Letters

Structure and Microstructure Study on Splat-Cooled Cadmium

In recent years several liquisol-quenching* techniques have been developed which enable metals and alloys to be quenched extremely rapidly from the liquid state. Although a large number of binary alloys rapidly quenched from the liquid state have been examined, only a few investigations have been made on pure metals. The aims of the present work were to study the influence of liquisol-quenching on the structure and microstructure of pure cadmium and the change of this microstructure under isothermal annealing at elevated temperatures.

Experiments were carried out on refined samples, with a stated purity of 99.9% pure cadmium. Charges of about 3g were melted in a graphite crucible using purified hydrogen atmosphere and then they were cooled slowly. The liquisol-quenched foils were obtained by a piston-and-anvil technique similar to that described by others [2-4]. The liquisol-quenching apparatus used for this work has been described in detail elsewhere [5]. The foils were circular up to about 20 mm in diameter and about 40 μm thick and quite uniform. The resulting thin foils were studied by means of X-ray methods and metallurgical microscopy.

Diffractometer recordings of cadmium foils were obtained by using CuK_α-radiation with an Ortec Si (Li)-detector. The Si (Li) semiconductor detector has an energy resolution (about 240 eV for 14.4 keV ^{57}Co γ-radiation) sufficient to eliminate both the K_β- and fluorescence radiation from the sample without using filters. X-ray diffraction charts of foils which have been (a) liquisol-quenched, (b) liquisol-quenched and then annealed for 1 h at 200°C, (c) the same, further annealed 19 h at 200°C and (d) a slowly cooled powder sample, are shown in fig. 1.

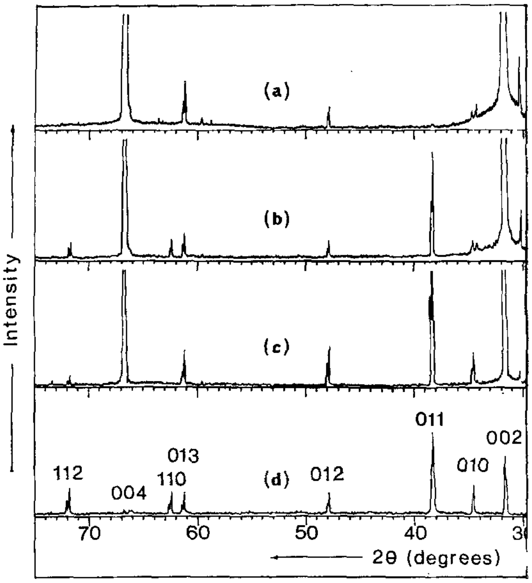

Figure 1 The diffraction patterns observed from a pure cadmium specimen. (a) Liquisol-quenched foil. (b) Previous foil annealed for 1 h at 200° C. (c) More annealed for 19 h at 200° C. (d) Slowly cooled powder specimen.

The very strong (002) and (004) reflections on the liquisol-quenched foil may be explained on the basis that the liquisol-quenched foil had an equiaxed microstructure and, at the same time, a high degree of preferred orientation. However, in some zones near the external surface of the foil which had been in contact with the copper anvil and the copper piston, the grains were columnar and parallel to the thermal gradient. This was found when a cross-section of liquisol-quenched foil was examined under optical microscope.

For the examination of preferred orientation, the single-channel analyser of the diffractometer system was replaced by a 512-channel pulse-height analyser and Bragg's law could be applied in a new way [6]. The sample was irradiated by polychromatic X-rays (Cu target at 16 mA and 40 kV) and the detector at a fixed 2θ angle determined the energies (wavelengths) which fulfil Bragg's law. The amplifier gain was adjusted so that the energy region was between 10 and 30 keV. The calibration of the energy range was performed with standard sources of ^{57}Co and ^{241}Am. The diffractometer was set to a predetermined low Bragg angle ($2\theta = 24°$) and the counting time in every exposure was 5 min. When a liquisol-quenched foil was etched in hydrogen peroxide solution (70 ml hydrogen peroxide (30%), 3 ml sulphuric acid and 927 ml water) for different times, remarkable changes were found on the spectrometric polycrystal diffraction chart as shown in fig. 2. This could

---

*The term liquisol-quenching refers to rapid cooling that involves transition from liquid to solid [1].

indicate a decrease in the degree of preferred orientation when moving from the surface to the interior of the foil.

Isothermal heat-treatments of the liquisol-quenched foils were carried out by using an Anton-Paar high temperature attachment for the diffractometer. In fig. 3 are shown four charts which give a record of counts per channel vs. X-ray energy or wavelength.

