

Thermally activated recovery of polycrystalline cadmium deformed by anisotropic thermal expansion

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Abstract

The recovery of polycrystalline cadmium plates, after being deformed by internal stresses due to anisotropic thermal expansion during cooling, has been investigated by measuring the increase in the vibration frequency of the plate with time and varying the temperature as a parameter. The recovery of frequency with time was shown to follow an exponential law with a characteristic time of the order of few hours, thus reaching a limiting frequency after sufficiently long time. This limiting frequency is found to increase with the increase in the annealing temperature. The activation enthalpy controlling the recovery process is about 0.12 eV. The recovery is explained in terms of elimination of dislocations kinks produced during the deformation.

1. Introduction

In hexagonal polycrystalline metals having high anisotropic thermal expansion and low mechanical strength, such as cadmium and zinc, the density of geometrical imperfections, particularly dislocations, is found to increase when the temperature of the metal is changed by about 1 K [1, 2]. Such an effect was almost hidden in hexagonal polycrystals having low thermal anisotropy and high mechanical strength, such as cobalt [2]. It was attributed to microplastic deformation taking place as a result of internal stresses produced between randomly oriented grains which expand or contract anisotropically when the metal is heated or cooled. The increase in the geometrical imperfections content showed itself as a sharp drop in the resonant frequency of a plate vibrating in one of its lowest flexural vibration modes. The frequency drop is accompanied by an enormous increase in the mechanical dissipation factor Q^{-1} .

It has been shown that the observed effect is not permanent; after a cyclic run, from room temperature to liquid air temperature and back to room temperature again, the vibration frequency resumes its original value. However, the recovery of the metal is not instantaneous but takes place over a period of time extending to several hours as has been thoroughly observed after the end of the cyclic run.

The purpose of the present work is to investigate the recovery process at different annealing temperatures and to find the type of imperfection being eliminated during recovery.

2. Experimental details

The specimens of polycrystalline cadmium were supplied by Johnson Matthey Chemicals in the form of square plates 26 mm on a side and 2 mm thick. The atomic purity is 99.999% with the following major impurities being detected (in atomic parts per million): Mg, 4; Ca, 2; Fe, 2; Cu, 1. The experimental technique used to vibrate the plates and to detect their vibrational frequencies has been fully described elsewhere [1, 3]. Each experimental run proceeds in the following steps:

(a) The cadmium plate is cooled from room temperature to about 210 K at an average cooling rate of about 1 K min⁻¹. At 210 K the cooling is stopped and heating takes place.

(b) Heating is continued to the temperature at which annealing will take place. It should be noted that as long as the temperature is varying, either on cooling or on heating, the frequency variation is assumed to be just temperature dependent but time independent. Hence, the measurements of frequency recovery with time ($f-t$ measurements) are started when the variation in temperature is negligibly small.

(c) The temperature of the specimen is kept constant by keeping it in a high vacuum cryostat at a pressure of 10⁻⁴ Pa. Thermal equilibrium is reached by balancing

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heat from an electrical furnace with liquid air in the cryostat. During the major part of the run, the maximum uncontrolled temperature fluctuations do not exceed 1 K, and the fluctuation rate does not exceed 0.2 K h⁻¹.

(d) The f - t measurements are carried out until the f - t variation appears to be fairly constant, and thus each run extends over 5 h. At the end of the run the specimen is brought back to room temperature where it is left under low pressure for more than 12 h. At the beginning of the next run it is checked that the specimen has resumed its original room temperature frequency.

3. Results

The symbols of Fig. 1 show the f - t experimental measurements at four annealing temperatures between 230 and 260 K. The gaps in the experimental results represent periods where the temperature fluctuations are large enough to affect the accuracy of the measurements. The recovery of the metal shows itself as an increase in the resonant frequency, a process opposite to that which occurred during deformation by cooling the plate. The frequency increases with time in an exponential manner following a law of the form

$$f(t) = f(\infty) - \Delta f \exp(-t/\tau) \quad (1)$$

where $f(\infty)$ is the limiting value of the frequency reached after sufficiently long time, τ is a characteristic time characterizing the temperature at which annealing takes place and Δf is a pre-exponential factor. By changing τ in infinitesimal steps, a least-squares regression fitting can be iterated, for each curve of Fig. 1, between the variables $f(t)$ and $\exp(-t/\tau)$. The value of τ which gives the highest correlation coefficient $|r|$ is taken as the characteristic time at the annealing temperature under consideration. The full curves of Fig. 1 represent the mathematical fittings. Apart from the small deviations, the calculated fittings appear to be satisfactorily good. Table 1 shows the limiting frequency values $f(\infty)$, the characteristic time constants τ , and the correlation coefficients $|r|$ at the four annealing temperatures. Figure 2 shows a plot of eqn. (1) together with experimental data. A few facts are worth considering.

