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Migration mechanism of self-interstitial atoms in Mo after low temperature irradiation
I. Relaxation peak

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Abstract

The relaxation peak due to ⟨110⟩ self-interstitial atoms (SIAs) in Mo after 20 MeV proton irradiation at 5 K was investigated in single-crystal specimens with various crystallographic orientations for Frenkel pair concentrations C_{FP} from 0.1 to 53 ppm using the vibrating reed technique at about 500 Hz. The relaxation peak is observed at around 41 K. For the peak height of the 41 K peak, Q_p^{-1}, observed in specimens with the same crystallographic orientation, $\ln(Q_p^{-1}/C_{FP})$ shows a linear increase with decreasing $\ln(C_{FP})$ over the whole C_{FP} range, while among different orientations good parallelism is found. The features of the 41 K peak other than Q_p^{-1}/C_{FP} remain unchanged. These facts suggest that the increase in Q_p^{-1}/C_{FP} reflects an increase in the fractional ratio F_I of SIAs responsible for the 41 K peak (SIA-Is hereafter), where F_I is found to decrease in proportion to $(C_{FP})^{1/3}$. All the observed results suggest that SIAs other than SIA-Is are not a result of SIA-Is interacting with each other but are SIAs of a different type (SIA-IIs hereafter). We surmise that both SIA-Is and SIA-IIs are formed during irradiation but that SIA-IIs cannot undergo three-dimensional migration.

1. Introduction

With regard to self-interstitial atoms (SIAs) in Mo introduced by low temperature irradiation, the model of the ⟨110⟩-split dumb-bell structure is widely accepted from anelastic [1, 2] and Huang-scattering [3] measurements as well as from molecular dynamical calculations [4]. A free-migration temperature of about 35 K is commonly reported from electrical resistivity [5], Mössbauer [6] and recent dislocation-pinning [7, 8] measurements. However, the migration mechanism and low temperature behaviour of SIAs in Mo still remain open questions. Figure 1 shows the low temperature internal friction Q^{-1} reported for Mo after various irradiations at 5 K [1, 7, 8], where a Q^{-1} peak at around 41 K and one at around 13 K can be seen (the 41 and 13 K peaks hereafter). Both the 41 and 13 K peaks are relaxation peaks due to the rotational motion of ⟨110⟩ defects. Recent 2 MeV electron [7] and 20 MeV proton [8] irradiations suggest that the 41 K peak is associated with SIAs and the 13 K peak with probable di-SIAs formed near cascade damage [7, 8]. After refs. 7 and 8 we revised the view reported in refs. 1 and 2 where the 41 K and 13 K peaks had been assumed to be related to di-SIAs and SIAs respectively. However, as reported by Jacques and Robrock from the anelastic relaxation peaks [9] or in refs.7 and 8, the peak height of the 41 K peak per 1

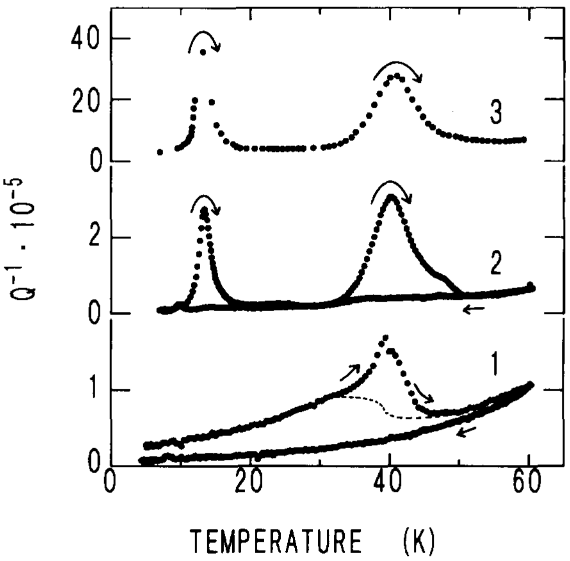

Fig. 1. Internal friction Q^{-1} of Mo after various irradiations at 5 K measured by means of the vibrating reed technique at about 500 Hz: curve 1, 2 MeV electron irradiation, $C_{FP}=0.5$ ppm [7]; curve 2, 20 MeV proton irradiation, $C_{FP}=21$ ppm [8]; curve 3, fast neutron irradiation, $C_{FP}=70$ ppm [1]. The crystallographic direction along the long axis of reed specimens is ⟨110⟩ for curves 1 and 2 and ⟨100⟩ for curve 3. The dashed curve depicted for curve 1 is the change in Q^{-1} due to dislocation pinning.

