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Temperature Dependence of Activation Energy in Stage II Recovery in Deformed Aluminium

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The activation energy of recovery in 99.999% aluminium deformed at 4.2 K is investigated at temperatures between 50 to 180 K by means of the change of slope method. The activation energy varies from 0.15 to 0.60 eV with raising temperature. This behaviour is simulated by considering an overlapping of several first order processes within stage II. It is supposed that the variation of activation energy in stage II is due to recovery of vacancies and their small clusters by pipe diffusion mechanism.

Die Aktivierungsenergie der Erholung in 99,999% bei 4,2 K deformiertem Aluminium wird bei Temperaturen zwischen 50 bis 180 K mittels Anstiegswechselmethode untersucht. Die Aktivierungsenergie variiert von 0,15 bis 0,60 eV bei steigender Temperatur. Dieses Verhalten wird unter Berücksichtigung einer Überlappung verschiedener Prozesse erster Ordnung in der Stufe II simuliert. Es wird angenommen, daß die Variation der Aktivierungsenergie in Stufe II durch Ausheilung von Leerstellen und ihrer kleinen Cluster über einen Pipe-Diffusionsmechanismus verursacht wird.

1. Introduction

It is well known that point defects are produced in deformed metals together with dislocations. Several mechanisms have been proposed for the production of point defects: (a) non-conservative motion of jogs on moving screw dislocations, (b) mutual annihilation of dislocations with an edge component, (c) dislocations cutting through an attractive tree of a dislocation forest [1]. A problem, argued for years, is whether the point defects produced are vacancies or interstitials or both.

Recently, experimental techniques such as perturbed angular correlation (PAC) and Mössbauer spectroscopy, which can clearly discriminate between vacancies and interstitials, were applied to study point defects in deformed metals [2 to 6]. These works all indicated that no signal of interstitial-probe complexes were detected while several signals of vacancy-probe complexes were observed. From these experimental results, it appears that the majority of point defects produced in deformed metals are vacancies. Especially for the stage II recovery in cold-worked aluminium, Sassa et al. [6] analyzed the defect line of the Mössbauer spectrum and concluded that the defects annealed at a temperature as low as 100 K were vacancies.

In our previous paper [7], we have proposed that defects recovered at stage II were of vacancy type on the basis of the following reason: the suppressive effect of impurities on stage II recovery was ordered as $\text{Ge} > \text{Si} > \text{Cu} > \text{Ag} > \text{Mg}$, consistent with the order of magnitude of the interaction between vacancies and impurities, in reactions leading to the formation of dislocation loops in quenched dilute aluminium alloys [8].

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It is worthwhile to measure the activation energy to clarify the mechanism of stage II recovery. The activation energy of the recovery around 100 K was estimated to be 0.2 to 0.3 eV by Sassa et al., according to the analysis of the temperature dependence of the defect line intensity [6]. Frois [9] obtained activation energies of 0.22 and 0.32 eV for the recovery peaks at about 80 and 125 K, respectively. As pointed out by this author, however, it seems that the activation energy increases gradually with increasing temperature and annealing should not be assigned to simple processes. For the separation of processes, the activation energy has to be measured with a temperature interval as small as possible, as described in the next section. Also, only an apparent activation energy is obtained experimentally, when some recovery processes occur simultaneously. We have examined the activation energy change in the region of 50 to 85 K (transition period between stages I and II) in deformed pure aluminium and its dilute alloys [10]. It was reported that the recovery in this temperature range can be interpreted by an overlapping of two processes consisting of dislocation rearrangement (below 60 K) and the annihilation of vacancies due to diffusion along dislocations.

Up to date, it has not sufficiently been clarified how defects recover at any temperature in stage II. In this paper, we examine the recovery of electrical resistivity in deformed aluminium and will try to simulate the temperature dependence of the activation energy. Then, stage II recovery will be discussed from the point of view of an overlapping of some recovery processes of vacancy-type defects.

2. Experimental Procedure

Polycrystalline wires of pure aluminium with 99.999% in nominal purity were prepared for the electrical resistivity measurements. The specimens of 0.2 mm diameter were annealed at 773 K for 30 min in vacuum and then extended by about 10% at 4.2 K. The electrical resistivity measurements were executed after the release of the stress. The detailed description of the electrical resistivity measurement technique has been presented in our previous paper [7].

After the deformation, isothermal annealings were carried out at intervals of about 10 K between 40 and 160 K. At every temperature, the time of annealing is fixed to 360 s and the electrical resistivity was measured every 120 s at 4.2 K. By the use of a series of isothermal annealings, activation energies were obtained by the change of slope method. The experimental data of each isothermal annealing are fitted to simple exponential decay curves by means of the least square method and slopes at the beginning and the end of each fitted curve are used for the calculation of the activation energy.

