Stress Exponent of Minimum Creep Rate and Activation Energy of Creep for Oxide Dispersion-strengthened Nickel-based Superalloy MA754

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The stress exponent of the minimum creep rate, n, and the activation energy of creep, Qc, were obtained for the oxide dispersion-strengthened nickel-based superalloy MA754 by conducting creep tests at 1 223–1 273 K in the stress range of 130–190 MPa. The values of n and Qc in MA754 were determined to be 26 and 862 kJ/mol, respectively. The causes of these high values were determined by measuring the internal stress, σ, using the strain dip test. The ratio of σ to applied stress, σi, was very high at lower stresses, while at higher stresses, σ decreased drastically with increasing stress, which reflected the large increase in creep rate. Such a large increase in creep rate with increasing applied stress led to an unpredictably higher value of n. With increasing temperature, the saturated σ decreased, which resulted in a relatively large creep rate. The larger creep rate at high temperatures led to a large value of Qc. In addition, the dislocation density, ρ, of the interrupted creep specimens at the time of the minimum creep rate increased with increasing stress and reached the saturated value. This change in ρ with stress must be reflected in a large change in n and Qc through a change in σ.

KEY WORDS: ODS; stress exponent of the minimum creep rate; activation energy of creep; internal stress; effective stress; dislocation substructure.

1. Introduction

The excellent high-temperature creep resistance of oxide dispersion-strengthened (ODS) nickel-based superalloys is due to the existence of uniformly dispersed oxides such as Y2O3 in the matrix.1) ODS alloys are expected to replace single-crystal nickel-based superalloys currently serviced as turbine blade components in aircraft engines. Many papers have reported the mechanical properties of ODS alloys at high temperatures.2–5) It is also well known that the values of the stress exponent of the minimum creep rate, n, and the activation energy of creep, Qc, are larger for ODS alloys than for solution-treated and precipitate-dispersion-strengthened alloys.

Nix et al. performed creep tests on the ODS nickel-based superalloy MA754 at 1 273–1 473 K and reported that n and Qc indicated very high values of 14–40 and 402–854 kJ/mol, respectively.5) Wilcox et al. also reported that a value of n near 40 was confirmed in thoria-dispersed nickel ODS alloy strengthened by ThO2 particles.6) The stress exponent of the minimum creep rate, n, is expressed as a guideline for the rate-controlling process in creep deformation.1) However, Kondo et al. reported that this rate-controlling process could not be identified by the value of n alone because n strongly depends on microstructural changes.5) That is, when solution-treated alloys at high stresses were strengthened by precipitates at low stresses, n increased due to the increase in creep resistance at low stresses. On the other hand, when uniform and fine precipitates of dispersion-strengthened alloys at high stresses coalesced and coarsened at low stresses, n decreased due to the decrease in creep resistance at low stresses. Therefore, the value of n was strongly affected by the changes in the dislocation substructures with stress.

Recently, many researchers have studied the internal stress to evaluate creep resistance.9–12) The internal stress, σi, is defined as back stress and is regarded as thermally activated stress operating in a wide range, while the effective stress, σe (σe = σa − σi), is regarded as thermally activated stress operating in the short range, that is, preceding the dislocation climb. Of course, the operating direction is the same for σe and σi.

Kondo et al. determined that the decrease in the minimum creep rate by the addition of solid-solution elements to carbon-free 25Cr–35Ni austenitic steels was explained by the increase in σi due to the increase in the dislocation density.9) In this way, σ can be considered as a structural factor that is based on the dislocation substructure. It would be very interesting to examine whether the large value of n could be
explained by microstructure changes using the $\sigma$ concept.

