Precipitation and growth of intermetallic phase in a high-temperature Fe–Ni alloy

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ABSTRACT

Purpose: The paper identifies the intermetallic phases, carbide and boride precipitating in the high-temperature Fe–Ni austenitic alloy during extended aging. Taking advantage of the LSW theory, at attempt was undertaken to provide a quantitative description of the γ' phase [Ni₃(Al,Ti)] particles growth as a function of temperature and aging time.

Design/methodology/approach: The samples were subjected to a solution heat treatment at 980°C/2h/water, and then aged at 715, 750 and 780°C, with holding times 0.5–500 h. Structural investigations were conducted using transmission electron microscopy (TEM) and X-ray diffraction.

Findings: Direct measurements on the electron micrographs allowed to calculate the structural parameters of the γ' phase: mean diameter (\(d\)), volume fraction (VV), and mean distance between particles (ld). In accordance with the LSW theory, linear dependencies of changes in \(d\) as a function of \(t^{1/3}\) were elaborated for the analysed aging temperatures. From the slope of the Arrhenius straight line, the activation energy (E) of the γ' phase coagulation process was determined, with its value estimated at 299kJ/mole.

Research limitations/implications: The obtained data of γ' phase particles growth as a function of temperature and aging time can be used to evaluate the degree of Fe–Ni alloys structure degradation during their operation at high temperatures.

Originality/value: The paper touches upon the problem of the development of modern quantitative metallography methods with the use of thin foil technique.

Keywords: Metallic alloys; Heat treatment; Precipitation and coagulation; LSW theory

1. Introduction

High-temperature Fe–Ni austenitic alloys achieve their optimum properties after multi-stage heat treatment consisting of solution treatment (or annealing) and various methods of aging. During preliminary heat treatment, the precipitation processes take place of γ'[Ni₃(Al,Ti)] and G (Ni₁₆Ti₆Si₇) intermetallic phases, as well as the carbide M₂₃C₆ and boride M₃B₂. During prolonged aging or utilization at elevated temperatures, processes of coagulation of γ' phase and overaging take place in Fe–Ni alloy [1-4]. The process of γ' phase particles growth can be described by means of the LSW (Lifshitz–Slyozov–Wagner) coagulation theory [5,6].

In the present paper the influence of prolonged aging on the course of precipitation and coagulation of γ' phase in the A-286 type high-temperature austenitic alloy was investigated. The basic stereological parameters of the γ' phase particles have been determined and the growth step of the γ' phase has been analyzed on the basis of the LSW theory.

2. Material and procedure

The examinations were performed on rolled bars, 16 mm in diameter, of an austenitic Fe–Ni alloy. The chemical composition of the material is given in Table 1.
The mean diameter ($D_{\bar{d}}$) of the particles was evaluated with help of the relation given by Czyrńska-Filemonowicz et al. [7,8]:

$$D_{\bar{d}} = \bar{d} / [t (t - \bar{d}) + (\pi A_{\Lambda} / L_{\Lambda})],$$  

(1)

where: $\bar{d}$ – the mean diameter of the circles in the projected plane (nm), $t$ – the foil thickness (nm), $A_{\Lambda}$ – the projection area, $L_{\Lambda}$ – the perimeter density (1/nm).

The volume fraction ($V_{\nu}$) of $\gamma'$ phase particles was calculated using the formula provided by Dubiel et al. [9]:

$$V_{\nu} = \pi \Sigma N_{i} d_{i}^{3} / 6A(t + \bar{d})$$  

(2)

where: $N_{i}$ – the number of particles with diameter $d_{i}$, $A$ – the total projection area (nm$^{2}$).

The mean distance between particles ($l_{d}$) was estimated using the equation given by Schröder and Arzt [10]:

$$l_{d} = \bar{d} \cdot [(\pi / 6V_{\nu}) \cdot (1 + s^{2} / \bar{d}^{2})]^{1/2} - (\pi / 4)\bar{d}$$  

(3)

where: $s$ – the standard deviation of the particle diameter distribution.

The analysis of the $\gamma'$ phase growth step was made on the basis of the LSW theory for coagulation on volume diffusion control according to the relationship provided by Kusabiraki et al. [11,12]:

$$\bar{d}^{3} - \bar{d}_{0}^{3} = 64\sigma D_{C} V_{m}^{2} / 9RT = K't$$  

(4)

where: $\bar{d}$ and $\bar{d}_{0}$ – average diameter of precipitates at time $t$ and $t = 0$ respectively, $\sigma$ – the interfacial energy between precipitates and 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 a particle of an infinite size, $V_{m}$ – the molar volume of precipitation phase, $R$ – the gas constant, $T$ – the absolute temperature, $K'$ – the growth rate constant.

