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Structural Transformation in Thin Films of Binary Alloys

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Structural transformation in thin films of binary alloys of 1st and 6th group elements, prepared by vacuum evaporation, has been studied by the author in detail by electron diffraction. The alloys chosen for the investigation were Ag_2Te, Ag_2Se, Ag_2S, Cu_2Te and Cu_2Se. The study of thin films of these alloys revealed that there occurs a transformation in structure and on heating, the temperatures of transformation are higher compared to the alloys in the bulk state. It has also been observed that the temperatures of structural transformation during heating and cooling are different. No quantitative explanation of the result has been given and it is expected that detailed discussion of the results will be published later.

1. Introduction

The study of the various properties of thin films of metals and alloys has been of much interest in recent years. Apart from their basic interest, such studies may be of practical utility because the properties of the same material in thin film state might differ from those in the bulk state. It is expected that the thinner the films the greater are the deviations from the properties of the bulk state. The studies of thin films have been extended from pure metals to binary and ternary alloys formed by vacuum deposition of the constituents. Various aspects of the study of the alloy films, such as formation of different phases in a system, alloying behaviour under different physical conditions, order/disorder and phase transformations have been recent topics of investigation.

The binary alloys chosen for the present investigation belong to 1st and 6th group elements and are Ag_2Te, Ag_2Se, Ag_2S, Cu_2Te and Cu_2Se. These alloys have not been much studied and have a complex behaviour as regards their physico-chemical properties. The most interesting feature of these alloys is that they have several polymorphic forms, i.e. their structure changes when they are heated. The structure of these alloys has been studied in the bulk state by X-ray diffraction by a few workers but the observed results are not mutually consistent. In the present investigation the author made a study of these substances in thin film form at various temperatures by electron diffraction. Their structure was examined while heating as well as while cooling and the results so obtained showed interesting features about the temperatures of structural transformation in thin films over the temperature cycle. The results observed in the present case are also compared with the results obtained by other workers concerning the bulk state.

2. Experimental and Technical Details

High purity metals were used: silver was supplied by Consolidated Mining & Smelting Co (Canada) and was 99.999% pure, and the other metals were supplied by Johnson Matthey & Co Ltd (London) and were of purity as given below: copper, 99.999%, selenium, 99.99%, tellurium, 99.999%, sulphur, 99.99%. The constituents of the alloys, weighed in stoichiometric proportions, were evaporated from tungsten baskets or from molybdenum boats under a vacuum of about 10^{-5} torr. The films were deposited on freshly cleaved single crystals of potassium chloride which were maintained either at room temperature or at elevated temperature and were kept at a distance of 6 cm from the source of evaporation. In certain cases the films were also formed directly on formvar supporting films.

After the constituents had been totally evaporated from the same boat, it was found that the compound was never formed immediately after evaporation (owing to the differential evaporation rates) and so in all cases the films were heated for a few hours at high temperatures to ensure compound formation. The annealing time and temperatures were different for the different alloy films and their optimum values were found by experimental trials.

Apart from the above method, simultaneous evaporation was also used for Ag_2Te alloy by evaporating the constituents from two separate tungsten baskets. The evaporation of both the constituents was so adjusted that evaporation was completed at the same time. It was found that the compound was formed in this method immediately after evaporation, no annealing being necessary.

In all the experiments the thickness of the films studied varied from 200 to 500 Å.

An RCA Emu-2A type of electron microscope, operated at a voltage of 50 kV, was used in the present investigation. The films were heated and cooled inside the diffraction unit at a rate of $\approx 2°$ C/min in all cases; the temperature was measured with an iron-constantan thermocouple. The calibration of the diffraction unit was performed using the (1 1 1) line of spectroscopically pure gold.

3. Results

The experimental results obtained for the different alloys with regard to the different conditions used in each particular case are described in the following sections.