To clarify the change in $n$ with the addition of solid-solution elements, Kondo et al. derived the equation for the minimum creep rate using the $\sigma$ concept as

$$\dot{\varepsilon}_m = [(\sigma_0 - \sigma)/E(T)]^{10} \exp(-Q_\infty/RT) \quad \ldots \ldots \ldots \ldots \quad (1)$$

where $E(T)$ is the elastic modulus, $Q_\infty$ is the apparent activation energy of creep under a constant $\sigma$, $R$ is the gas constant, and $T$ is the absolute temperature.\(^{13}\) The correlation between $n$ and the effective stress exponent of the minimum creep rate, $n_0$, was expressed as follows:

$$n = n_0 [1 - (d\sigma/d\sigma_0)] / (1 - \sigma_0/\sigma_a) \quad \ldots \ldots \ldots \ldots \quad (2)$$

Therefore, the large value of $n$ in ODS alloys seemed to result from the low $\sigma_0$ dependence of $\sigma_a$ and/or the high ratio of $\sigma$ to $\sigma_a$.

In general, the activation energy of creep under constant stress, $Q_c$, was obtained from the following equation:

$$Q_c = -R [d \ln \dot{\varepsilon}_m / d \sigma_a] (1/T) \ldots \ldots \ldots \ldots \quad (3)$$

Wilshire et al. reported that the values of $Q_c$ in Nimonic 80A and Nimonic 115 were 110 and 515 kJ/mol, respectively.\(^{14-16}\) Here, the minimum creep rate was plotted as a function of $\sigma$, and the values of $Q_c$ obtained were 305 and 310 kJ/mol, respectively; these values are close to that of the activation energy for self-diffusion, $Q_d$, in pure Ni ($293$ kJ/mol). Tien et al. reported that $Q_c$ was larger than $Q_d$ due to both the temperature dependence of $\sigma$, $K_m$, and the temperature dependence of the elastic coefficient, $K_E$.\(^{17,18}\) That is, the relationship between $Q_c$ and $Q_d$ was obtained as the following equation:

$$Q_c = Q_d + K_m + K_i \quad \ldots \ldots \ldots \ldots \quad (4)$$

$$K_m = -(n/mRT^2/E(T)) (dE(T)/dT)$$

$$K_i = -[nRT^2/(\sigma_a - \sigma)] (d\sigma/dT)$$

However, Kondo et al. evaluated the value of $K_E$ for various kinds of nickel-based heat-resistant alloys.

The contribution of $K_E$ to $Q_c$ in Eq. (4) was up to 42 kJ/mol, and the measured $Q_c$ obtained from Eq. (3) corresponded to the sum of $K_i$ and $Q_\infty$. From these results, an increase in $Q_c$ with the addition of solid-solution elements was explained by the temperature dependence of $\sigma$.\(^{13}\) Therefore, the large values of $Q_c$ for ODS alloys are attributed to the temperature dependence of $\sigma$. It would be very interesting to determine if the $\sigma$ concept is applicable to ODS alloys with large values of $n$ and $Q_c$ using the Eqs. (2) and (4). However, there have not been any such systematic studies on ODS alloys as of yet.

In this study, the values of $n$ and $Q_c$ for the ODS nickel-based superalloy MA754 were investigated through microstructural observation of specimens interrupted at the minimum creep rate and the measurement of $\sigma$ by creep tests at 1223 and 1273 K in the stress range of 130 to 190 MPa.

2. Experimental Procedure

An ODS nickel-based superalloy of MA754 (with a chemical composition in wt% of 19.67Cr, 0.21Fe, 0.25Al, 0.42Ti, 0.07Mo, 0.66Y$_2$O$_3$, balance Ni) prepared by mechanical alloying and extruding was obtained in the form of a 33.5 × 75.2 × 1200 mm bar. Specimens were cut parallel to the extruded direction by an electron discharge machine. The alloy was tempered at 1588 K for 3.60 × 10$^3$ s. Creep test specimens were prepared with a gage diameter of 6 mm and a gage length of 30 mm. Creep tests were performed at 1223 and 1273 K in the stress range of 130 to 190 MPa under constant load. Creep strain was measured automatically using linear variable differential transformers (LVDTs) attached to extensometers, and internal stress was measured by the strain dip test. The creep tests were interrupted at the time of the minimum creep rate.

