Stacking Faults and Transformation of $\gamma'$ Metastable Precipitates in an Fe–29Ni–22Co–4Nb–2Cr–1Ti–0.5Al–0.5Si Alloy

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In this study, we investigate an Fe–29Ni–22Co–4Nb–2Cr–1Ti–0.5Al–0.5Si heat resistant alloy (refer to herein as alloy 929C), in which the $\gamma'$ phase is the precipitation-strengthening phase. The specimens of alloy 929C are solid-solution heat treated and aged within a temperature range of 993 to 1 073 K for up to 1 440 ks. The morphological and structural changes of the precipitates in the alloy are analyzed by transmission electron microscopic observation. Internal-fringe contrast, which suggests the existence of stacking faults on the (111)$_{\gamma'}$ plane, is found in many of the large $\gamma'$ precipitates formed in the specimens at the latter stage of aging at temperatures above 1 033 K. The metastable $\gamma'$ precipitates, of which some have stacking faults, are gradually transformed into a stable $\eta$ phase during aging. The effects of stacking faults introduced by cold-rolling into the $\gamma'$ particles on the formation of $\eta$ phase are studied by subsequent annealing heat treatments. The selected-area electron diffraction (SAED) patterns of the cold-rolled and annealed particles show that the metastable $\gamma'$ precipitates with stacking faults are transformed intensively into a stable $\eta$ phase. In this paper, we discuss in detail the basis of these morphological and structural changes of the precipitates in heat-resistant alloys.

KEY WORDS: superalloy; precipitation; age hardening; gamma prime phase; stacking fault; eta phase; transformation; nucleation; transmission electron microscopy.

1. Introduction

Incoloy alloy 909, an Fe–38Ni–13Co–5Nb–1.5Ti–0.4Si alloy, is a low thermal expansion heat-resistant alloy that is attractive for aerospace and land-based gas turbine engine applications.1–7) The recently developed alloy 929C, an Fe–29Ni–22Co–4Nb–2Cr–1Ti–0.5Al–0.5Si alloy, is another low thermal expansion heat-resistant alloy.8) Both Incoloy 909 and alloy 929C are strengthened by the fine precipitation of $\gamma'_1$ phase (Ni$_3$(Al, Ti): cubic, L1$_2$-type, metastable) in $\gamma$ matrix (austenite: fcc) brought about by aging after solution heat treatment. However, when these alloys are used for a long time at a high temperature, the $\gamma'$ phase shifts to plate-like $\eta$ precipitates formed in the $\gamma$ matrix. The metastable $\gamma'$ precipitates, of which some have stacking faults, are gradually transformed into a stable $\eta$ phase during aging. The effects of stacking faults introduced by cold-rolling into the $\gamma'$ particles on the formation of $\eta$ phase are studied by subsequent annealing heat treatments. The selected-area electron diffraction (SAED) patterns of the cold-rolled and annealed particles show that the metastable $\gamma'$ precipitates with stacking faults are transformed intensively into a stable $\eta$ phase. In this paper, we discuss in detail the basis of these morphological and structural changes of the precipitates in heat-resistant alloys.

2. Materials and Methods

Alloy 929C was melted and cast in a high-frequency induction vacuum furnace. The alloy ingots of 10 kg were forged to a size of 20 mm x 20 mm x 200 mm, and the forged bars were heated at 1 253 K for 3.6 ks (1 h) and then air-cooled.

| Table 1. Chemical composition of alloy 929C (mass%) |
|-------|-------|-------|-------|-------|-------|-------|
| Fe   | Ni   | Co   | Nb   | Cr   | Ti   | Al   |
| 40.25| 29   | 22.39| 3.97 | 1.93 | 1.25 | 0.58 |
| Si   | Mn   | C    | B    | P    | S    |
| 0.48 | 0.11 | 0.03 | 0.004| 0.002| 0.001|

