the structures of Ag–Zn alloy films prepared by co-evaporation onto substrates held at room temperature. Under equilibrium conditions, the system Ag–Zn is known to form a γ brass-type phase, Ag_5Zn_8, around 61.5 at. % Zn. Michel [7] noted that the γ brass structure phase does not form during deposition, electron diffraction patterns denoting a β' phase (CsCl type) and a δ phase (close packed hexagonal). After ageing (three months at room temperature), the seven first electron diffraction peaks of the γ brass structure appeared on the spectra. Similar behaviour was observed on Cu–Al alloy films [7]. On the other hand, foils of Cu–Zn alloys prepared by L.Q. contain stable γ brass Cu_5Zn_8 [8]. Moreover, metastable γ brass structure phases were reported to appear in samples of Au–Si [9] and Au–Sn [10] obtained by L.Q.; Au–Si and Au–Sn are two alloy systems in which no γ brass structure phases exist under equilibrium conditions, constituting exceptions to the Hume-Rothery's empirical rules.

The above examples illustrate the fact that if one seeks in a given research for instance, to try and cancel the remaining exceptions to Hume-Rothery's empirical rules, preparing metastable γ brass structure phases, L.Q. will prove more effective than V.Q. The limitations of V.Q. and L.Q. are surely different. Apart from the rate of quenching, the important factors which seem to govern these limitations are the size of the unit cell (and the number of atoms in it) and maybe the degree of compactness of the desired alloy phase. These two points need investigation if an answer to the question "What are the controlling factors in the preparation of non-equilibrium alloys by vapour-quenching and rapid cooling from the melt?" is required.

Acknowledgements

The author wishes to thank Professor P. Duwez and Mr. J. Wysocki for a critical reading of the manuscript as well as Professor L. Danguy for his constant support.

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Received 14 January
and accepted 27 February 1974.

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Small-angle X-ray study of splat-cooled cadmium

There are only a few pure splat-cooled metals such as aluminium [1-4] and cadmium [5-7] that have been studied by X-ray diffraction methods. A reduction in lattice parameters of splat-cooled specimen both in aluminium and in cadmium has been reported in previous papers. This effect has been explained to be due to the excess vacancy concentration. Prodan and Bonefačić [2] as well as Dartyge *et al.* [3] have presented evidence for vacancy clustering in aluminium quenched from the liquid state by small-angle X-ray scattering. We have not found corresponding small-angle X-ray diffraction studies of splat-cooled cadmium in the literature. The second reason for this study was that we have a solid state detector by which it is possible to measure very weak scattering intensities from vacancy clusters.

The diffraction measurements were carried out by using a Kratky small-angle Kratky scattering camera. An Ortec Si(Li) semiconductor detector was used the energy resolution of which, FWHM, was about 300 eV for Mo$K\alpha$-radiation.

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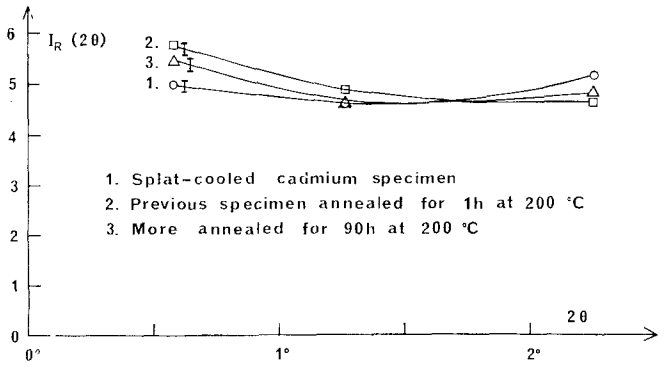

Figure 1 Intensity $I_R(2\theta)$ of diffuse scattering by 99.999% pure specimens as a function of 2θ. The measurements were made by using Mo$K\alpha$-radiation.

This resolution is sufficient to separate $K\alpha$- and $K\beta$-radiations. More details of measuring system are described in another paper [8]. Splat-cooled cadmium foils were produced by the piston and anvil technique, which has been reported previously [9].

The results have been collected in Fig. 1. Curve 1 has been obtained from splat-cooled cadmium specimens. Every point is the average of four measurements of different foils. Curves 2 and 3 represent the relative intensities of the same splat-cooled specimens for different annealing times at 200°C. All the measured intensities were corrected for the thickness of a foil. They also include thermal, Compton, double Bragg and background scatterings. In the case of pure metals, the total intensity is the same order of the magnitude as the sum of the parasitic ones and the major part of the parasitic scatterings is background scattering. The background scattering without a specimen was always measured before the measurement proper. The changes of the intensities were very small (about 1%). We can also assume that the magnitude of the thermal and Compton scatterings of a splat-cooled cadmium foil do not change essentially during the annealing treatment. The effect of the double Bragg scattering will be discussed below. Thus, the sum of the parasitic scatterings has a constant value and the changes between the three curves in Fig. 1 are primarily due to the changes of a small-angle scattering of a specimen. The features of these intensity curves considerably resemble those obtained by Dartyge *et al.* [3] from splat-cooled aluminium specimens.

