X-Ray Diffraction Study of HCP Metals
II. Line Broadening in Polycrystalline Zn and Mg Powder

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Microstructures of polycrystalline hexagonal close packed (hcp) Zn and Mg have been studied by x-ray diffraction line broadening analysis using the integral breadth method, and the Fourier coefficient method. For these two methods, several diffraction peaks were considered to obtain two suitable peak combinations.

For the room temperature powder samples, the root mean square (rms) strain was observed to be extremely small. The particle size was anisotropic in both samples with the Zn powder showing more particle size variation than Mg. The average particle size for Zn was about 750 Å, which was over twice the average particle size of 295 Å observed in Mg. The two fault probabilities for Zn turned out to be negligible or zero. Mg, on the other hand, was found to have small, but definite fault probabilities. The deformation fault probability α was 4.5×10^{-4} and the growth fault probability β was 6.5×10^{-4}. These results can be compared with the previous work of hcp Cd at room temperature, which was found to have no growth fault probability β and a deformation fault probability α amounting to 3×10^{-3}. This value is higher than that observed in Mg, because for Cd the two fault probabilities were obtained by neglecting the particle size of about 650 Å which actually did exist in the sample.

I. Introduction

The purpose of this study is to extend our earlier experimental x-ray investigation[1, 2] on the low melting point hexagonal close packed (hcp) metals which was started several years ago in our solid state physics laboratory here at USF. This is the second series of experiments performed after studying Cd, under analogous conditions to obtain a better understanding of the phenomenon of x-ray line broadening in hcp Zn and Mg. Up to that point most of the x-ray line broadening studies have been made with face centered cubic (fcc) and body centered cubic (bcc) metals.

Of the hcp metals studied, almost all the works have been done on the high melting point metals. Co, with a relatively high melting point of 1495 °C, has perhaps been most extensively studied[3]. These results showed that the fault probabilities decreased as the annealing temperature increased. Zr, with a melting point of 1857 °C, was investigated[4] and found to have no faulting. Re, with a melting point of 3160 °C, had[5] a fault probability for β, but α was estimated to be zero. Some hcp alloys, for example Co-Ni, Ag-Sn and Ag-In, have been also investigated[6, 7]. These studies showed that the fault probabilities increased as the alloy compositions approached the fcc phase from the hcp phase.

Our literature survey indicates that still not much is known about the low melting point hcp metals, except perhaps our own measurements[1, 2] on hcp Cd and some inconclusive results[8] of hcp Mg. We shall summarize some of the important results here that are relevant to this investigation. Mitra and Misra[8] used the Pines[9] single reflection method to separate the strain and particle size in polycrystalline Mg with no consideration taken to the effcets due to faulting. The results of their study did reveal some anisotropy in particle size. On the other hand Hunter[1], and Halder and Hunter[2] extensively studied polycrystalline Cd using both the Fourier coefficient and integral breadth method. Cd was found to have small root mean square (rms) strain 0.001 at room temperature which decreased with increasing annealing temperature. The growth fault probability β turned out to be extremely small or zero, but the deformation fault probability α had a value of approximately 0.003 at room temperature. The particle size in the 002 – 004 direction increased very little with the increase in annealing temperature, pointing out that Cd is much less affected by mechanical deformation compared to other hcp metals, which have higher melting point.

Thus from the above review, we expect that the line broadening in Mg will be more pronounced than in Zn, which in turn should be more pronounced than in Cd. This is because the melting point of a metal is directly proportional to the re-

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crystallization energy and the self-annealing processes of that metal. The strain and fault probabilities in these metals should be rather small, but still larger than Cd due to respective higher melting temperatures. We would like to test these predictions and arive at a quantitative interpretation through the present investigation.

II. Experimental

In this investigation, the samples being studied are polycrystalline materials; the primary requirement for obtaining a strong x-ray diffraction would therefore be to have as many small crystalline regions in the samples as possible that are randomly oriented and have extremely flat surfaces with respect to the x-ray incident beam. The best procedure to accomplish this is to pack the powdered sample being studied into a suitable holder that will not produce any undesirable x-ray diffraction peaks. This process insures that some of the appropriate hkl planes will be properly oriented to the x-ray beam.

