$$\Delta G_0 = \Delta H(T_E - T)/T_E \quad (7)$$

where ΔH is the latent heat in transformation per unit volume and T_E the equilibrium transformation temperature. Thus Eq. (6) results in Eq. (8).

$$d = 4\sigma T_E / [\Delta H(T_E - T)] \quad (8)$$

Equation (8) represents a linear relationship between the reciprocal of interlamellar spacing, d^{-1} , and the degree of supercooling, $T_E - T$.

Figure 12 shows the relation between the aging temperature and the reciprocal of interlamellar spacing of cellular δ phase. A linear relationship holds between d^{-1} and temperature. From Eq. (8), the most probable temperature of $\gamma \rightleftharpoons \gamma + \delta$ transformation in equilibrium, T_E^C , was calculated to be 1279 K. Similar analysis for the Widmanstätten type δ phase yielded $T_E^W = 1313$ K. The lower transformation temperature of the cellular type than the Widmanstätten type is consistent with the microstructure observations on precipitation behavior of the δ phase. In order to verify the validity of the derived T_E^C and T_E^W , precipitation behavior of the δ phase was observed in X-750M specimens aged at around the estimated transformation temperatures for 36 ks. No δ precipitates were detected in the specimens aged at higher temperatures above 1355 K. The Widmanstätten type precipitates were formed very little in grain interior after aging at 1336 K and abundantly after aging at 1308 K. At 1274 K a small amount of cellular δ precipitates appeared on grain boundaries besides a large amount of Widmanstätten type precipitates. At 1225 K both types of precipitates were observed in a large number. The observed temperature was higher for the T_E^C but near to the T_E^C . Therefore the equilibrium temperature of transformation from γ matrix to cellular δ phase agrees well with the prediction based on the diffusional transformation theory. For the Widmanstätten type, application of this theoretical analysis seems to be difficult because of the fluctuations in measured interlamellar spacing. The kinetics of cellular precipitation have been analyzed in detail by Chan¹²⁾ and Turnbull¹³⁾ besides

Fig. 12. Relations between reciprocal of mean interlamellar spacing of δ phase precipitated in X-750M and aging temperature.

Zener.¹¹⁾ However, since the values of physical constants of this alloy system are indefinite, detailed analysis remains to be a future problem.

4. Conclusion

A modified alloy, X-750M, was made by substituting a substantial amount of Al and Ti in the Inconel X-750 alloy (X-750) with Nb to study the differences in behavior of the precipitation strengthening due to γ' in the X-750 superalloy and due to γ'' in other Ni base superalloys. The precipitation strengthening phase in the aged X-750M was the metastable phase of γ'' , which tended to transform gradually into the stable phase of δ in aging. The present study clarified the morphology of δ precipitates, the crystallographic relationship between δ and γ , and the equilibrium transformation temperatures, based on the study on the aging characteristics of X-750M in terms of hardness measurement and microstructure observation with optical and transmission electron microscopy.

The results of the present study will be summarized as follows.

(1) During aging of the X-750M alloy after solution treatment γ'' phase precipitates and grows in the matrix, and subsequently δ phase precipitates in grain boundaries of the matrix and grows gradually.

(2) The delta phase cannot be detected in the X-750 alloy for all the temperature and time conditions of aging in the present study. In the X-750M alloy the δ phase tends to precipitate as the cellular type in the temperature range of 943 to 1073 K and as the Widmanstätten type above 1123 K.

(3) Both cellular and Widmanstätten type precipitates have an crystallographic orientation relationship of $\{111\}_{\gamma} // (010)_{\delta}$ and $\langle 1\bar{1}0 \rangle_{\gamma} // [100]_{\delta}$ with the γ phase.

(4) Both morphological types of δ phase show a tendency to precipitate at a regular interval. The interlamellar spacing depends solely on the aging

temperature in both types, decreasing with lowering of the aging temperature.

(5) By applying the diffusional transformation theory derived for the growth of eutectoid phase, the equilibrium temperature of transformation is estimated to be 1279 K for the cellular type and 1313 K for the Widmanstätten type δ phase. These temperatures agree fairly well with the observed temperatures for both the types of δ phase.

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REFERENCES

- 1) Ed. by C. T. Sims, N. S. Stoloff and W. C. Hagel: Superalloys II, High-Temperature Materials for Aerospace and Industrial Power, John Wiley and Sons, New York, (1987), 165.
- 2) Y. Han, P. Deb and M. C. Chaturvedi: *Met. Sci.*, **16** (1982), 555.
- 3) E. L. Raymond and D. A. Wells: Superalloys-Processing, Battelle Columbus Laboratories, MCIC 72-10, Columbus, Ohio, (1972), N1.
- 4) K. Kusabiraki, S. Araie and T. Ooka: *Tetsu-to-Hagané*, **78** (1992), 650.
- 5) K. Kusabiraki, H. Nagahama, L. Wang and T. Ooka: *Tetsu-to-Hagané*, **75** (1989), 1354.
- 6) K. Kusabiraki, L. Wang, T. Ooka and K. Yamada: *Tetsu-to-Hagané*, **76** (1990), 1341.
- 7) I. Kirkman: *J. Iron Steel Inst.*, **207** (1969), 1612.
- 8) M. Sundararaman, P. Mukhopadhyay and S. Banerjee: *Metall. Trans. A.*, **19** (1988), 453.
- 9) B. R. Clark and F. B. Pickering: *J. Iron Steel Inst.*, **205** (1967), 70.
- 10) J. Burke: The Kinetics of Phase Transformations in Metals, Chap. 6.7, Pergamon Press Ltd., New York, (1965).
- 11) C. Zener: *Trans. AIME*, **167** (1946), 550.
- 12) J. W. Cahn: *Acta Metall.*, **7** (1959), 18.
- 13) K. N. Tu and D. Turnbull: *Scr. Metall.*, **1** (1967), 173.

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