AN X-RAY STUDY OF SILVER-CADMIUM ALLOYS*

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ABSTRACT. An X-ray investigation of the silver-cadmium system of alloys has been carried out to determine the phase boundaries at temperatures below 300°C with particular attention to the β-field. The presence of the β' phase, which occurs in the β-field at temperatures below 228°C has been confirmed. The lattice parameter and structure of the α, β' and ζ phases have been determined. An approximate boundary of the β' phase has been obtained. The boundaries of the other phases as obtained by us agree with those of Owen *et al.* The results are discussed in the light of the Hume-Rothery rule and the zone-theory.

INTRODUCTION

The equilibrium diagram of the silver-cadmium system of alloys, published in Metals Handbook (1948) is based on the thermal and microscopical work of Durrant (1931, 1935). In this diagram a phase β' (ordered body-centred cubic with CsCl type of structure) is given in the β-field. The diagram presented by Owen *et al.* (1939) from the X-ray investigation of the system differs from that given in Metals Handbook in respect of the exact position of the phase boundaries, though the arrangement of the different phases is similar. They, however, could not get the β'-phase at the lower temperature as their samples, according to them, could not be brought to a satisfactory state of equilibrium by annealing within a reasonable time.

The earlier X-ray investigations of the alloys by Astrand and Westgren (1928) and Natta and Freri (1928) revealed only the β and ζ phases. The only evidence of the β' phase from the X-ray study was given by Kosolapov and Trapeznikov (1936) who studied a single 51 atomic percent cadmium alloy in a high temperature camera and got the β' phase at 270°C and ζ phase at 500°C. Later work (Owen *et al.*), however, proved that the temperatures recorded by them were incorrect. Thus at present there is no satisfactory confirmation of the boundaries of the β' phase by X-ray methods. In the present work an attempt has been made to determine the phase boundaries of the silver-cadmium alloys at temperatures below 300°C with particular attention to the β-field where the β' phase occurs. The ζ to β' transformation was studied in detail by taking X-ray

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powder diffraction photographs of the alloys in the high temperature camera and also by taking photographs of quenched specimens of the alloys.

EXPERIMENTAL PROCEDURE

X-rays are intensively used to study the equilibrium diagram of metallic systems and are extremely valuable for the identification of phases in alloys. They may be used for this purpose even when it is not possible to index the diffraction lines or to solve the crystal structure. There are two general ways of applying *X*-rays to study the equilibrium diagrams : (a) the lattice parameter method and (b) the method of vanishing lines.

(a) *The lattice parameter method* :

In general the lattice parameter of pure metals changes, either decreases or increases, with the addition of a second metal i.e. on alloying. If the system does not form a continuous range of solid solutions, a break will occur in the lattice parameter composition curve, from which the limit of solid solubility can be determined. In the same way the limit of other intermediate phases, if any, can be established. Thus by applying this lattice parameter method the interphase boundaries between two phases, when they occur due to the change in composition, can be determined at any temperature.

(*b*) *The method of vanishing lines* :

If a standard film of a particular phase has been obtained, a simple visual examination of X-ray films is often sufficient to establish the existence of that particular phase in a polyphase alloy. The boundaries of the phase fields are determined by a method of X-ray bracketing, in which, if the diffraction lines due to a phase are present on one film and absent in another, the boundary is drawn between the temperatures or compositions to which the two films refer. The sensitivity of this method, however, depends on the width of the two-phase region and also whether the phases give rise to strong diffraction lines which do not overlap. In a favourable case as little as 1% of a given phase can be determined visually on a Debye-Scherrer film.

PREPARATION OF ALLOYS

Small amounts of silver-cadmium alloys up to 68 per cent by weight of cadmium where prepared from spectroscopically pure metals obtained from Johnson Matthey & Co., London. Accurately weighed quantities of silver and cadmium in the form of turnings (cleaned and dried) were taken in pyrex tubes, evacuated and sealed under very low pressure of helium, and heated in an electric furnace. The mixture was first heated for an hour at 500°C, when cadmium melted and got absorbed in silver by diffusion thereby lowering the melting point of silver. The temperature of the furnace was then raised till the alloy melted, when it was made homogeneous by shaking and quenched in water to prevent segregation and inhomogeneity which might occur during slow cooling.