The cadmium foils were heated at 155, 186 and 220°C and the change of the corrected relative intensity, k, is plotted against the annealing time in fig. 4. The corrected relative intensity, k, of the (002) line was obtained from the relation

$$k = \frac{I_{002}}{I_{\mathrm{Cd}K_\alpha}} : \frac{I^0{}_{002}}{I^0{}_{\mathrm{Cd}K_\alpha}},$$

where $I^0{}_{002}$ and $I^0\mathrm{Cd}K_\alpha$ are the integrated intensities from the liquisol-quenched foil. (Here $I_{\mathrm{Cd}K_\alpha}$ is the intensity of the CdK_α fluorescent emission, which is not affected by crystallographic changes).

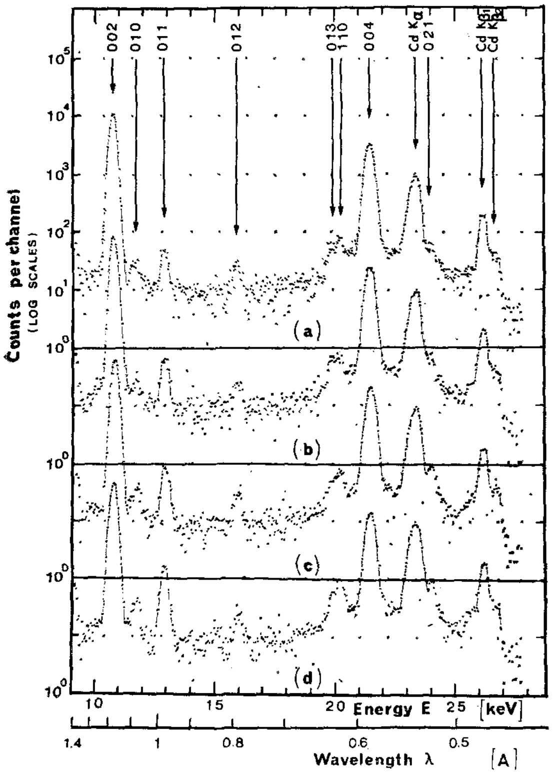

Figure 2 Variation of the spectrometric polycrystal diffraction chart of a pure cadmium specimen after the following sequential treatments. (a) Liquisol-quenched foil. (b) After 60 sec etch. (c) After 240 sec etch. (d) After a heavy etching.

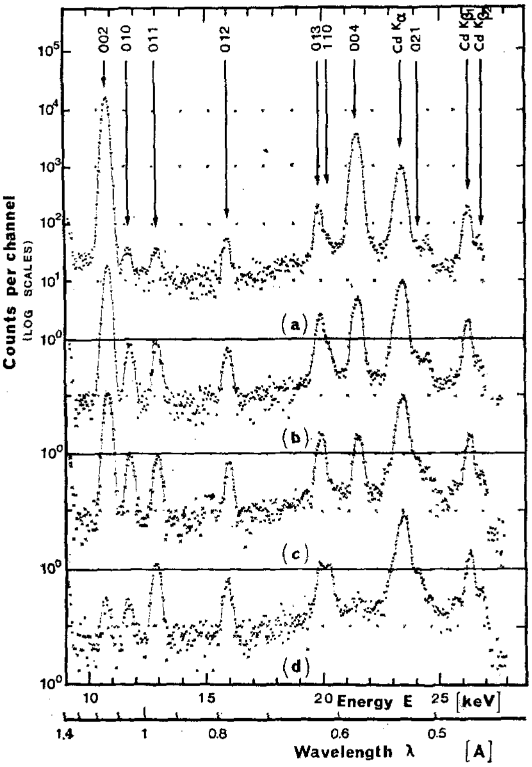

Figure 3 Variation of the spectrometric polycrystal diffraction chart of a pure cadmium specimen. (a) Liquisol-quenched foil. (b) Previous foil annealed for 1 h at 200°C. (c) More annealed for 19 h at 200°C. (d) Slowly cooled powder specimen.

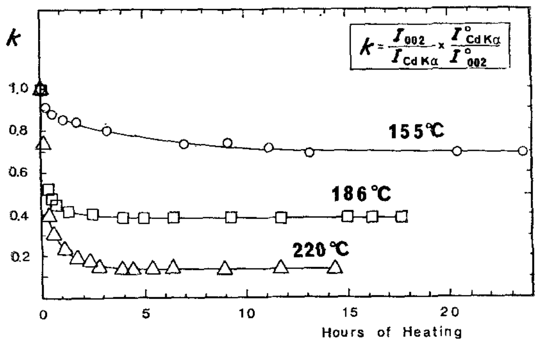

Figure 4 The corrected relative intensity of 002 reflection, *k*, as a function of the annealing time for three different temperatures.