Microstructural observations were performed using optical microscopy, field emission scanning electron microscopy, and transmission electron microscopy (TEM) on the specimen sections parallel to the extruded plane. TEM foils were prepared by electropolishing using a twin-jet polisher with a 10% perchloric acid-alcohol solution. The dislocation density was measured on the TEM micrographs using Hirsch’s method.\(^{19}\)

3. Results and Discussion

3.1. Microstructure of the Tempered Specimen

The optical micrograph and scanning electron micrograph of the tempered MA754 are shown in Fig. 1. This figure shows the elongated grains introduced by the extrusion array along the extruded direction (Fig. 1(a)); it also shows that there are no precipitates or dispersed phases at the grain boundaries (Fig. 1(b)).

3.2. Creep Properties of MA754 at 1273 K

The creep rate-time curves of MA754 at 1273 K in the
stress range of 130 to 180 MPa are shown in Fig. 2. All of the creep curves consist of a transient creep stage and an accelerating creep stage. The open circles on the curves indicate the times at which the creep tests were interrupted, which correspond to the minimum creep rate.

The stress-minimum creep rate curves of MA754 at 1223 and 1273 K are shown in Fig. 3. The correlations between the minimum creep rate and the stress are linear on the log-log scale, and the stress exponent of the minimum creep rate, \( n \), has a large value of 26.

### 3.3. Internal Stress

Figure 4 shows typical graphs (original records) plotting creep elongation as a function of time after starting the strain dip test at 1273 K and 170 MPa. For a reduction stress, \( \Delta \sigma \), of 10.4 MPa, a positive creep rate appears immediately after the stress reduction (Fig. 4(a)). On the other hand, for a \( \Delta \sigma \) of 24.3 MPa, a negative creep rate appears after the stress reduction (Fig. 4(c)). For a \( \Delta \sigma \) of 17.3 MPa, a zero creep rate appears after exhibiting an elastic strain response (Fig. 4(b)).

The relationship between the reduction stress and the creep rate is shown in Fig. 5. From this figure, \( \sigma \) (the applied stress minus \( \sigma_i \)) at 1273 K and 170 MPa is determined to be 22 MPa by estimating the stress where the creep rate is zero. Values of \( \sigma \) at other applied stresses are obtained using a similar technique. Additionally, \( \sigma \) is calculated from the difference between \( \sigma_i \) and \( \sigma \).

The relationships between \( \sigma_i \) and \( \sigma_a \) in the higher stress range at 1223 and 1273 K are shown in Fig. 6. At stresses lower than 140 MPa, \( \sigma_i \) cannot be defined because of the difficulty in measuring strain with a good resolution just after the stress reduction. At high stresses, the values of \( \sigma_i \) at temperatures of 1223 and 1273 K are determined to be constant values of 162 and 145 MPa, respectively, independent of \( \sigma_a \). It is clear that there is no \( \sigma_a \) dependence of \( \sigma_i \).

### 3.4. Examination of \( n \)

Where \( \sigma_e \) is defined by the strain dip test, \( n_{\text{cal}} \) is calculated using Eq. (2). Then, this value is compared with the mea-
sured value, \( n_{\text{meas}} \). In this section, it is confirmed that Eq. (2) is applicable to ODS alloys.

The curves showing the relationships between \( \sigma_e \) and the minimum creep rate at 1 223 and 1 273 K are shown in Fig. 7. Using the log-log scale, the curves correlating the minimum creep rate and \( \sigma_e \) become linear with an \( n_0 \) of 4.

The curves showing the relationship between \( \sigma_e \) and the minimum creep rate of MA754 are shown in Fig. 8, along with those for the polycrystalline Ni–20Cr alloy at 1 173 and 1 273 K reported by Nakajima. The plots show the relationships between the minimum creep rate and \( \sigma_e \) in these two types of alloys as straight lines in the log-log scale. Of course, the effective stress exponent of the minimum creep rate is independent of the testing temperature.