The prepared alloys were weighed to ensure that no loss had occurred during heating. The alloys were again sealed in evacuated pyrex tubes and homogenized at 600°C for 24 hours and then examined for homogeneity by taking filings from different parts of the lump. From the homogeneous lumps, powdered samples were prepared and taken in small pyrex tubes, evacuated and sealed. The tubes were suspended by means of a fine copper wire in a vertical tube furnace and annealed at different temperatures. The tubes could be dropped into cold water placed just below the furnace by opening the bottom door and cutting the suspension. The method yielded very efficient quenching. Specimen for the high temperature camera was prepared by taking the powder in thin-walled pyrex capillaries.

APPARATUS

Philips precision cameras with 57.3 and 114.5 mm diameter were used to take the powder photograph of the quenched alloys. High temperature X-ray photographs were taken in Unicam 19 cm high temperature camera, which was calibrated by measuring the lattice spacing of pure silver up to 500°C. CuK_α radiations from a sealed off Philips X-ray tube were used to obtain the diffraction photographs.

EXPERIMENTAL RESULTS

Powders of the silver-cadmium alloys situated within the range of composition from 47 to 58% by weight of cadmium were quenched from different temperatures and X-ray pictures were taken. A preliminary survey shows that this region contained a single body-centred cubic β' (ordered) phase below about 228°C bordered on either side by double phase regions. The alloy 47* is in $(\alpha+\beta')$ field below 228°C and in $(\alpha+\zeta)$ above it (See Fig.1). Both the alloys 56.4 and 58 are mixtures of β' ond γ, a complex body-centred cubic with 52 atoms per unit cell, below 220°C, above which they are in $(\zeta+\gamma)$ region. All the four alloys included between 50.8 to 53% by weight of cadmium are in the β'-field below about 228°C, and in the ζ phase above it. A second transformation from ζ to β (body-centred cubic with same lattice parameter as that of β') was also observed with these alloys. Thus when 51.57 alloy was-quenched from 450°C it yielded β phase. The β phase was also obtained with 51.3 alloy when an exposure was given at 440°C in the high temperature camera. According to Owen this transformation occurs at 427°C for the alloys with compositions from 43.7 to 50% by weight of cadmium, and 445°C for the alloys from 56 to 60% cadmium. No attempt has been made here to redetermine this transformation

*Alloy 47 indicates an alloy with 47% by weight of cadmium.

temperature, but the observation on the two alloys mentioned above, confirmed their results.

(i) *The* $\alpha/(\alpha+\beta')$ *and* $\alpha/(\alpha+\zeta)$ *phase boundaries.*

Three α phase alloys with 25.1, 30.1 and 34.7% by weight of cadmium were prepared. In order to get a relation between lattice parameter and composition in the α phase, the lattice parameter of these alloys were measured. Powders of alloy 47 were annealed at 235°C for five days and quenched in water and X-ray powder photograph was taken. Sharp lines of α and ζ phases were obtained. The lattice parameter of α phase was calculated from (511) lines and those of ζ were obtained from $(21\bar{3}3)$, $(30\bar{3}2)$ and (0006) lines (the wave length used for CuK_α radiations are $CuK\alpha_1 = 1.54051$ and $K\alpha_2 = 1.54433$ Å). The alloy was again quenched from 224°C after annealing for five days, which yielded α and β' lines, from which the lattice parameters for α and β' phases were calculated. The results are given in the Table I. The α phase in the 47% alloy corresponds to 43.5 and 43.4% by weight of cadmium at 235 and 224°C respectively, as obtained by extrapolating the lattice parameter composition curve for α phase alloys. These gave the limit of the α phase. By narrowing the limits of annealing temperatures a temperature of 228°C±1 was obtained for this alloy at which $\beta'-\zeta$ transformation occurs.

