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The influence of antimony-additions on the creep behaviour of a 25 wt % Cr–20 wt % Ni austenitic stainless steel

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The effect of antimony on the creep behaviour (dislocation creep) of a 25 wt% Cr–20 wt% Ni stainless steel with ~ 0.005 wt % C was studied with a view to assessing the segregation effect. The antimony content of the steel was varied up to 4000 ppm. The test temperature range was 1153 to 1193 K, the stress range, 9.8 to 49.0 MPa, and the grain-size range, 40 to 600 μm. The steady state creep rate, $\dot{\epsilon}_s$, decreases with increasing antimony content, especially in the range of intermediate grain sizes (100 to 300 μm). Stress drop tests were performed in the secondary creep stages and the results indicate that antimony causes dislocations in the substructure to be immobile, probably by segregating to them, reducing the driving stress for creep.

Nomenclature

σ_a	Creep stress in a constant load creep test without stress-drop
σ_A	Initial applied stress in stress-drop tests
$\Delta\sigma$	Stress decrement
$(\sigma_A - \Delta\sigma)$	Applied stress after a stress decrement, $\Delta\sigma$
Δt_i	Incubation time after stress drop (by the positive creep)
σ_c	Strain-arrest stress
σ_i	Internal stress
σ_s	σ_s-component $(= \sigma_i - \sigma_c)$
$\dot{\epsilon}_s$	Steady state creep rate (average value) in a constant load creep test
$\dot{\epsilon}$	Strain rate at time, t, in a constant load creep test
$\dot{\epsilon}'_s$	New steady state creep rate (average value) after stress drop from σ_A to $(\sigma_A - \Delta\sigma)$
$\dot{\epsilon}'$	Strain rate at time, t, after stress drop

1. Introduction

It is widely accepted that additional elements and impurities have an influence on the mechanical properties of polycrystalline metals, especially Ni–Cr steels [1–5]. Some of the elements tend to segregate to grain-boundaries and subgrain-boundaries, resulting in embrittled grain-boundaries [2], or stabilized subgrain-boundaries [3]. This indicates that the creep properties are affected by the segregation, rather than by the solid solution effect. Antimony is an element which exists in bulk as substitution type [6] and segregates to the boundaries [7].

In their previous paper [8], the authors reported the creep behaviour of a 25 wt % Cr–20 wt % Ni austenitic stainless steel doped with antimony. According to [8], the effect of antimony additions on the "dislocation-creep" is striking in the intermediate grain-size range (d = 100 to 300 μm, where d is the mean grain diameter).

The creep behaviour in this range is strongly associated with the formation of dislocation substructures [9–12]. Thus, the internal stress field can be influenced by antimony additions, because antimony atoms must segregate to the substructure (subgrain boundaries).

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TABLE I Chemical compositions of the various specimens

Specimens	Elemental composition (wt %)			
	Cr	Ni	C	Sb
Sb-free	22.77	21.39	0.005	nil
Sb-100	22.83	21.86	0.004	0.01
Sb-300	22.99	21.57	0.005	0.03
Sb-1000	23.07	21.81	0.006	0.10
Sb-4000	23.20	22.64	0.005	0.40

The purpose of the present paper is to interpet the effect of antimony additions on the creep behaviour of an austenitic stainless steel, based on the results of stress drop tests.

2. Experimental procedures

The chemical compositions of the vacuum-melted austenitic stainless steels used in this study are shown in Table I. The content of nickel was planned to be higher and that of chromium lower than that of the AISI 310 stainless steel, to prevent sigma-phase formation. The carbon content was as low as possible in order to restrain carbide-precipitation.

Specimens were prepared from the steels as detailed previously [10]. Primary annealing under various conditions resulted in various mean grain diameters, d. This was followed by secondary annealing at the test temperature for 55 ksec*. All heat treatments prior to the creep tests were performed in a vacuum (~ 0.1 Pa).

The creep tests were performed in air after heating for 3.6 ksec at test temperatures. The range of stress, temperature and grain-size were settled according to the previous paper [8], that is, the test temperature range was 1153 to 1193 K, the stress range 9.8 to 49.0 MPa and the grain size ranged between 40 and 600 μm. This is the field of "dislocation (power law) creep", based on the deformation mechanism maps [8, 9].

Stress-drop tests were carried out in the steady state creep stage which had previously been ascertained by conventional creep tests. The elongation was measured with an accuracy of $\pm 0.5\,\mu$m, using precision-dial and standard-dial gauges.