3.1. Silver Telluride

Thin films of Ag_2Te were prepared both by evaporation from two baskets and by evaporation from the same basket. Deposition was made on to formvar or on to freshly cleaved single crystals of potassium chloride maintained at room temperature or at 300° C. The films formed by simultaneous evaporation from two baskets showed compound formation immediately after evaporation and no annealing was necessary in these cases, but in the later method (evaporation from the same basket) the films did not show alloy formation until they had been annealed for a few hours. In this case the films formed onto formvar or KCl, kept at room temperature during evaporation, were homogenised for two hours at an annealing temperature of 120° C and showed polycrystalline structure of the alloy. The films formed onto single crystals of potassium chloride at 300° C and annealed at the same temperature for $1\frac{1}{2}$ h showed oriented growth. The electron diffraction examination of the low-temperature phase (α-phase) of the alloy showed an orthorhombic structure with the following lattice parameters which are in agreement with the observations of Zorll [1]: $a = 13.03$ Å; $b = 12.72$ Å; $c = 12.22$ Å. The films were later heated inside the diffraction unit and it was observed that at 157° C the orthorhombic structure of the α-phase of Ag_2Te was transformed to a face-centred cubic structure (β-Ag_2Te) with $a = 6.58$ Å as already reported [2]. Figs. 1a and 1b depict the electron diffraction patterns of the oriented films of the alloy before and after structural transformation, respectively. Both the oriented and the polycrystalline films showed the same temperature of structural transformation within $\pm 2°$ C over the entire thickness range investigated. After the transformation in structure had taken place the films were cooled and the diffraction patterns were again recorded when the temperature was decreasing. Repeated observations showed hysteresis: the original phase was only regained at 115° C and below [3].

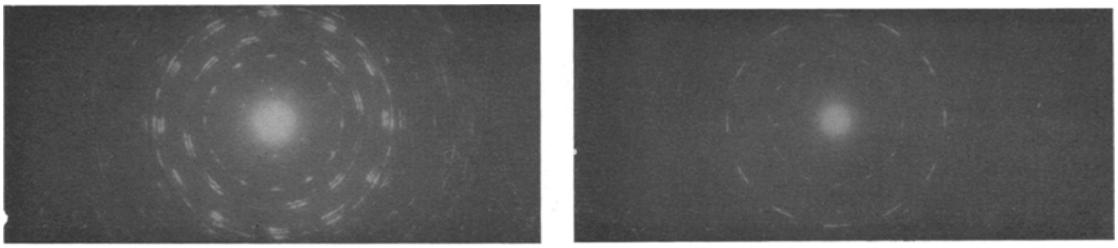

(a) (b)

Figure 1 Transmission electron diffraction patterns of Ag_2Te showing oriented structure of the alloy (a) before and (b) after structural transformation, respectively.

Regarding the earlier controversy Tokody [4], Frueh [5] and Wyckoff [6] identified the α-phase as having monoclinic structure, but with different lattice parameters and interaxial angles. However, using the same technique Koern [7], and Rowland and Berry [8] reported that the α-phase has an orthorhombic structure, again with different lattice parameters. Chou Ching-Liang *et al* [9] confirmed the results of Frueh [5]. All the above authors including Rahlfs [10] have recognised the β-phase as having a face-centred cubic structure with the same lattice constants as determined in the present case. The temperature of structural transformation has been reported between 135° and 150° C.

Miyatani [11] has made electrical conductivity measurements of bulk Ag_2Te with temperature and found that the variation of electrical conductivity is not reversible with temperature. He reported the phenomenon of hysteresis in bulk Ag_2Te similar to the present results in thin films of Ag_2Te.

3.2. Silver Selenide

The fact that the alloy silver selenide exists in two modifications has been known since 1904, but since then very little work on it has been reported. In the present work thin films of Ag_2Se alloy were prepared by evaporating its constituents in stoichiometric proportion from the same boat and were deposited onto freshly cleaved single crystals of potassium chloride maintained at room temperature. After evaporation the films were annealed at different temperatures for homogenisation and their electron diffraction study [3] showed the following different orientations.