TABLE I

Lattice parameter of α-phase alloys

Alloy composition in wt. % of Cd.	Lattice parameter at 30°C in Å	Quenching temperature °C
25.1	4.1400	—
30.1	4.1518	—
34.7	4.1635	—
47.0	4.1839	235
47.0	4.1837	224
47.0	4.1835	180

(ii) *The* $(\alpha+\zeta)/\zeta$ *and* $(\alpha+\beta')/\beta'$ *phase boundaries*

The four alloys included between 50.8 and 53% cadmium by weight are all in the β' field below the transformation temperature and in the ζ phase above it. Alloy 51.3 was studied in the high temperature camera up to 440°C. The photograph taken at 440°C shows that the alloy again changed to body-centred cubic phase.

The $\beta'-\zeta$ transformation was studied in detail for the 51.3 alloy using the high temperature camera. For that purpose exposures in the high temperature camera were made at several temperatures between 220 to 240°C. A temperature hysteresis was observed in course of taking these photographs. Thus it has been observed that β' transforms to ζ at about 225°C when photographs were taken at successive increasing temperatures i.e. when going from β' to ζ field, and ζ transforms to β' at about 220°C in the reverse process. But when the specimen was annealed in the camera for six hours before recording the pictures at every temperature, no such temperature hysteresis was observed. This revealed that $\beta'-\zeta$ transformation is not rapid and requires time to be completed. This phenomenon was also observed in the case of quenched alloys. An alloy, originally in the ζ state, when annealed at 220°C for two hours and quenched, gave ζ phase only, whose diffraction lines were not sharp but diffuse. This shows that the atoms of the ζ phase have started moving and are slightly displaced from the normal positions still-keeping the hexagonal symmetry i.e. the lattice is strained. However, the results obtained with the high temperature camera are that the alloy 51.3 is in the ζ phase at 230°C and in β' at 225°C. The mean value 227.5°C was accepted as the approximate transformation temperature for this alloy.

Powders of the 51.3 alloy were annealed at temperatures of 224°C, 227°C, 230°C and 234°C for five days and quenched in water and their diffraction photographs were taken. The results are that at 224°C the alloy is in the β' phase, at 227°C both β' and ζ are present, and at 230 and 234°C there is only the ζ phase. Hence 227°C was accepted as the transformation temperature.

The lattice parameter of the β' and ζ phases corresponding to all the four alloys were determined. The variation of the lattice parameter of β' phase with composition was rather small. No variation in the 'c' parameter of the hexagonal ζ phase was observed and only the 'a' parameter changed with composition. The lattice parameter of β' and ζ phases as well as the annealing temperatures are included in the Table II.

TABLE II

Lattice parameter of β' and ζ phases

β'			ζ				
Composition wt. % of Cd.	Annealing temp. °C.	Lattice parameter in Å	Composition wt. % of Cd.	Annealing temp. in °C	Parameter 'c' in Å	Parameter 'a' in Å	c/a
47.0	224	3.3314	47.0	235	4.8236	2.9835	1.617
50.8	224	3.3315	50.8	234	4.8240	2.9835	1.617
51.3	224	3.3316	51.3	235	4.8238	2.9840	1.616
51.57	224	3.3318	51.57	235	4.8238	2.9843	1.616
53.0	216	3.3323	53.0	226	4.8239	2.9854	1.615
56.4	215	3.3325	56.4	224	4.8238	2.9860	1.615
58.0	210	3.3326	58.0	230	4.8234	2.9862	1.614

The transformation temperatures of all the other alloys were established by examining the quenched powders. The results are given in the Table III. Alloy 53 when annealed for 15 days at 220°C, the accepted transformation temperature for this alloy, yielded both β' and ζ phases.

TABLE III

$\beta'-\zeta$ transformation temperatures

Composition of alloys; wt. % of cadmium	β'—ζ transformation temperature °C.	Phases
47.0	228	$(\alpha+\beta')-(\alpha+\zeta)$
50.8	228	$\beta'-\zeta$
51.3	227	,,
51.57	226	,,
53 0	222	,,
56.4	220	$(\beta'+\gamma)-(\zeta+\gamma)$
58.0	220	,,

An approximate value of thermal expansion for the β' and ζ phases were obtained from the high temperature photographs. For β' phase a value of 24×10^{-6} °C^{-1}, and for ζ phase values of $\alpha_c = 22\times 10^{-6}$ °C^{-1} and $\alpha_a = 36\times 10^{-6}$ °C^{-1} corresponding to the c and a axes respectively were obtained. The axial ratio c/a for the ζ phase changes from 1.617 to 1.614 with increasing cadmium concentrations. The value of c/a also decreases with increasing temperature.