The critical stress decrement, $\Delta\sigma_c$, corresponds to values, such that when $\Delta\sigma < \Delta\sigma_c$, the incubation time, Δt_i, after a stress decrement, $\Delta\sigma$, rapidly increases with increasing $\Delta\sigma$, and also negative creep is observed immediately after stress dropping, as reported in previous papers [10, 11]. The strain-arrest stress, σ_c, is defined as $(\sigma_A - \Delta\sigma_c)$.

It is said that the steady state creep rate, $\dot{\epsilon}_s$, in the dislocation creep field can normally be expressed by

$$\dot{\epsilon}_s = A\sigma_a^n \exp(-Q_c/RT), \qquad (1)$$

where A is a constant (if d is constant), n is the stress exponent, R is the gas constant, T, the absolute temperature, and Q_c is an activation energy for creep. In this study, Equation 1 was applied to the steady state creep rates, $\dot{\epsilon}_s$, in order to understand the effect of antimony-additions on $\dot{\epsilon}_s$.

3. Experimental results and discussion

3.1. Constant load creep tests

Fig. 1 shows the grain-size dependences of $\dot{\epsilon}_s$, which reduces with increasing antimony content. The effect of the antimony additions on $\dot{\epsilon}_s$ is striking for intermediate grain sizes of 100 to 300 μm. When the grain size is larger than 300 μm, the effect diminishes with increasing grain-size, as with decreasing grain-size from 100 to 400 μm.

Fig. 2 shows the stress dependences of $\dot{\epsilon}_s$ for $d \simeq 160$ and 300 μm as the representative results of this range ($d = 100$ to 600 μm). The effect of antimony additions on $\dot{\epsilon}_s$ is made clear by Fig. 2, that is, the effect is enhanced with decreasing stress and increasing antimony content, resulting in n-values higher than those of the steel without antimony. The steel with 4000 ppm of antimony has an n-value approximately equal to six for $d = 160\,\mu$m, and above seven for $d = 300\,\mu$m. Such high values of n have been obtained for several austenitic stainless steels [13–16] and Nimonic 80 [17], for instance and in contrast to those of many pure metals ($n =$ 4 to 5) [18] and Ni–20 wt% Cr alloy ($n = 4.8$) [17]. Also the apparent activation energy for creep, Q_c, is often much higher than that of volume self-

*The stainless steel without antimony had no precipitates even during creep tests, but those with antimony already had grain boundaries dotted with precipitates after the secondary annealing. It is thus suggested that some of the antimony atoms segregate to grain boundaries as the second phase. The second phase increased insignificantly during creep, indicating that the secondary annealing led to an equilibrium state.

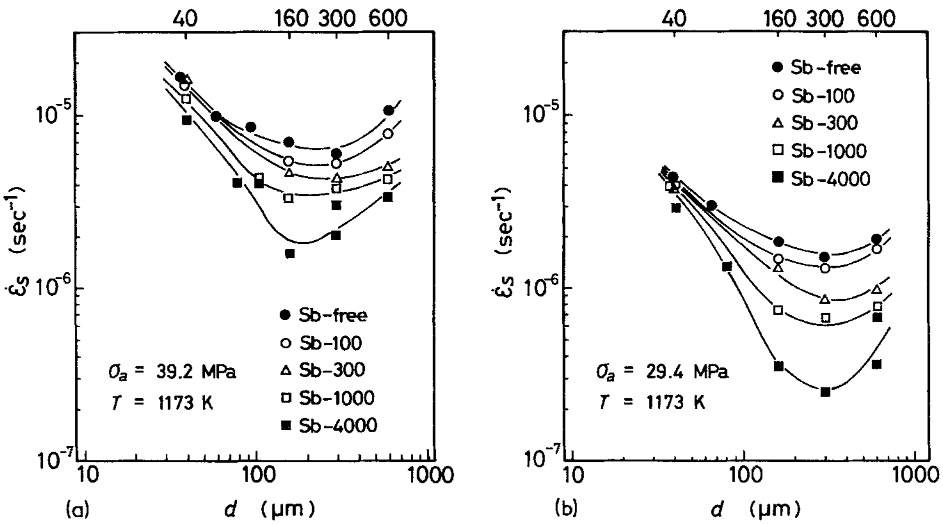

Figure 1 The effect of Sb-additions on the grain-size dependences of $\dot{\epsilon}_s$. (a) $\sigma_a = 39.2$ MPa, (b) $\sigma_a = 29.4$ MPa.

diffusion, Q_v when high values of n are observed [10, 14], as reported in the previous paper [8]†.