This study clarifies the transformation process from $\gamma'$ phase to $\eta$ phase through stacking faults formed in the $\gamma'$ precipitates by using alloy 929C.
up to 72 ks (20 h) in a vacuum, then used as the sample. For transmission electron microscopic (TEM) observation, the aged specimens were polished with emery papers and chemical-polished to a thickness of about 30 \(\mu\)m with a solution of 10% sulfuric acid+6% hydrochloric acid+9% hydrofluoric acid+31% hydrogen peroxide+44% water. They were then punched into discs of 3 mm in diameter, and electrically polished (45 V, 500 A/m\(^2\)) by twin jet method in a solution of 12% perchloric acid+88% acetic acid to make foil specimens. To prepare the carbon extraction replica of the precipitation phase, we used a two-step replicating method. An aqueous solution of 1% citric acid+1% ammonium sulfate was used as the electrolytic extraction liquid. The details of its procedure were described previously.10) A TEM with an acceleration voltage of 200 kV was used to observe the microstructures of the aged specimens and to analyze the crystal structures of the precipitates.

3. Results and Discussion

3.1. Microstructures of \(\gamma'\) and \(\eta\) Precipitates

Figure 1 shows the transmission electron micrographs of the specimens aged at 1 033 K (A=aged for 90 ks (25 h); B=aged for 180 ks (50 h); C=aged for 360 ks (100 h); D=aged for 720 ks (200 h)). These micrographs indicate the formation in the specimens of fine precipitates which gradually grow with the progress of aging time, A→B→C→D. Selected area electron diffraction (SAED) patterns, not shown here, indicated that the fine precipitates were a \(\gamma'\) phase coherent with the \(\gamma\) matrix. The \(\gamma'\) phase has crystallographic orientation relationships with the \(\gamma\) matrix: \(\{100\}^\gamma//\{100\}^\gamma\) and \(\{001\}^\gamma//\{001\}^\gamma\). The \(\gamma'\) precipitates have been shown to be fine spheres at the early stage of aging, but they gradually become cuboidal in form as a result of the growth that occurs with the progress of aging time.

If this alloy is aged at above 1 063 K for a sufficient long time, such as the specimen aged at 1 063 K for 180 ks (50 h) shown in Fig. 2, the \(\gamma'\) precipitates with the size of 150–200 nm change to a star-like form with eight horns according to the growth of \(\langle 111\rangle^\gamma\) direction. As the growth rate of the \(\gamma'\) precipitates in the alloy 929C dissimilar to those of conventional heat resistant alloys such as Inconel 718 and so on is relatively large, the \(\gamma'\) precipitates in this alloy grew with ease to the size of 150–200 nm after long time aging. The details of the age-hardening, precipitation,
growth, and morphological changes of the $\gamma'$ phase of this alloy were reported earlier.\(^9\)

**Figure 3** shows the transmission electron micrograph of the specimen aged at 1033 K for 360 ks (100 h). Under this aging condition, elongated plate-like precipitates appeared in the $\gamma$ matrix. **Figure 4** shows the transmission electron micrograph of the plate-like precipitate formed in the specimen aged at 1073 K and its SAED pattern. The SAED pattern shows that the plate-like precipitate in this alloy is $\eta$ phase, and that there are crystallographic orientation relationships, consistent with previous reports,\(^5,11\) between the $\gamma$ matrix and the $\eta$ phase: \{111\}/(001)\(_\gamma\) and \{110\}/(110)\(_\eta\)\(_\gamma\). The $\eta$ phase formed after the precipitation of the $\gamma'$ phase in the latter stage of aging and grew in a Widmanstätten-like shape in the grain interior. This study has confirmed the $\eta$ phase to be a stable precipitate of alloy 929C.

It is important to note that alloy 929C aged at temperatures higher than 1073 K showed a peculiar tendency to precipitate the $\gamma'$ phase intensively on some \{111\} planes of the $\gamma$ matrix and formed regions without dispersed $\gamma'$ precipitates, as shown in **Fig. 5**. The SAED pattern in Fig. 5 shows that the localized precipitates on the (111) plane are $\gamma'$ phase. In this case, the $\gamma'$ precipitates also changed into $\eta$ phase, as described below with the progress of aging time. The internal-fringe contrasts decorated by many $\gamma'$ precipitates in the $\gamma$ matrix, shown in Fig. 5, are thickness-fringe due to a stacking fault, probably, formed in the (111) plane.

