Suzuki Segregation and Dislocation Locking in Supersaturated Co–Ni-Based Alloy

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The stress relaxation experiment has been performed at temperatures ranging from room temperature to 1073 K to study changes in motion and structure of the dislocations induced into the Co–Ni-based alloy. The resultant zero rate of stress relaxation at room temperature can be assumed to be due to the immobilization of the induced dislocations originating from an elastic interaction between dislocation cores and solute atoms. At elevated temperatures where the dynamic strain aging (DSA) occurs, the zero rate of the stress relaxation at an initial stage can be attributed to the dislocation locking effect caused by the Suzuki segregation. The stress relaxation at the DSA temperature range occurs by the sole movement of leading partial dislocations, resulting in wide dislocation dissociations. At exceeding the DSA temperature range, the dislocation locking effect caused by the Suzuki segregation fades away and the two partial dislocations simultaneously glide by viscous motion, resulting in the lack of the observed wide dislocation dissociation. The phase diagram calculation and microstructure observations reveal that the present alloy SPRON 510 is a supersaturated solid solution and that the occurrence of the Suzuki segregation is strongly associated with the degree of the supersaturation of the solid solution.

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1. Introduction

Co-based alloys are generally used in applications which require wear resistance, corrosion resistance, low thermal expansion and high-temperature strength, as well as magnetic properties. In numerous applications of Co-based alloy, the alloy SPRON510 (the trademark of a Co–Ni-based alloy provided by SII Micro Parts Ltd., Japan), primarily containing chromium, molybdenum, niobium and iron, has also been used in the production of springs of small precision instruments, medical instrument parts, diaphragms, and so on. Although the alloy SPRON510 (essentially quaternary alloys of cobalt, nickel, chromium and molybdenum) are commercial alloys, with practical uses as described above, from an academic standpoint, several interesting properties in the high-temperature strength were found in the previous investigation.\(^1\) In the previous paper,\(^1\) it was demonstrated that the alloy SPRON 510 exhibits a high work hardening rate both at room temperature and elevated temperatures where the dynamic strain ageing (DSA) operates. It was considered, in that paper, that in the DSA temperature range, the so-called Suzuki segregation\(^2\) into stacking faults bounded by Shockley partials could occur so that the dislocation dissociation is extended, thereby causing suppressing the cross-slip event. Since it is difficult for the stress relief mechanism, due to the cross-slip event, to occur in the temperature range where the DSA operates, deformation twinning begins as an alternative mechanism to reduce the internal stress. Thus it was concluded in the previous paper\(^1\) that the DSA in the alloy SPRON 510 is responsible for the higher work-hardening rate and the occurrence of the deformation twinning at elevated temperatures.

It is generally accepted that the DSA is related to the dynamic interaction between diffusing solute atoms and mobile dislocations with edge character.\(^3\) In such a DSA mechanism, elastic interaction between solute atoms and dislocation cores of edge dislocations are responsible for the jerky motion of the dislocations, as typically observed in a system of Fe–C. However, as stated above, in the alloy SPRON 510 the DSA is thought to come from the Suzuki segregation, that is, chemical interaction between solute atoms and stacking faults bounded by the Shockley partials. Thus it is thought that the dislocations are strongly locked by the solute atoms at elevated temperatures, especially at the DSA temperature range. It should be considered how the locking force coming from the Suzuki segregation affects the dislocation motions.

In the present paper, we studied the dislocation behavior using stress relaxation experiments from room temperature to elevated temperatures and reveal difference in the dislocation motion between the DSA temperature range and non-DSA temperature range. Furthermore, we will discuss the occurrence of the Suzuki segregation in the present alloy on the basis of the considerations on the calculated phase diagram and microstructure observations.