The authors pointed out that the steady state creep rate, $\dot{\epsilon}_s$, can be more meaningfully represented by

$$\dot{\epsilon}_s = A^* (\sigma_a - \sigma_c)^{n^*} \exp(-Q_c^*/RT), \quad (2)$$

where A^* is constant, n^* is an effective stress exponent, which is independent of T and σ_a, with a value of approximately four, and Q_c^* is the true activation energy for creep, equivalent to Q_v and independent of σ_a. Q_c^* is obtained from the relationship $Q_c^* = -R\ [\partial \ln \dot{\epsilon}_s / \partial \ln(1/T)]$ under the condition $(\sigma_a - \sigma_c) = \text{constant}$ [10].

In the following section, Equation 2 will be applied to the stress dependence of $\dot{\epsilon}_s$.

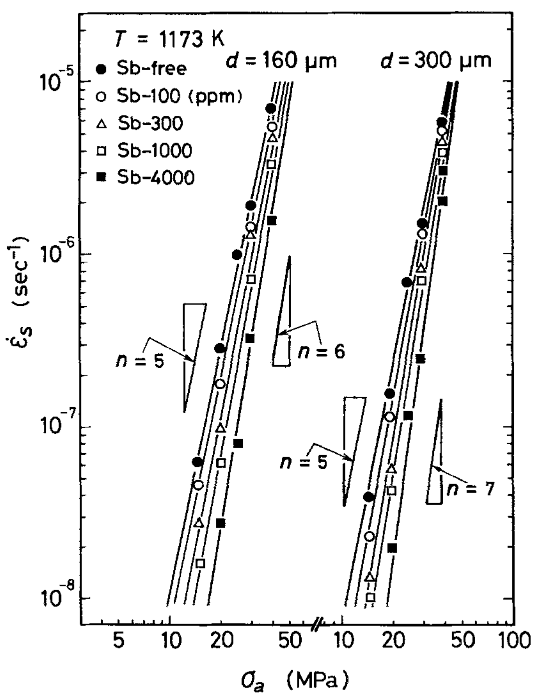

Figure 2 The effect of Sb-additions on the stress dependences of $\dot{\epsilon}_s$.

3.2. Stress drop tests

The results of the stress drop tests exhibit signs of the internal stress verging on the applied stress, regardless of the antimony content. There is always an incubation time, Δt_i, even after the smallest stress decrement (1.0 MPa), and then creep deformation recommences to reach a new steady state creep stage with an average strain rate of $\dot{\epsilon}_s$. The internal stress is close to the applied stress ($\sigma_i \simeq \sigma_A$ or σ_a) implying that the power law creep in austenitic 25Cr–20Ni stainless steel is controlled by "recovery" (climb controlled) [9, 19, 20].

Thus the strain-arrest stress, σ_c, may be only one component of the internal stress, but a significant one, because there remains a possibility of systematically arranging the steady state creep rates by using Equation 2.

Fig. 3 shows the variation of the strain-arrest

†In austenitic stainless steel, often $Q_c > 400\ \text{kJ mol}^{-1}$, which is much higher than bulk self-diffusion of Fe ($Q_v \simeq 285\ \text{kJ mol}^{-1}$).

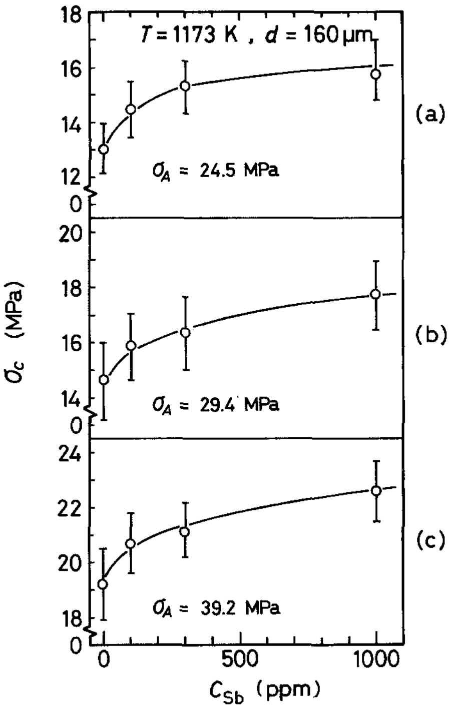

Figure 3 Variations of the strain-arrest stress, σ_c, with Sb-content, C_{Sb}. (a) $\sigma_A = 24.5$ MPa, (b) $\sigma_A = 29.4$ MPa, (c) $\sigma_A = 39.2$ MPa.

stress with antimony content, C_{Sb}, for $d = 160\,\mu$m. The strain-arrest stress, σ_c, increases with increasing C_{Sb}. This is related to the stabilization of the dislocation-substructure, because σ_c is considered to be the long-range stress field owing to metastable substructures [9, 14]. This indicates that antimony segregation to the substructures reduces the number of mobile dislocations. As a result, the steady state creep rate, $\dot{\varepsilon}_s$, is decreased by antimony addition, as seen in Fig. 2.

