Annealing and Creep of Dispersion-Strengthened Ni-Al₂O₃ Alloys*

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Changes in the hardness and structure of dispersion-strengthened Ni-Al₂O₃ alloys (1~5 wt% Al₂O₃) were observed by vacuum annealing at 1200°C for 5 hr. According to the result, the Ni-1%Al₂O₃ alloy showed the disappearance of the fiber texture and a slight change in hardness by further annealing. Hence the alloy was selected as a material suitable for the study of the steady-state creep mechanism, and creep tests were carried out at 650°~800°C under a stress of 2~6 kg/mm².

The results of the creep tests were compared with those theoretically obtained by assuming the fittest parameter values n and Q in the equation $\dot{\epsilon} = A \sigma^n \exp(-Q/kT)$, where $\dot{\epsilon}$ is the steady-state creep rate and Q is the activation energy, as proposed by Ansell et al.

The values obtained by the authors are $n=4.3-6.5$ and $Q=34.0-71.7$ kcal/mol which are approximate to the theoretical ones on the assumption that dislocation climb is the rate-determining process. Moreover, it has been established that the activation energy for steady-state creep decreases with increasing applied stress.

The values of the shear modulus μ , calculated from the theoretical formula $\dot{\epsilon} = (2\pi\lambda^2)/(h\mu^3kT)\sigma^4 D_0 \exp(-Q/kT)$ by use of the experimental values, $\dot{\epsilon}$ and Q , are in the range of 10^{12} dyne/cm² which is comparable with those of nickel.

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I. Introduction

A characteristic feature of dispersion-strengthened alloys is a large value of creep strength at high temperatures. Accordingly, the study of the creep mechanism of the dispersion-strengthened alloys is of great importance from the theoretical and practical points of view.

Ansell and Weertman have carried out creep tests on the annealed, recrystallized SAP (Al-Al₂O₃) alloy at a comparatively high temperature at which a considerable amount of dislocation climb occurs. From these results, they proposed a theoretical equation for the steady-state creep of the dispersion strengthened alloys in a fixed range of stress and temperature⁽¹⁾. There is room for further discussion in their equation, and in the previous work, the authors compared their theory with the present results of creep tests at 650°~800°C on the extruded Ni-Al₂O₃ alloys⁽²⁾. It is evident that there is a remarkable difference in the values of n and Q in the equation, $\dot{\epsilon} = A\sigma^n \exp(-Q/kT)$, where $\dot{\epsilon}$ is the steady-state creep rate, σ is the applied stress, n is the power number and Q is the activation energy. Such a difference is considered to be due to the large effect of residual stress and worked structure in the extruded materials used. Therefore, in this experiment, creep tests were carried out on sufficiently annealed, recrystallized materials. The structure of the dispersion-strengthened alloy, however, is too stable to apply the heat-treatment for ordinary metallic materials, so that an annealing condition under which the recrystallization can occur sufficiently was determined by X-ray analysis and hardness measurement.

Creep tests were carried out at temperatures above 650°C on the Ni-Al₂O₃ alloys which were annealed in vacuum, and the values of n and Q were estimated to compare with the theoretical ones.

II. Experiments and Results

Specimens of nickel containing 1-5wt% alumina were used to determine the annealing condition for the dispersion-strengthened Ni-Al₂O₃ alloys. Specimens were prepared by the mixing method described elsewhere⁽³⁾, and all of the specimens were extruded with an extrusion ratio of higher than 20:1 at a rate of about 4 m/sec in dice pass over a temperature range of 1000°~1100°C. The specimens were then annealed in vacuum (about 10^{-4} mmHg) over a temperature range of 800°~1400°C in order to determine annealing conditions of the specimens, then at each annealing temperature and time, Vicker's hardness were measured and the X-ray and electron microstructures were observed.

Fig. 1(a) and (b) show the relation between annealing time and room temperature hardness for Ni-1% Al₂O₃ and Ni-5%Al₂O₃ alloys at 800° and 900°C, respectively, whereas Fig. 2 (a), (b), (c) and (d) show the relations between them after annealing over a temperature range of 1000°~1300°C for 1-3% Al₂O₃ alloys. From these measurements it is recognized that the hardness change of Ni-1%Al₂O₃ alloy with annealing temperature and time is smaller than in other high alumina specimens. Fig. 3 shows the hardness change in case of annealing at 1400°C, and there is the tendency that Vicker's hardness of 3~5% Al₂O₃ alloys decreases at first and then increases slightly with annealing time.

