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ANNEALING STUDIES OF VAPOUR QUENCHED Al-Sn FILMS

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Abstract: Mestable solid solutions of Al + up to 5% at. Sn have been obtained by means of »vapour quenching« in vacuum. The morphology and kinetics of structural changes have been observed by electrical resistance measurements and electron microscopy investigations. The »as deposited« thin films are found to be single phase solid solutions with an f. c. c. structure, while after annealing above 500 K they transform into a two phase structure where Al and Sn are separated. The activation energy for this process is found to be (1.45 ± 0.15) eV. The influence of the Sn impurity and defects on the electric resistance has been observed in the temperature interval of 250 — — 350 K.

1. Introduction

Investigations of Al-Sn alloys are difficult owing to a very low mutual solubility of these metals[1]. Very recently this solubility has been extended by the use of splat cooling method to about 0.25at% of Sn in Al[2]. However, electrical measurements on such small samples are very difficult[3]. One of the most efficient methods of approach indicated in such cases is vapour quenching. This method yields solid solutions with greatly augmented concentrations of Sn (the solubility limit is yet to be found) while the films thus obtained are quite suitable for electrical measurements and for electron microscopy.

2. Experiment

Thin films of Al-Sn alloy were prepared by evaporation of master alloy of predetermined concentration in high vacuum. This is possible because both constituents have suitable vapour pressures at the temperature of evaporation. The master alloy was prepared using 99.997% pure aluminium and

99.97% pure tin by induction melting in pure helium atmosphere and throughly mixing. During evaporation the pressure in the vacuum system was maintained at about $3 \cdot 10^{-6}$ torr.

The alloy was evaporated from a tungsten filament on to a polished copper substrate which itself was mounted on a copper block cooled by liquid nitrogen. Just prior to evaporation of the alloy the copper substrate was covered with a film of SiO a few thousand angstroms thick evaporated from a separate filament. This SiO film served the purpose of rendering the surface of the substrate essentially amorphous and making the electrical measurements possible. The latter were effected through gold contacts evaporated on the substrate. The alloy was then evaporated on top of these contacts at a rate of abaout 10 Å/s. to a thickness of 300 — 500 Å. The temperature rise of the substrate during the evaporation was estimated to be 6 °C at most. The concentrations of tin in the films were calculated with the help of the Langmuir-Raoult expression[4] using the vapour pressure values given

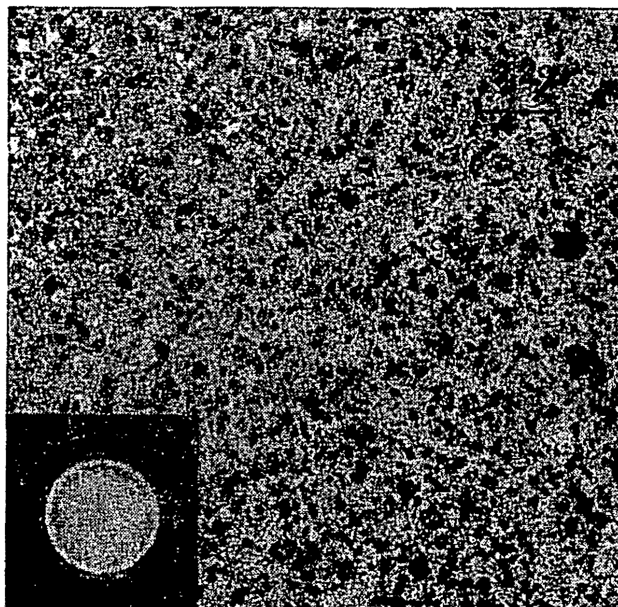

Fig. 1. Vapour quenched Al — 1.26 at % Sn thin film, as deposited. Inset: electron diffraction pattern.

by Dushman[5]. These concentrations were subsequently verified by means of an electron probe analysis. It was found that film composition, can be predicted with a high accuracy taking into account the vapour pressures of the metallic components. The thickness of the films was determined by means of a Sloan interferometer using test films evaporated at the same time on substrates placed in the immediate vicinity of the main substrate.