The films annealed at 120° C for 1½ h, when examined by electron diffraction at room temperature revealed polycrystalline growth showing the orthorhombic structure of the α-phase of the alloy, with the lattice parameters: $a = 7.05$ Å; $b = 4.32$ Å; $c = 7.82$ Å.

The other set of films annealed at 140° C for 1½ h showed oriented growth of the alloy. On the other hand the films annealed at 150° C for 1½ h showed mosaic single crystal structure.

On heating the alloy films inside the diffraction unit it was found that the orthorhombic structure of α-Ag_2Se was transformed to β-Ag_2Se having body-centred cubic structure (with $a = 4.98$ Å) at 166° C [12] and was stable up to high temperatures. Figs. 2a and 2b show the transmission electron diffraction patterns respectively of the α-phase and β-phases of Ag_2Se, showing mosaic single crystal structure. On cooling the β-phase, the films of all thicknesses showed a transformation in structure at 107 ± 2° C, thus showing the phenomenon of hysteresis.

Regarding the previous work on this alloy, Bellati and Lussana [13] and Pellini [14] studied it in bulk state at high temperatures and reported that the temperatures of structural transformation had been observed as 133 and 122° C respectively. On the other hand Rahlfs [10] found that the temperature of structural transformation was 128 ± 5° C. Zorll [15] and Chou Ching-Liang and Pinsker [16] studied the thin films of this alloy by electron diffraction and reported that it had an orthorhombic structure. The values of the lattice parameters obtained in the present experiment are in agreement with those determined by these authors. The former author found that the high temperature phase is only stable above 140° C while the latter authors did not quote any value of the temperature of the phase transformation. The phase stable at high temperatures has been shown by all the authors to have a body-centred cubic structure with the same lattice parameters as determined in the present study. Miyatani [17] made electrical

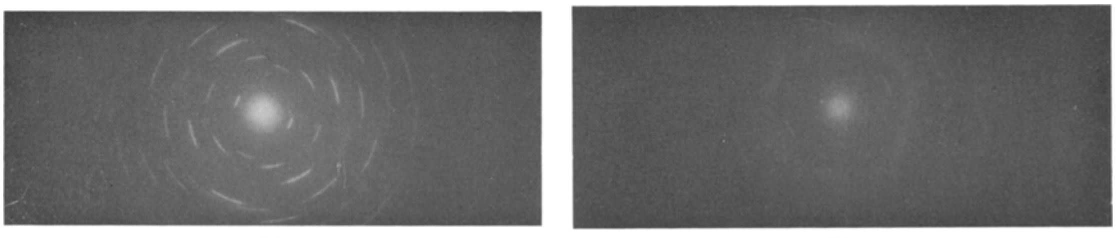
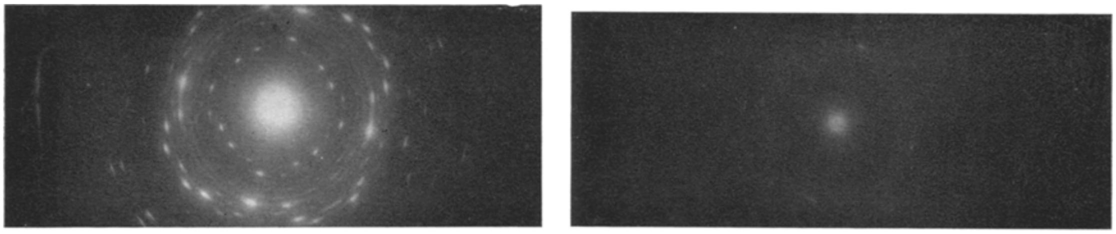

(a) (b)

Figure 2 Transmission electron diffraction patterns of Ag_2Se alloy films showing mosaic single crystal growth (a) before and (b) after structural transformation in the film respectively.