(a) All runs for f - t measurements start from a saturated state of imperfections introduced by internal stresses during cooling. This state was found to be reached near 210 K for cadmium [2], the same temperature at which cooling is stopped and heating is started in each run.

(b) Carrying out f - t measurements at temperatures higher than 260 K is very difficult since most recovery takes place before this temperature is reached.

(c) The limiting value of the frequency, which represents the final state of the metal annealed at a certain temperature, appears to increase linearly with the annealing temperature as can be seen from Fig. 3. This means that the higher the annealing temperature the

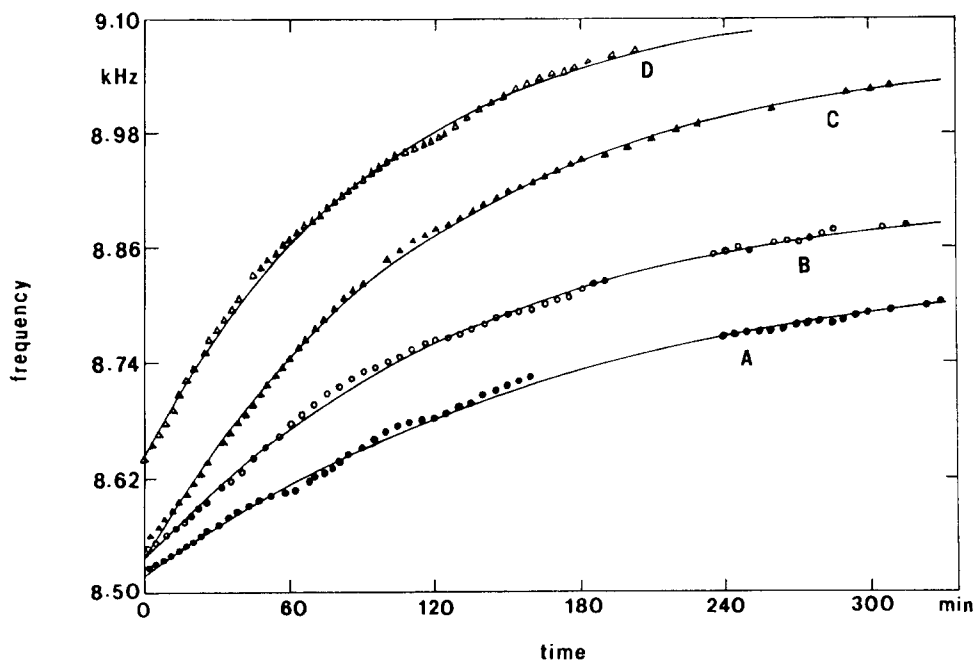


Fig. 1. Resonant frequency-time recovery measurements in cadmium plate at different annealing temperatures: points A, $T=232.6$ K; points B, $T=243.3$ K; points C, $T=251.5$ K; points D, $T=258.4$ K; —, mathematical fitting.

TABLE 1. Values of the annealing temperatures T , characteristic times τ of recovery, limiting frequencies $f(\infty)$ and the correlation coefficients $|r|$

T (K)	τ (min)	$f(\infty)$ (kHz)	$ r $	$1000/T$ (K^{-1})	$\ln \tau$
232.6	176.2	8.854	0.9989	4.30	5.17
243.3	136.0	8.922	0.9990	4.11	4.91
251.5	117.5	9.066	0.9993	3.98	4.77
258.4	97.2	9.124	0.9992	3.87	4.57