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ppm Frenkel pairs, $Q_p{}^{-1}/C_{FP}$, appears to be too low to be explained by the strain field tensor $\boldsymbol{\lambda}$ around an SIA reported from Huang scattering [3]. That is, when ⟨110⟩ SIAs can rotate during migration (three-dimensional migration hereafter), the relaxation peak due to the rotational motion can be expected to be much higher than the 41 K peak observed. To explain this fact, Jacques and Robrock proposed a migration model without rotation, *i.e.* two-dimensional migration of ⟨110⟩ SIAs [9, 10]. However, our recent work suggested that $Q_p{}^{-1}/C_{FP}$ tends to increase with decreasing C_{FP} [7, 8]: in Fig. 1, $Q_p{}^{-1}/C_{FP}$ of curve 1 is about 10 times larger than that of curve 2, suggesting a strong increase with decreasing C_{FP}. To pursue this issue, in the present study we perform further careful measurements of the 41 K peak over a wide C_{FP} range from 0.1 to 53 ppm and discuss the migration mechanism of SIAs in Mo.

2. Experimental procedures

Mo single-crystal rods purchased from the Material Research Corporation were cut into reed specimens of dimensions 0.15×3×15 mm^3, with a thick end of dimensions 0.5×3×5 mm^3 for clamping. The shaped specimens were annealed at 2273 K in a vacuum of 10^{-7} Pa for 1 h. The nominal residual resistivity ratio (RRR) is about 4100 after annealing. The crystallographic direction of these specimens is ⟨100⟩ or ⟨110⟩ along the long axis of the reeds (⟨100⟩ and ⟨111⟩ specimens hereafter). We also prepared ⟨100⟩ and ⟨111⟩ specimens from high purity Mo single-crystal rods received from Professor A. Seeger. Some of the as-annealed specimens were deformed at room temperature before irradiation in order to observe the dislocation pinning more clearly (see Part II and ref. 8 for Q^{-1} in the as-deformed state). The low temperature irradiations were performed at 5 K using 20 MeV protons from the Tandem Accelerator at the University of Tsukuba. Using the flexural resonant vibration of the reed specimens at about 500 Hz, the vibration frequency f and Q^{-1} were measured. The apparatus and measurement procedures were similar to those described in ref. 8. After each irradiation at 5 K, f and Q^{-1} were measured during heating at 2 K min^{-1} to minimize the recovery of the 41 K peak during measurements. The heating was continued up to 60 K to anneal out the low temperature defects introduced by irradiation.

3. Results and discussion

To observe the 41 K peak at low dose or C_{FP}, we used the as-annealed specimens in which saturation of the dislocation pinning can be expected at a very low dose. The C_{FP} dependence of the 41 K peak was investigated by successive irradiations with increasing dose. Separately, the effect of dislocations on the 41 K peak was investigated using the deformed specimens. Figure 2 shows the C_{FP} dependence of $Q_p{}^{-1}/C_{FP}$ for the 41 K peak observed in ⟨100⟩, ⟨110⟩ and ⟨111⟩ specimens. For the as-annealed specimens the following features are found. In each crystallographic direction $Q_p{}^{-1}/C_{FP}$ increases linearly with decreasing C_{FP}. Among different crystallographic directions good parallelism can be seen over the whole C_{FP} range, suggesting that the anisotropy in the strain field tensor $\boldsymbol{\lambda}$ of SIAs responsible from the 41 K peak remains unchanged (these SIAs will be referred to as SIA-Is below). $Q_p{}^{-1}/C_{FP}$ increases in the order of ⟨111⟩, ⟨110⟩ and ⟨100⟩ specimens when it is compared at the same C_{FP}, suggesting ⟨110⟩ symmetry of the defects responsible for the 41 K peak. Although not shown here, both the peak profile of the 41 K peak, which can be described as a slightly broadened Debye peak, and the peak temperature of the 41 K peak remain almost unchanged over the whole C_{FP} range, suggesting that the increase in $Q_p{}^{-1}/C_{FP}$ with decreasing C_{FP} can be related to an increase in the fractional ratio of SIA-Is in C_{FP}. In fact, dislocation-pinning measurements given in Part II also suggest an increase in the fractional ratio of SIA-Is with decreasing C_{FP}, where extrapolation shows that the fractional ratio of SIA-Is reaches 100% at $C_{FP} = 0.001$ ppm (see Fig. 3 in Part II).

