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X-ray line profile analysis of silver base Ag-Cd-In alloys

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Abstract. X-ray diffraction line profiles of five silver base ternary alloys in α-phase with varying atomic percentages of cadmium and indium were recorded in both cold-worked and annealed states of the samples. Detailed studies on the profiles involving peak shift, peak asymmetry and Fourier analysis of line shapes have been carried out to evaluate microstructural parameters such as deformation fault probabilities, RMS strains and dislocation densities. It was found that the addition of indium has a marked effect in producing deformation fault probabilities in comparison to that of adding cadmium in ternary silver base alloys. Compound fault probability was found to be maximum for the alloy Ag-10Cd-15In.

Keywords. Microstructure; line profile analysis; cold-worked state; silver base ternary alloys; stacking fault probabilities.

1. Introduction

Extensive studies of microstructural analysis of various silver base binary alloys using x-ray methods have been made (Wagner 1966; Anantharaman *et al* 1972; Adler and Wagner 1962; Sen Gupta and Goswami 1967; De 1969; Sen Gupta 1967; Sen Gupta and De 1970; Chatterjee *et al* 1976). These studies have indicated that addition of solutes such as cadmium and indium to pure silver increases the stacking fault probability. According to phase diagram, α-phase silver base ternary alloys can be prepared with cadmium and indium as solutes up to about 25 at % (Snyder 1966). Krishnan *et al* (1971) evaluated only the intrinsic fault probabilities (α′) in some Ag-Cd-In alloys from a measurement of peak shift of (111) and (200) reflections. Recently the present authors reported that in four of the Ag-Cd-In alloys, in which the concentration of one of the constituent metals (indium) was kept constant at 5 at %, the deformation fault probability increases with increasing cadmium content (Reddy and Suryanarayana 1983). The present paper is an extension of our earlier work and the results on microstructural analysis of five more silver base ternary alloys using x-ray diffraction technique are included along with a detailed discussion on the deformation fault probabilities, root mean square (RMS) microstrains, effective domain size and dislocation densities on all the nine alloys.

2. Experimental procedure

The desired alloy samples were prepared from high purity silver, cadmium and indium metals. The details of the preparation of the samples and homogenization were

reported earlier (Reddy and Suryanarayana 1983). The x-ray data on annealed and cold-worked samples were collected by point counting method using a Philips goniometer fitted on to a PW 1730 x-ray generator and proportional counter; copper K_α radiation was used. The line profiles of the (111), (200), (220), (311), (222) and (400) reflections were recorded taking all necessary precautions (Reddy and Suryanarayana 1983).

The faulting parameters $\alpha(= \alpha' - \alpha'')$ and $4{\cdot}5\ \alpha'' + \beta$ were calculated from peak shift and peak asymmetry measurements of the profiles using well-known relations of Wagner (1966) and Cohen and Wagner (1962). The peak and the centre of gravity of the line profiles were determined by standard methods (Bearden 1933; Halder *et al* 1977).

Observed line profiles for cold-worked state of the alloys were corrected for instrumental broadening using the technique developed by Stokes (1948) and expressed as Fourier series (Warren 1969). The Warren-Averbach method (Warren and Averbach 1950; Warren 1959) was applied to separate the particle size coefficients $(D_e)_{hkl}$ and RMS strains $\langle \varepsilon^2 \rangle_{hkl}^{1/2}$ in [111] and [100] directions and also to evaluate compound fault probability $[1{\cdot}5(\alpha' + \alpha'') + \beta]$. Subsequent line shape analysis (Adler and Wagner 1962) also provides information about particle size due to faulting (D_{SF}) and minimum value of domain size (T_{min}) as defined by Warren (1961).

All the numerical calculations were done on Integra/1001 computer adopting a suitable program.

3. Results and discussion

3.1 *Lattice parameters and peak shift analysis*

The lattice parameter of each alloy specimen was calculated from a plot of a_{hkl} vs $\cos\theta \cot\theta$. In table 1 the data on lattice parameters of annealed and cold-worked samples are given and the results are shown in figure 1. It can be seen that for annealed samples all the a_{hkl} values fall on a straight line but for cold-worked samples the values of a_{hkl} scatter from the line and this scatter is consistent with Paterson's theory (Paterson 1952). From an analysis of the data on lattice parameters, one can infer that cold working causes contraction of the lattice in all these alloys of Ag-Cd-In system. These results are in agreement with those obtained on binary silver base alloys namely Ag-In, Ag-Cd, Ag-Sn and Ag-Ga (Adler and Wagner 1962; Chatterjee *et al* 1976).