The powder samples of Zn and Mg were prepared at room temperature by filing blocks of these metals of purity 99.999% obtained from Ventron Corporation. The process of filing and details of sample preparation have already been described previously[2]. The x-ray source was a Philips XRG-2500 unit provided with a Cu target. The powder patterns were recorded on a vertical diffractometer with a Bragg-Brentano focusing condition. A single crystal graphite monochromator was used to eliminate the white radiation and the Kβ components of the Cu radiation. The CuKα_1 wavelength (1.54051 Å), and the CuKα_2 wavelength (1.54433 Å) remained, with CuKα_2 being one-half the intensity of the CuKα_1 line.

The reflections recorded in this study for both Zn and Mg were selected according to the requirement for hcp metals described by Halder and Hunter[2]. The strong available reflections with faults such as 101, 102 and 103 were recorded. These were then supplemented by the reflections without faults, i. e. 100, 002, and 004. Several samples were run on the x-ray machine, but the ones which seemed to be the best after visual inspection with regard to the background and smoothness of the tails were retained for analysis.

III. Results and Discussions

A) Correction Factors

The diffraction peaks directly measured from the samples are to be treated[10] first for several correction factors. These factors are the usual Lorentz polarization factor for nonpolarized x-ray beam, Rachinger[11] correction for the separation of CuKα_1 peak from CuKα_2 peak, and the geometrical correction for the pure instrumental broadening[12]. For the first two, the standard procedures as described previously[1, 2] have been utilized. However, for the instrumental broadening we chose to use a well annealed, pure tungsten powder of lattice constant 3.1652 Å. The straightforward method of using the well annealed powder of the same material, i. e., Zn an Mg, failed due to two main reasons. The first one is that these metals have rather low melting points, 420 °C for Zn and 651 °C for Mg, and therefore, at room temperature which is quite close to the respective recrystallization temperatures, very little broadening properties would remain. For this reason the annealed samples did not show adequate contrasting behavior to the cold worked samples. The second reason is that these metals get very easily oxidized, especially Mg, with heating even in very high vacuum. Pure Mg undergoes a structural phase transition from hcp to fcc to become MgO accompanied by a change in the lattice parameter. Similar situation, although less severe, is also noted for Zn.

The above problems were easily remedied by the isotropic and non-reactive lattice properties of metal tungsten. The metal was heated in evacuated sealed tube for 24 hours and all the diffraction peaks from 110 to 321 were recorded. These peaks were found to be smooth, noise-free and much sharper than the Zn and Mg peaks under study. Then the standard Stokes[12] correction was employed with the various Fourier coefficients, and finally the corrected Fourier coefficients free of instrumental broadening were obtained.

B) Separation of Particle Size, Strain and Faults

Our method of separating the particle size, strain and faults is the same as has been described in our earlier publications[13, 14]. Therefore, we shall not repeat the theory and equations here which are explained and already wellknown. However, it should be pointed out that because of the higher probability of oxidation[15] in Zn and Mg, a somewhat different approach due to Pines[9] was introduced to obtain the particle size and strain. Pines devised a single reflection method when the double reflection method is not applicable. In our case the usual pair 002 and 004 was not satisfactory due to the nature of the 004 peak which was found to be very weak, broad and showed some overlap of ZnO and MgO peaks.