As was noted in a previous paper [7], an isochronal annealing at every 5 K was performed, while Takamura and Okuda [11] and Swanson [12] adopted every 10 and 15 K, respectively. The former annealing at every 5 K was suitable for the study of stage II_A recovery (between 60 and 100 K), because of the large recovery rate. In the case of a small recovery rate in stage II_B (between 100 and 160 K), the latter annealing at 10 or 15 K intervals will be successful, on account of the demand for an accurate calculation of slopes at the beginning and the end of each isothermal annealing. If we liked to investigate the recovery stage II (between 60 and 160 K) all over, then the latter annealing was adopted.

3. Results

A typical series of isothermal annealings of the electrical resistivity is given as a function of temperature in Fig. 1, where $\Delta\rho$ and $\Delta\rho_0$ are the residual resistivity increment and the total residual resistivity increment just after the deformation, respectively.

Fig. 1. Isothermal annealing curves of 5N Al at temperatures between 40 and 180 K

The isochronal annealing curve together with the differential isochronal annealing curve are also given as shown in Fig. 2. As is shown by the differential isochronal curve in Fig. 2, two substages (a large recovery at around 85 K (stage II_A) and a rather wide and small recovery stage from 100 to 160 K (stage II_B)) are obtained obviously. But subpeaks in stage II_A appearing at 75 and 90 K, which are newly found in our previous work [7] and investigated in detail by Ohtaki [13], are not observed. This comes from the difference in annealing treatment, 6 min pulse every 10 K, as mentioned in the preceding section. Though it is clear that every 10 K is not close enough to analyze stage II_B, the temperature interval of the annealing is chosen as mentioned above, in an effort to make accurate measurements of activation energies throughout stage II, especially the small recovery stage II_B.

The temperature dependence of the activation energy is shown in Fig. 3 where temperatures are determined as an average temperature of two subsequent isothermal annealings. The activation energy proves to vary gradually with temperature all over

Fig. 2. Isochronal annealing curve obtained from data in Fig. 1 (○) and its differential curve (●)

Fig. 3. Temperature dependence of activation energy between 40 and 180 K (present work: ○). Also shown are Frois's data (●)

stage II. This is consistent with Frois's results [9], which are also shown in Fig. 3, making an exception for a few data points in the temperature region of 150 to 180 K. It is considered that in this region the temperature was not sufficiently stabilized to determine the activation energy accurately in the present work. Excluding this region, the temperature dependence of the activation energy for the recovery of 15% deformed specimens shows no evident difference in comparison with 10% cold-worked specimen. At present, it will be considered that the amount of extension has no apparent effect on the activation energy in stage II. As has been shown before, the activation energy certainly increases with increasing temperature.

4. Analysis

As suggested in Section I, the recovery stage II occurs as an overlapping of several recovery processes. In these processes, we assume that N defect species are recovered. In such a case, the electrical resistivity increase contributing to stage II, $\Delta\rho_{II}$, which is caused by the production of defects during low-temperature deformation, will be described by

$$\Delta\rho_{II} = \sum_{n=1}^N \Delta\rho_{II,n} \quad (1)$$

with a summation of $\Delta\rho_{II,n}$ due to the recovery of a species n among N species. Since the mechanism of the recovery is not clear at present, we assume for simplicity that it obeys a first-order process, that is,

$$\Delta\rho_{II,n}(t) = \Delta\rho_{II,n}(0) \exp(-A_n t), \quad (2)$$

where $\Delta\rho_{II,n}(0)$ represents the initial electrical resistivity contribution of defects of the species n . The rate constant is given by

$$A_n = B_n \exp(-E_n/kT), \quad (3)$$

where E_n is the migration energy of the species n , and B_n is the constant given as the product of geometrical factor g_n , jump-attempt frequency ν_n , and sink concentration C_s . Combining (1) to (3), $\Delta\rho_{II}$ in recovery at temperature T for time t can be written as

$$\Delta\rho_{II}(T, t) = \sum_{n=1}^N \Delta\rho_{II,n}(0) \exp[-B_n \exp(-E_n/kT) t] \quad (4)$$

The annealing temperature T and time t can be chosen according to the experimental heat treatment. On the contrary, other parameters appearing in (4), $\Delta\rho_{II,n}(0)$,

Table 1

List of parameters used for the simulation of isothermal annealing curves

n	E_n (eV)	B_n (s ⁻¹)	$\Delta\rho_{II,n}(0)/\Delta\rho_0$ (%)
1	0.16	5.9×10^8	6.35
2	0.18	2.6×10^8	6.23
3	0.22	1.7×10^9	4.66
4	0.30	3.8×10^{10}	1.48
5	0.34	2.9×10^{13}	2.16
6	0.37	6.5×10^{12}	1.69
7	0.41	7.4×10^{11}	1.83
8	0.42	2.4×10^{13}	1.39

B_n and E_n are not available at present. So we take B_n and E_n as adjustable parameters, and try to simulate the series of isothermal annealing curves at temperatures between 60 to 150 K in Fig. 1. From the simulated curves, we can calculate activation energies by means of the change of slope method, which can be compared with the experimental results in Fig. 3 directly. Also here the number N of species is not known, so we carried out simulations for different N and compared calculated activation energies with experimental ones and estimated the required number of N .