Electrical measurements were performed »in situ« without breaking the vacuum. The film resistance was measured by the four-point method using a microvolt recorder. The films were all evaporated on the substrate held at liquid nitrogen temperature and then using a resistance heater were heated at a constant rate of 1 — 3 K/min.

In some cases isothermal annealing periods were incorporated into the annealing program. The temperature was recorded simultanously with the resistance by means of a Cu-constantan thermocouple which was glued to the substrate very close to the film.

3. *Electron microscope measurements*

The quenched Al-Sn films were investigated by means of a Philips type EM 300 electron microscope using the hot stage. The as-deposited films were found to be crystalline with the grain size of the order of 100 Å (Fig. 1). Visual inspection of the intensities of diffracted electron beams showed that the texture, if any, is very weak. The Al-5.1 wt% Sn alloy electron diffraction pattern showed no tin reflections (Fig. 1, inset).

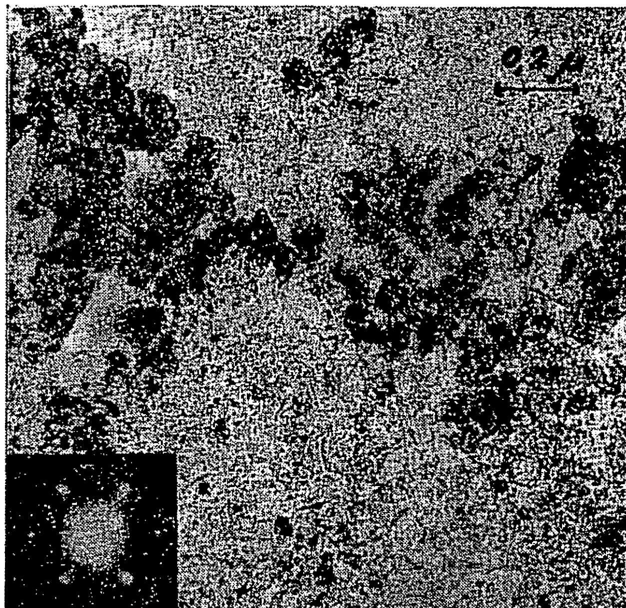

Fig. 2. Vapour quenched Al — 1.26 at % Sn thin film, annealed up to 300 °C. Inset: electron diffraction pattern showing Al and Sn reflections.

After annealing the films in the microscope through an isochronal annealing procedure, an exaggerated grain growth of quenched Al-Sn alloy was

observed. The low index axes of the grains were observed to be perpendicular to the supporting SiO layer, as shown in Fig. 2, and determined from a number of diffraction pattern. Rapid grain growth was observed to start at about 250 °C and to continue to 400 °C. At about 450 °C sublimation of the film from the SiO substrate began to take place.

The appearance of β-Sn precipitates after annealing and the absence of tin diffraction rings in the as-deposited alloy films indicate that a solid solutions of tin in aluminium was obtained. The composition of 5.1 wt% Sn corresponds to 1.26 at% Sn and is about sixty times the equilibrium solubility.

4. Electrical measurements

A few thin films of Al + 1.26 at% Sn were subjected to electrical resistance measurements during the annealing. A typical annealing curve obtained through constant heating rate is shown in Fig. 3. Since the resistance depends on the structural state of the material such a curve contributes to the insight in the morphology of recovery and the phase transition. This curve is essentially different from similar curves obtained with thin films of pure metals as well as dilute alloys[6]. Thin films of pure metals[7] show a

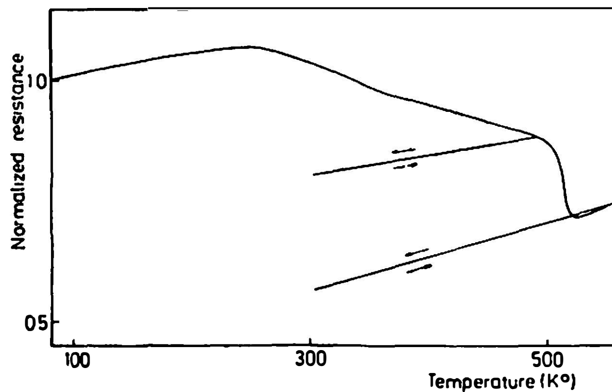

Fig. 3. Normalized resistance versus annealing temperature for constant rate heating of about 1 K/min of an Al + 1.63 at % Sn thin film.