The lattice parameter of β' and ζ phases were plotted against composition, and by extrapolation it was observed that the β' and ζ phases in 47% alloy correspond to 50.6 and 50.7% by weight of cadmium respectively. These gave the composition of the $(\alpha+\zeta)/\zeta$ and $(\alpha+\beta')/\beta'$ boundaries.

(iii) *The* $\zeta/(\zeta+\gamma)$ *and* $\beta'/(\beta'+\gamma)$ *phase boundaries*

The alloys 56.4 and 58% by weight of cadmium were studied by quenching method. A transformation temperature of 220°C$\pm$1 was obtained for both the alloys. The alloy 56.4 was also studied up to 400°C in the high temperature camera. The high temperature study of the alloy yielded 219°C$\pm$1 as the transformation temperature. The lattice parameters of the phases were calculated from the high angle lines. Lattice parameter of γ was 9.9704 Å for both the alloys. By extrapolating the lattice parameter for β' and ζ corresponding to these two alloys, the boundary between $\beta'/(\beta'+\gamma)$ and $\zeta/(\zeta+\gamma)$ was obtained. Alloys 47 and 56.4 were annealed for more than 15 days at 180°C and yielded an approximate boundary composition at that temperature. The results are included in the Table IV.

DISCUSSION OF RESULTS

The presence of the β' phase, which was suspected by Durrant and others from thermal and microscopical studies of the silver-cadmium alloys, has been confirmed by our X-ray investigation of the system. The β' phase boundaries determined by us are found to differ considerably from those given in Metals Handbook, these latter being based on the microscopical work of Durrant. The boundaries of the α and ζ phases obtained in the present work agree with those found by Owen *et al.* The boundary compositions of the different phases, as obtained in course of the present work along with those obtained by Owen, are given in Table IV. $\beta'-\zeta$ transformation temperatures of all the alloys examined are given in the Table III. These differ from those given in Metals Handbook by about 12°C.

TABLE IV

Boundaries in the silver-cadmium system of alloys

Temp. °C.	Boundary composition (cadmium weight percent) $\alpha/(\alpha+\beta')$	$(\alpha+\beta')/\beta'$	$\beta'/(\beta'+\gamma)$	$\alpha/(\alpha+\zeta)$	$(\alpha+\zeta)/\zeta$	$\zeta/(\zeta+\gamma)$	$(\zeta+\gamma)/\gamma$	Author
180	43.3	50.6	53.6					1
215		50.6	53.65					1
224	43.4			43.5	50.7			1
235				43.5	50.7	53.75		1
250				43.5	50.75	54.0		2
270					50.75	54.0		2
300				43.6			59.6	2
210							59.6*	2
190							59.6*	2

1 Present work. 2 Owen, Roger and Guthrie (1939). *Corresponds to $(\beta'+\gamma)/\gamma$.

With the help of these data the equilibrium diagram of the Ag-Cd system between the compositions of 40 to 60% by wt of cadmium and up to 300°C was constructed and is given in Fig. 1. The complete diagram of the system, shown in Fig. 2 was obtained by combining the results of Owen *et al.* with those of the present observations. This ropresents a complete diagram for the silver-cadmium system obtained from the X-ray study of the alloys in the solid state. However, the liquids and solids curves were not determined in the present investigation.

A duplex $(\beta'+\zeta)$ phase eld is also included in the diagram, based on the observations on three alloys as mentioned earlier. It has not been possible to determine the extent of this duplex region precisely, but observations show that it is confined within $\pm 2°C$ of the corresponding ($\beta'-\zeta$) transformation temperature. The general arrangement of the phase fields is similar to that in the silver

