FIZIKA 2 Suppl. 2 (1970) 

# STUDY OF Al-RICH Al-Sn ALLOYS RAPIDLY QUENCHED FROM THE VAPOUR PHASE

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## Introduction

By applying the "two piston" method(1), highly extended solid solubility was obtained in Al-Sn(2) system. The solubility of tin in aluminium was extended to 0,26 at.% Sn, i.e. eleven times the equilibrium solubility at 610°C(3), as reported by A. Kirin and A. Bonefačić.

The "freezing effect" is expected to increase with the quenching rate, so that intimate mixtures of atoms of unfavourable stacking factors can be realized by applying sufficiently high quenching rates. This can be well demonstrated by the use of the "vapour quenching" technique (4) in which the components are co-evaporated onto a cold substrate. The substrate is kept at such a low temperature that the mobility of the arriving atoms is greatly reduced. When different atoms arrive succesively at the substrate, they are forced to mix at random and homogeneously. The quenching rates are considered to be of the order of $10^7$ to $10^8$ deg/s(5), which is approximately a hundred times the rates obtained by splat-cooling techniques (1,5).

This paper reports on the results of an investigation of vapour quenched Al-rich Al-Sn alloys by means of electron probe analysis and hot-stage electron microscopy.

## Experimental

Carefully weighed batches of Al-Sn alloys of 2,5 and 19 wt.% Sn nominal concentrations were prepared by induction melting in vacuum at $3 \cdot 10^{-5}$ Torr and 800°C. Pure Al and the Al-Sn alloy films were obtained by deposition onto polished copper substrates, coated with an amorphous SiO layer approximately 300 Å thick. The temperature of the liquid-nitrogen-cooled copper substrate was 83°K, and its increase during evaporation 6 deg. maximum. The alloy was evaporated from a single source at 1000°C and at a pressure $3 \cdot 10^{-6}$ Torr in the evaporation unit. The deposition rate was calculated to be 10-20 Å/s approximately. The concentrations of tin in quenched alloy films were calculated with the help of the Langmuir-Raoult expression(6), using the vapour pressure values given by Dushman (7).

## Results and discussion

These concentrations were measured and determined by means of the electron probe analysis, using the method developed by Hutchins(8) and Djurić and Cerović(9). The results of calculations are shown in Table I. Comparing the calculated ($c^{NC}$) and measured ($c^{ME}$) values, one can see that the concentrations of tin in aluminium can be predicted with great accuracy using evaporation from a single source and taking into account the vapour pressure effect.

TABLE I

$c^{N}$, $c^{NC}$ and $c^{ME}$ are nominal, calculated and measured concentrations, respectively. p-vapour pressure, M-atomic mass, I-characteristic X-ray intensity in the probe analysis.

Vapour quenched Al-Sn alloys
Concentration calculation and measurement:

$$\frac{C_{Sn}^{NC}}{C_{Al}^{NC}} = \frac{C_{Sn}^{N}}{C_{Al}^{N}} \cdot \frac{p_{Sn}}{p_{Al}} \sqrt{\frac{M_{Al}}{M_{Sn}}} \qquad (1)$$

$$a\frac{C_{Sn}^{ME}}{C_{Al}^{ME}} = b \qquad C_{Sn}^{ME} + C_{Al}^{ME} = 1 \qquad (2)$$

$$a = \frac{\left(\frac{I_F}{I_M}\right)_{Sn}^{ST}}{\left(\frac{I_F}{I_M}\right)_{Al}^{ST}} \qquad b = \frac{\left(\frac{I_F^{ALL}}{I_M^{ST}}\right)_{Sn}}{\left(\frac{I_F^{ALL}}{I_M^{ST}}\right)_{Al}}$$

| $C_{Sn}$ (wt%) | N | NC | ME | $\frac{C^{ME}-C^{NC}}{C^{ME}}$ |
|---|---|---|---|---|
| | 2 | 0.65 | 0.72 | + 10 % |
| | 5 | 1.63 | 1.44 | - 10% |
| | 19 | 6.85 | 5.1 | - 35% |

Al and Sn reference films, evaporated onto a glass substrate at room temperature, together with the quenched Al and Al-Sn films were investigated by means of an electron microscope using the hot stage. The as-obtained Al and Al-Sn quenched films were observed 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.2).