drastic and almost linear decrease of resistivity from the temperature of deposition to room temperature where the recovery of the films is more or less complete. In the case of dilute alloys[6] a continuous decrease of resistivity from the temperature of deposition is slower and continues beyond room temperature to the temperature of decomposition where it is somewhat more rapid. Beyond this temperature the resistivity increases indicating that the transition is complete.

All the Al-1.63 at% Sn films that we investigated showed five regions where the electrical resistance behaved differently. This special behaviour we may attribute to the presence of Sn as a component of the alloy.

The first region between 80 K and 250 K is characterised by a slow, almost linear, increase in resistance. A high residual resistivity of freshly evaporated films shows a highly disordered structure which thermal agitation cannot »repair« by heating in this region. The resistivity of the films is calculated[8, 9] to be about 36 $\mu\Omega$ cm. Between 250 K and 350 K a relatively fast drop in resistance is observed. A high binding energy between vacancies and Sn atoms in aluminium suggests[10, 11] that vacancy trapping takes place here together with the formation of complexes which contribute less to resistivity[12]. After 350 K we observe a somewhat slower decrease in resistance up to 490 K which suggests a recombination of the complexes and a gradual anihilation of vacancies. The interval from 490 K to 525 K is characterised by a sudden and drastic drop in resistance which strongly suggests a phase transition. This is supported by electron microscopy examination which shows that decomposition of a single phase solid solution of an f. c. c. structure takes place with the emmergence of separate Al and Sn stable phases. Beyond 575 K the resistance begins to rise indicating that the phase transition is complete. Fig. 3 also shows two plots obtained by fast cooling of the sample to room temperature and immediate reheating to the original temperature both before and after the phase transition. Such cycles are characterised by reversible behaviour of the resistance with a somewhat greater

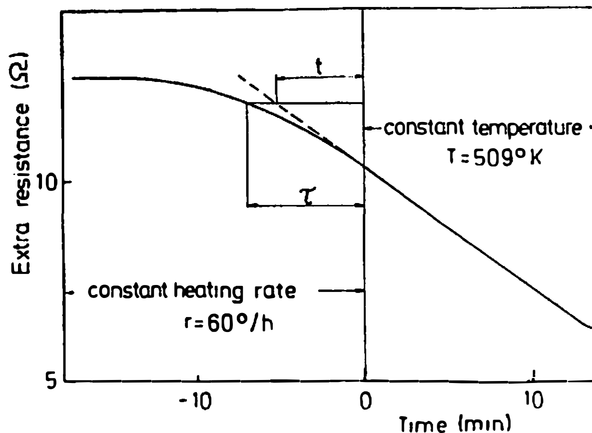

Fig. 4. Combination of isochronal and isothermal annealing used for activation energy determination of an Al + 1.26 at % Sn thin film.

positive temperature coefficient after the phase transition. These plots are used in calculating the activation energy and resistivity of the film sample.

Since the energy of vacancy — Sn coupling as well as the energy of vacancy migration are both known for bulk material, our main interest is

centered on the activation energy of Al-Sn alloy decomposition. In order to avoid exposing the films to air and thus to introduce an uncertainity factor in the annealing process, its kinetics was investigated by a combination of isochronal and isothermal annealing. The result of a modified Meechan-Brinkman[13] analysis used for calculating the activation energy of the film decomposition is shown in Fig. 4. In this case the standard formula for activation energy is

$$\ln\left(\frac{\Delta t_i}{\Delta \tau_i}\right) = \frac{E}{k}\left(\frac{1}{T_0} - \frac{1}{T_i}\right),$$

