

INTERRELATIONS BETWEEN METASTABLE PHASES FORMED BY
RAPID SOLIDIFICATION AND BY MARTENSITIC TRANSFORMATION

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If solidification or a solid state transformation are induced by rapid cooling, both types of phase transformation and their products assume common characteristics. The transformation mechanism is characterised by a complete elimination or severe restriction of diffusion. The transformation products may, apart from being stable phases, be metastable extensions of stable phases or new metastable phases. Furthermore, lattice defects are introduced which are characteristic of the mode of transformation. In this paper investigations of the rapid solidification and martensitic transformations of Cu, Ag and Au base alloys, i.e. of the so-called Hume-Rothery phases or electron compounds, will be compared.

Stable and Martensitic Phases in Cu, Ag and Au Base Alloys

In a recent review (1) it has been shown that the electron-to-atom ratios of the stable Hume-Rothery phases ($e/a < 3/2$ for α (fcc); $e/a = 3/2$ for β (bcc) and ζ (hcp); $e/a = 21/13$ for γ ($D8_{1-3}$)) are but rough approximations for the characteristic concentrations. Metastable phases comply rather well to the valency electron rules. The actual occurrence of stable and metastable β , γ and ζ phases in a particular system is a function of the solvent and solute atom properties and is related to their position in the periodic system.

The martensitic phases in Cu, Ag and Au base alloys (2) are formed by quenching the β phases or by deforming them in the supercooled, metastable state. The martensite phase symbols⁺)

x) It should be noted that the Greek letters used as phase symbols of the Hume-Rothery phases and of the martensitic phases do not signify the same structures. But the notation is straight forward since the Hume-Rothery phases have unprimed, and the martensitic phases have primed, symbols.

and structures are (3): β' phase, fcc or long-period stacking (LPS) structure; β'' phase, consisting of alternating lamellae of two structures (fcc + LPS or hcp + LPS); γ' phase, hcp. In the present context it is interesting to note that the fcc martensitic structures correspond to a supersaturated α phase, the hcp martensitic variants correspond to a ζ phase, and the LPS structures, in particular the 3R-variant, are occasionally found as stable phases as well (4).

Experimental Observations on Splat Cooled Alloys

The most characteristic features of Cu, Ag and Au rich alloys which have been rapidly quenched from the melt are: (i) metastable extensions of the α and ζ phase fields, (ii) formation of ζ and γ phases which do not occur in stable equilibrium, (iii) formation of metastable phases with LPS structures, (iv) heavy faulting up to a fault density and distribution which leave no ordered stacking sequence to be recognizable by x-ray or electron diffraction, (v) stabilization of high-temperature β phases at room temperature. Most of these characteristics are also observed in alloys which have been transformed martensitically (2). The stable phase equilibria (5) and the phases (structures) formed by rapid solidification and martensitic transformation in three typical alloy systems are compiled in FIG. 1. It is immediately evident that the new metastable phases formed by both modes of transformation occur in the same concentration ranges and that the crystal structures are closely interrelated. Moreover, our recent study of a splat-cooled Cu-Al alloy by electron microscopy (6) has shown that the transformation leads to a microstructure which is almost identical to that of martensitically transformed Cu-Al alloys (7-9) as well as to splat cooled Ag-Ge alloys (16), FIG. 2. The metastable extension of α and ζ phase ranges and the formation of new metastable ζ phases by both rapid solidification as well as martensitic transformation appears to be directly related to the suppression of diffusion and the concomitantly enforced formation of phases with comparatively simple structures at or near the gross alloy composition. Consequently, the α phase is formed at low solute concentrations and its range is extended up to e/a