2. Experimental Procedure

The sample of the alloy SPRON 510 (hereafter designated by the Co–Ni based alloy) was supplied by SII Micro Parts Ltd., Japan. The Co–Ni-based alloy, which has the chemical composition listed in Table 1, was melted in a vacuum induction-melting furnace. The phase diagram of the present alloy system, Co–31Ni–19Cr–1.5Nb–2.1Fe–0.8Ti–0.01Zr–xB(Mo) (x = 0 to 20 mass%) was calculated using the database of the Thermo-Calc.\(^5\)

The ingot was forged into a rod of diameter 18.5 mm at approximately 1323 K. The rod-shaped alloy was swaged from 18.5 to 13.5 mm in diameter at room temperature and
subsequently annealed at 1323 K for 24 h to attain chemical homogeneity and to produce a recrystallized microstructure. Through these processes, recrystallized grains with an average grain size of approximately 100 μm were obtained. Crystal structures, and identification of second phase precipitates were determined by an X-ray diffractometer using monochromated CuKα radiation over 20° ≤ 2θ ≤ 100°. The disc specimen for X-ray diffraction was cut perpendicular to the longitudinal direction of the sample rod.

Tensile tests and subsequent stress relaxation experiments were performed using an Instron type 8562 electromechanical testing machine at room temperature, 773 K, 873 K, 943 K, 1023 K and 1073 K at an initial strain rate of 5.2 × 10^-4 s^-1 in a vacuum of approximately 10^-3 Pa. The gauge size of the tensile sample was as follows: thickness, 1 mm; width, 3 mm; length, 16 mm. The stress relaxation experiments were performed by stopping the motion of the crosshead and measuring the resulting variations in stress rate and strain rate in the sample. The crosshead was stopped at a total strain of 12% of each tensile sample.

In order to examine the deformation microstructure, transmission electron microscope (TEM) observations were conducted. Thin discs with a thickness of approximately 1 mm were cut by the wire-cut spark machine from the tensile-deformed samples and mechanically polished with emery papers to a thickness of approximately 0.1 mm. The thin foils for TEM observations were prepared by jet-electropolishing the disc at a voltage of 12 V at 243 K in a solution of 90 parts methanol plus five parts sulphuric acid. TEM observations were performed using a Hitachi H-800 at an accelerated voltage of 200 kV.

3. Results

3.1 Microstructure analysis

X-ray diffraction pattern of the Co–Ni-based alloy is indicated in Fig. 1. The diffraction pattern exhibits peaks being identified as the FCC phase and no appreciable peaks corresponding to second phases, indicating that the present Co–Ni-based alloy is a single-phase structure. It is found that intensity of the (220) peak is weak as compared with that of (111), or (200) peaks. This is because that a specimen has a weak (111) fiber texture, since the fabrication of the specimens includes the hot and cold swaging process.

3.2 Stress relaxation tests

Figure 2(a) shows tensile stress-strain curves, obtained before the relaxation experiments started. As shown in the figure, serrated flow associated with the DSA can be found in the stress-strain curves except at room temperature. As previously reported by the present authors, DSA can be attributed to the chemical interaction between solute atoms and stacking faults bounded by the Shockley partials. This suggests that the dislocations become interactive with the solute atoms as the temperature increases.

Figure 2(b) shows the stress relaxation curves, i.e., variation in stress with passage of time after stopping the motion of the crosshead. At room temperature, the stress relaxation does not occur virtually. At temperatures of 773 K, 873 K, and 943 K, approximately up to 1000 seconds, the stresses exhibited almost constant and then decreased gradually; the stress at 873 K led to zero. However, at 773 K and 943 K, the stresses did not reach complete relaxation. The stresses at 1023 K and 1073 K decreased gradually with time and reached zero at approximately 2500 seconds and 800 seconds, respectively.