Pines[9] showed that when the strain distribution function is the usual Gaussian-type, the derivatives of the total Fourier Coefficients $A(L)$ can be related[16] to that of the pure particle size coefficient $A^{\mathrm{P}}(\mathrm{L})$ by

$$-\left(\frac{\mathrm{d}A(L)}{\mathrm{d}L}\right)_{L=0} = -\left(\frac{\mathrm{d}A^{\mathrm{P}}(L)}{\mathrm{d}L}\right)_{L=0} = \frac{1}{D}, \tag{1}$$

where D is the particle size. The above equation is especially true for 100, 002 and 004 reflections which contain no faults. Therefore, from the slope of the $A(L)$ versus L curve in the limit $L \rightarrow 0$, one can get $1/D$. We have performed this calculation to determine the particle size in two directions, 100 and 002. Once the particle size is known, it is a simple matter to calculate the strain, since the strain coefficients $A^{\mathrm{D}}(L)$ can be found from

$$A^{\mathrm{D}}(L) = A(L)/[\exp\{-L/D\}]. \tag{2}$$

The remaining part of the calculation is exactly identical with the previous work[2].

C) Overall Characterstics of Zn and Mg

The x-ray diffraction peaks of Zn and Mg were rather sharp at room temperature, the Zn peaks being sharper than those of Mg. The corrected peaks obtained after introducing various correction factors are shown in Figs. 1 through 2, the well annealed, pure tungsten peaks were still sharper than either of these metals and, therefore, useful for the geometrical correction. The sharp peaks seem to be the characteristic of the low melting point hcp metals.

The experimentally observed lattice parameters c are shown in Figure 3. The observed 2θ value of various reflections are also presented in Table I along with the corresponding theoretical 2θ values. Here the angle θ is the Bragg angle, and theoretical 2θ values are considered with reference to crystalline solids at 0 °K. As can be seen, some systematic changes are observed. These changes can be interpreted in terms of two major factors: one is the difference in temperature between the theoretical and observed values, and the other is the difference between the crystalline structure of the solid and the deformed structure of the polycrystalline sample. Lele[17] theoretically calculated the effects of layer faults in hcp crystals, suggesting that in the region of stacking faults the changes in structure may allow a spacing fault. The appearance of a spacing fault causes a peak shift such that the reflections with $h-k=3N$ will shift twice as much as those of reflections with $h-k=3N\pm1$, but in opposite direc-

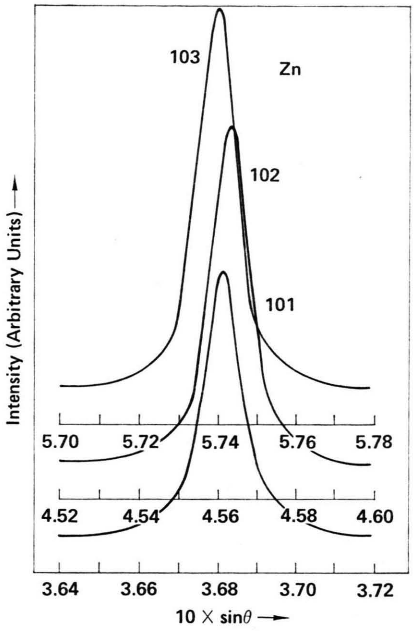

Fig. 1. The corrected diffraction peaks for 101, 102 and 103 reflections in cold worked Zn at room temperature.

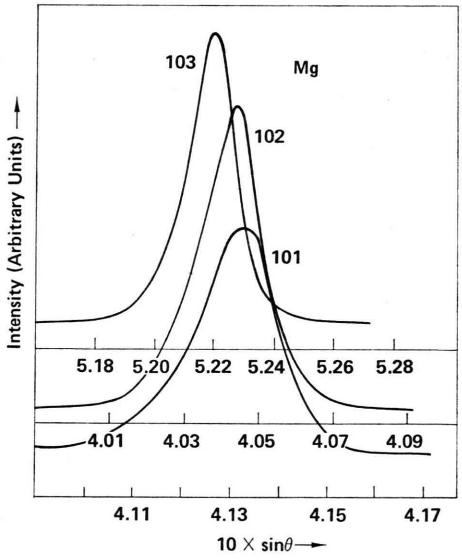

Fig. 2. The corrected diffraction peaks for 101, 102 and 103 reflections in cold worked Mg at room temperature.