where Δt_i and $\Delta \tau_i$ are the times measured from the boundary point between the isothermal and constant rate curves. T_0 is the isothermal annealing temperature while T_i is the temperature corresponding to a fixed value of electrical resistance on the constant heating rate curve. The values of activation energy obtained for various values of t and τ are found to be between 1.36 and 1.59 eV. In order to find out whether or not we are dealing with a unique activation process in this temperature interval one uses the following expression

$$\ln \Delta t_i = c' + c'' - \frac{E}{k T_i}.$$

So $\ln \Delta t_i$ bears a linear relationship with $\frac{1}{T_i}$ and the slope of the line is $-\frac{E}{k}$ for a unique activation process. Within the experimental error involved, we have obtained a rather good linear fit which is shown in Fig. 5. The mean activation energy which determines the slope of the line is found to be 1.46 eV.

5. Conclusion

Solid solutions of Al + up to 5.1 wt% Sn were obtained by means of a »vapour quenching« technique on a substrate held at liquid nitrogen temperature. The freshly evaporated films were of a single phase crystalline f. c. c. structure. Sn impurity is known to have a high energy for vacancy binding. The influence of its interaction on electrical resistance has been observed during the annealing of Al—Sn alloy in the temperature interval of 250—350 K. This influence is qualitatively similar to that in diluts Al—Sn bulk alloys and so it can be described in the same way as being due to the formation complexes of Sn atoms and vacancies. A single transition is detected in the temperature interval between 495 K and 525 K where a single phase solid

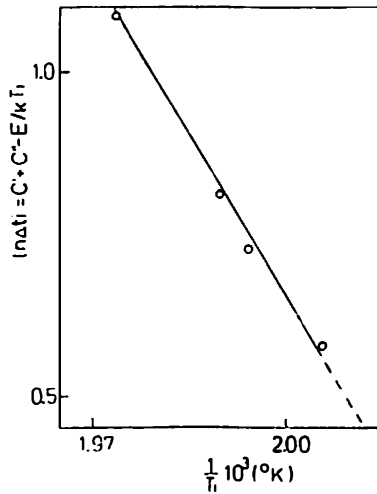

Fig. 5. Curve $\ln \Delta t_i$ versus $\frac{1}{T_i}$ indicating existence of unique activation process.

solution is transformed into a two-phase structure of separated Al and Sn which is confirmed by electron microscopy observations as well as by electrical measurements. The activation energy for this process is calculated to be (1.45 ± 0.15) eV.

On the basis of the value of activation energy as well as the electron microscopy observation it seems likely that the decomposition process proceeds by heterogenous nucleation at the grain boundaries and the growth proceeds by grain boundary diffusion.

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NAPUŠTANJE Al-Sn TANKIH SLOJEVA KALJENIH IZ PLINOVITE FAZE

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Sadržaj

Tanki slojevi čvrstih otopina Al sa raznim koncentracijama Sn dobiveni su pomoću tehnike kalenja iz plinovite faze. To je jedina metoda, koja omogućuje šire istraživanje ovih legura, zbog vrlo slabe međusobne topivosti ovih metala.

Dobiveni tanki slojevi istraživani su korištenjem elektronske mikroskopije i električnih mjerenja. Upravo napareni tanki slojevi bili su jednofazne kristalinične fcc metastabilne čvrste otopine čija homogenost i koncentracija je ustanovljena pomoću elektronske mikroskopije. Električna mjerenja vršena »in situ«, bez prekidanja vakuuma, pokazala su jak utjecaj interakcije Sn nečistoća i vakancija u području 250—350 K.

Ponašanje električnog otpora, kvalitativno slično onome na vrlo razrijeđenim Al—Sn legurama, dade se objasniti velikom energijom vezanja Sn atoma i vakancija. U području iznad 500 K detektiran je i pomoću EM i električnih mjerenja jedinstveni fazni prijelaz koji rezultira u dvofaznom sistemu gdje su Al i Sn separirani. Iz električnih mjerenja proračunata je i vrijednost aktivacione energije za taj proces koja iznosi (1.45 ± 0.15) eV.