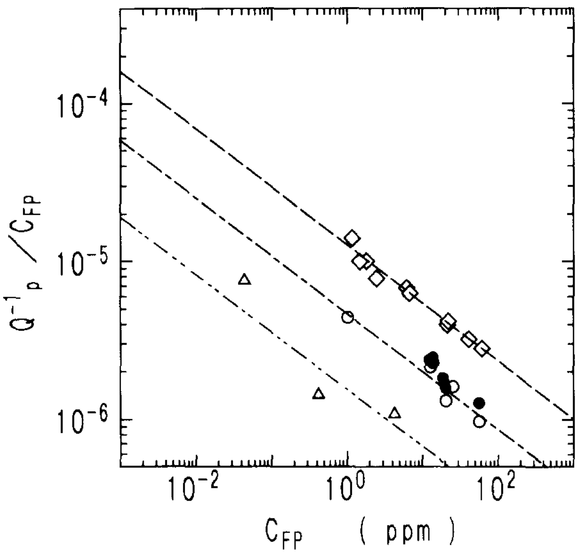

Fig. 2. C_{FP} dependence of the peak height of the 41 K peak per 1 ppm Frenkel pairs, $Q_p{}^{-1}/C_{FP}$, observed for Mo after various irradiations at 5 K: ◇, ○ and △, as-annealed ⟨100⟩, ⟨110⟩ and ⟨111⟩ specimens respectively; ●, deformed ⟨110⟩ specimens after 20 MeV proton irradiation. Dashed lines are fitted to the data observed for as-annealed ⟨100⟩, ⟨110⟩ and ⟨111⟩ specimens (see text).

In Fig. 2, Q_p^{-1}/C_{FP} in the ⟨100⟩ specimens expected at $C_{FP} = 0.001$ ppm is comparable with that expected from $\boldsymbol{\lambda}$ reported from Huang-scattering measurements [3]. However, the detailed features of $\boldsymbol{\lambda}$ calculated from the present data are considerably different from those reported from Huang scattering, as seen in Table 1. For the stress-induced ordering of ⟨110⟩ SIAs through their rotational motion, the relaxation strength $\Delta E_{\langle hkl\rangle}$ in an ⟨*hkl*⟩ reed specimen [11] can be given by

$$\Delta E_{\langle hkl\rangle} = \frac{C_0 \Omega E_{\langle hkl\rangle}}{9kT} \Psi_{\langle hkl\rangle}^2 \qquad (1)$$

where C_0 is the concentration of ⟨110⟩ SIAs which can contribute to the relaxation, Ω is the atomic volume, $E_{\langle hkl\rangle}$ is the Young modulus along the ⟨*hkl*⟩ direction, k is the Boltzmann constant and T is the temperature at which the relaxation shows a maximum. $\Psi_{\langle hkl\rangle}$ is the shape parameter measuring the anisotropy in $\boldsymbol{\lambda}$, *e.g.* $\Psi_{\langle 100\rangle}^2 = [(\lambda_1 + \lambda_2)/2 - \lambda_3]^2$ and $\Psi_{\langle 111\rangle}^2 = (\lambda_1 - \lambda_2)^2$, where λ_i are the principal values of $\boldsymbol{\lambda}$. We calculated λ_i from the data shown in Fig. 2 assuming that all the SIAs introduced at $C_{FP} = 0.001$ ppm are SIA-Is and $\mathrm{tr}\boldsymbol{\lambda} = 1.1$ atomic volumes as reported in ref. 3. The results listed in Table 1 suggest that the λ_i values reported in ref. 3 represent SIAs other than SIA-Is (these SIAs will be referred to as SIA-IIs below), because the C_{FP} dependence of Q_p^{-1}/C_{FP} shown in Fig. 2 predicts a negligible fractional concentration of SIA-Is at the concentration $C_{FP} = 300$ ppm used in ref. 3.

Figure 3 is a redrawing of the data shown in Fig. 2, but here the fractional concentrations of SIA-Is, F_I, are plotted assuming $F_I = 100\%$ for C_{FP} below 0.001 ppm. For $C_{FP} \geqslant 0.001$ ppm, F_I decreases in proportion to $(C_{FP})^{1/3}$, *i.e.* with the mean spacing between SIAs. On the other hand, the results for the decrease in the Young modulus due to the pile-up of irradiation defects [8] suggest a linear increase in C_{FP} with increasing dose in the present C_{FP} range. Combining these results, one can say that the decrease in F_I is compensated by an increase in the fractional ratio of SIA-IIs, F_{II}, and $\mathrm{tr}\boldsymbol{\lambda}$ is comparable between SIA-Is and SIA-IIs. In elastic after-effect measurements, where the 26 K elastic after-effect corresponding to the 41 K peak can be observed below the migration temperature of SIA-Is, a monotonic decrease in the 26 K elastic after-effect during annealing at higher temperature is reported [2]. We also observed that the 41 K peak always shows a monotonic decrease during measurements over the whole C_{FP} range [7, 8]. These facts belie the view that SIA-IIs are SIA-Is whose rotational motion is hindered by some interaction between SIA-Is. That is, one can again say that there exist SIAs of two different types and they are both formed during irradiation. As will be reported in Part II, SIA-IIs cannot undergo three-dimensional migration.