Deformation fault probability (α) was evaluated by using the following relation (Adler and Wagner 1962).

$$(\Delta a/a')_{hkl} = G_{hkl}\,\alpha, \tag{1}$$

where G_{hkl} is the planar parameter and $(\Delta a)_{hkl}$ is the difference between the measured cold-worked lattice parameter (a_{hkl}) and hypothetical lattice parameter (a'_{hkl}). The mean values of stacking fault probability (α) as obtained from equation (1) and also obtained from the peak shift of neighbouring pairs of reflections namely (111), (200), (220) and (311) are given in table 1. The results of Krishnan *et al* (1971) are also included in table 1. A general agreement can be seen between the results obtained in the present work and those reported by Krishnan *et al* in respect of the observation that deformation fault probability increases with increasing solute content. However, there is difference between the individual values reported. In this context, it is worth mentioning that while Krishnan *et al* evaluated α only from one neighbouring pair of reflections, the

Table 1. The values of lattice spacings and stacking fault probabilities α', α'' and β from line profile analysis in Ag-Cd-In alloys

Sl No.	Composition of the alloy in at % Ag-Cd-In	Lattice spacings $(a_0)_{Ann}$ (Å)	Lattice spacings $(a_0)_{CW}$ (Å)	$\alpha_{(\times 10^3)}$ Krishnan *et al* (1971)	$\alpha_{(\times 10^3)}$ Present work: From peak shift	$\alpha_{(\times 10^3)}$ Present work: From lattice parameter	$4{\cdot}5\alpha'' + \beta$ $(\times 10^3)$	$1{\cdot}5(\alpha' + \alpha'') + \beta$ $(\times 10^3)$	α' $(\times 10^3)$	α'' $(\times 10^3)$	β $(\times 10^3)$
1.	90– 5– 5	4·1103	4·1064	12·2	13·09	13·17	8·69	36·91	7·38	−5·71	34·41
2.	85–10– 5	4·1220	4·1172	17·0	17·78	19·89	13·94	29·27	25·34	7·56	−20·08
3.	75–20– 5	4·1432	4·1407	29·1	28·14	29·69	12·54	53·88	28·72	0·58	9·93
4.	70–25– 5	4·1594	4·1547	32·4	25·96	27·35	17·24	62·39	21·82	−4·14	35·87
5.	85– 5–10	4·1272	4·1235	31·6	24·89	25·19	24·29	53·25	30·47	5·58	−0·82
6.	80–10–10	4·1415	4·1375	39·5	25·69	22·68	20·04	36·37	40·49	14·80	−45·56
7.	75–15–10	4·1468	4·1416	—	34·43	36·70	15·75	51·82	44·81	10·38	−30·96
8.	80– 5–15	4·1431	4·1407	64·7	39·77	42·81	1·40	40·59	53·41	13·64	−59·98
9.	75–10–15	4·1556	4·1522	70·8	49·19	51·35	8·10	70·40	56·85	7·66	−26·37
	Error limits	±0·0002			±3 to ±5		±4 to ±10	±2 to ±10	±5 to ±8	±2 to ±3	±5 to ±10

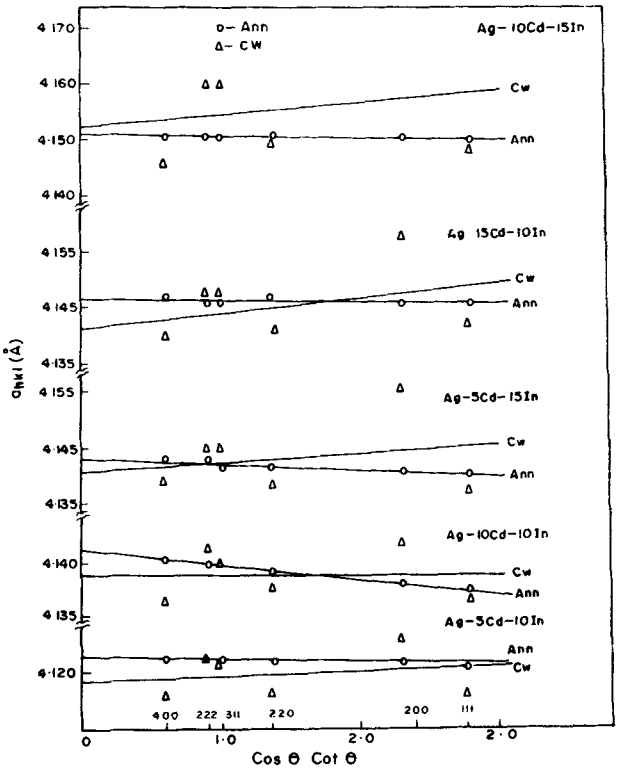

Figure 1. The plots of a_{hkl} vs extrapolation function $\cos\theta \cot\theta$ for Ag-Cd-In alloys.

present datum reported in table 1 is an average from three pairs of reflections.

