Micro-mechanisms and precipitation kinetics of delta (δ) phase in Inconel 718 superalloy during aging
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**A B S T R A C T**
The formation of δ phase in Inconel 718 superalloy during aging was quantitatively studied based on improved analyzing techniques to unambiguously determine the mechanism of δ phase precipitation and its kinetics. Based on the general transformation rate expressed in terms of the time corresponding to the transformed fraction of 0.5 or 50% and also the modified Johnson–Mehl–Avrami–Kolmogorov (JMAK) equation, the average activation energy for the formation of δ phase was determined as 212.4 kJ/mol and 197.5 kJ/mol, respectively. These values are comparable to the activation energy for diffusion of Nb in Ni (202.59 ± 4.71 kJ/mol). Therefore, the micro-mechanism for the formation of δ phase was characterized as the diffusion of Nb in the matrix. Based on the kinetic studies, the temperature of 1055.7 K (782.7 °C) was found as the lower bound for the formation of δ phase, which was consistent with the precipitation-temperature-time (PTT) plot developed for this material. Finally, a formula was obtained to quantitatively show the effects of aging temperature and cold rolling reduction on the transformation rate for the precipitation of δ phase.

**1. Introduction**
Due to its desirable mechanical properties at elevated temperature and low cost, Inconel 718 is known to be one of most common nickel-based superalloys [1–4]. The FCC Ni3(Al,Ti) γ′ phase, the BCT Ni3Nb γ phase, and the orthorhombic Ni3Nb δ phase precipitate during aging of Inconel 718 superalloy [5–8]. The γ′ and γ phases are known as the main strengthening phases but δ phase is normally regarded as an undesirable phase.

The γ and δ phases are Nb-based intermetallics, where γ′ phase is a metastable phase and the δ phase is the equilibrium one. As a result, the growth of the δ phase occurs at the expense of γ′ phase [9,10]. Therefore, formation of δ phase is associated with the decreased precipitation hardening effect by depletion of the coherent γ precipitates. The increased susceptibility to hot cracking has been also noted in the δ phase containing alloys [9]. However, this phase with appropriate morphology is noted for inhibition of grain growth during thermal processing [11], increased resistance to grain boundary creep failure [12], and providing the possibility to design efficient thermomechanical processing by affecting the dynamic recrystallization (DRX) [13–18], post-dynamic recrystallization [19,20], and interaction with the recrystallization of the cold rolled alloy [21,22]. Whether the detrimental or beneficial effects of the δ phase are taken into account, the study of its precipitation kinetics [9,10,23–27] or dissolution [28,29] is vital. It has been shown that the prior cold rolling before aging for the formation of precipitate phases can significantly accelerate the kinetics of precipitation [10,21,23,24,26].

The so-called apparent activation energy for precipitation of δ phase (Q) in the cold rolled Inconel 718 superalloy has been reported in the range of 1113 to 577 kJ/mol by Liu et al. [23,24], where increasing the rolling reduction from 25 to 65% resulted in the decreased Q in this range. However, the same authors have noted that the value of Q should be less than 500 kJ/mol if the precipitation of δ phase is controlled by diffusion of alloying elements. Therefore, they concluded that the formation of δ phase involves a structure change, and hence, requires higher activation energy. As a result, it seems that this subject needs more attention with improved analyzing techniques to unambiguously determine the mechanism of δ phase precipitation and its kinetics.

Accordingly, in the present work, the micro-mechanisms and precipitation kinetics of delta phase in Inconel 718 superalloy during aging were investigated, which are important for the industrial production. For this purpose, the precipitation mechanism
of delta phase and its kinetics were determined not only by experimental observations but also by a Johnson–Mehl–Avrami–Kolmogorov (JMAK) approach.