After annealing the films in the microscope applying an isochronal annealing process, an exaggerated grain growth of quenched Al and Al-Sn alloys was observed. The low index axes of the grains were observed to be perpendicular to the supporting amorphous SiO layer, as shown in Fig.3, and determined from a number of

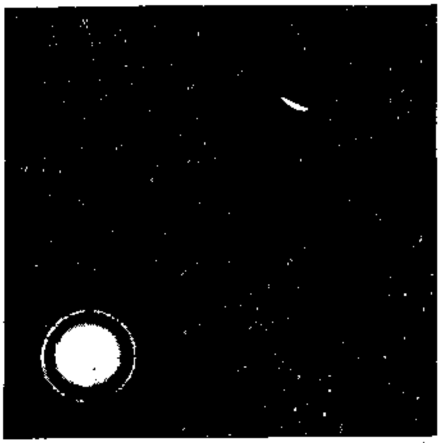

FIG. 1

Vapour quenched (VQ) aluminium thin film, as obtained.

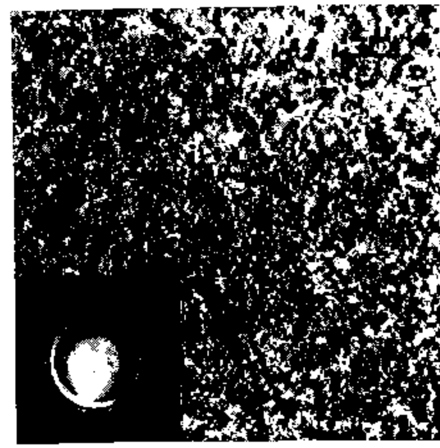

FIG. 2

VQ Al-5.1 Wt.%(1.26 at.%)Sn thin film, as obtained.


FIG. 3

Aluminium thin film, VQ and annealed up to 200°C.


FIG. 4

Al-5.1 wt.% Sn alloy, VQ and annealed up to 300°C.

diffraction patterns. Rapid grain growth in pure Al films was observed to start at about 200°C and continue to 400°C when the entire polycrystalline film was consumed by a few big grains of 4 μm or more in lateral size. Rapid grain growth in the Al-Sn alloy films was observed to start at about 250°C and to continue to 400°C (Fig.4). The sublimation of the films out of the SiO substrate took place at approximately 450°C.

Examination of several diffraction patterns of the Al-5.1 wt.% Sn alloy showed that the $\beta$-Sn $\{200\}$ reflections are at a definite orientation to the matrix (Al) reflections, i.e. close to $\{111\}$. (Fig.4). The analysis of possible orientation relationships between Al matrix and $\beta$-Sn precipitates showed the $\{111\}_{Al} \parallel \{100\}_{Sn}$ and $\langle 110 \rangle_{Al} \parallel \langle 001 \rangle_{Sn}$ orientation relationships as the most probable.

We attribute the exaggerated growth of the low index zone axis grains to the influence of amorphous SiO substrate, as no such grain growth was observed in the aluminium and tin films evaporated onto the glass substrate and annealed in the microscope.

The appearance of $\beta$-Sn precipitates after annealing, and the absence of tin diffraction rings in the as-obtained alloy films, we take as arguments for the statement that a solid solution of tin in aluminium was obtained. The maximum concentration of solid solution was estimated to be 5.1 wt.% (1.26 at.%) Sn. This is approximately sixty times the equilibrium solubility. We have not as yet found an upper limit of tin solid solubility in aluminium obtainable by this technique.

Acknowledgements

This work was sponsored by the Federal Fund for Scientific Research, Belgrade, and by the Republican Fund for Scientific Research, Zagreb, Yugoslavia.

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## DISCUSSION

**R.W. Cahn:** What do you mean by temperature as applied to a single atom moving in a straight like through a vacuum ?

**D. Kunstelj:** I haven't mentioned the temperature of atoms in my report. The alloy was evaporated from a single source at 1000°C. The vapour pressure of Al at this temperature is $3 \cdot 10^{-4}$ torr and that of Sn $2 \cdot 10^{-4}$ torr (see Dushman ). The temperature rise of the substrate during the evaporation I have reported to be 6° max. (Radiation of the heated source + kinetic energy transfer from arriving atoms + heat of crystallisation).

**P. Duwez:** How did you estimate the rate of vapour quenching $10^7$–$10^8$ °C/sec ?

**D. Kunstelj:** All I have said was that it is considered that the C.R. is $10^7$–$10^8$ °C/sec, and this was reported by L.M. Burow and A.A. Iakunin (Zh.Fiz.Himii 424(1968) 1028/z).