Fig. 4 (a), (b), (c) and (d) show the relations between hardness and annealing temperature against 1,3,5

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Fig. 1 Effect of annealing time at 800° and 900°C upon room temperature hardness for extruded Ni-1%Al₂O₃, Ni-5%Al₂O₃ alloys.
(a) 800°C, (b) 900°C

Fig. 2 Effect of annealing time at 1000°~1300°C upon room temperature hardness for extruded Ni-Al₂O₃ alloys.
(a) 1000°C, (b) 1100°C, (c) 1200°C, (d) 1300°C

Fig. 3 Relation between room temperature hardness and annealing time at 1400°C for extruded Ni-Al₂O₃ alloy.

and 9 hr annealing, respectively. The room temperature hardness does not change so remarkably in 1%Al₂O₃ alloy, but it shows minimum values in the vicinity of 1100°~1200°C in 3-5%Al₂O₃ alloys and the tendency toward the decrease of hardness with temperature appears only in 2%Al₂O₃ alloy. The hardness changes of the specimens annealed for 5 and 9 hr in vacuum are similar to those annealed for a short time, the hardness being almost invariable in 1%Al₂O₃ alloy.

X-ray patterns of the annealed specimens at 1200°C for 5 hr in vacuum are shown in Photo. 1. Photo. 1 (a) represents a diffraction pattern of the extruded Ni-1%Al₂O₃ alloy and spots due to the (100) fiber structure appears clearly on the (111) line. Photo. 1 (b)~(f) are the structures of the annealed specimens. Although a fiber structure is slightly recognized except 1%Al₂O₃ alloy, the presence of coarse grains is apparent. The change in X-ray pattern due to the disappearance of the worked structure and the growth of grains, depends on the annealing temperature and time rather than the alumina content.

Photo. 2 shows electron microstructure of the as-extruded Ni-1%Al₂O₃ alloy (a) and Ni-1%Al₂O₃ alloy annealed at 1200°C for 5 hr (b). From these photographs, coagulation of alumina particles seldom occurs under this annealing condition, so it will be possible to neglect the change in the dispersion state of the extruded and annealed materials.

From the above experimental results, it has been considered that the use of Ni-1%Al₂O₃ alloy annealed at 1200°C for 5 hr in vacuum is favorable to the creep test.

The method of the creep test is the same as described before⁽³⁾, but the applied stress was changed in the range of 2~5 kg/mm² at an interval of 50°C within the testing temperature range of 650°~800°C for creep rupture tests under a fixed condition of stress and temperature. The results obtained are shown in Figs. 5 and 6 in logarithmic scale. The relation between stress-rupture life and stress-steady state creep rate are linear for the annealed Ni-1%Al₂O₃ alloys. When Fig. 6 is contrasted to the equation $\dot{\epsilon} = A\sigma^n \exp(-Q/kT)$, it can be easily understood that the value of n corresponds with the gradient of the straight line (where $\dot{\epsilon}$ is the steady-state creep rate

Fig. 4 Relation between room temperature hardness and various annealing temperature for extruded Ni-Al₂O₃ alloys. (a) after 1-hr annealing, (b) after 3-hr annealing, (c) after 5-hr annealing, (d) after 9-hr annealing.

Photo. 1 X-ray diffraction patterns of extruded Ni-1%Al₂O₃ alloy and annealed Ni-1~5%Al₂O₃ alloys at 1200°C for 5 hr.

(a) As extruded Ni-1%Al₂O₃ alloy. (b) Ni-1%Al₂O₃ alloy. (c) Ni-2%Al₂O₃ alloy. (d) Ni-3%Al₂O₃ alloy. (e) Ni-4%Al₂O₃ alloy. (f) Ni-5%Al₂O₃ alloy. (b)~(f) Annealed Ni-Al₂O₃ alloys.

(%/hr). The n values were obtained from the above relation and parameters of creep tests are shown in Table 1. The n value becomes smaller with increasing temperature and is 4.3 at 800°C which nearly equals the theoretical value $n=4$ as proposed by Ansell et al. Paying attention to the value of n , it is by far smaller than the value previously obtained for the creep of

the extruded material⁽²⁾, being about one-half.

The semi-log plots of steady-state creep rate vs. inverse absolute temperature are shown in Fig. 7, where all the values fall on a straight line. Fig. 7 is plotted by estimating the values from Fig. 6. The gradient of the straight line becomes smaller with increasing applied stress. Activation energy of the

Photo. 2 Electron microstructures of as-extruded Ni-1%Al₂O₃ alloy (a) and annealed at 1200°C for 5 hr Ni-1%Al₂O₃ alloy (b).

Fig. 5 Stress-rupture results for annealed Ni-Al₂O₃ alloys, tested at 700°, 750° and 800°C.