In general the diffusion coefficient ($D$) is expressed as:

$$D = D_{0} \cdot \exp(-E/RT)$$  

(5)

where $D_{0}$ – is the pre-exponential factor, $E$ – is the activation energy of diffusion. Therefore, the $K'$ constant in equation (4) takes on the following form:

$$K' = [64\sigma D_{C} V_{m}^{2} \exp(-E/RT)] / 9RT$$  

(6)

where $D_{0}$ – is the pre-exponential factor, $E$ – is the activation energy of diffusion.

On assumption that the values of $\sigma$, $C_{e}$ and $V_{m}$ are nearly independent of temperature, the value of diffusion activation energy ($E$) can be obtained from the slope of Arrhenius plot being the linear relationship between $\ln(TK')$ and $T^{-1}$.

### 3. Experimental results

The investigated Fe–Ni alloy after solution heat treatment at 980°C/2h/water is characterized by a structure of twinned austenite with elevated dislocation density and a small amount (ca. 0.3%) of undissolved precipitates (Fig. 1). In phase composition of extracted precipitates discovered the occurrence of titanium compounds, i.e. carbide TiC, nitride TiN, carbonitride Ti(C,N), carbosulfide TiC$_{3}$S$_{2}$, and Laves phase Ni$_{3}$Si

![0.5µm](image)

Fig.1. Structure of the alloy after solution heat treatment at 980°C/2h/w. Twinned austenite with increased dislocation density and undissolved particle of carbonitride Ti(C,N)

The application of single-stage aging after solutioning at 715, 750 and 780°C for 0.5–500h initiates the precipitation processes of intermetallic phases, carbide and boride (Figs. 2-5). The main phase precipitating during alloy aging was the $\gamma'$ [Ni$_{3}$(Al,Ti)] intermetallic phase. At initial stages of aging, at a temperature of 715°C, this phase precipitated homogeneously in the form of dispersive particles coherent with the matrix (Fig. 2).

An increase of aging temperature up to 750°C intensifies diffusion processes of the $\gamma'$ phase particles growth and coagulation (Fig. 3). First transcrystalline plates of the $\eta$ [Ni$_{3}$Ti] phase appeared in the near-boundary austenite areas (Fig. 4). The phase transition $\gamma' \rightarrow \eta$ was accompanied by a dissolution of the neighbouring $\gamma'$ phase particles in the matrix.

At the highest aging temperature of 780°C, the alloy structure demonstrated visible effects of overaging connected with the coagulation of $\gamma'$ phase particles (Fig. 5). The cellular $\eta$ phase nucleated at a vicinity of grain boundary of matrix by celluar reaction and grew up in clusters.

### Table 1.

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>V</th>
<th>Ti</th>
<th>Al</th>
<th>B</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content (wt.%)</td>
<td>0.05</td>
<td>0.55</td>
<td>1.25</td>
<td>14.3</td>
<td>24.5</td>
<td>1.34</td>
<td>0.41</td>
<td>1.88</td>
<td>0.16</td>
<td>0.007</td>
<td>0.0062</td>
</tr>
</tbody>
</table>

The samples for testing cut off these rods were subjected to solution heat treatment at 980°C for 2 h and water quenched, and then to aging at temperatures 715, 750 and 780°C at holding time from 0.5 to 500 h.

Observations of the alloy substructure were carried out using the thin foil technique on a Jeol JEM-2000 FX transmission electron microscope (TEM). The X-ray phase analysis of isolates was carried out with a Philips PW-1140 X-ray diffractometer.

A quantitative analysis of secondary $\gamma'$ phase particles, which phase precipitated in the alloy during ageing, was performed on TEM images in bright field mode. Based on direct counting, basic stereological parameters of the $\gamma'$ phase were determined from binary images, i.e.: the mean diameter ($D$), the volume fraction particles ($V_{\nu}$) and the mean distance between particles ($l_{d}$).

The chemical composition of the investigated alloy was determined by X-ray fluorescence spectrometry using a Philips PW-1150/00 device.

