Letters

A comparison of the limitations of vapour-quenching and liquid-quenching in the presentation of non-equilibrium alloys

Vapour-quenching (V.Q.) and liquid-quenching (L.Q.) [1] are two apt methods for preparing non-equilibrium phases in amorphous and crystalline alloys. Vapour-quenching refers to the process of condensing a vapour onto a substrate held at a sufficiently low temperature. Early papers on supersaturated solid solutions [2] prepared by both methods stated that V.Q. techniques are more effective than L.Q. ones for preparing metastable phases, the effectiveness of a method being defined here as its capability of preparing non-equilibrium phases of a given type. In view of the present application of both methods to an increasing number of alloy systems, the above point should be considered more thoroughly.

In the case of V.Q. and L.Q., the rate of quenching is usually regarded as the controlling parameter. As far as L.Q. is concerned the rates of quenching range approximately from 10^5 to 10^8 K sec^{-1} whereas in V.Q. they are difficult to estimate but are, however, generally regarded as higher than those of L.Q. in the case of the condensation of a vapour onto a substrate held at liquid nitrogen temperature. However, in V.Q. processes, the formation of alloy films depends on the nature of individual species in the gaseous state and on the evaporation conditions (temperature and nature of the support, evaporation rate, temperature, nature and shape of the evaporation source, evaporation equipment, etc.).

On the other hand, the structure of alloy foils obtained by L.Q. techniques usually depends on the structure and properties of the melt (and the temperature the melt is quenched from). Therefore, owing to these differences, if one accepts the rate of quenching to be a limiting parameter for alloys prepared by L.Q., it is hard to conceive that the same parameter should be applied to the quite different V.Q. experiments and, *a fortiori*, that this parameter should be used in order to compare results obtained on alloys prepared with V.Q. and L.Q. techniques. Comparison between non-equilibrium phases produced using both methods is difficult because of a lack of experimental results, particularly for metastable crystalline phases prepared by V.Q.

Some general considerations may, however, be drawn. The different techniques of L.Q. have proved able to prepare a large number of non-equilibrium intermediate phases in a variety of alloy systems. These have unit cells ranging from simple cubic with one atom per unit cell [3] (~ 3 Å) to complex fcc with 500 atoms per unit cell [4] (~ 20 Å). V.Q. techniques do not appear capable of preparing large unit cells containing a high number of atoms but, on the contrary, show a tendency to form close-packed structures. The differences between results obtained by the two sets of techniques seem attributable to the fact that in the process of quenching from the liquid state the arrangements of atoms existing for a given liquid alloy (nature of the bonds, co-ordination numbers, atom clusters) may prove sources of nucleation. By way of illustration of this, it has so far not been possible to quench in an amorphous state any congruent melting compound; three different non-equilibrium intermediate phases [5] have been produced by quenching the Au–Ge eutectic melts from three different temperatures, etc.

In V.Q. processes the vapour species striking a cold substrate first form highly compact configurations which can be readily frozen in, but the displacements necessary to form less compact crystalline equilibrium phases would require a higher activation energy. As an illustration of this statement it is worth considering a few results obtained on Hume-Rothery γ brass structure phases. The γ brass type of structure [6] occurs in noble metal alloys at an electron concentration of $21/13 = 1.615$ and may be regarded as based on a defective body-centred cubic structure. The unit-cell of the γ brass type of structure, made up by stacking 27 of the usual body-centred cells together, contains 52 atoms and, depending on the nature of the alloy, shows a lattice parameter of the order of 10 Å. The γ brass type of structure has been found in some 35 equilibrium binary alloys [6] mainly in noble metal alloys in agreement with Humer-Rothery's empirical rules. Owing to its relatively large unit cell, the γ brass type of structure seems appropriate for testing the capabilities of V.Q. and L.Q. and for showing their relative differences.

Using electron diffraction, Michel [7] studied

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-

*Aspirant au F.N.R.S.

equilibrium alloys by vapour-quenching and rapid cooling from the melt?" is required.

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M. R. ANSEAU*
*Université de l'Etat à Mons,
Faculté des Sciences,
Laboratoire de Physique du Solide,
7000 Mons, Belgium*

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 $MoK\alpha$-radiation.