Estimated parameters are given in Table 1, where $\Delta\rho_{II,n}(0)$ are calculated with parameters E_n and B_n so as to minimize the difference between experimental data and calculated ones and the quantity $\Delta\rho_0$ is the total residual resistivity increase due to the deformation. The species are characterized by these three parameters. The activation energy calculated with these parameters is shown in Fig. 4 together with experimental results. They show very good mutual agreement between about 80 and 140 K. Here we used $N = 8$, which is the number of defect species contributing to stage II. It is difficult to reproduce the temperature dependence of activation energy with $N < 8$. So eight species of defects are considered as a minimum for the simulation of isothermal curves in this temperature range. The origin is discussed in the following.

It is found from Table 1 that the recovery processes are divided into two different groups by values of parameters E_n and B_n . Group 1 ($n = 1$ to 3) have a relatively low activation energy E_n and low-rate constant B_n compared to those of group 2 ($n = 4$ to 8). At first we discuss the parameters E_n of the species in group 1, recovered at stage II_B (between 60 and 100 K).

Fig. 4. Calculated values of the activation energy (●) between 70 and 140 K using parameters given in Table 1. Experimental data are also shown for comparison (○)

As discussed in our previous papers [7, 10], stage II_A is caused by the annihilation of vacancies due to enhanced diffusion along dislocation and the activation energy associated with the main recovery peak around 85 K is 0.21 eV. But three parameters (see Table 1) obtained here for species $n = 1$ to 3 give an impression that not only single vacancies but also small vacancy clusters such as di- and trivacancies contribute to stage II_A recovery. Collins [3] performed a PAC study of heavily deformed Au at 77 K and resolved the recovery stage III into three different processes due to tri-, di-, and single vacancies. He found that in stage III of deformed Au trivacancies recovered at the lowest temperature, then divacancies and finally single vacancies were annealed out in stage III. So he concluded that tri- and divacancies were created during deformation without a reaction of single vacancies. Müller [4] also pointed out that long-range migration of divacancies occurred around 200 K in Al elongated by 5 to 20% at 77 K. Moreover, it is well known that the activation energy of stage III in deformed Al is 0.57 eV [1], which is different from a migration energy of 0.65 eV for single vacancies in quenched Al [14]. From the experimental results stated before and considering the production mechanisms of point defects by low-temperature deformation (b) and (c) mentioned in Section 1, it is likely that small clusters of vacancies, which have smaller migration energies, are created simultaneously with deformation. So the species in group 1, which mainly recover at about 85 K, will be assigned to vacancies and their small clusters. We suppose that tri-, di-, and single vacancies move by diffusion along dislocations [7] with activation energies of about 0.16, 0.18, and 0.22 eV (Table 1), respectively, and are finally annihilated at jogs.

Recovery of defects in group 2 is considered to correspond to the recovery stage II_B (between 100 and 160 K). As is mentioned in our previous paper [7], the recovery in this temperature region is strongly affected by impurities. Though the differential isochronal recovery curve of 5N Al is almost flat throughout the stage II_B except for a small peak at about 140 K, the addition of each impurity up to an amount of about 60 ppm produces small peaks at subsequent temperatures. So the recovery in this substage is thought to be related to vacancy-impurity complexes. As shown in Table 1, they have activation energies of 0.3 to 0.42 eV, which are smaller than the migration energies of 0.47 to 0.65 eV for vacancy-type defects in the lattice [14]. So the recovery may occur by enhanced diffusion along dislocations, in the same way as in stage II_A. The difference between the activation energy of stage II_A (group 1) and that of stage II_B (group 2) can be explained by binding energies between vacancies and impurities. The binding energy between single vacancies and impurities in the lattice is smaller than 0.1 eV [15], while that for small clusters is not known. When the vacancies are trapped at impurities, a summation of migration energy and binding energy between them is required for detrapping and annihilation of the vacancies. As is mentioned before, migration energies of tri-, di-, and single vacancies are estimated to be 0.16, 0.18, and 0.22 eV, respectively. Assuming that binding energies between impurities and tri-, di-, or single vacancies in the dislocation pipe are about 0.1 eV, i.e. the same as in the lattice, the activation energy is estimated to be 0.26 to 0.32 eV. Another possibility of distributing the activation energy is the emission of vacancies from the small clusters and their annihilation at sinks. The formation of small vacancy clusters during deformation are likely as mentioned before. In the lattice, binding energies of vacancies with their small clusters are estimated to be 0.22 to 0.25 eV [9], and the activation energy for the annihilation of single vacancies detrapping from small clusters containing 4 to 10 vacancies is estimated to be 0.44 to 0.47 eV. Thus, if we assume pipe diffusion of vacancies detrapped from vacancy-impurity complexes and from small vacancy clusters, activation energies for stage II_B recovery may be distributed between 0.26 and 0.47 eV. Here we use binding energies