TABLE 1. Principal values of the strain field tensor $\boldsymbol{\lambda}$ around SIAs estimated from extrapolation of Q_p^{-1}/C_{FP} to 0.001 ppm in Fig. 2 and those reported from Huang-scattering measurement at around 300 ppm [3]. In the calculation, $\mathrm{tr}\boldsymbol{\lambda} = 1.1$ atomic volumes [3] is assumed

Principal value	Q_p^{-1} (present study)	Huang scattering [3]
λ_1 (at.vol.)	0.5	0.7
λ_2 (at.vol.)	0.4	−0.4
λ_3 (at.vol.)	0.2	0.8

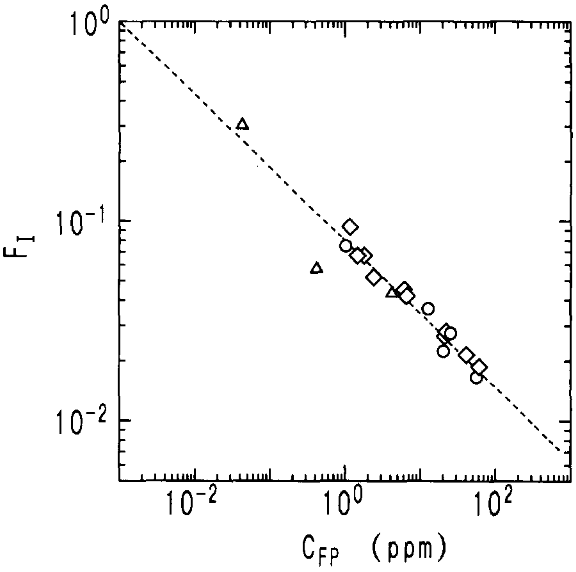

Fig. 3. Redrawing of Fig. 2, but here plotted as the fractional ratio of SIA-Is, F_I, in C_{FP}, deduced from the data in Fig. 2 assuming that the anisotropy of the elastic dipole for SIA-Is remains unchanged over the whole C_{FP} range and $F_I = 100\%$ for $C_{FP} = 0.001$ ppm: ◇, ○ and △, ⟨100⟩, ⟨110⟩ and ⟨111⟩ specimens respectively. The dashed line is fitted to the observed data (see text).

In Fig. 2 one can see that Q_p^{-1}/C_{FP} for the 41 K peak found in the deformed specimens is about 10% larger than that observed in the as-annealed specimens, indicating an increase in SIA-Is in the deformed specimens. We surmise that this fact suggests that local distortion of the host lattice can assist the formation of SIA-Is during irradiation. However, a simple model for defect production during irradiation cannot explain the fact that F_I decreases in proportion to $(C_{FP})^{1/3}$.

4. Conclusions

The 41 K Q^{-1} peak due to ⟨110⟩ SIAs in Mo after 20 MeV proton irradiation at 5 K was investigated in single-crystal specimens with various crystallographic orientations for Frenkel pair concentrations C_{FP} from

0.1 to 53 ppm by means of the vibrating reed technique at about 500 Hz. For the peak height of the 41 K peak, $Q_p{}^{-1}$, found in specimens with the same crystallographic orientation, $\ln(Q_p{}^{-1}/C_{FP})$ shows a linear increase with decreasing $\ln(C_{FP})$ over the whole C_{FP} range, while among different orientations good parallelism is found. The features of the 41 K peak other than $Q_p{}^{-1}/C_{FP}$ remain unchanged. These facts suggest that the increase in $Q_p{}^{-1}/C_{FP}$ reflects an increase in the fractional ratio F_I of SIAs responsible for the 41 K peak (SIA-Is), in C_{FP}, where F_I is found to decrease in proportion to $(C_{FP})^{1/3}$ or shows a saturation at 100% for $C_{FP} \leqslant 0.001$ ppm. All the observed results suggest that SIAs other than SIA-Is are not a result of SIA-Is interacting with each other but are SIAs of a different type (SIA-IIs) which cannot undergo three-dimensional migration. We surmise that both SIA-Is and SIA-IIs are formed during irradiation.

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