(a) (b)

Figure 3 Transmission electron diffraction patterns of Ag_2S alloy showing (a) α-phase and (b) β-phase of the alloy respectively.

conductivity, and Hall coefficient measurements of Ag_2Se alloy in bulk state and found that β-Ag_2Se was only stable above 130° C.

As in the case of thin films of Ag_2Te, the thin films of Ag_2Se also showed a rise in temperature of structural transformation compared to the bulk alloy, and the phenomenon of hysteresis was also equally well marked.

3.3. Silver Sulphide

Thin films of Ag_2S were formed on to freshly cleaved single crystals of potassium chloride maintained at 150° C, by evaporation of the constituents of the alloy from the same basket, and were annealed at the same temperature for 3 h. The electron diffraction study of the films so formed revealed formation of a compound of orthorhombic structure. Fig. 3a shows the electron diffraction patterns of the alloy showing the oriented growth in the film. The films grown onto the substrate kept at room temperature did not show compound formation even after annealing.

On heating the alloy films in the diffraction unit it was found that the low temperature phase of Ag_2S* (α-phase) transformed at 218° C to β-Ag_2S having body-centred cubic structure with $a=4.89$ Å and this was found to be stable at high temperature as reported earlier [3, 18]. Fig. 3b depicts the diffraction patterns of β-Ag_2S. On cooling the films the transformation from β-phase to α-phase took place at 156° C, a much lower temperature than that observed for the transformation from α-phase to β-phase.

The present electron diffraction results concerning the structure of the α-phase are similar to those of Nowotny and Zahn [19] and Kracek [20], who concluded by X-ray diffraction that the α-phase has an orthorhombic structure. Ramsdell [21], Frueh [22] and Wyckoff [6] attributed a monoclinic structure to α-Ag_2S but gave different lattice parameters. They also attributed a body-centred cubic structure to β-Ag_2S. Investigations regarding the temperature of structural transformation of the alloy in bulk state have been made by many workers and different results have been reported. Hansen [23] has quoted the temperature of transformation of the bulk alloy as lying in the range from 175 to 178° C. Emmons *et al* [24] reported that the transformation in structure takes place only at 180° C in the bulk alloy. Wilman and Sinha [25] studied the evaporated thin films of Ag_2S by electron diffraction and observed that α-Ag_2S has a monoclinic structure which transformed to β-Ag_2S having a body-centred cubic structure. They also observed that such a transformation was reversible but if the films were heated at a temperature between 350 and 400° C for 1 to 2 min, the structure of β-phase was changed irreversibly to face-centred cubic.

Thus it can be seen that in the case of Ag_2S thin films also, there is a rise in the temperature of structural transformation compared to that for the alloy in the bulk state and the phenomenon of hysteresis is well marked, parallel to the observations already made in the cases of thin films of Ag_2Te and Ag_2Se alloys.

3.4. Copper Telluride

The various phases formed in the copper-tellurium system have not yet been completely determined. But in the case of Cu_2Te, phase transformation has been reported by X-ray diffraction study and so only this alloy of the system was of interest in the present work.

The thin films of Cu_2Te were grown on to single crystals of potassium chloride maintained

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*The diffraction patterns of α-Ag_2S could not be indexed properly and hence the lattice parameters could not be determined. The structure was identified by comparison only.

at room temperature by evaporating its constituents from the same basket, and were annealed at 300° C for 3 h for complete homogenisation. The alloy films so formed were examined by electron diffraction and the diffraction patterns of the phase stable at low temperature (α-Cu_2Te) showed polycrystalline growth having hexagonal structure with the following lattice parameters: $a = 12.54$ Å; $c/a = 1.731$.