The small-angle scattering intensity depends both on the scattering angle and the annealing time, as can be seen from Fig. 1. The vacancies are probably distributed nearly at random in the splat-cooled specimen. The very large reduction of lattice parameters of the splat-cooled cadmium specimen gives support to this interpretation [5-7]. Thus the small-angle scattering intensity of the splat-cooled cadmium specimen is very weak. When the specimen is annealed 1 h at 200°C, the vacancies begin to form small clusters. Thus the slope of the intensity curve increases (Fig. 1). The wide-angle X-ray diffraction measurements show that an anneal of 1 h at 200°C does not appreciably change the volume of the unit cell [5, 6]. Hence, most single vacancies have disappeared. When the annealing treatment is continued, the slope of the intensity curve decreases slightly. From this we conclude that the vacancies partly disappear.

On closer consideration of the weak small-angle scattering intensity of metal specimens, we have to take into account a possible double Bragg scattering. The wide-angle X-ray diffraction measurements show that the splat-cooled cadmium foil has a high degree of preferred orientation. The [001] direction is nearly parallel to the normal of the specimen surface [5]. In small-angle scattering measurements, the primary beam is perpendicular to the surface of the specimen. Therefore, the strongest Bragg reflections can be avoided. For this reason, the intensity of the double Bragg scattering from the splat-cooled specimen is extremely weak.

When the splat-cooled specimen is annealed, the preferred orientation is reduced and the grain size grows slightly (Fig. 2). The weak continuous diffraction rings in Fig. 2a are due to (106) and (213) planes. The increase of the Bragg reflections may also cause a small addition to the double Bragg scattering. The double

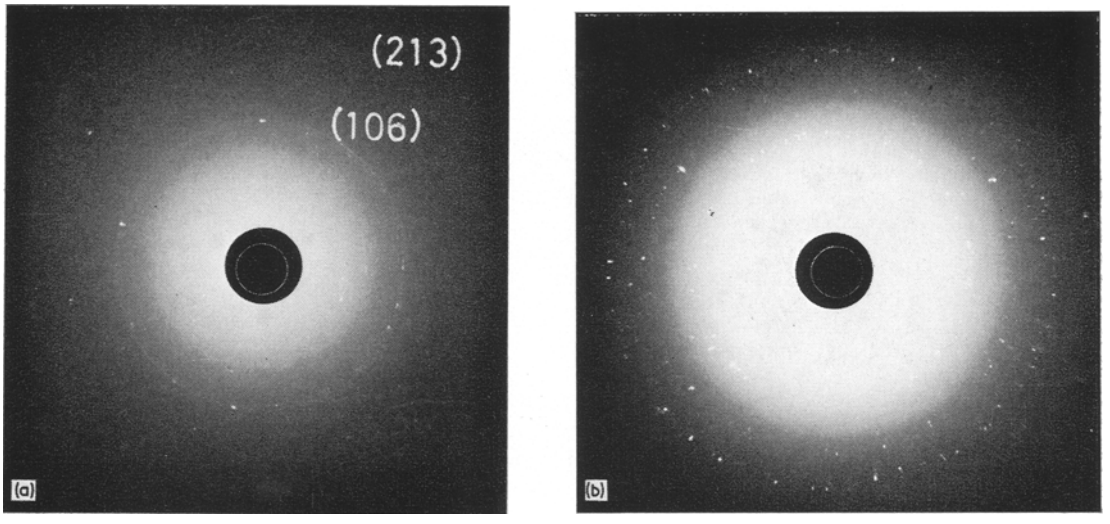

Figure 2 Back-reflection pinhole patterns of a cadmium foil obtained by using Cu$K\alpha$-radiation (45 kV, 18 mA). (a) As-splat-cooled foil. (b) The same foil after annealing. The exposure time was 2.5 h.

Bragg scattering intensity is insignificant compared with the small-angle scattering intensity caused by the vacancy clusters.

Considering the curves 2 and 3 in Fig. 1, we can conclude that the reduction of the average size of the vacancy clusters is dominant. The theoretical determination of the double Bragg scattering is difficult. Because the measured scattering intensities are very weak, we have not performed any quantitative calculations for the determination of the size of the vacancy clusters. The intensity measurements, however, indicate that the average size of the clusters must be small. Furthermore, we can conclude that the excess vacancies in splat-cooled specimens during annealing constitute clusters, which migrate out of the grains upon prolonged annealing.

Acknowledgement

The authors wish to express their thanks to Professor M. Hämäläinen Head of the Department, for extending the facilities of the laboratory. The grant received from the Finnish State Committee for Natural Science in support of this study is gratefully acknowledged.

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Received 17 January
and accepted 27 February 1974

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