With a view to studying the individual effects of solutes (cadmium and indium) on microstructural parameters of Ag-Cd-In alloys, the nine alloys so far studied and listed in table 1 are divided into four sets where in each set, the concentration of one of the solutes was constant. The data for the alloys at serial numbers 1–4 are taken from Reddy and Suryanarayana (1983). The other three sets of alloys considered now are with constant indium concentration of 10 at. % (Sl. Nos. 5, 6, 7 referred to as 2nd set), with constant cadmium concentration of 5 at. % (Sl. Nos. 1, 5, 8 referred to as 3rd set) and with constant cadmium concentration of 10 at. % (Sl. Nos. 2, 6, 9 referred to as 4th set). The plots of deformation fault probabilities (α) vs combined solute (Cd + In) at. % for the four sets of alloys are shown in figure 2. It is observed from these plots that adding either indium or cadmium in the ternary silver base alloys would increase the deformation fault probability. However, it is noteworthy that adding indium has a marked effect in producing deformation fault probability in Ag-Cd-In alloys with constant cadmium (3rd and 4th sets) in comparison to the effect of adding cadmium to the alloys with constant indium concentration (1st and 2nd sets). The present observations agree with those on binary Ag-In, Ag-Cd alloys (Adler and Wagner 1962).

The concept of electron-to-atom (e/a) ratio has been widely used as a normalizing parameter in correlating the changes in α with composition in most of the binary alloys. However, in the case of the ternary alloys, e/a ratio is not such a useful parameter since

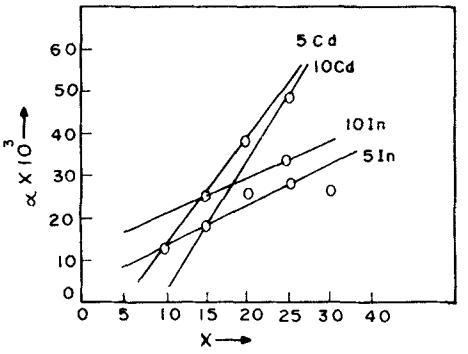

Figure 2. The plots of deformation fault probability (α) vs X, at. % of solute (Cd + In) for some Ag-Cd-In alloys.

one can prepare a number of alloys with the same e/a (Ag-25Cd-5In, Ag-15Cd-10In, Ag-5Cd-15In). So Krishnan *et al* (1971) extended the concept of solvent solute valence difference for ternary alloys which was originally proposed by Delehouzee and Deruyttere (1967) for binary alloys to explain the compositional dependence of α through the following expression

$$\alpha = \alpha_0 \exp(k|\Delta Z|p), \tag{2}$$

where α is the deformation fault probability in the alloy containing p atomic percentage of solute, α_0 is the deformation fault probability in the solvent metal alone, $|\Delta Z|$ the difference between the solute and solvent valences and k, a constant for a series of alloys based on particular solvent. The plot of $\ln\alpha$ versus $p|\Delta Z|$ for the present data on Ag-Cd-In alloys is shown in figure 3. The values of α_0 and k are evaluated from intercept and slope of this plot and these values are $6{\cdot}8 \times 10^{-3}$ and 0·05 respectively. Liu and Gallaghar (1971) reported the value of k in the case of silver base binary alloys as 0·08.

3.2 *Peak asymmetry analysis*

The asymmetry analysis of (111) and (200) line profiles was made from measurements of the centre of gravity of the line profile and the peak maximum. The values of the parameter $4{\cdot}5\alpha'' + \beta$ obtained in this analysis are given in table 1 for calculating individual fault parameters α', α'' and β. It was observed that asymmetry parameter $(4{\cdot}5\alpha'' + \beta)$ in the first set of alloys (with constant indium concentration of 5 at.%) increases with the addition of cadmium while in the second set of alloys a reverse effect was observed. However, no systematic variations of this asymmetry parameter with solute concentration (Cd + In) were observed in 3rd and 4th sets of these alloys.