2. Experimental material and procedure

The data for the formation of δ-phase at different holding times and temperatures for various cold working (CW) reductions were taken from the reported references [9,10,23–26]. By consideration of maximum amount of the formed δ-phase at long holding times (δ_max) and the current value (δ_t), the transformed fraction (X) was determined as follows:

\[ X = \frac{\delta_t}{\delta_{\text{max}}} \]  

Accordingly, the obtained data were plotted as shown in Fig. 1. It can be seen that the data for the formation of δ-phase at cold rolling reductions in the range of 0–50%, temperatures in the range of 810–910 °C, and holding times up to 71 h are available. The time corresponding to the transformed fraction of 0.5 or 50% (t_0.5) can be estimated from Fig. 1 (the dotted line). It can be seen that increasing the cold rolling reduction and aging temperature result in the increased transformation kinetics (decreased t_0.5).

However, there is a lack of data for the temperature of 810 °C in the case of cold rolling reduction of 0%, which should be investigated for the kinetics analysis. As a result, a forged Inconel 718 superalloy (Ni-5.25Nb-2.93Mo-17.21Cr-18.91Fe-0.87Ti-0.54Al-0.021C, wt%) was solution treated at 1050 °C for 6 h followed by water quenching to suppress the formation of precipitates. The selection of the solution temperature was based on the precipitation-temperature-time (PTT) plot for Inconel 718 superalloy [30], where it showed that at temperatures higher than 1000 °C, the dissolution of γ’, γ, and δ phases takes place and Nb comes back to the solid solution. While the holding time of 1 h at 1050 °C [31] and 0.75 h at 1045 °C [13] has been reported in the literature, the holding time of 6 h at 1050 °C was used in the present work to ensure the dissolution of these phases.

Afterward, the samples were aged at 810 °C for 4, 8, 14, 24, 41, and 71 h for the precipitation of the δ-phase. The microstructures were etched by Kalling’s reagent number 2 (100 ml HCl – 100 ml ethanol – 5 g CuCl_2) [32,33]. Field-emission scanning electron microscopy (FEI Nova NanosTEM 450) and X-ray diffraction (PHILIPS diffractometer with Cu-kα radiation) were used for microstructural and phase analyses, respectively.

3. Results and discussion

3.1. δ phase precipitation at 810 °C in the solution-annealed sample

Fig. 2 shows the microstructures of the solution annealed sample and aged ones at 810 °C for 4, 8, 14, 24, 41, and 71 h. The figure clearly shows that the δ phase firstly forms on grain boundaries (Fig. 2b–d), and then, by increasing the holding time, it forms on twin boundaries (Fig. 2e and f) and grain interiors (Fig. 2f and g). Fig. 2i at high magnification reveals the presence of γ’ and γ phases. Fig. 2b also reveals that at the vicinity of δ phase, depletion from the γ’ phase has been happened, which implies that the transformation of γ’ to δ might be also a possibility [23,24]. The XRD patterns of the solution annealed, 41 h aged (Fig. 2f), and 71 h aged (Fig. 2g) samples are shown in Fig. 3. It can be seen that the diffraction peaks of both γ’ [34] and δ can be seen in the 41 h and 71 h aged samples, confirming the presence of these phases. The volume fraction of the δ phase was obtained from the microstructures based on the area fraction and the results are summarized in Fig. 4. The figure reveals that the amount of δ phase slowly increases with increasing holding time due to the slow kinetics at low temperature of 810 °C. Then, a sigmoidal curve (with a formula shown in the figure) was fitted to the data to estimate δ_max (74.5 vol %) and t_0.5 (95.06 h).
3.2 Activation energy for the precipitation of δ phase

Based on the reported references [9,10,23–26] and the results of Section 3.1, the data for the precipitation of δ phase at different temperatures and holding times for the cold rolling reductions of 0, 25, 40, and 50 are available for analysis. In general, the transformation rate can be expressed as Equation (2), where \( c_0 \) is a constant and \( f \) is a function of \( X \) only [35,36]. Integration of Equation (2) from 0 to \( t_{0.5} \) results in Equation (3). Taking natural logarithm from this equation gives Equation (4).
\[
\frac{dX}{dt} = f_0 \exp(-Q/RT) \tag{2}
\]

\[
\int_{t_0}^{t_5} dt = \exp\left(\frac{Q}{RT}\right) \times \int_{t_0}^{t_5} (c_0f)^{-1} dX \tag{3}
\]

\[
\ln t_{0.5} = \left(\frac{Q}{R}\right)(1/T) + \ln\left(\frac{c_0f}{k_0}\right) \tag{4}
\]

