

Preparation of Tin Single Crystals for Transmission Electron Microscopy*

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THE investigation of metals by transmission electron microscopy has become almost general in its application. Accordingly, methods of preparing thin foils have been developed for a large number of metals and alloys.^{1,2} However, a preparation method for tin has not been reported and this paper will describe an electropolishing technique used for thinning down single crystals of tin.

The crystals, which had been grown by a controlled orientation technique (Chalmers³), originally had dimensions 1×20×40 mm. The orientations of the large faces were generally either (001) or (110).

The thinning by electropolishing was carried out in two stages. The first stage brought about rapid dissolution of the specimen down to a thickness of about 0.2 mm without producing a bright polish. In the second stage, which required a much lower current density, a mirror like polish was obtained. The details of the two stages are as follows:

(i) Rapid dissolution of bulk specimen. First, the edges of the specimen were insulated. For this purpose a lacquer known as "Microstop" (manufactured by Michigan Chrome and Chemical Company of Detroit) was found to be excellent.

The specimen was then mounted symmetrically between two stainless steel cathodes, each about four times the area of the specimen. The specimen was parallel to the cathodes and spaced about 2 cm from them.

The polishing bath consisted of 20% perchloric acid (62%), 10% ethylene glycol monobutyl ether (butyl cellosolve) and 70% ethyl alcohol. About 12 v was applied to the cell which was kept at a temperature of 15–20°C. The rate of stirring was moderate. It is important to ensure that the stirrer does not cause a turbulence at the specimen surface, since this produces a rippled surface. After the specimen had reached a thickness of about 0.2 mm, this stage of the polishing was discontinued.

(ii) Final stage. One side of the specimen was blanked off completely with lacquer, while the other was masked along the edges leaving exposed a slightly smaller area than before.

The electrolyte consisted of 5% perchloric acid (62%), 10% butyl cellosolve, and 85% ethyl alcohol. A potential of about 30 v was applied to the electrode arrangement, which was similar in principle to that described by Boswell and Smith.² The main differences were that only one pointed cathode was used and the specimen was mounted at 60° to the vertical, tilted toward the cathode. The separation between the cathode point and the specimen was about 5 mm.

The reason for the slantwise arrangement of the specimen was to slow down the flow of the viscous layer of reaction products, since this produced a better polish. For the same reason the stirring was so arranged that the flow of the electrolyte over the specimen surface would retard the flow of the viscous layer. It is again important that no turbulence should be produced at the surface, and the viscous layer should flow at a slow but uniform rate.



FIG. 1. Dislocations and a twin in a deformed single crystal foil of tin. ×60 000.

The bath temperature was kept at 10°C.

The first side was polished until a mirror like finish was obtained, after which the sample was washed in a stream of water and then placed in acetone to dissolve the lacquer. The polished side was then blanked off completely with lacquer and the same polishing procedure carried out on the other side. On this occasion, however, polishing was continued until holes appeared in the center of the specimen, after which it was washed in water and ethyl alcohol and dried. The material near the edges of the holes was generally sufficiently thin for electron transmission.

It should be noted that during the final stage of polishing, the specimen was at all times backed with a thick layer of lacquer, which prevented any deformation from being introduced during polishing. Thus it was possible to preserve the single crystal nature of the foils, which were later examined⁴ with special reference to the formation and growth of twins. An example of twins and dislocations as they appeared in a deformed single crystal foil of tin, is shown in Fig. 1.

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¹ P. M. Kelly and J. Nutting, *J. Inst. Met.* **87** (12), 385 (1959).

² F. W. C. Boswell and E. Smith, ASTM Special Technical Publication **245**, 31 (1959).

³ B. Chalmers, *Can. J. Phys.* **31**, 136 (1953).

⁴ J. T. Fourie, F. Weinberg, and F. W. C. Boswell (to be published).

Continuous Series of Metastable Solid Solutions in Silver-Copper Alloys*

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A TECHNIQUE has been devised by which small amounts of liquid alloys can be cooled at rates high enough to prevent the normal process of nucleation and growth of equilibrium phases. The classical method for achieving high rates of cooling consists of injecting a small droplet of molten alloy into a liquid quenching bath. Olsen and Hultgren used such a technique in a study of the effect of the rate of cooling on the homogeneity of solid solutions.¹

The rate of heat transfer between a metallic liquid droplet and the quenching liquid is limited by the formation of a gaseous layer due to the evaporation of the quenching liquid. This limitation can be removed by replacing convective heat transfer through the vapor layer by conductive heat transfer between the liquid alloy and a solid wall made of a good heat conductor. In this case two conditions must be satisfied. First, the liquid alloy must strike the cold surface at high speed in order to spread the liquid into a thin layer. Secondly, a good contact must be assured between the liquid alloy and the target material during the process of solidification. The first condition has been satisfied by propelling a small liquid droplet (about 25 mg) by means of a shock wave against a solid copper target. In regard to the second condition, a high speed rotating cylinder was used as the target; the liquid was ejected against the inside surface of the cylinder at a suitable angle. The centrifugal force acting on the molten material insured a good thermal contact with the target. The relative motion of the target and the droplet also helped in spreading the liquid over a larger area. This spreading led to a thinner layer of solidified material, and hence a large over-all heat transfer rate.

Experiments were made with copper-silver alloys. In this system a eutectic exists at 60.1 at. % Ag, 39.9 at. % Cu, and there is a limited solid solubility range at both ends of the phase diagram.