**Figure 6** shows the transmission electron micrograph of the specimen aged at 1073 K for 43.2 ks (12 h). Patient and detailed observation of the transformation process of the $\gamma'$
phase into the \( \eta \) phase revealed that the \( \gamma' \) precipitates change into \( \eta \) phase directly, as shown in this figure. Although according to the TEM images, the transformation seems to proceed soon from the \( \gamma' \) phase to the \( \eta \) phase, such an immediate transformation is difficult to accept because the crystal structures of the two phases are so different from each other.

The transmission electron micrograph and SAED pattern of the specimen aged at 1073 K for 36 ks (10 h) are shown in Fig. 7. The SAED pattern indicates that the precipitates are \( \gamma' \) phase, since the superlattice diffraction spots from (100)\(_x\), (110)\(_x\) and so on appear besides the fundamental diffraction spots from the \( \gamma \) matrix. The photograph shows that some largely grown \( \gamma' \) precipitates have internal-fringe contrast within their structure, as indicated by arrows. This internal-fringe contrast in the \( \gamma' \) precipitates suggests the existence of stacking faults in the crystal structure. Similar observations were often made with the long term aged specimens as well.

### 3.2. Crystallographic Relation between \( \gamma' \) and \( \eta \) Phases

As well known, the unit cell of the \( \gamma' \) phase \([Ni_3(Al,Ti)]\) has a cubic form with an \( L1_2 \) structure. In Fig. 8 we see the atomic arrangement of the closed-packed (111)\(_x\) plane in which the stacking faults seem to be formed. In this representation, solid circles represent titanium or aluminum atoms and open circles represent nickel atoms. In the case of \( \gamma' \) phase, assuming the position of titanium or aluminum atoms in Fig. 8 to be \( a \), the titanium atoms in the second layer would move to position \( b \). Similarly, the titanium atoms in the third layer would move to position \( c \). Thus, the \( \gamma' \) phase consists of a three-layer stacking-sequence structure with a single cycle of \( abc \). The atomic arrangement returns to its original state at the fourth layer. Each (111)\(_x\) plane shifts by a vector of \( a/3[121] \) on the plane just below it. The orientation relationships of the (111)\(_x\) plane are shown in Fig. 8.

**Figure 8**: The arrangement of atoms on the closed-packed (111) and (001) plane of the \( L1_2 \) and \( DO_{24} \) structure, respectively.

**Figure 9**: The unit cell of the \( \eta \) phase (\( DO_{24} \) type structure).

Consider again the atomic configuration shown in Fig. 8, in which the \( \gamma' \) phase contains a stacking fault on (111)\(_x\). Assuming that the stacking fault is formed on the b plane in this structure, the stacking sequence changes to \( abcabc \cdots \). The stacking sequence structure \( hcbc \cdots \) formed here is essentially the same as that of the \( \eta \) phase, which is a stable precipitation phase for alloy 929C. Therefore, we can reason that the transformation from \( \gamma' \) precipitates with the stacking faults into \( \eta \) phase can occur as a transformation from the metastable phase to the stable phase in order to stabilize the crystal structure by maintaining high temperatures.
3.3. \(\gamma' / \eta\) Transformation Induced by Cold-rolling

Then, we studied the effects of stacking faults introduced by cold-rolling into the \(\gamma'\) precipitates on the formation of \(\eta\) phase. Figure 10 shows the transmission electron micrograph of alloy 929C aged at 1063 K for 180 ks (50 h) and cold-rolled at a reduction of 15% at room temperature and its SAED pattern. This micrograph shows that the precipitates are \(\gamma'\) phase and many stacking faults were introduced into them by cold-rolling.