By substituting the values of \( n_0 \) and \( \sigma_i \) measured by the strain dip test into Eq. (2), the calculated value of the stress exponent, \( n_{\text{cal}} \), is obtained. The values of \( n_{\text{meas}} \) are plotted as a function of \( \sigma_e \), together with \( n_{\text{cal}} \) at a higher stress region, as shown in Fig. 9. The values of \( n_{\text{meas}} \) are in good agreement with the values of \( n_{\text{cal}} \). Consequently, it is supposed that the large value of \( n \) in MA754 at the higher stress region is attributed to the \( \sigma_e \) dependence of \( \sigma_i \) in Eq. (2).

3.5. Dislocation Substructures of the Interrupted Creep Specimens

The internal stress, \( \sigma_i \), can be considered as the amount of stress needed to maintain the evolved dislocation substructure; therefore, it was suggested that \( \sigma_i \) depends on the dislocation density, \( \rho \). With increasing \( \sigma_e \), \( \rho \) saturates at a
higher stress. To confirm this, the $\sigma_i$ dependence of $\rho$ at the higher stress region is investigated by microstructure observation. The measurements of $\rho$ are performed on the specimens interrupted in the creep tests at the time of the minimum creep rate.

The transmission electron micrographs of the specimens interrupted at the time of the minimum creep rate at 1 273 K and at 150 and 180 MPa are shown in Fig. 10. The stress axis and the extruded direction are indicated by the arrows. A number of dislocations are observed in the $\gamma$ matrix that correlate with $Y_2O_3$ oxide particles and are tangled with each other. The number of dislocations in the $\gamma$ matrix seems to be independent of $\sigma_i$. Also, $\rho$ is measured using Hirsh’s method.

The correlation between $\rho$ of the interrupted creep specimens at the time of the minimum creep rate and $\sigma_i$ is shown in Fig. 11. At stresses higher than 150 MPa, $\rho$ becomes saturated with increasing $\sigma_i$. This change in $\rho$ with $\sigma_i$ corresponds to the change in $\sigma_i$ with $\sigma_a$ at high stresses shown in Fig. 6. A one-to-one correspondence between $\sigma_i$ and $\rho$ is confirmed in the ODS alloy. However, at the lower stress region, $\rho$ decreases with decreasing $\sigma_i$.

### 3.6. Examination of $\sigma_i$ at Low Stresses

The stress dependence of $\sigma_i$ at the lower stress region is confirmed for $\sigma_i$ values lower than 170 and 150 MPa and at temperatures of 1 223 and 1 273 K, respectively. The estimated $\sigma_i$ at low stress is obtained using the following equation:

$$\sigma_i = A\sigma_a^2 + B\sigma_a$$

The relationships between $\sigma_i$ and $\sigma_a$ at low stresses are estimated as shown in Fig. 12, together with the measurements at higher stresses from Fig. 6. From the $\sigma_i$ dependence of $\sigma_a$, it is estimated that the ratio of $\sigma_i$ to $\sigma_a$ is very high at low...
stresses. Therefore, a large increase in \( \sigma \) occurs with increasing \( \sigma_i \) in the stress range of 150 to 180 MPa. Consequently, for MA754, it is concluded that the large \( n \) at high stresses is attributed to the lack of \( \sigma_i \) dependence of \( \sigma \) through \( \rho \), and the large \( n \) at low stresses is attributed to the high ratio of \( \sigma \) to \( \sigma_i \) in Eq. (2).

3.7. Examination of \( Q_c \)

3.7.1. Measured Values of \( Q_c \) and \( Q_c^* \)

Figure 3 shows the relationship between the minimum creep rate and \( \sigma \) at 1 223 and 1 273 K. A linear relationship is obtained for each curve in the log-log scale, and all of the curves are parallel. From these results, the value of \( Q_c \) is constant in the stress range of 130 to 190 MPa and is determined to be approximately 962 kJ/mol from Eq. (3). This \( Q_c \) is three-times larger than the activation energy, \( Q_d \), for the self-diffusion of pure Ni, which is approximately 293 kJ/mol.