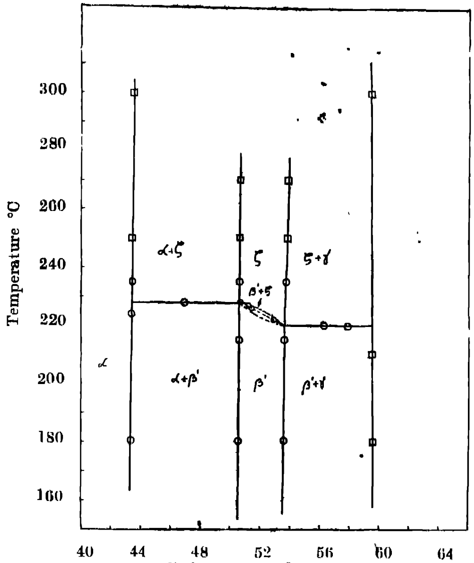

Fig. 1. Boundaries of the β'-phase in the Ag-Cd system

zinc system except that in the case of Ag-Zn there is only one ($\beta-\zeta$) transformation at about 260°C, whereas in Ag-Cd system there are two transformations in the β-field.

The structures of the different phases in the diagram are : α phase, face-centred cubic, β phase, body-centred cubic; β' phase, ordered body-centred cubic with CsCl type of structure; γ phase, complex body-centred cubic with 52 atoms to the unit cell; and ζ, δ and ϵ phases are close-packed hexagonal. It is not possible to get evidence of long range order in β' phase from x-ray investigations in this case as the super-lattice lines cannot be recorded on account of the nearly equal scattering powers of silver and cadmium atoms. However, there is evidence from nuclear magnetic resonance experiments (Drain, 1959) that the silver and cadmium atoms strongly attract each other which shows that unlike atom pairs will be favoured in this alloy. It may de concluded that the β to ζ and again ζ to β' transformations are probably controlled by the order parameters and energy considerations.

The alloy 68% by weight of cadmium, which is in the δ phase field, was studied. The lattice parameters of the δ phase are: $a=3.037$ Å, $c=4.824$ Å and $c/a=1.588$.

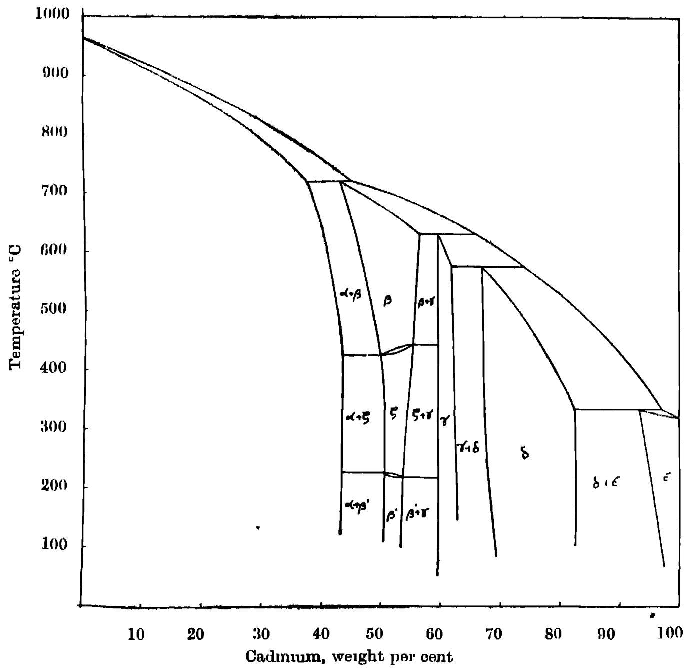

Fig. 2. Equilibrium Diagram of silver-cadmium alloys based on the work of Owen *et al.*, and the present investigations.

The formation of the intermediate phases β, ζ and γ can be explained by the Hume-Rothery rule for electron compounds. Assuming that the electrons are nearly free and the Fermi energy is the most significant factor determining the stability of these phases, Jones (1934, 1937) has given a theoretical explanation of the Hume-Rothery rule from the zone theory of metals. According to this rule the α phase having f.c.c. structure should become unstable at the electron concentration 1.4 while from the equilibrium diagram (Fig. 1) of Ag-Cd alloys it comes out to be 1.425 Similarly, for the $(\alpha+\beta')/\beta'$ boundary the Hume-Rothery rule gives 1.5 as against 1.496 found here. For the $\beta'/(\beta'+\gamma)$ and $(\beta'+\gamma)/\gamma$ boundaries we find the electron concentrations 1.528 and 1.586 as against 1.5 and 1.6 from the Hume-Rothery rule.

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