Fig. 4 shows the change in $\dot{e}$ and $\dot{\varepsilon}$ with time, where $\dot{e}$ and $\dot{\varepsilon}$ are as defined earlier. The abscissa of Fig. 4 represents the time after stress decrement for $\dot{e}$, and also the time from the beginning of the creep for $\dot{\varepsilon}$. The strain rate, $\dot{e}$, has a maximum value around $t \simeq 10^3$ sec for the conditions of Fig. 4, and then gradually becomes the new steady state creep rate, $\dot{e}_s$. On the other hand, the strain rate, $\dot{\varepsilon}$, monotonically decreases to reach the secondary creep stage. The maximum value in the strain rate, $\dot{e}$, is very often observed when $\Delta\sigma < \Delta\sigma_c$ but it is rarely observed when $\Delta\sigma \geqq \Delta\sigma_c$, where $\Delta\sigma_c = \sigma_A - \sigma_c$.

As can be seen in Fig. 4, $\dot{e}_s$ is much less than $\dot{\varepsilon}_s^{\ddagger}$. This indicates that the substructures developed before stress-reduction remain metastable even after stress-drop.

Fig. 5 shows the steady state creep rates, $\dot{\varepsilon}_s$, which are re-arranged as a function of $(\sigma_a - \sigma_c)$. It is found that the antimony additions have no influence on $\dot{\varepsilon}_s$ as a function of $(\sigma_a - \sigma_c)$, and the stress exponent, n^*, is nearly equal to 4. This consequently indicates that $(\sigma_a - \sigma_c)$, i.e. σ_s-component $(= \sigma_i - \sigma_c)$ is comparable to the driving stress, which is considered to be derived from the mobile dislocations [19, 20].

σ_c-component must be due to immobile dislocations, being probably similar to the friction stress in [19]. On this basis, the large values of n can be rationalized. Similarly, it appears that the large values of Q_c may also be explained in terms of the strain-arrest stress [10].

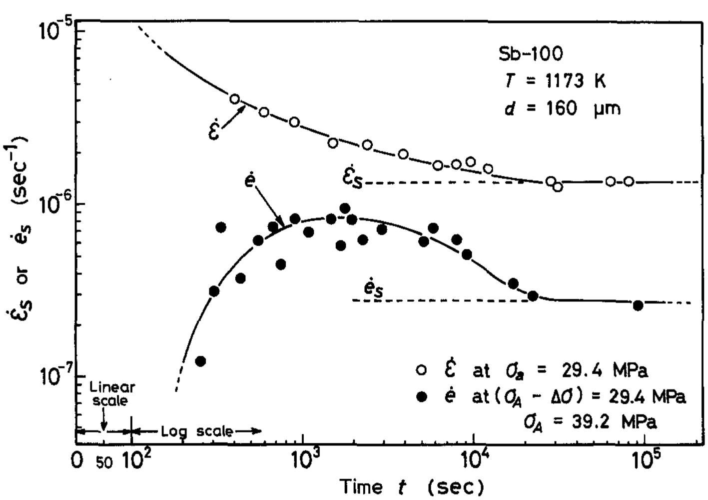

Figure 4 The change in the strain rates $\dot{\varepsilon}$ and $\dot{e}$ with time.

‡It is in the accelerated creep stage when $\dot{e}$ is equal to $\dot{\varepsilon}_s$ for $\sigma_a = (\sigma_A - \Delta\sigma)$.

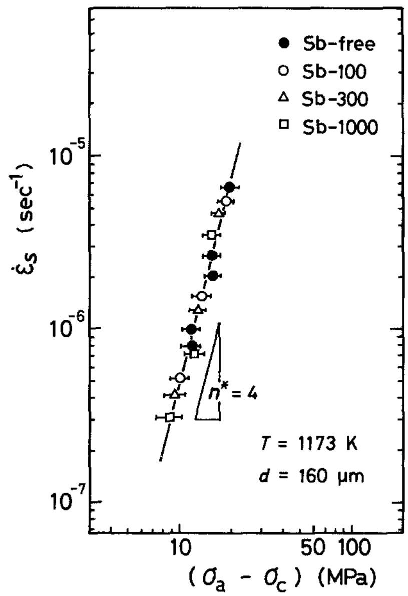

Figure 5 The steady state creep rates, $\dot{\epsilon}_s$, as a function of $(\sigma_a - \sigma_c)$.

4. Conclusion

As mentioned above, it could be concluded that antimony atoms in 25Cr–20Ni stainless steel cause dislocations in substructures such as subgrain boundaries to be "immobile", probably by segregating to them, resulting in an increased strain-arrest stress, that is, a reduced strain rate.

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