3.3 TEM observations

The dislocation structure of a sample aged at 943 K for 2 h after deformation approximately 10% at room temperature is
shown in Fig. 3(a). It should be noted that, unlike the dislocations without aging treatment as shown in Fig. 3(b) reproduced from Ref. 1, all the dislocations accompany wide ribbons of stacking fault fringes, indicating that the dislocations dissociate into the Shockley partials. These dislocation dissociations must have occurred during the aging treatment; for example, during aging at 943 K, solute atoms migrate to the dislocations and segregate into the stacking fault bounded by the two Shockley partials, resulting in the reduction of the stacking fault energy (SFE) and widening the width of the stacking fault. Such microsegregation of the solute atoms into the stacking faults of the dissociated dislocations, known as the “Suzuki segregation”, is a cause for solid-solution hardening in FCC alloys.2

Figures 4(a), (b), (c), (d) and (e) show TEM micrographs of the dislocation configurations observed after stress relaxation experiments at 773 K, 873 K, 943 K, 1023 K and 1073 K, respectively. No dissociated dislocations appear within the resolution of the present study at 773 K (Fig. 4(a)), essentially the same as the dislocations observed at room temperature shown in Fig. 3(b). On the other hand, extended stacking fault fringes, associated with widely dissociated dislocations are seen at 873 K and 943 K (Figs. 4(b) and (c)). Dislocations are not dissociated widely at 1023 K and 1073 K (Figs. 4(d) and (e)). Such behavior of the dislocation dissociation corresponds to that of the DSA. We can point out that the dislocation dissociation widely occurs at temperatures where the DSA significantly appears.

4. Discussions

4.1 Supersaturated solid solution and Suzuki segregation

Since the experimental phase diagram of the present alloy is not available in the literature, we have calculated the phase diagram as a function of molybdenum concentration using database of the Thermo-Calc.5 Figure 5(a) shows the calculated phase diagram of Co–31Ni–19Cr–1.5Nb–2.1Fe–0.8Ti–0.01Zr–xMo (x = 0 to 20 mass%). As can be seen in the figure, γ FCC phase is found to exist stable at temperatures higher than 1223 K. The GCP (Geometrically Close Packed) phase, i.e., η phase and the TCP (Topologically Close Packed) phases, i.e., μ, and δ can coexist with the γ phase in the lower temperature region. The TCP σ phase appears at molybdenum concentration higher than 10 mass% at temperature of approximately 1173 K. According to the calculated phase diagram, the present alloy containing 10 mass% Mo is thought to consist of γ, σ, η, μ, and δ phases. However, it is evident from the optical microstructure1 and X-ray diffraction pattern shown in Fig. 1 that the present alloy has a FCC single-phase structure. These apparent inconsistencies between calculations and experiments seem to be due to low precipitation rate of the secondary phases in the present alloy. In fact, it was found that the secondary phases precipitated from the aged sample at 1173 K after the heavy pre-straining of 83% reduction in the cross sectional area of the sample. Although further details on the precipitations are not described in the present paper, it can be thought that since pipe diffusion of solute atoms through dislocation cores introduced by the pre-straining can be facilitated, the precipitations of the secondary phases in the pre-strained samples become easier than those in the as-recrystallized samples without deformations. Thus we can consider that since the precipitation reactions of the secondary phases, indicated in the calculated phase diagram, are too sluggish to occur, a supersaturated solid solution is produced even in the temperature region where the secondary phases can exist in equilibrium state.

Although the secondary phases in the calculated phase diagram will precipitate by prolonged aging treatment, in the previous paper1 we have detected no precipitates during tensile testing in the temperature range between room temperature and 1123 K. Instead, wide dissociation of the dislocations, presumably resulted from the microsegregation of the solute atoms into the stacking faults bounded by the Shockley partials, was observed in the samples tensile-tested at temperatures around 973 K.1 It was considered in that paper1 that the Suzuki segregation takes place during tensile testing at elevated temperatures, resulting in the wide dissociation of gliding dislocations. We consider from the present study that it is in a supersaturated alloy that the wide dissociation caused by the Suzuki segregation occurs at elevated temperatures. Ac-
accordingly, we can point out that a degree of supersaturation of the solid solution plays an important role in the occurrence of the Suzuki segregation.