The activation energy for the decrease in the degree of the preferred orientation was determined from the curves of fig. 4 by using the well-known Arrhenius equation. A value of

TABLE I Lattice parameters of Cd at room temperature (25° C).

Specimen	a[Å]	c[Å]	V[Å^3]	c/a
Liquisol-quenched foil	2.9775	5.6126	43.0921	1.8850
+ 1 h at 200° C	2.9787	5.6149	43.1446	1.8850
+ 19 h at 200° C	2.9785	5.6166	43.1518	1.8857
slowly cooled powder	2.9789	5.6184	43.1773	1.8861
slowly cooled powder [8]	2.9794 (2.9734 kX)	5.6186 (5.6073 kX)	43.1933	1.8858

The accuracy of the measurements is estimated to be 0.03 Å for a and 0.0010 for c/a.

(17.0 ± 1.8) kcal/mole was obtained for the activation energy.

The microstructure of liquisol-quenched foils and that of a melted and then slowly cooled specimen are shown in figs. 5a and b, respectively.

The grain size of liquisol-quenched foils varied from less than 5 μm up to about 10 μm in diameter. A small grain size resulted from very high solidification rate which can be obtained by liquisol-quenching.

According to Eshelby [7] a vacancy in a crystal lattice causes a change in the lattice parameter. Considerable increase in vacancy concentration

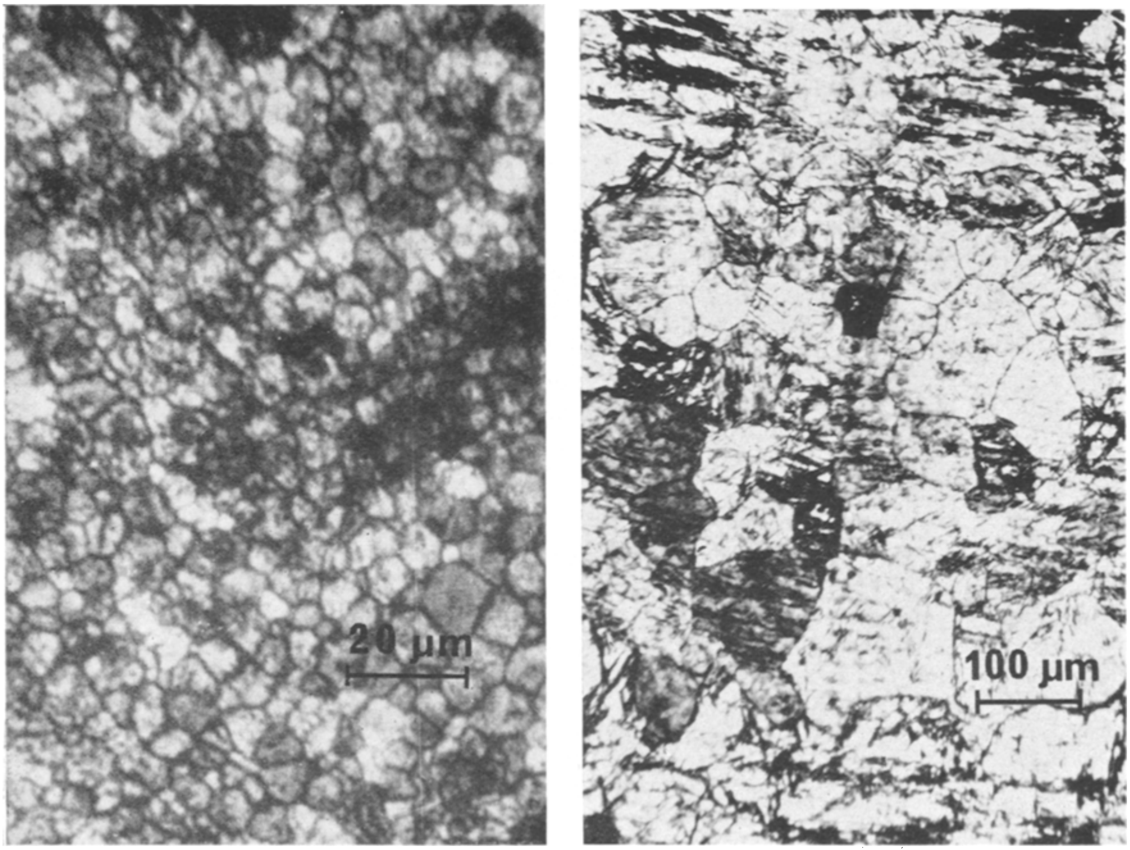

Figure 5 (a) Optical micrograph of an etched liquisol-quenched cadmium foil (× 750). (b) Optical micrograph of an etched slowly cooled cadmium foil (× 130).

can be obtained by liquisol-quenching. That is the reason why we decided to determine the lattice parameters of the liquisol-quenched foil. The lattice parameters of foils were determined by means of a Guinier X-ray diffraction camera, type XDC-700. These data, which are collected in table 1, can in principle be used to estimate vacancy concentrations.