hkl	$2\theta^0$ (theo)	$2\theta^0$ (obs)	$\Delta 2\theta^0$	$2\theta^0$ (theo)	$2\theta^0$ (obs)	$\Delta 2\theta^0$
	Zn			Mg		
002	36.303	36.288	−0.015	34.395	34.289	−0.106
004	77.079	77.022	−0.057	72.503	72.379	−0.124
100	39.007	38.977	−0.030	32.180	32.085	−0.095
101	43.235	43.201	−0.034	36.614	36.515	−0.099
102	54.340	54.303	−0.037	47.813	47.720	−0.093
103	70.102	70.048	−0.054	63.063	62.943	−0.120

Table I. The theoretical and observed 2θ values for Zn and Mg. The theoretical values are obtained for crystalline solid at 0 °K. The error bar in the observed value is ±0.0063 and $\Delta 2\theta = \Delta 2\theta(\text{obs}) - 2\theta(\text{theo})$.

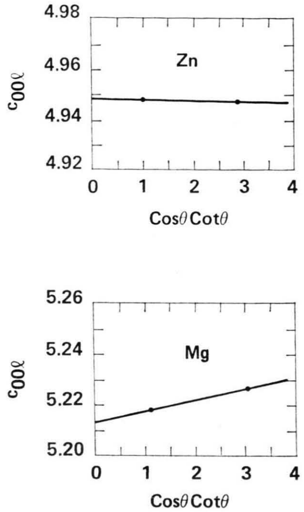

Fig. 3. The plot of the lattice parameter C_{00l} obtained from 002 and 004 reflections. The error bar in the measured value is $\pm 2\times10^{-4}$ Å.

Table II. Average values of the fault probabilities in Mg.

hkl	Term	Value	α (avg)	β (avg)
101	$(3\alpha+\beta)$	1.5×10^{-3}		
103	$(3\alpha+\beta)$	2.83	4.5×10^{-4}	6.5×10^{-4}
102	$(3\alpha+3\beta)$	3.29		

tion. However, peaks with $l=0$ will remain unshifted. From Table I, we could not detect any such systematic change.

The plots of the Stokes corrected Fourier coefficients for the two metals are illustrated in Figs 4 through 5. From the pair of 002 and 004 reflections the rms strain turned out to be zero or negligible (less than 10^{-5}) for both the metals. The average values of particle size $\overline{D}$ were 650 Å for Zn and 295 Å for Mg. No physical values of rms strain could be calculated with these average values of particle size $\overline{D}$ employing Eq. (2), because the strain coefficients turned out to be greater than 1,

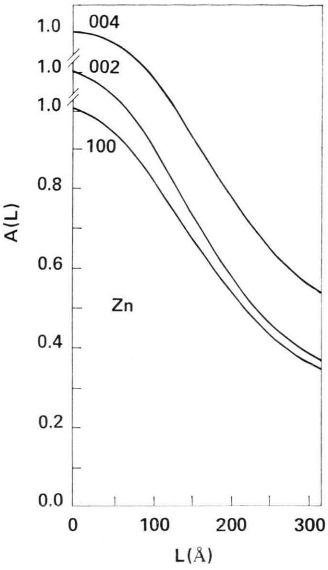

Fig. 4. The plot of the Stokes-corrected Fourier coefficients for several reflections in Zn.

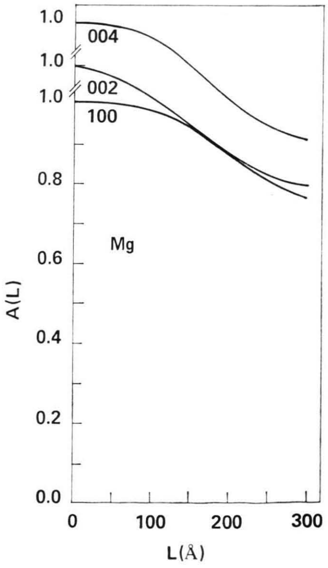

Fig. 5. The plot of the Stokes-corrected Fourier coefficients for several reflections in Mg.

which were unphysical and, therefore, immediately rejected. One could, of course, get unphysical Fourier coefficients due to 'hook effect' due to prematurely terminating the tails of the diffraction peaks. However, the 'hook effect' occurs only in the region of small L (say below 25 Å), whereas our observed effect remained well beyond this limit.