3.3 *Line shape analysis*

The values of effective particle size $(D_e)_{hkl}$, RMS strain $\{\langle \varepsilon^2_{L=50\text{Å}} \rangle^{1/2}\}$, particle size due to faulting $(D_{SF})_{hkl}$ and minimum value of domain size (T_{min}) are listed in table 2. The variation of RMS strain $\{\langle \varepsilon^2_L \rangle^{1/2}\}$ with L (distance in Å normal to reflecting planes) as shown in figure 4 describes the usual picture of the strain field around the dislocation in deformed lattice and it is found that RMS strain and particle size along [100] direction

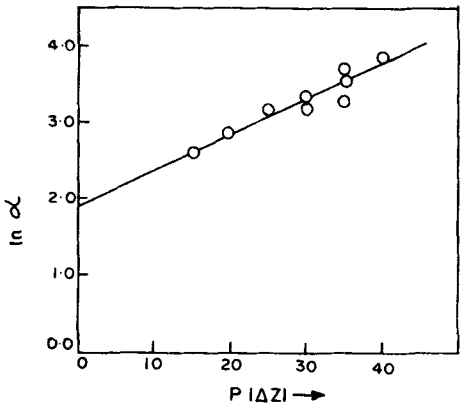

Figure 3. Variation of $\ln\alpha$ with $p\,|\Delta Z|$ for Ag-Cd-In alloys.

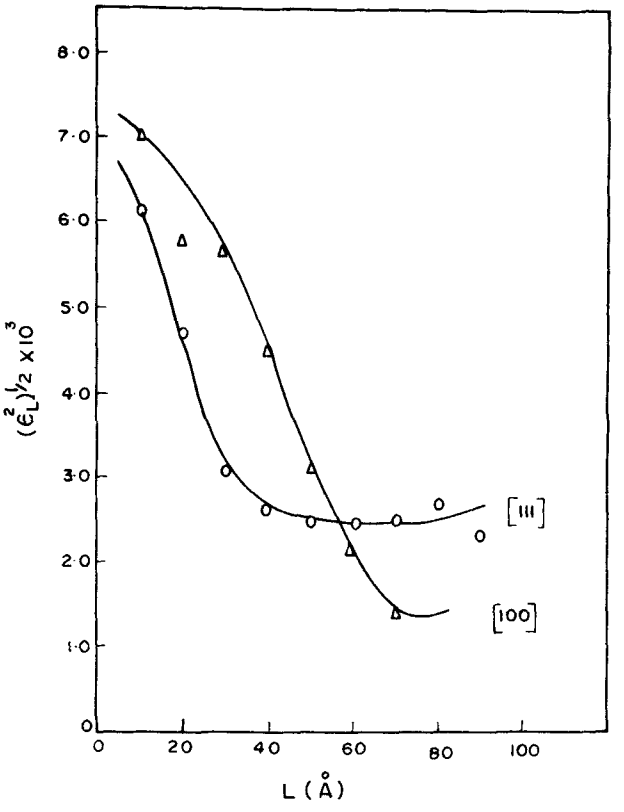

Figure 4. The plots of the RMS strains $\langle\varepsilon_L^2\rangle^{1/2}$ vs L (in Å) for Ag-10Cd-15In alloy.

are greater than those along [111] direction in these alloys (anisotropy in particle size and in RMS microstrains). It is also observed that the values of particle size $(D_e)_{hkl}$ along [111] and [100] directions decrease with increasing sum of the solutes (Cd + In) concentration for all the four sets of alloys. The particle size due to faulting (D_{SF}) is

Table 2. The values of effective domain sizes, RMS microstrains, D_{SF}, T_{min}, dislocation densities ρ and γ/μ parameters for Ag-Cd-In alloys

Sl No.	Compositions of the alloy in at % Ag-Cd-In	D_e(Å)		$\langle \varepsilon_{L=50Å}^2 \rangle^{1/2}$ ($\times 10^3$)		D_{SF}(Å)		T_{min} (Å)	ρ ($\times 10^{-11}$ cm/cm^3)		ρ_{av} ($\times 10^{-11}$ cm/cm^3)	γ/μ ($\times 10^{11}$ cm)
		[111]	[100]	[111]	[100]	[111]	[100]		[111]	[100]		
1.	90– 5– 5	100	73	1·91	2·35	354	153	87	4·95	8·33	6·64	2·70
2.	85–10– 5	118	80	1·95	3·90	325	141	116	4·17	12·58	8·37	2·52
3.	75–20– 5	87	53	1·80	2·95	178	77	107	5·31	14·29	9·80	1·89
4.	70–25– 5	87	50	2·28	2·90	154	67	125	6·70	14·83	10·76	2·87
5.	85– 5–10	92	55	2·35	2·00	179	78	118	6·58	9·37	7·98	1·73
6.	80–10–10	72	53	1·40	2·93	263	114	62	4·99	14·19	9·59	2·47
7.	75–15–10	52	38	2·30	2·90	183	80	67	11·34	19·57	15·46	2·45
8.	80– 5–15	90	60	2·03	2·60	235	102	91	5·79	11·12	8·46	1·16
9.	75–10–15	65	40	2·54	3·70	136	59	78	9·85	23·69	16·77	1·87
	Error limits	±5 to ±10										

inversely proportional to compound fault probability $[1{\cdot}5(\alpha'+\alpha'')+\beta]$ so that the effective particle size decreases with increasing compound fault probability when the solute concentration is more.