The copper-silver system was chosen as a crucial test of the method because the existence of a eutectic is not in agreement with the Hume-Rothery rules, which would predict complete miscibility of the two metals. Four alloys containing 23.0, 39.9 (eutectic composition), 62.9, and 88.5 at. % copper were quenched from melt. The x-ray diffraction patterns of these alloys showed a single phase. On a plot of unit cell size vs concentration, the lattice parameters obtained with the four metastable alloys fell on a smooth curve connecting the two previously known segments of curves within the solubility limits at both ends of the phase diagram (14.1 and 95.1 at. % Cu). The maximum deviation from linearity (Vegard's law) was less than 1% at 50% Cu. Such a deviation is not unusual in solid solution binary alloys. These results establish without doubt that, during solidification, the two stable phases, copper rich and silver rich, did not have time to nucleate and grow, and metastable solid solutions were obtained.

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¹ W. T. Olsen, Jr. and Ralph Hultgren, *Trans. AIME*, **188**, 1223 (1950).

acteristic of a body-centered cubic structure, has a prominent role in lowering the free energy of this phase at high temperatures.

The interpretation of the structure of alloys containing less than 16.4 at. % Ge has not been completed. It appears, however, that the solubility of germanium in face-centered cubic silver is extended beyond 9.6 at. % Ge. In the alloys containing more than 25.7 at. % Ge, both the hexagonal compound and diamond cubic germanium were found. No measurable change in the lattice parameter of the diamond cubic germanium could be observed. Because of the nearly equal size of silver and germanium (as deduced from the change in lattice parameter at the silver-rich end of the phase diagram),⁴ and the openness of the diamond cubic lattice, silver could probably be retained in the germanium structure without any appreciable change in the cell size. Therefore, measurements other than the lattice parameter will be necessary to establish whether there is any significant solubility of silver in germanium.

¹ P. Duwez, R. H. Willens, and W. Klement, Jr., *J. Appl. Phys.* **31**, 1136 (1960).

² M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill Book Company, Inc., New York, 1958).

³ W. Hume-Rothery, G. V. Raynor, P. W. Reynolds, and H. K. Packer, *J. Inst. Metals* **66**, 209 (1940).

⁴ E. A. Owen and V. W. Rowlands, *J. Inst. Metals* **66**, 361 (1940).

Metastable Electron Compound in Ag-Ge Alloys

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IN the previous Letter to the Editor,¹ the existence of a continuous series of metastable solid solutions in Cu-Ag alloys was reported. By quenching the molten alloys rapidly enough, the normal processes of nucleation and growth were prevented and solid solutions were obtained. These metastable solid solutions were predictable since copper and silver satisfy the criteria for complete solid solubility proposed by Hume-Rothery.

In Ag-Ge alloys complete solid solubility is precluded because of dissimilar crystal structures. The Ag-Ge equilibrium phase diagram² is of the eutectic type with a maximum solubility of germanium in silver of 9.6 at. % and negligible solubility of silver in germanium. The eutectic composition is at 25.9 at. % Ge. It was expected that the solubility limits on both ends of the phase diagram would be extended by rapid quenching. An alloy containing 25.7 at. % Ge was quenched from the melt. This alloy had a crystal structure that was neither face-centered cubic nor diamond cubic, but rather hexagonal close-packed with $a=2.987\pm 0.003$, $c=4.716\pm 0.002$, and $c/a=1.628\pm 0.003$. The presence of a small amount of a diamond cubic germanium phase was indicated by a few weak diffraction peaks on the x-ray pattern. The new metastable hexagonal phase is considered to be an electron compound with an electron concentration of 7/4 electrons/atom.

In 1940, Hume-Rothery *et al.*³ suspected the existence of a $\frac{3}{2}$ electron compound in Ag-Ge alloys, but failed to detect it under equilibrium conditions. In order to determine if such a compound could be synthesized by rapid quenching, an alloy containing 16.4 at. % Ge was investigated. No body-centered cubic phase was found, but again a hexagonal close-packed structure occurred with $a=2.891\pm 0.002$, $c=4.718\pm 0.006$, and $c/a=1.632\pm 0.003$. The existence of the hexagonal structure instead of the body-centered cubic structure at the electron concentration of $\frac{3}{2}$ has been noted in other alloy systems. Satisfactory explanations for the occurrence of a hexagonal close-packed structure in the region of a $\frac{3}{2}$ electron concentration have not been advanced. It might be noted, however, that when a $\frac{3}{2}$ electron compound (β -phase) does exist, it is usually more stable at high temperatures. It is probable that the electronic configurational energy is not the main factor in creating a $\frac{3}{2}$ electron compound (β -phase). It is suggested that the high-lattice entropy contribution, char-

Erratum: Motion of High-Speed Arc Spots in Magnetic Fields

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J. Appl. Phys. **30**, 1813 (1959).]

IN Fig. 5, the A at the left of the figure should be replaced by (b) and the B at the left side of the figure should be replaced by (a).

Books Reviewed

Prompt, noncritical reviews appear in this column. Critical reviews of many of the books described here will appear in Physics Today, The Review of Scientific Instruments, or American Journal of Physics.

Exploding Wires. W. G. CHACE AND H. K. MOORE, EDITORS.
Plenum Press, Inc., New York, 1959. Price \$9.50.

The collection of papers which were presented at the conference on the exploding wire phenomenon (April, 1959) comprises the first book published on this topic. These have been arranged into three broad groups: theoretical and experimental, shock wave, and applications and techniques. For those who are not acquainted with this field, the editor, W. G. Chace, has written an introduction which is compact and informative. In the papers which follow, many aspects dealing with the electrical, optical, spectroscopic, and radiometric observations are covered. The variety of uses of exploding wires listed and the collection of specialized techniques which have been developed, as described in this volume, will make a useful addition to the store of "knowhow" for operations in this range of very rapid discharges from high-capacity condensers, of the production of intense light sources, and of very high temperatures.