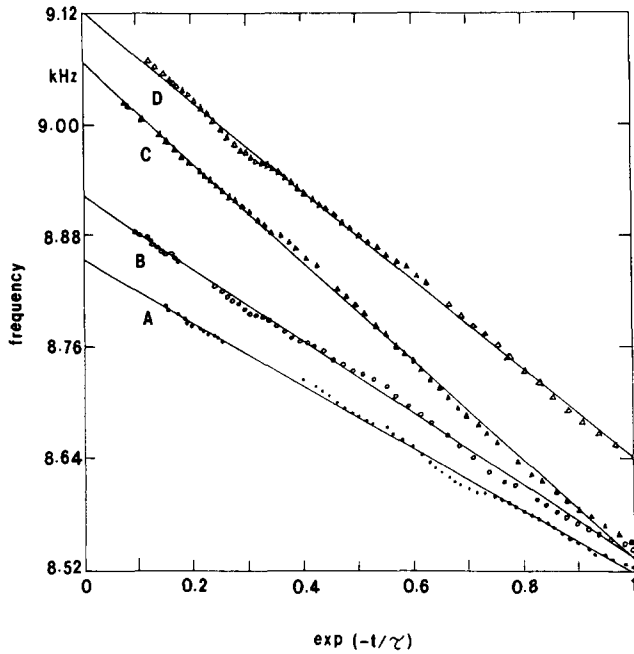


Fig. 2. Mathematical fitting (—) according to eqn. (1) for different annealing temperatures, with experimental measurements: points A, $T=232.6$ K; points B, $T=243.3$ K; points C, $T=251.5$ K; points D, $T=258.4$ K.

lower the imperfection content after a sufficiently long time, a fact which is generally accepted in annealing experiments.

(d) Each experiment indicates the existence of a single characteristic time for the $f-t$ variations carried out at a certain annealing temperature. In turn this indicates the elimination of a single type of imperfection in this temperature interval.

Accordingly, the characteristic time dependence on the annealing temperature T can be assumed to follow an Arrhenius relation of the form

$$\tau(T) = \tau(\infty) \exp(W/kT) \tag{2}$$

where W is the activation enthalpy of the process governing the recovery and k is Boltzmann's constant. A linear regression analysis between $\ln \tau$ and $1/T$ yields

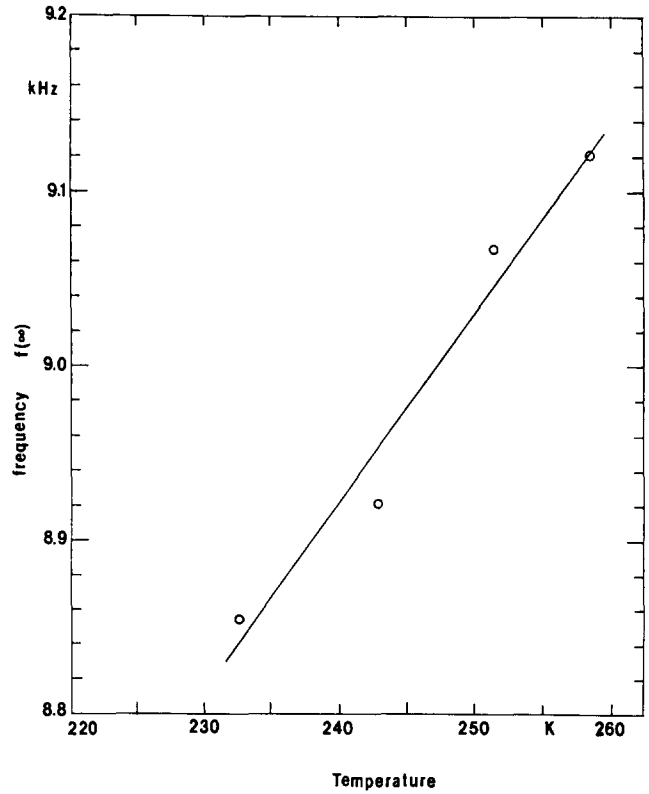


Fig. 3. Variation in the limiting frequency $f(\infty)$ with annealing temperature.

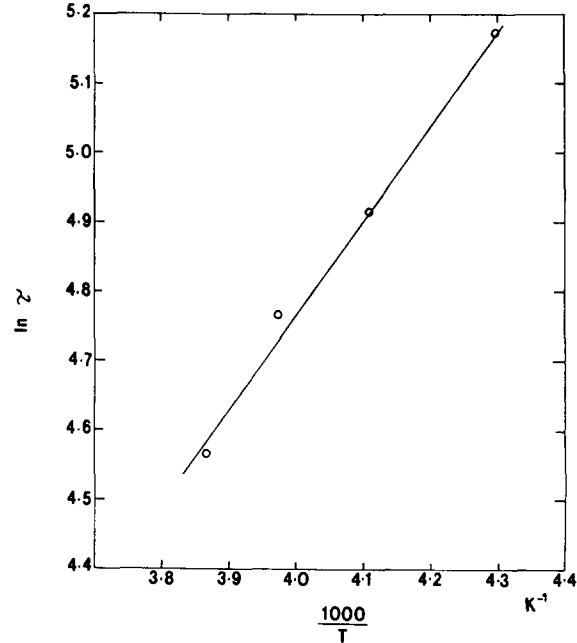


Fig. 4. Arrhenius relation between the characteristic time and the annealing temperature represented by eqn. (2), giving an activation enthalpy $W=0.12$ eV.

the values of $W=0.12 \pm 0.01$ eV, $\tau(\infty) \approx 0.5$ min and a correlation coefficient $|r|=0.9985$. The regression line is shown in Fig. 4 with the values of $\ln \tau$ in Table 1.

