Electromigration in Single Crystal Cadmium [1,*]

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Measurements of electromigration in single crystals of cadmium have been made as a function of orientation. The resulting values for the effective charge numbers are

$$Z_{\parallel} = 1.5_4 \pm 0.15 \quad \text{and} \quad Z_{\perp} = 3.2_0 \pm 0.3 \,.$$

The results are also expressed in terms of the effective charges for the separate atomic jumps, (1) to a vacancy in the same basal plane and (2) to a vacancy in an adjoining plane. While the parallelism of these findings with those for zinc is apparent, there is one significant difference. In cadmium vacancy creation (and annihilation) tends to alter the c-axis dimension preferentially.

The investigation of electromigration in cadmium parallels that of zinc[3] in many respects. The experimental procedure using the vacancy flux method was practically identical. In Fig. 1 are shown sample plots of marker motion and change in specimen diameter versus position for the sample crystal (orientation 62° to the *c*-axis and run at a maximum temperature of 286 °C). The compilation of all the data on atom velocities is shown as a function of reciprocal temperature in Fig. 2. The slopes of these curves agree quite well with the activation energies for selfdiffusion in cadmium as measured by MAO[4]. After dividing by the respective $(D^* \varrho)$, one obtains the following values:

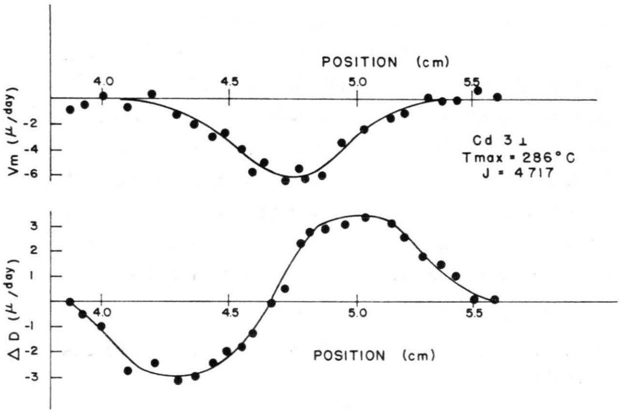

Fig. 1. Sample electromigration data for cadmium single crystal, $\Theta = 62°$, maximum temperature 286 °C.

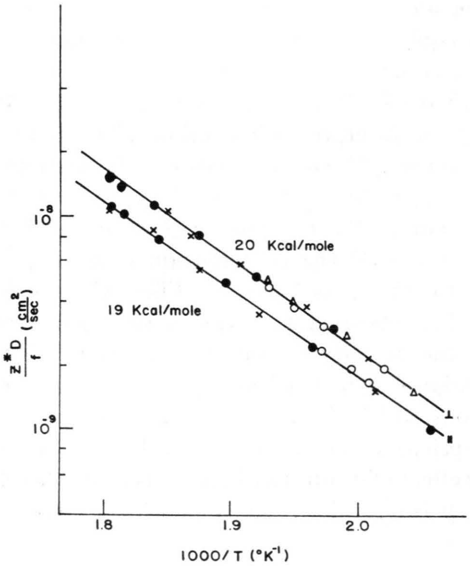

Fig. 2. Ln of $Z^* D/f$ for all cadmium runs plotted vs. T^{-1}. Data are converted to perpendicular and parallel orientations.

$$(Z^*/f)_{\parallel} = -2.0 \pm 0.2; \quad (Z^*/f)_{\perp} = -4.1 \pm 0.4. \quad (1)$$

The effective charge number, Z^*, is defined as the quantity which is multiplied by the electric field strength and the absolute charge of the electron to give the driving force for electromigration. The sub-

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[2] Deceased June 30, 1970. Manuscript prepared from notes by H. B. Huntington.

[3] J. L. ROUTBORT, Phys. Rev. **176**, 796 [1968]; see also an article on Anisotropy in Electromigration by H. B. HUNTINGTON, W. B. ALEXANDER, M. D. FEIT, and J. L. ROUTBORT, Proc. Marstrand Conf. At. Transp. Sol. Liq., Verlag Z. Naturforsch., Tübingen 1971.

[4] CHIH-WEN MAO, part of a doctoral research in progress at Rensselaer Polytechnic Institute. See also E. S. WAJDA, G. A. SHIRN, and H. B. HUNTINGTON, Acta Met. **3**, 39 [1955].

scripts $\parallel$ and $\perp$ denote parallel and perpendicular to the c-axis. The f's stand for the correlation factors for the assumed vacancy mechanisms. For the parallel case the meaning is clear cut since only one type of vacancy jump is involved. For the perpendicular flow the $f_\perp$ is defined by an appropriate average, or the ratio of the actual diffusion coefficient determined by isotope measurement to that diffusion coefficient determined conceptually by setting all the atomistic correlation coefficients equal to unity.