The films formed onto the heated substrate also revealed polycrystalline growth, indicating that for obtaining oriented growth one would have to use still higher temperatures. The films on heating in the diffraction unit showed transformation in structure at 410° C [3] and the high temperature phase (β-Cu_2Te) showed a face-centred cubic structure with $a = 6.11$ Å. This phase was found to be stable up to 600° C. On cooling the alloy films, it was found that the original structure was not regained at the same temperature as on heating but at 340° C, thus showing the phenomenon of hysteresis. It is interesting to note that there exists no difference of opinion in the literature regarding the structure of the low temperature phase of the alloy in bulk state. However, the different authors [26-30] have given different lattice parameters for the hexagonal structure. Using X-ray diffraction technique, all the workers have reported the same structure and lattice parameters for the high temperature phase of the alloy as observed in the present investigation for thin films.

About the temperature of structural transformation, no clear information is available in the literature for either the bulk or the thin films of the alloy. However, some thermal effects investigated in the bulk solid state of the alloy indicated a transformation in structure at a temperature of 387° C [23].

3.5. Copper Selenide

The structural study of Cu_2Se alloy was begun as early as 1923 by Davey [31] and he pointed out that it has calcium fluoride structure with lattice constant $a = 5.751$ Å. Rahlfs [10] also studied this alloy in bulk state by X-ray diffraction and found that the alloy showed a transformation in the structure between two face-centred cubic phases, one stable at high temperatures and the other stable at lower temperatures, and these phases had lattice constants of 5.84 and 5.72 Å, respectively. Later these results were confirmed by Boettcher *et al* [32].

The thin films of this alloy prepared by the method described in section 2 showed face-centred cubic structure with $a = 5.8$ Å. No change in the lattice constants could be observed even on heating up to 300° C [18, 33].

In the bulk state the structural transformation in Cu_2Se has been reported to occur at 110° C by Bellati and Lussana [13]. In the present case, as mentioned above, no transformation in structure could be observed.

4. Discussions

As a result of the present electron diffraction study of thin films of binary alloys belonging to the A_2B class of compounds the following conclusions were drawn:

(1) On heating, the temperature of structural transformation in thin films of the alloys investigated is higher than that in the bulk state.

(2) There is hysteresis of the temperatures of phase transformation on heating and cooling.

The results (1) and (2) above seem to be general, and apply for other alloys than those investigated in the present work. In this connection Bahadur and Sastry's work [34] and the work of Hull [35] may be mentioned. The former authors studied the thin films of AgCd and AgZn alloys by electron diffraction and found that no phase transformation occurs in the thin films of these alloys up to the temperatures of 300 and 350° C respectively. They could not study these alloys at still higher temperatures as vaporisation of one of the constituents had started at these temperatures. On the other hand it had already been reported that these alloys in bulk state, when studied by X-ray diffraction, undergo a structural transformation at 250 and 270° C respectively. The above authors suggested that in the case of thin films the temperatures of phase transformation, if observable, are expected to be greater than those found for the alloys in the bulk state. Hull [35] found in the case of thin foils of β-brass and Fe-30% Ni alloys that the transformation in these foils occurs at temperatures higher than those observed for the normal alloys in bulk state. The phenomenon of hysteresis has also been observed by Kuznetsov and Rabezolva [36] and Miyatani [11] in the bulk state. Recently Parshad and Sharma [37] have tried to explain the physical basis of the phenomenon of hysteresis in both thin film and bulk states.

At this stage it is not possible to explain the observed results quantitatively until detailed activation energy data are available, but it is believed that the differences observed in the thin film and bulk states may be due to the following differences in their structure:

(1) Thin films have much larger surface volume ratio.

(2) The presence of a large density of dislocation and other defects in thin films.

(3) Smaller crystallite size in thin films.

During the course of investigation it was observed that the time period needed to transform one phase to another was of the order of a few seconds and could not be recorded accurately. It is expected that these results will be discussed at a later date when more information about activation energy data and time of transformation is available.

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