The integral breadth particle size D_{I} for these metals were found to be 783 Å for Zn and 597 Å for Mg. Once again no physical integral breadth strain could be recorded.

Using the theory of hcp metals as outlined previously[2] the two fault probabilities were calculated from 101, 102 and 103 reflections. The necessary equations for this maneuvering can be summarized by writing

$$\frac{1}{D_{\mathrm{eff}}}=\frac{1}{D}+\frac{|l|\,d_{hkl}}{c^2}\,(3\,\alpha+\beta)\,, \tag{3}$$

for $k-k=3\,N\pm1$ with l = even integer, and

$$\frac{1}{D_{\mathrm{eff}}}=\frac{1}{D}+\frac{|l|\,d_{hkl}}{c^2}\,(3\,\alpha+3\,\beta)\,, \tag{4}$$

for $h-k=3\,N\pm1$ with l = odd integer, where D_{eff} stands for the effective particle size to be calculated from the above reflections. For Zn the factor $(3\,\alpha+\beta)$ and $(3\,\alpha+3\,\beta)$ turned out to be zero. However, for Mg these two quantities are not zero and shown in Table II. Finally, solving for α and β, we found for Mg at room temperature $\alpha=4.5\times10^{-4}$ and $\beta=6.5\times10^{-4}$. These values are indeed small compared to high melting point hcp metals, where these are on the order of $10^{-1}\sim10^{-2}$. Mitra and Mishra[8, 18] have earlier reported a study on Mg with somewhat larger particle size of about 700 Å, small rms strain of about 10^{-3}, but no faults. We have not been able to reconcile with these results, although our method of measurement and analysis are substantially different, but quite reproducible to high degree of accuracy.

IV. Concluding Remarks

The x-ray diffraction patterns from Zn and Mg were recorded using the CuKα radiation and a graphite crystal monochromator. The peak positions were checked and calibrated with reference to a well annealed, pure tungsten powder of lattice constant 3.1652 Å. Several peaks with faults 101, 102 and 103, and without faults 100, 002 and 004 were examined.

At room temperature both Zn and Mg were found to have a small variation of particle size with respect to 100 and 002 directions. The rms strain in both the metals were negligibly small or zero, and therefore were considered unimportant in the analysis of the broadening of the 101, 102 and 103 peaks.

The average particle size in Zn was about 675 Å, and the two fault probabilities α and β were found to be extremely small (less than 10^{-5}). The small variation in the broadening of the peaks 101, 102 and 103 in Zn is interpreted as due to the small effect of particle size anisotropy.

Contrastingly, the average particle size in Mg was rather small, about 295 Å. The two fault probabilities were not zero, but found to be $\alpha=4.5\times10^{-4}$ and $\beta=6.5\times10^{-4}$.

The above results can be compared with the previous study of Cd at room temperature which showed average particle size of about 650 Å, negligible rms strain (about 10^{-3}), $\alpha=3\times10^{-3}$ and $\beta=0$. It should be noted here that α in that study was found neglecting the particle size of 650 Å. When this effect is taken into account, α will be less than 1×10^{-4} which is consistent with Zn and Mg result.

In summary, cold working produces only small changes in the microstructure of low melting point hcp metals. The smaller changes observed in the microstructure of cold worked Cd, Zn and Mg than those in high melting point metals Co, Re seem to have been caused by an increasing self-annealing process and perhaps higher stacking fault energies. It is predicted that the effect of mechanical deformation could probably be considerably enhanced by cold working and analyzing the samples at low temperatures, possibly near the liquid nitrogen temperature[2, 19]. A low temperature study would provide a further insight into the various deformation properties of these low melting point hcp metals.

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