Acknowledgements

The authors wish to express their cordial thanks to Professor M. Kantola for valuable discussions and comments. They also wish specially to thank Dr S. Seitsonen for his critical reading of the manuscript. Thanks are also due to Mr V. Viljanen for lattice parameter measurements.

References

1. C. SURYANARAYANA and T. R. ANANTHARAMAN, *J. Mater. Sci.* **5** (1970) 992.
2. P. PIETROKOWSKY, *Rev. Sci. Instr.* **34** (1963) 445.
3. J. N. BAKER, C. E. MIGHTON, and W. R. BITLER, *ibid* **40** (1969) 1065.
4. D. R. HARBUR, J. W. ANDERSON, and W. J. MARAMAN, *Trans. Met. Soc. AIME* **245** (1969) 1055.
5. E. LAINE, E. HEIKKILÄ, and I. LÄHTEENMÄKI (1971), to be published.
6. B. C. GIESSEN and G. E. GORDON, *Science* **159** (1968) 973.
7. J. D. ESHELBY, *J. Appl. Phys.* **25** (1954) 255.
8. D. A. EDWARDS, W. E. WALLACE, and R. S. CRAIG, *J. Amer. Chem. Soc.* **74** (1952) 5256.

Received 2 July
and accepted 13 July 1971

E. LAINE
I. LÄHTEENMÄKI
Institute of Physics 2
University of Turku,
Turku, Finland

Residual Stresses in Glass-Crystal Composites

When a body is composed of two or more constituents that differ in their thermal expansion behaviour, internal stresses occur within and in between the constituents. Several nondestructive techniques, such as X-ray diffraction [1] and thermal deflection [2], have been widely used for measuring these stresses. Bogardus and Roy [3], and Foster and Hughes [4], measured changes in the transition temperature of crystals in glass-crystal composites and calculated the stresses using the Clausius-Clapeyron equation. The present work is aimed at determining the transition temperature of well-known crystals in glass-crystal composites that were carefully prepared to minimise any chemical reactions between the glass and the crystal.

Two glasses and two crystals were chosen for the study. Glasses having thermal expansion coefficients of 13.80 and 6.70 × $10^{-6}/°C$ were selected [5]. The crystals chosen were cristobalite and silver iodide: cristobalite ($T_c = 260°C$) because of its very high thermal expansion coefficient; and silver iodide [6] ($T_c = 152°C$) because of its low thermal expansion coefficient. Both crystals have transition temperatures well below the softening point of the glasses. To minimise the chemical reactions between the glass and the crystal, the glass-crystal composites were fabricated by hot pressing at high pressures (10000 psi) for short periods of time (2 min.)

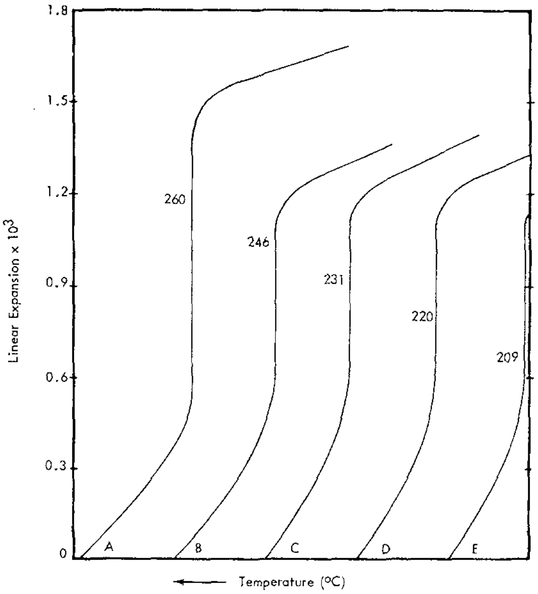

Figure 1 Dilation curves corresponding to various heating conditions imposed on a composite of cristobalite and glass I. Glass I had a thermal expansion coefficient of 13.80 (× $10^6/°C$).