4. Discussion

A quick inspection of the obtained activation enthalpy suggests that it lies in the range of migration of self-interstitials in most metals (ref. 4, p. 102). For cadmium this is not the case. Recently, Seeger [5] reported activation enthalpies of the *c* dumbbell self-interstitials, the most stable configuration in Cd, as 0.23 eV parallel to the *c* axis and 0.35 eV perpendicular to it. Furthermore, this migration takes place in the recovery stage III which ends at 130 K [5] and can at most extend to 160 K [6]. In addition, the formation enthalpies of monovacancies in Cd are dispersed from 0.39 eV [7] to 0.52 eV [8], while their migration enthalpy is 0.38 eV [9], values which are quite far from our activation enthalpy. However, the binding enthalpy of divacancies in Cd is 0.15 eV [9], a defect which exists only at temperatures much lower than the range employed in our experiments. In addition, clusters of self-interstitials are found [5] to break up in the temperature range 150–165 K with an activation enthalpy of 0.5 eV, while break-up of vacancy clusters occurs in the temperature range 200–217 K with an activation enthalpy of 0.7 eV. Therefore, the elimination of any point defect, which may be created during deformation by cooling, is thus excluded as a cause of the observed recovery.

It has been assumed [1, 2] that microdeformation in Zn and Cd occurs by slip of dislocations in the basal plane (0001). It is well known that intersection of basal dislocations during their glide with forest dislocations, having their lines along the *c* axis, may produce two jogs if the two dislocations are cut by each other. The formation energy of a jog is approximately given by (ref. 4, p. 61)

$$U_j \approx \mu b_1^2 b_2 / 10 \quad (3)$$

where $\mu = 2.46 \times 10^{10} \text{ N m}^{-2}$ is the shear modulus for Cd, b_1 is the Burgers vector of the jog formed on the forest dislocation and b_2 is the Burgers vector of the jog formed on the gliding basal dislocation. This energy would be a minimum if the forest dislocation is an edge dislocation having its Burgers' vector along $[11\bar{2}0]$ and the basal dislocation has its Burgers' vector in the same plane. For Cd the shortest b has a length $2.98 \times 10^{-10} \text{ m}$, and thus the minimum value of U_j is about 0.3 eV. This means that jogs cannot be the type of defect eliminated during recovery.

As has been mentioned before [1], under the action of internal stresses dislocation sources emit loops which are piled up against the grain boundaries. The release of these loops continues until the back stress created by the pile on the source neutralizes the activating stress. Kinks are formed on gliding dislocations so as to contribute to the glide motion. When the metal is

heated, on its way back to room temperature, the activating stress on the dislocation source is removed and the back stress, acting alone on the pile, drives the dislocation back to the source which acts now as a sink. During this process kinks are eliminated and it is expected that our activation enthalpy is that for kink formation given as [10]:

$$U_k = (2a/\pi)(\mu ab^3 \sigma_p / \pi)^{1/2} \quad (4)$$

where a is the distance between Peierls' valleys, b is the magnitude of the Burgers vector, μ is the appropriate shear modulus and σ_p is the Peierls stress. For screw and mixed (60°) dislocations in the slip system $[11\bar{2}0](0001)$ we assign $a = b = 2.98 \times 10^{-10} \text{ m}$ and $\sigma_p = 1.5 \times 10^8 \text{ N m}^{-2}$ [11] from which $U_k = 0.11 \text{ eV}$, a value which is very close to our activation enthalpy and can account for the recovery mechanism.

5. Conclusion

The recovery of flexural vibration frequency of a cadmium plate deformed microplastically by internal stresses produced by anisotropic thermal contraction has been studied with time. The activation enthalpy of the recovery is found to be about 0.12 eV, a value very close to that of kink formation for basal slip in Cd. The elimination of these kinks is assumed to be the dominant recovery agent.

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