Therefore, the plot of \(\ln t_{0.5}\) versus \(1/T\) can be used to obtain the value of \(Q/R\). The corresponding plot is shown in Fig. 5 for different cold rolling reductions. It can be seen that the slopes of all curves are nearly equal, indicating a nearly same value of \(Q\). Based on this figure, it can be seen that \(Q\) does not change with the cold rolling reduction, and hence, the mechanism of the formation of \(\delta\) phase is the same and does not depend on the rolling reduction. These values are comparable to the activation energy for diffusion of \(Nb\) in Ni (202.59 ± 4.71 kJ/mol [37,38]). Therefore, the controlling mechanism of \(\delta\) phase formation should be the diffusion of this element.

This is in contrast to the work of Liu et al. [23], where the “apparent” \(Q\) in the range of 1113 to 577 kJ/mol was reported for the cold rolled alloy. Based on the obtained relations, these authors estimated the \(Q\) value of 1450 ± 90 kJ/mol for the undeformed sample. Therefore, it is required to analyze the data presented by Liu et al. [23]. These authors used the JMAK equation of the form of \(X = W_c/W_{max} = 1 - \exp\left(-a \times t^n\right)\), where \(W_c\) denotes the weight percentage of \(\delta\) phase. Based on its rearrangement (\(\ln\left(1\left(1 - X\right)\right) = \ln a + n \ln t\)), the values of \(a\) and \(n\) were obtained respectively from the intercept and slope of the plot of \(\ln\left(1\left(1 - X\right)\right)\) versus \(\ln t\). The reported results are summarized in Table 1.

However, via analyzing the precipitation reactions in the 17-4 PH stainless steel, Mirzadeh [36] showed that the modified JMAK equation of the form of Equation (5) should be used for obtaining the activation energy, where the exponent \(n\) has been considered not only for \(t\) but also for the temperature-dependent parameter \(k\).

\[
X = 1 - \exp\left(-\left(kt\right)^n\right) \tag{5}
\]

Based on Equation (5), \(\ln\left(1\left(1 - X\right)\right) = n \ln k + n \ln t\). Therefore, \(\ln k = \ln a/n\). The obtained values of \(\ln k\) are also shown in Table 1. The temperature dependency of \(k\) can be expressed by

\[
k = k_0 \exp\left(-\frac{Q}{RT}\right) \tag{6}
\]

\[
\ln k = \ln k_0 + \left(-\frac{Q}{R}\right)(1/T) \tag{7}
\]

Therefore, the slope of the plot of \(\ln k\) versus \(1/T\) can be used for obtaining the value of \(-Q/R\). The corresponding plot is shown in Fig. 6, where the average value of \(Q\) can be obtained as 197.5 kJ/mol. This value is near the obtained values of \(Q\) based on Equation (2).

The present analyses were based on two different methods (Equation (2) and Equation (5)), which solidifies its reliability. Moreover, this also supports the argument that the diffusion of \(Nb\) in Ni is the controlling micro-mechanism for the formation of \(Ni\)\(Nb\) \(\delta\) phase regardless of cold rolling.

### 3.3 Precipitation kinetics of \(\delta\) phase

In phase transformations, the reciprocal of the time corresponding to transformation percent of 50% (\(t_{0.5}\)) is indicative of the transformation rate. Therefore, the data shown in Fig. 5 were plotted in the form of Fig. 7a. It can be seen that by increasing the aging temperature and cold rolling reduction, the transformation rate increases. However, the temperature dependency of transformation rate increases by increasing the cold rolling reduction. The fitted lines also tend to a common point.

Via equating the formula obtained for cold rolling reductions of 0 and 50% in Fig. 7a, the intersection point was estimated as 1055.7 K (782.7 °C). Therefore, the temperature of 782.7 °C can be considered as the lowest temperature for the formation of \(\delta\) phase. The precipitation-temperature-time (PTT) plot for the precipitation in Inconel 718 superalloy is shown in Fig. 8 [30]. It can be seen that the temperature of 782.7 °C is nearly consistent with the lowest bound for the formation of \(\delta\) phase, which provides another evidence for the validity of the kinetics analyses of the present work.