of vacancy-impurity complexes and of vacancy clusters in the lattice, but they may have almost the same values as those in the dislocation pipe. So the estimated value of E_n in Table 1, 0.3 to 0.42 eV, may be reasonable for the mechanisms mentioned above.

Another point of discussion is the parameter B_n given in Table 1. The values B_n of the species in group 1 are of the order of 10^8 to 10^9 s⁻¹, while those in group 2 are 10^{11} to 10^{13} s⁻¹. These values are understandable within the scope of the above-presented discussion. Parameter B_n consists of frequency factor ν_n , geometrical factor g_n , and sink concentration C_s . The values of ν_n and g_n are estimated to be of the order of 10^{12} s⁻¹ and 10, respectively. These values for groups 1 and 2 will not be different from each other, only the values of C_s can change. The recovery of defects in group 1, corresponding stage II_A, may be controlled by their diffusion processes. Then the value of C_s estimated from B_n in Table 1 with the value of ν_n and g_n shown above is of the order of 10^{-5} to 10^{-4} . This is coincident with the jog concentration on dislocations in metals deformed by about 10% [16]. On the other hand, by the same estimation as above, C_s has a value of the order of 10^{-1} to 1 for the species in group 2. Assuming pipe diffusion of vacancies for stage II_B recovery, it will be natural that it has the same sink concentration as stage II_A. But the estimated value is different by an order of three to five. This is understood from the fact that the recovery processes of species in group 2 are controlled by the emission process of vacancies from vacancy-impurity complexes or small vacancy clusters. Then the emitted vacancies diffuse quickly along dislocations and are annihilated at jogs, so that vacancies can reach sinks with only one jump process.

The last problem is the contribution of each species to the electrical resistivity change $\Delta\rho_{II,n}(0)$. The change is expressed by the product of concentration C_n of species n and electrical resistivity change due to the annihilation of 1 at% of that species. From the value of $\Delta\rho_{II,n}(0)/\Delta\rho_0$ in Table 1 and the experimental value of $\Delta\rho_0 = 5.15 \times 10^{-9}$ Ω cm, the order of C_n can be estimated. Electrical resistivities of di- and trivacancies are different from that of two and three isolated vacancies. But it is sufficient for checking the order of C_n to use the value of electrical resistivity of single vacancies of 1 at%, i.e. 3×10^{-6} Ω cm [1]. The value of C_n are estimated to be about 1×10^{-6} for group 1 and about 2×10^{-7} for group 2. The total of them, about 5×10^{-6} , and the value for group 1 is reasonable for metals cold-worked by about 10% [1]. If impurity trapping of vacancies is assumed for group 2 species, the order of the concentration of impurity-vacancy complexes is surprising in the 5N aluminium specimen. General considerations indeed lead to the conclusion that the concentration of complexes is expressed as the product of that of vacancies and impurities, and estimated to be of the order of 10^{-11} . But Collins [2, 3] and Müller [4] have suggested that 20 to 50% of probe ¹¹¹In atoms in their PAC study captured vacancies. This enhancement of trapping of vacancies is not made clear at present, but it may be necessary to consider the peculiarity of recovery in deformed metals such as an inhomogeneous distribution of impurities according to impurity-dislocation interactions and/or the peculiarity of one-dimensional diffusion of vacancies along dislocations. It is not sufficient, however, to explain the amount of group 2 only by enhanced trapping of vacancies with impurities, so it is required to assume the existence of small vacancy clusters created during deformation.

5. Conclusions

(1) The measured activation energies of stage II recovery in deformed Al varies from 0.15 to 0.50 eV with rising temperature, and it has been explained by the overlapping of eight first-order processes.

(2) According to the simulation, stage II_A is considered to be due to the annihilation of single, di-, and trivacancies along dislocation pipes associated with activation energies of 0.22, 0.18, and 0.16 eV, respectively.

(3) Stage II_B consists of five processes whose activation energies are between 0.3 and 0.42 eV. Each species of defects could not been assigned to these recovery processes one by one, but they are considered to be due to detrapping of vacancies from both vacancy-impurity complexes and small vacancy clusters and successive vacancy annihilation at sinks.

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