4.2 Dislocation locking and wide dissociation by Suzuki segregation

In this section, we discuss the dislocation locking effects by the solute atoms caused by the Suzuki segregation at elevated temperatures through considering the stress-relaxation behavior indicated in Fig. 2(b).

If the dislocations move by viscous motion, average velocity of dislocations, \( \bar{v} \), and strain rate, \( \dot{\varepsilon} \), are formulated as follows:

\[
\bar{v} = B(\sigma_{eq})^{n^*} \tag{1}
\]

\[
\dot{\varepsilon} = \phi \rho_m \bar{v} \tag{2}
\]
Where \( B \) and \( \Phi \) are constant, \( \sigma_{\text{eff}} \) the effective stress, \( m^* \) the effective stress exponent,\(^5\) \( \rho_m \) the mobile dislocation density.\(^7\) Flow stress, \( \sigma \), consists of the sum of the internal stress, \( \sigma_i \), and effective stress, \( \sigma_{\text{eff}}; i.e., \sigma = \sigma_i + \sigma_{\text{eff}} \). Results from stress relaxation experiment are generally interpreted by assuming that the total strain rate in the sample, \( \dot{\varepsilon} \) (the sum of the elastic, \( \dot{\varepsilon}_e \), and plastic, \( \dot{\varepsilon}_p \), strain rates), is zero, so that the plastic strain rate is proportional to the stress rate, in the sample. The relationship between the plastic strain rate and the stress rate is given by:

\[
\dot{\varepsilon}_p = \dot{\varepsilon}_e + \dot{\varepsilon}_p = 0
\]

\[
\dot{\varepsilon} = \frac{\dot{\varepsilon}_p}{\dot{E}_a} \quad (3)
\]

where \( \dot{\varepsilon}_p \) is the plastic strain rate of a sample, \( E_a \) the young modulus of the testing system including the sample. From eqs. (1) through (3), we obtain following relation:

\[
\dot{\varepsilon} = -E_a\phi \rho_m b B (\sigma - \sigma_i)^{m^*} \quad (4)
\]

In the present stress relaxation tests, as indicated in Fig. 2(b), it is revealed that the stress relaxation almost does not occur at room temperature. According to eq. (4), the stress relaxation rate is approximately zero suggests the two possible explanations: (I) the stress term in eq. (4), \( \sigma - \sigma_i \) is almost zero, \( i.e., \) lack of the effective stress, and (II) the mobile dislocation density, \( \rho_m \), is almost zero, because other factors, \( E, \phi, b \) and \( B \) are constant. However, since the dislocations are assumed to move by viscous motion in eq. (4), explanation (I) is in conflict with this assumption. In the previous study,\(^1\) it had been established in the Co–Ni based alloy that the high planarity of dislocation array induced at room temperature is associated with high friction forces acting on moving dislocations. Accordingly, it can be thought that the dislocations are strongly locked by solute atoms immediately after the beginning of the stress relaxation test. At room temperature, since dislocations do not dissociate as illustrated in Fig. 3(b), it can

be assumed that the origin of the locking force exerting dislocations comes from the elastic interaction between the solute atoms and the dislocation cores. Thus we can conclude that the resultant zero rate of stress relaxation at room temperature is due to the immobilization of the induced dislocations, \( i.e., \rho_m \approx 0 \), and simultaneously stress term, \( \sigma - \sigma_i \approx 0 \), in eq. (4).