Fig. 6 stress versus steady-state creep rate for annealed Ni-Al₂O₃ alloys, tested at 650°, 700°, 750° and 800°C.

steady-state creep was calculated from these gradients and are shown in Table 2 against applied stress. The activation energy of the steady-state

Table 1 Stress-rupture and creep results for annealed Ni-1%Al₂O₃ alloys.

Temperature (°C)	Stress (kg/mm ²)	Rupture life (min)	Steady-state creep rate (%/hr)	Power
650	4.0	—	4.75×10^{-3}	6.5
	5.0	—	2.25×10^{-2}	
	6.0	—	—	
700	4.0	3054	1.80×10^{-2}	5.2
	4.5	1615	2.86×10^{-2}	
	6.0	360	2.49×10^{-1}	
750	3.0	2932	2.68×10^{-2}	4.5
	3.5	1494	4.86×10^{-2}	
	4.0	727	7.35×10^{-2}	
	5.0	365	2.04×10^{-1}	
800	2.0	7419	1.66×10^{-2}	4.3
	2.5	1600	7.33×10^{-2}	
	3.0	925	8.36×10^{-2}	
	4.0	270	3.05×10^{-1}	

Table 2 Activation energy of steady-state creep at 650°~800°C for Ni-1%Al₂O₃ alloys.

Stress (kg/mm ²)	Activation energy (kcal/mol)
2	71.7
3	65.0
4	50.9
5	40.2
6	34.0

creep at a stress of 3 kg/mm² is about 65.0 kcal/mol and the value is close to 65.8 kcal/mol⁽⁴⁾ which is the activation energy of self-diffusion of nickel in the temperature range of 700°~1100°C. Osipov et al.⁽⁵⁾ have also reported that the activation of creep is lowered with increase in applied stress. Fig. 8 shows the relation between stress and activation energy.

III. Considerations

The characteristics of the specimens subjected to the annealing experiments are that they are prepared by heavy hot working of a sintered powder material

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Fig. 7 Steady-state creep rate of annealed Ni-Al₂O₃ alloys as a function of temperature.

Fig. 8 Activation energy for steady-state creep of Ni-1% Al₂O₃ alloy as a function of applied stress.

and fine particles of alumina are dispersed in nickel. Accordingly, though the specimen are the material worked at a high temperature, an (100) fiber structure and pronounced lattice distortion can be observed by the X-ray diffraction technique. Moreover, the recovery from the worked structure is considered to be delayed by the above dispersion effect. The relations of annealing time and temperature against room temperature hardness in Figs. 1~4 arose from the above conditions, and the reason why the hardness change did not occur in Ni-1%Al₂O₃ alloy might be attributed to the substantial softening induced by a high working temperature prior to the disappearance of the fiber structure. In addition, the low content of alumina seems to contribute to the high softening rate.

The softening process of the specimens was not studied in detail because the purpose of the present experiments was to determine a sufficient recrystallization condition. From the experimental results, however, it was recognized that the hardness became a

minimum by annealing at about 1100°C and the hardness once decreased had a tendency to increase with annealing time at the annealing temperature of 1400°C. The α - γ modification of alumina dispersion particles has been reported to occur at about 1200°C⁽⁶⁾, so the result of hardness change may be linked with the α - γ modification.

From the results of the above investigation Ni-1% Al₂O₃ alloys annealed at 1200°C for 5 hr in vacuum (10⁻⁴mmHg) were used for the measurement of steady-state creep.

Ansell et al. studied on the steady-state creep of SAP (Al-Al₂O₃ alloy) in the temperature range where the climb of dislocations plays a main part in the rate-determining process, thus leading the equation,

$$\dot{\epsilon} = \frac{2\pi\lambda^2}{h\mu^3kT} \sigma^4 D_0 \exp(-Q/kT) \quad (1)$$

where $\dot{\epsilon}$ is the steady-state creep rate, λ is the inter-particle spacing of alumina which is the dispersion phase, h is the height of the dislocation climb, μ is the shear modulus of the nickel base phase, D_0 is the frequency factor, Q is the activation energy of self-diffusion, σ is the applied stress and k is Boltzmann's constant.

The temperature at which the dislocation climb becomes the rate-determining process for creep is considered to be about a half of the melting point (°K)⁽⁷⁾, e.g., about 600°C for nickel. Accordingly the creep test range of 650~800°C is regarded as most appropriate. The power numbers in Table 1 range 4.3~6.5 and are approximate to the theoretical ones, but the activation energy of steady-state creep changes with applied stress as shown in Fig. 8. This can be written in the following equation:

$$Q = Q_0 - \gamma\sigma, \quad (2)$$

where Q_0 is the constant energy, γ is the coefficient which varies with stress. Q is the activation energy obtained from the temperature dependence of steady-state creep and may be considered as the activation energy of dislocation climb. It is thought that the dislocation climb is caused by diffusion of vacancies to the leading dislocations of the piled-up group at a barrier, as calculated by Weertman⁽⁸⁾. Therefore, in this case the activation energy of steady-state creep appears to be the activation energy of self-diffusion. Moreover, it should be noted that the stress-dependence in formula (2) seems to give an experimental support to the proposed mechanism of Friedel⁽⁹⁾, and Shoek⁽⁷⁾ based on the dislocation climb.