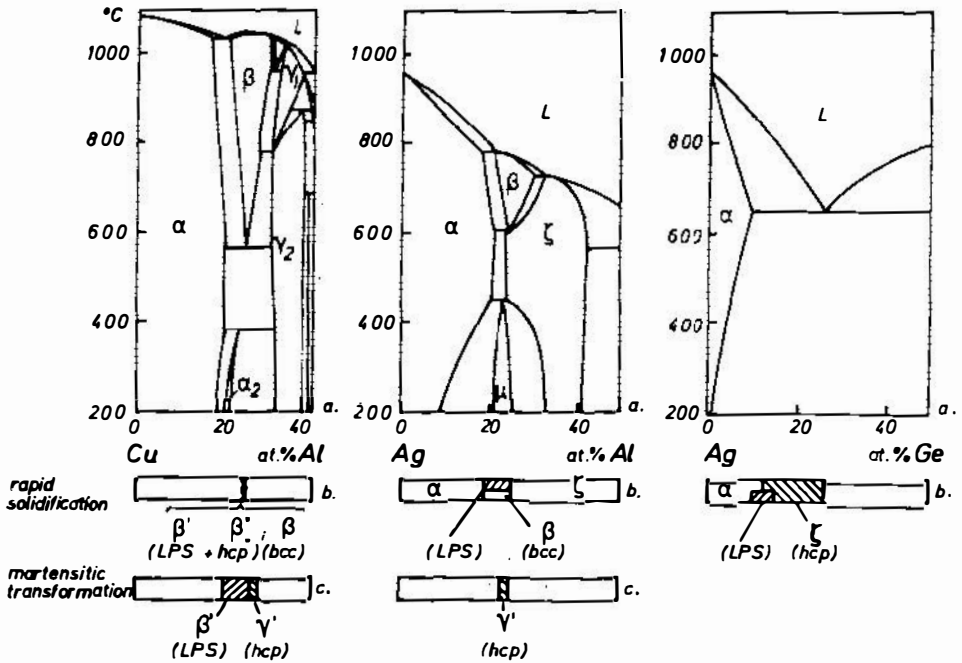


FIG. 1

Phase diagrams (a.) and phases formed by rapid transformations (b. and c.) of Cu-Al (b: 6; c: 7-9), Ag-Al (b: 10; c: 11, 12) and Ag-Ge (13-16) alloys.

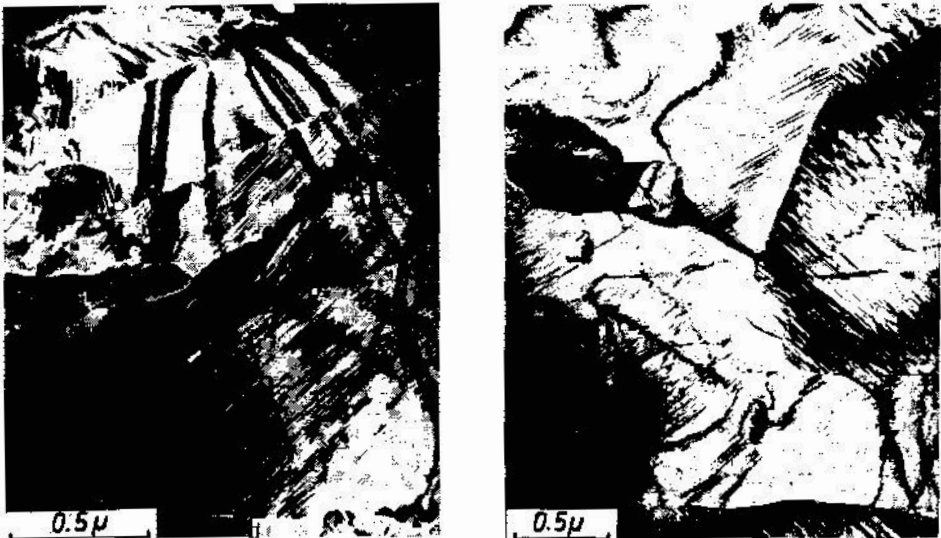


FIG. 2

Microstructures of splat cooled Ag-15 at.% Ge (a.) and Cu-25 at.% Al alloys. Transmission electron micrographs taken directly from thin regions of the foils.