Now in terms of an atomistic theory one is concerned with how the electric field affects the atom jumps in the basal plane (B) and from plane to adjoining plane (A). Then one can obtain $(D^* Z^*/f)$ as follows:

$$(D^* Z^*/f)_{\parallel} = \tfrac{3}{4} n c^2 \omega_{\mathrm{A}} Z \tag{2 a}$$

and $$(D^* Z^*/f)_{\perp} = \tfrac{1}{2} n a^2 (3\, \omega_{\mathrm{B}} Z + \omega_{\mathrm{A}} Z) \tag{2 b}$$

where n is the fractional number of vacant sites and the ω's are the frequencies respectively for the two kinds of jumps involved. The ω_{A} and ω_{B} also determine the diffusivities through

$$D^*_{\perp} = \tfrac{1}{2} n a^2 (3\, \omega_{\mathrm{B}} f_{\mathrm{B}\perp} + \omega_{\mathrm{A}} f_{\mathrm{A}\perp}), \tag{3 a}$$

$$D^*_{\parallel} = \tfrac{3}{4} n c^2 \omega_{\mathrm{A}} f_{\mathrm{A}}. \tag{3 b}$$

Consequently it is possible to determine $Z^*_{\parallel}$ and $Z^*_{\perp}$ for a microscopic model. Conversely the Eqs. (2) and (3) can be used to determine Z^*_{A} and Z^*_{B} from macroscopic measurements

$$Z^*_{\mathrm{A}} = f_{\mathrm{A}} Z^*_{\parallel}/f_{\parallel}, \tag{4 a}$$

$$Z^*_{\mathrm{B}} = f_{\mathrm{B}\perp} (Z^*/f)_{\perp} \frac{[1 - \frac{2}{3}(a/c)^2 (D^*_{\parallel}/D^*_{\perp}) (Z^*/f)_{\parallel} (Z^*/f)_{\perp}^{-1}]}{1 - \frac{2}{3} (a/c)^2 (D^*_{\parallel}/D^*_{\perp})}. \tag{4 b}$$

For $(c/a) = 1.89$, $D^*_{\parallel}/D^*_{\perp} \cong 1.5$ and the values of Eq. (1) one obtains

$$Z^*_{\mathrm{A}} = -1.54 \pm 0.15, \quad Z^*_{\mathrm{B}} = -3.88 \pm .4$$
$$\text{and} \quad Z^*_{\mathrm{B}}/Z^*_{\mathrm{A}} = 2.51. \tag{5}$$

If one takes the point of view that Z^* is made of two contributions one from the electrostatic force and the other from the so-called "electron wind"

$$Z^* = Z_{\mathrm{el}} + Z_{\mathrm{wd}}, \tag{6}$$

and one further assumes Z_{el} to be the normal valence[5] (2 for cadmium and zinc) then

$$Z_{\mathrm{wd,\,A}} = -3.54, \quad Z_{\mathrm{wd,\,B}} = -5.9,$$
$$Z_{\mathrm{wd,\,B}}/Z_{\mathrm{wd,\,A}} = 1.67. \tag{7}$$

The same procedure applied to zinc gives

$$Z^*_{\mathrm{A}} = -1.9_6, \quad Z^*_{\mathrm{B}} = -5.6_6 \quad \text{and} \quad Z^*_{\mathrm{B}}/Z^*_{\mathrm{A}} = 2.9, \tag{8 a}$$
$$Z_{\mathrm{wd,\,A}} = -3.9_6, \quad Z_{\mathrm{wd,\,B}} = -7.6_6$$

and

$$Z_{\mathrm{wd,\,B}}/Z_{\mathrm{wd,\,A}} = 1.9_3. \tag{8 b}$$

In one respect cadmium did behave quite differently from zinc. This was with respect to the ratio of expansions along different crystallographic axes. In dealing with the dimensional changes along the specimen axis and transverse to the same axis we have customarily introduced a quantity α which is defined as the ratio of longitudinal extension to total dilatation. For a thin isotropic specimen one would expect a constant value of 1/3 for α. In Fig. 3 are shown plots of α as a function of position for specimen axes both parallel and perpendicular to the c-axis. It is apparent that α was always larger for the parallel specimen than for the perpendicular specimen, which is the opposite from the situation for zinc[6]. The result is quite interesting in view of the

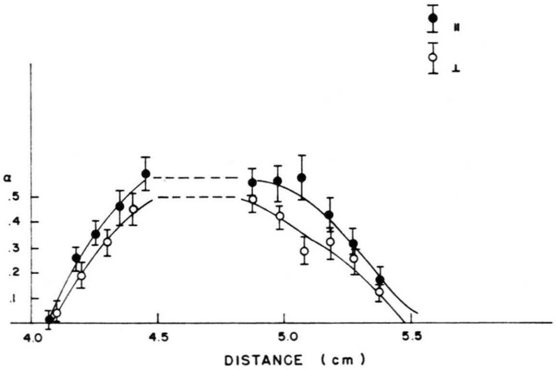

Fig. 3. Data for α vs. positions for two cadmium specimens.

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[5] This assignment for Z_{el} is open to some question. G. FROHBERG, Proceedings of the Marstrand Conference and H. B. HUNTINGTON, Trans. AIME **245**, 2671 [1969].

[6] Reported measurements on thermal expansion and lattice constant in cadmium by R. FEDER, H. CHARBNAU, and A. S. NOWICK, Bull. Amer. Phys. Soc. **12**, 388 [1967] bear out the conclusion that in this metal vacancy creation (and annihilation) is revealed primarily by changes in length along the c-axis.

fact that cadmium behaves plastically quite differently from zinc with less clearly marked basal cleavage and basal slip. Perhaps the growth (or shrinkage) of sessile loops in the basal plane is significant.

Also the shape of the a curve is interesting. The values higher than 1/3 in the center are a common feature in many investigations. They result from the interactions of the expanding half on the contracting half of the specimen and vice versa. The mutual interaction tends to inhibit transverse dimensional change and to increase a. The small values of a at the ends of the heated regions in the specimen occur because in this region the curve of diameter change versus position is convex toward the axis. (Whereas it is concave toward the axis in the region of large a.) This configuration gives rise to stresses which augment the radial distortion or cause it to exist where it might not otherwise be expected. Hence a is decreased — even to zero at the ends.