On the other hand, linear relationships between the minimum creep rate and \( \sigma_i \) at 1 223 and 1 273 K are also obtained for each curve in the log-log scale, as shown in Fig. 7. Then, the value of \( Q_c^* \) is determined to be approximately 282 kJ/mol. This value is similar to that of \( Q_c \) for pure Ni as well as the value of \( Q_c^* \) that Wilshire et al. reported for Nimonic 80A and Nimonic 115.\(^{14-16}\)

3.7.2. Calculated \( Q_c \)

The change in \( K_i \) from Eq. (4) (the temperature dependence of \( \sigma_i \)) with \( \sigma \) is shown in Fig. 13. Here, \( K_i \) is determined from the difference between \( Q_c \) and \( Q_c^* \); this value saturates to 690 kJ/mol at a stress above 150 MPa.

To investigate \( K_i \) for MA754, the relationship between \( \sigma_i \) under a constant \( \sigma \) (between 150 and 180 MPa) and temperature is determined and is plotted in Fig. 14 with that of a \( \gamma \) single-phase Ni–20Cr alloy at 29.4 MPa determined by Nakajima.\(^{20}\) It has been believed that the temperature dependence of the dislocation substructure is negligibly small. However, Nakajima indicated the temperature dependence of the dislocation substructures through the temperature dependence of \( \sigma \), as shown in Fig. 14. The temperature dependence of the internal stress for MA754 is far larger than for Ni–20Cr alloy. However, at stresses below 160 MPa, the temperature dependence of \( \sigma_i \) becomes slightly smaller, but \( \sigma_i \) becomes much smaller because of the internal stresses caused by extrusion. Consequently, it is concluded that the large value of \( Q_c \) in MA754 is attributed to the high temperature dependence of \( \sigma \) at high stresses and the high ratio of \( \sigma \) to \( \sigma_i \) at low stresses.

4. Conclusions

The stress exponent of the minimum creep rate, \( n \), and the activation energy of creep, \( Q_c \), for the ODS nickel-based superalloy MA754 were investigated through the microstructure observation of specimens interrupted at the time of the minimum creep rate. Additionally, \( \sigma_i \) was measured by conducting creep tests at 1 223 and 1 273 K in the stress range of 130 to 190 MPa. The following conclusions were obtained:

(1) The values of \( n \) and \( Q_c \) for MA754 were determined to be 26 and approximately 962 kJ/mol, respectively.

(2) At high stresses, there is no \( \sigma_i \) dependence of \( \sigma \), but the ratio of \( \sigma \) to \( \sigma_i \) is very high at low stresses.

(3) The dislocation density, \( \rho \), of the specimen interrupted at the time of the minimum creep rate becomes saturated with increasing \( \sigma_i \). Therefore, there is no \( \sigma_i \) dependence of \( \rho \) at high stresses. On the other hand, at low stresses, \( \rho \) decreases with decreasing \( \sigma_i \).

(4) The actual measured stress exponent, \( n_{\text{meas}} \), correlates well with the calculated value, \( n_{\text{cal}} \).

(5) The activation energy of creep, \( Q_c \), under a constant \( \sigma_i \) correlates well with the sum of \( Q_c^* \) and \( K_i \).
The temperature dependence of $\sigma_i$ is very high at high stresses, and the ratio of $\sigma_i$ to $\sigma_a$ is high at low stresses. Consequently, it is concluded that the high values of $n$ and $Q_c$ in MA754 are attributed to the lack of $\sigma_a$ dependence of $\sigma_i$ and the high temperature dependence of $\sigma_i$ at high stresses and the very high ratio of $\sigma_i$ to $\sigma_a$ at low stresses, respectively.

REFERENCES