$< 3/2$, e.g. Ag-Ge (13), Ag-Sn (17). Since the Hume-Rothery rules indicate a stabilizing effect of $e/a = 3/2$ for ζ phases at low temperatures this phase is expected to form if the formation of more stable phases in this range is suppressed for kinetic reasons. The degree metastability may be expressed as the difference in free energy of formation between the metastable ζ phase and the corresponding equilibrium mixture of stable phases. The difference has been determined for Au-Sb alloys (18) to be $\Delta G (298^\circ\text{K}) = 0.67 \pm 0.15$ kcal/g-atom. This is typical of the amount of free energy differences between different solid alloy phases. Therefore, it is to be expected and actually found that the suppression of the stable phases for kinetic reasons can lead to the formation of new hexagonal phases by martensitic transformation (2) and by rapid solidification (Ag-Si: 17, 19; Ag-Ge: 20, 13; Au-Ge: 21, 22; Au-Sb: 18, 22) and of γ phases by rapid solidification (Au-Si: 22; Au-Sn: 23).

Metastable states with LPS structures in rapidly solidified alloys have been reported for the Cu-Al (6), Cu-Sn (24), Ag-Al (10), Ag-Ge (14-16), Au-Ge (21) and Au-Si (19) systems. They may have formed directly from the melt. But alternatively they can be due to the martensitic transformation of a β phase which had crystallized from the melt first. This latter two-stage process cannot be derived from x-ray diffraction alone but it can only be determined by a combination with electron microscopic observations. It has been firmly established to occur in Cu-Al (6), Cu-Sn (24) and Au-Cd (25) alloys and may be supposed to occur in Ag-Al alloys from indirect evidence (10). LPS structures which have formed directly from the melt can be recognized from the prevalence of growth faults (but this is not a sufficient criterium) and from their microstructure (grain shape and fault distribution).

The high fault density in rapidly solidified alloys which has been observed by x-ray diffraction line broadening and shifting in numerous cases as well as by electron microscopy (6, 16) is closely related to the metastability of the α or ζ (or LPS) phases since it is well known that the stacking fault energy

decreased considerably towards the phase boundaries of close-packed phases. Growth faults are most likely to be due to the process of rapid solidification. Deformation faults can be due to plastic deformation during further cooling in the solid state or to martensitic transformation. The high fault densities may sometimes preclude or falsify structure determination based solely on x-ray diffraction. Electron diffraction patterns combined with dark field electron microscopy reveal thin lamellae with several different stacking sequences within one specimen (16) of alloys which have been assigned very large unit cells based on x-ray diffraction (14). It is interesting to note that the high temperature β phase is partially retained in splat cooled and martensitically transformed Cu-Al (6), Ag-Al (10) and Au-Cd (25) alloys. This is unusual since residual β has never been found in Cu-Al alloys quenched from the β phase field. However, recent observations on Fe-Ni alloys have shown that the scarcity of potent martensite nuclei in thin foils may result in a severe depression of M_s (26). The same effect is likely to occur in splats which are locally extremely thin as shown by the fact that they are partially transparent to 100 kV electrons, i.e. $< 1000 \text{ \AA}$ in thickness.

Conclusions

Rapidly solidified and martensitically transformed Cu, Ag and Au alloys have numerous common structural characteristics. These are due to their mode of formation and to the stability criteria for Hume-Rothery phases. In rapidly solidified alloys the structures observed at room temperature may either have formed directly from the melt or by martensitic transformation of a transiently stable β phase.

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DISCUSSION :

- M. Paić : What kind of splat cooling have you used ?
- H. Warlimont : The gun technique according to Duwez.
- K. Mukherjee: How soon after splat cooling did you observe the micro structure ? Also did you perform any thermal annealing after the splat cooling to study the reverse transformation?
- H. Warlimont : Within a few minutes to a few hours. We observed no time dependent change in the foils.