The above consideration on dislocation motions at room temperature is applicable to the one at elevated temperatures to approximately 943 K, \( i.e., \) DSA temperature range, if we consider the Suzuki effect\(^2\) as a locking force of dissociated dislocations. As described in the previous sections, the solute atoms at elevated temperatures can be dynamically absorbed to the stacking faults bounded by the Shockley partials during tensile testing; referred to as “dynamic” Suzuki segregation. The dissociated dislocations, accompanied by the solute atoms in the stacking faults, glide jerkily on slip planes during tensile testing at elevated temperatures, led to the DSA. Thus in the temperature range where the DSA operates, \( i.e., \) 800 to 1000 K, just after the crosshead motion is stopped, the gliding dislocations become immobile because atmosphere of the solute atoms lock the dislocations, resulting in the stress relaxation rate being zero from the initial stage to passage of time, up to approximately 1000 seconds. After approximately 1000 seconds from the beginning of the stress relaxation experiments, since the solute atoms in the matrix migrate into the stacking faults of the dissociated dislocations, a leading dislocation can solely move, leaving behind the trailing one, because the segregated solute atoms in the stacking faults hinder the movement of the trailing dislocations. This results in widening the spacing between the Shockley partials, namely, width of the stacking fault bounded by the Shockley partials (see Fig. 6). Although it is difficult to quantitatively evaluate the amount of stress relaxation resulting from the movement of the individual partial dislocations, above-described sole glide motion of the leading dislocations can be responsible for one of the mechanisms of the stress relaxation actually observed at 873 and 943 K where the dislocations are significantly dissociated after the relaxation experiments have finished, as shown in Figs. 4(b) and (c).\(^5\)

At temperatures higher than 1023 K where the DSA diminishes, as shown in Fig. 2(b), the stress relaxations gradually occur from the beginning of the stress relaxation experiments. This indicates that the two partial dislocations of the dissociated dislocations are thought to simultaneously glide by viscous motion during stress relaxation experiments. In fact,
as can be seen in the dislocation arrangement illustrated in Figs. 4(d) and (e), the stacking fault fringes of the dislocations practically disappear, suggesting that dislocation dissociation originating from Suzuki segregation is eliminated at temperatures higher than 1023 K where the DSA does not operate. Accordingly we can find that dislocation locking effect by the Suzuki segregation fades away at temperatures higher than approximately 1023 K.

5. Conclusions

In order to investigate changes in motion and structure of the dislocations introduced into Co–Ni based alloy, the alloy SPRON 510, the stress relaxation behavior and observations of the dislocation structure have been examined in the temperature range between room temperature and 1073 K. Obtained results are as follows:

(1) According to X-ray analysis, the alloy SPRON510 is a single-phase with a FCC crystal structure. On the other hand, a calculated phase diagram suggests that the alloy has multiphase of γ, σ, η, μ and δ phases at room temperature. These observations suggest that the present Co–Ni based alloy is a supersaturated solid solution. It is assumed that a degree of supersaturation of the solid solution plays an important role in the occurrence of the Suzuki segregation at elevated temperatures.

(2) The resultant zero rate of stress relaxation at room temperature can be assumed to be due to the immobilization of the induced dislocations originating from an elastic interaction between dislocation cores and solute atoms. On the other hand, at elevated temperatures where the DSA operates, the zero rate of the stress relaxation at an initial stage comes from the Suzuki segregation.

(3) After approximately 1000 seconds from the beginning of the stress relaxation experiments at 873 and 943 K, the occurrence of the stress relaxation results from the sole movement of leading partial dislocations, leaving behind the trailing ones. As a result, since the spacing between the Shockley partials becomes extended, the wider stacking faults bounded by the two Shockley partials are formed in the DSA temperature range, especially at approximately 943 K.

(4) At temperatures higher than 1023 K where the DSA diminishes, the stress relaxations gradually occur from the beginning of the stress relaxation experiments. Dislocation locking effect by the Suzuki segregation fades away at temperatures higher than approximately 1023 K where the DSA does not operate.

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REFERENCES

8) It should be recognized that the movement of the dislocations without the solute segregation could be responsible for the stress relaxation in this temperature range. Thus in the present study we cannot quantitatively discuss the amount of stress relaxation based on the movement of the individual partial dislocations.