For analysis, the data points were plotted in the form of Fig. 7b by consideration of \(T-1055.7\). Therefore, the fitted lines with the formula of \(y = ax\) were determined. While the slope (\(a\)) depends on the cold rolling reduction. The obtained values of \(a\) are plotted against cold rolling reduction (CR) in Fig. 9. It can be seen that the data points can be fitted by an exponential function. Now, based on Fig. 7b and 9, the transformation rate can be expressed as Equation (8), where \(T\) and CR are expressed in Kelvin and percent, respectively.

\[
Rate_5 = 1/t_{0.5} = 0.0005(T - 1055.7)\exp(0.0405 \times CR) \tag{8}
\]

Equation (8) quantitatively shows the effect of cold rolling reduction and aging temperature on the transformation rate of

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**Table 1**

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Rolling Reduction (%)</th>
<th>(a)</th>
<th>(n)</th>
<th>ln(k_0)</th>
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<tr>
<td>910</td>
<td>25</td>
<td>3.20E-04</td>
<td>0.78</td>
<td>-1.03E+01</td>
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<tr>
<td>910</td>
<td>40</td>
<td>1.00E-03</td>
<td>0.69</td>
<td>-1.00E+01</td>
</tr>
<tr>
<td>910</td>
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<td>3.40E-03</td>
<td>0.61</td>
<td>-9.32E+00</td>
</tr>
<tr>
<td>910</td>
<td>65</td>
<td>1.50E-02</td>
<td>0.5</td>
<td>-8.40E+00</td>
</tr>
<tr>
<td>860</td>
<td>25</td>
<td>8.40E-07</td>
<td>1.3</td>
<td>-1.03E+01</td>
</tr>
<tr>
<td>860</td>
<td>40</td>
<td>3.90E-05</td>
<td>0.98</td>
<td>-1.04E+01</td>
</tr>
<tr>
<td>860</td>
<td>50</td>
<td>1.70E-04</td>
<td>0.86</td>
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<td>0.64</td>
<td>-8.84E+00</td>
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<tr>
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<td>25</td>
<td>9.10E-09</td>
<td>1.53</td>
<td>-1.21E+01</td>
</tr>
<tr>
<td>810</td>
<td>40</td>
<td>2.00E-07</td>
<td>1.33</td>
<td>-1.16E+01</td>
</tr>
<tr>
<td>810</td>
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<td>5.50E-06</td>
<td>1.07</td>
<td>-1.13E+01</td>
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<tr>
<td>810</td>
<td>65</td>
<td>7.00E-05</td>
<td>0.92</td>
<td>-1.04E+01</td>
</tr>
</tbody>
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**Fig. 5.** Plot used for obtaining \(Q\) based on Equation (2).
d phase, which is of upmost importance for the processing of this superalloy.

4. Conclusions

The mechanism of δ phase precipitation and its kinetics were studied in an Inconel 718 superalloy based on improved analyzing techniques. The following conclusions can be drawn from this study:

Fig. 6. Plot used for obtaining Q based on Equation (5).

Fig. 7. Transformation rate versus aging temperature for different rolling reductions.

Fig. 8. Precipitation-temperature-time (PTT) plot for the precipitation in Inconel 718 superalloy up to 1000 h [30].
Based on different methods, the average activation energy for the formation of $\delta$ phase was determined to be 212.4 kJ/mol and 197.5 kJ/mol. These values are comparable to the activation energy for diffusion of Nb and Ni. Therefore, the micro-mechanism for the formation of $\delta$ phase was characterized as the diffusion of Nb in the matrix.

The temperature of 1055.7 K (782.7 °C) was found as the lower bound for the formation of $\delta$ phase, which was consistent with the PTT plot developed for this material up to the aging time of 1000 h.

The following formula was obtained to quantitatively show the effects of aging temperature and cold rolling reduction on the transformation rate for the precipitation of $\delta$ phase:

$$\text{Rate}_\delta = \frac{1}{t_\frac{1}{2}} = 0.0005 e^{0.0045 \cdot \text{CR}} \cdot (T - 1055.7)$$

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References