The values of compound fault probability $[1{\cdot}5(\alpha'+\alpha'')+\beta]$ for all the alloys are given in table 2. This parameter has been found to increase at higher solute concentration and the result of a maximum value ($70{\cdot}4 \times 10^{-3}$) for Ag-10Cd-15In alloy is noteworthy. In our earlier studies (Reddy and Suryanarayana 1984) on x-ray Debye temperatures of Ag-Cd-In alloys, it was reported that the same alloy shows a maximum value for θ_M (317° K).

3.4 *Stacking fault concentrations*

The individual values of α', α'' and β were estimated from all the parameters obtained from peak shift, peak asymmetry and peak broadening (table 1). It is found that the intrinsic faults (α') are greater than the extrinsic faults (α'') in these alloys. The twin fault probability (β) is found to be negative for the alloys with Sl. Nos. 2 and 5–9 indicating total absence of such type of faults in these alloys. However, the twin fault probability (β) is found to be positive for the alloys with Sl. Nos. 1, 3 and 4. These positive values of β may be attributed to the segregation of solutes at stacking faults in these three alloys. According to Wilson (1962), the asymmetry in profiles may also be produced by the segregation of solutes at stacking faults (Suzuki effect) in addition to the extrinsic and twin faults. However it is difficult to detect Suzuki effect and also to eliminate asymmetry due to extrinsic and twin faults. It may also be mentioned here that the determination of parameter $4{\cdot}5\alpha''+\beta$ involves the accurate determination of peak maximum position and centre of gravity (CG) of profile but the determination of CG suffers from the experimental limitations such as long tails of peak and peak overlap and hence much reliance cannot be placed on the values of β.

Finally it may be concluded that cold working produces appreciable intrinsic faults and to a small extent extrinsic faults, but fails to produce twin faults in most of these Ag-Cd-In alloys. These observations are similar to the results on some binary and ternary alloys namely Cu-Ga, Cu-Sb, Cu-In, Cu-Sn, Ag-Zn, Ag-Sb, Ag-Ga and Cu-Ni-Zn (Chatterjee *et al* 1976, 1977; Halder *et al* 1977; Sen Gupta and De 1970).

3.5 *Dislocation density (ρ) and stacking fault energy (γ)*

The values of dislocation density $(\rho)_{hkl}$ are calculated using the method suggested by Williamson and Smallman (1956) and the results are given in table 2. The average values of ρ and α were used to determine the parameter γ/μ for these alloys. It was not possible to calculate the stacking fault energy (γ) as the values of shear modulii (μ) for these alloys are not available. It is observed that the dislocation density along [100] direction is greater than that along [111] direction for the same alloy and the effect of adding a solute is to increase the dislocation density.

3.6 *Anomaly in Ag-10Cd-15In alloy*

As mentioned in §3.3, the value of compound fault probability of this alloy was found to be maximum. This alloy also had shown an anomalously high value of Debye temperature (317° K) when compared to the value of 244° K in the case of pure silver (Reddy and Suryanarayana 1984) and for the other silver alloys. Another observation from the present work is that due to cold work the lattice parameter of the alloy

decreases causing a contraction of the lattice. Such a behaviour in binary and ternary alloys has earlier been attributed to the Suzuki effect (Halder *et al* 1977). While the Suzuki effect may be present in all the nine alloys studied, in the particular alloy (Ag-10Cd-15In) the anomalous behaviour may also be due to a possible order-disorder phenomenon. To investigate this proposition, the authors have taken another diffractogram to look for any additional low angle peak. No such extra reflection was observed. Since the differences between the atomic scattering factors of Ag, Cd and In are small for x-rays, even if the phenomenon of order-disorder persists, it would be difficult to detect it from x-ray work. Therefore, it may be intuitive to subject the sample for careful resistivity measurements under different heating and cooling cycles to detect the presence of any such behaviour. Presently such a study is being undertaken by the authors.

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