Experimental results

The investigated Fe–Ni alloy after solution heat treatment at 980°C/2h/water is characterized by a structure of twinned austenite with elevated dislocation density and a small amount (ca. 0.3%) of undissolved precipitates (Fig. 1). In phase composition of extracted precipitates discovered the occurrence of titanium compounds, i.e. carbide TiC, nitride TiN, carbonitride Ti(C,N), carbosulfide TiC$_{3}$S$_{2}$, and Laves phase Ni$_{3}$Si
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X-ray examinations of the sample isolates after aging showed the appearance of the same phases as those observed in the supersaturated state, i.e. TiC, TiN, Ti(C,N), Ti₄C₂S₂ and Ni₂Si. Besides, in aged alloy often the following phases were discovered: γ'[Ni₃(Al,Ti)], G phase [Ni₆Ti₆Si₇], η phase [Ni₃Ti], carbide M₂₃C₆ and boride M₃B₂.

The quantitative analysis of γ' phase particles precipitating in the alloy during aging was carried out at for aging temperatures of 715, 750 and 780°C and holding times from 4 to 500 hrs. Table 2 provides the results of quantitative examinations obtained for selected times of aging, i.e.: 4, 150 and 500 h.

The growth process of γ' phase particles in the examined Fe–Ni alloy was analyzed using the LSW theory according to equation (4) given by Kusabiraki et al. [11,12]. The relationship between the mean diameter of precipitates (D) and the cube root of the aging time is presented in Fig. 6. For the analyzed aging temperatures, the obtained relationships are linear, which proves the fact that coagulation of γ' phase particles proceeds in accordance with the LSW theory and is controlled by volume diffusion.
Table 2. Stereological parameters of the γ’ particles in the tested alloy

<table>
<thead>
<tr>
<th>Stereological parameters</th>
<th>Time of aging (h) at 715°C</th>
<th>Time of aging (h) at 750°C</th>
<th>Time of aging (h) at 780°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (%)</td>
<td>2.1 16.5 10.9</td>
<td>9.2 24.3 13.6</td>
<td>5.6 11.5 15.5</td>
</tr>
<tr>
<td>d (nm)</td>
<td>7.4 15.7 19.9</td>
<td>9.2 24.3 13.6</td>
<td>12.7 47.2 70.7</td>
</tr>
<tr>
<td>D (nm)</td>
<td>7.5 17.1 23.0</td>
<td>9.2 24.3 13.6</td>
<td>10.6 28.8 45.1</td>
</tr>
<tr>
<td>V (%)</td>
<td>0.07 1.0 1.4</td>
<td>0.1 1.1 2.1</td>
<td>2.1 7.7 8.4</td>
</tr>
<tr>
<td>l (nm)</td>
<td>195 106 121</td>
<td>217 128 164</td>
<td>153 89 124</td>
</tr>
</tbody>
</table>

The activation energy of the γ’ phase coagulation process in the examined Fe–Ni alloy was determined from the Arrhenius straight line slope (Fig. 7). The value obtained (E = 299 kJ/mole) is close to the value of activation energy (283 kJ/mole) determined for the A-286 alloy by Kusabiraki et al. [11].

![Fig. 6. Relationship between the mean diameter of γ’ phase particles and the cube root of aging time at temperatures of 715, 750 and 780°C](image)

Fig. 6. Relationship between the mean diameter of γ’ phase particles and the cube root of aging time at temperatures of 715, 750 and 780°C

![Fig. 7. Arrhenius plots for determination of the activation energy for growth of γ’ phase precipitates in the examined Fe–Ni alloy and in the A-286 alloy (Kusabiraki et al. [11])](image)

Fig. 7. Arrhenius plots for determination of the activation energy for growth of γ’ phase precipitates in the examined Fe–Ni alloy and in the A-286 alloy (Kusabiraki et al. [11])

4. Conclusions

The application of a single-stage aging, after solution heat treatment, at temperatures of 715, 750 and 780°C, with holding times from 0.5 to 500h, causes precipitation processes of γ’, η and G intermetallic phases in the investigated alloy, as well as the carbide M23C6 and boride M23B2.

During the precipitation of the γ’ phase one may distinguish three characteristic stages, i.e. coherent zones, coherent spheroidal particles (10 ÷ 35 nm) and coagulated spheroidal particles (40 ÷ 85 nm).

It was found that the mean diameter of γ’ phase precipitations increases as a function of the cube root of aging time, which is consistent with the predictions based on the LSW theory for the coagulation controlled by volume diffusion. The determined value of activation energy for the process of γ’ phase coagulation in the examined alloy was 299 kJ/mole.

References