Figure 11 shows the transmission electron micrograph of a large \(\gamma'\) precipitate extracted from alloy 929C aged at 1063 K for 180 ks (50 h) and cold-rolled at a reduction of 15% at room temperature. The micrograph was taken from \(\{110\}_\gamma\) direction. Figure 11 indicates that the precipitate extracted has stacking faults on \(\{111\}_\gamma\) plane. Since the \(\gamma'\) precipitates have stratified structure within its structure and superlattice diffraction spots of \((111)_{\gamma'}\), \((\overline{1}1\overline{1})_{\gamma'}\), and so on have streaks normal to \((111)_\gamma\) and \((\overline{1}1\overline{1})_\gamma\) planes. There looks no distinct change except for the internal-fringe contrast in the appearance of \(\gamma'\) particles. Similar analyses were carried out for many \(\gamma'\) precipitates which showed internal-fringe contrast in the cold-rolled samples. Streaks indicating the existence of stacking faults in the \((111)_\gamma\) plane were observed in the SAED patterns of these \(\gamma'\) precipitates in all cases.

Next, we examined how the stacking faults that had been introduced by cold-rolling into the \((111)_\gamma\) plane of the \(\gamma'\) phase changed as a result of the annealing of the samples. Figure 12 shows the transmission electron micrographs of alloy 929C aged at 1063 K for 180 ks (50 h), cold-rolled at a reduction of 15% at room temperature, and then annealed at 1063 K for 72 ks (20 h). Internal-fringe contrast is found in some of \(\gamma'\) precipitates as shown in the photograph A. They have nearly same appearance (A) as that before annealing. However, many other \(\gamma'\) precipitates changed into new appearance with small platelets (B, C and D). We analyzed one of the \(\gamma'\) particles with small platelets formed during annealing of the aged and cold-rolled sample. Figure 13 shows the transmission electron micrograph and its SAED pattern of alloy 929C aged, cold-rolled and then annealed at the same conditions shown in Fig. 12. The annealed \(\gamma'\) precipitates have plural plate-like structures in their structure. The SAED pattern shows that the \(\gamma'\) precipitate particle contains \(\eta\) phase. This micrograph shows clearly that some parts of \(\gamma'\) phase transformed into \(\eta\) phase. It has been shown that stacking faults on the \(\{111\}\) plane in \(\gamma'\) precipitates act as one of the most effective nucleation sites for precipitation of \(\eta\) phase.

We concluded that long-term aging of a \(\gamma'\)-strengthened heat-resistant alloy such as alloy 929C (as well as alloy 909, X-750, · · ·) after plastic deformation can induce degradation of the strengthening effect due to the phase transformation from the \(\gamma'\) to the \(\eta\) phase.

4. Conclusions

An Fe–29Ni–22Co–4Nb–2Cr–1Ti–0.5Al–0.5Si alloy (alloy 929C) was used to study the transformation process of \(\gamma'\) precipitates to \(\eta\) phase. Specimens of this alloy were solid-solution heat treated and aged in a temperature range between 993 K and 1073 K for up to 1440 ks (400 h). To clarify the effects of the stacking faults on the phase transformation of the precipitates, some of the aged samples were cold-rolled at room temperature and annealed at the same temperature as the aging. Morphological and structural changes from the \(\gamma'\) phase to the \(\eta\) phase were studied in detail through transmission electron microscopy.
The results obtained in this study are as follows:

(1) TEM observation showed not only the \(\gamma'\) precipitates formed intensively on the (111) plane, but also the precipitates dispersed in the \(\gamma\) matrix transform to a stable \(\eta\) phase after long time aging.

(2) Stacking faults are often observed in large \(\gamma'\) precipitates grown in aged alloy 929C. Stacking faults seem to be introduced in the \{111\} plane of the \(\gamma'\) phase during the aging process.

(3) The \(\gamma'\) phase with stacking faults and the stable \(\eta\) phase have a similar stacking sequence of crystal planes and crystal lattice. Therefore, changes from \(\gamma'\) precipitates of which some contain stacking faults to \(\eta\) phase are attributable to the transformation of the metastable \(\gamma'\) phase into the stable \(\eta\) phase, in order to stabilize the crystal structure of the precipitates in the alloy.

(4) It was confirmed experimentally that the stacking faults on the \{111\} plane of the \(\gamma'\) precipitates act as one of the most effective nucleation sites for the \(\eta\) phase.

(5) Long-term aging of a \(\gamma'\)-strengthened alloy such as alloy 929C after plastic deformation can induce degradation of the strengthening effect due to the phase transformation from the \(\gamma'\) to the \(\eta\) phase.

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