In this case, if the stress becomes larger and the rate of deformation increases, the range of the steady-state creep becomes smaller or can hardly be recognized. Therefore some other deformation mechanism will need to be considered. In the present

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Table 3 The calculated shear modulus μ and the values used to obtain μ .

σ (kg/mm ²)	σ (dyne/cm ²)	$\dot{\epsilon}$ (hr ⁻¹)	Q (cal/mol)	T (°K)	A (dyne ⁻¹ cm ²) ⁴ hr ⁻¹)	μ (dyne/cm ²)
2	1.96×10^8	1.66×10^{-4}	71700	1073	4.48×10^{-23}	1.63×10^{12}
3	2.94×10^8	8.36×10^{-4}	65000	1073	1.99×10^{-24}	4.60×10^{12}
4	3.92×10^8	3.05×10^{-3}	50900	1073	2.79×10^{-27}	4.11×10^{13}

$$k: 1.380 \times 10^{-16} \text{ erg deg}^{-1} \quad D_0: 1.27 \text{ cm}^2 \text{ sec}^{-1}$$

experiments, a half of about 10 kg/mm²(10), which is the yield strength of this material at 800°C, was selected as the upper limit of applied stress in creep.

Now the n values determined by the equation, $\dot{\epsilon} = A\sigma^n \exp(-Q/kT)$, are in the range of 4.3~6.5, but when the effective stress is $\sigma - \sigma_0$ as considered before(2), n can be set as 4, where σ_0 is the internal stress. Then the value A can be estimated by introducing Q and $\dot{\epsilon}$ to the above equation. The value A is comparable to $2\pi\lambda^2 D_0 / h\mu^3 kT$ in equation (1), so the value μ can be calculated by using the following constants: The average value of interparticle spacing measured by electrophotometric observation is $\lambda = 10^{-4}$ cm; the height of the dislocation climb $h = 10^{-5}$ cm(8); $D_0 = 1.27$ cm²/sec(4). The calculated shear modulus μ and the values used are shown in Table 3. The values μ are comparable with the ones in reference(11)(12), indicating the validity of this theory. The tendency to the increase of apparent values of μ with applied stress needs to be related with the stress-dependence of activation energy of creep mentioned before.

Equation (1) was derived mathematically from some ideal patterns and it is apparent that further studies are necessary on the steady-state of creep which is the premise of this equation and on the behavior of extended dislocations, the concentration of vacancy, etc.. Nevertheless, an attempt of theoretical analysis of the creep mechanism will give a clue to the experimental examination of the creep phenomena.

IV. Summary

From the results obtained by creep tests for extruded materials, the power numbers of stress versus steady-state creep rate for fully annealed and recrystallized materials are close to the theoretical

ones determined by Ansell et al. and the activation-energy comparable with that of self-diffusion was obtained. The results of annealing and creep rupture tests are:

(1) In the experiments of annealing of dispersion-strengthened Ni-Al₂O₃ alloys containing 1~5wt% alumina in the temperature range of 850°~1400°C, X-ray diffraction patterns which showed softening and recrystallization were observed in every specimen annealed at 1200°C for 5 hr. Particularly in 1%Al₂O₃ alloy, the fiber structure due to working disappeared under the above condition and the hardness changed very little. Therefore the alloy can be used in creep tests as the recrystallized material.

(2) It is recognized that the hardness of 3~5wt% Al₂O₃ alloys have a tendency to increase at the annealing temperature of about 1100°C.

(3) The relations between stress-rupture life and stress-steady-state creep rate for annealed Ni-1%Al₂O₃ alloys are linear in the double log plot under the creep conditions of 650°~800°C and 2~6 kg/mm². The power number of stress versus steady-state creep rate are in the range of 4.3~6.5 and these values are very close to those proposed by Ansell et al.

(4) The semi-logarithmic plots of steady-state creep rate versus reciprocal temperature (1/°K) are linear and the activation energy of steady-state creep obtained from these straight lines are in the range of 34.0~71.7 kcal/mol and they decreased with increase in stress.

(5) The shear modulus μ of nickel in Ni-1%Al₂O₃ alloy were calculated by using a theoretical equation of steady-state creep, the measured steady-state creep rate and activation energy. The values of μ have an order of 10¹² dyne/cm² which is comparable to that of pure nickel.

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