

ELECTRON-MICROSCOPIC EXAMINATION OF A SPLAT-COOLED SILVER-GERMANIUM ALLOY

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Received November 29, 1971

ABSTRACT

Extremely rapid solidification of a Ag-15 at.% Ge alloy results in the formation of a highly irregular structure. The individual grains consist of a lamellar mixture of close-packed structures with different stacking sequences (f.c.c. and h.c.p. phases as well as long-period stacking structures), superposed with a high density of randomly arranged stacking faults. It is concluded that the structure observed at room temperature may have formed by martensitic transformation of a metastable b.c.c. phase which is formed first upon solidification.

INTRODUCTION

RAPID quenching from the melt results in the formation of new crystalline phases in a number of alloy systems.¹ Most of these phases have elemental structures; but, especially in some noble metal alloys, complicated structures with as many as 500 atoms per unit cell have been derived from X-ray diffraction data. The formation of metastable phases during rapid solidification is usually favoured, if their structure is simple such that the incorporation of the atoms does not require highly correlated jumps and if the required chemical partitioning of the components is minimized. If, on the other hand, complicated structures are observed after rapid solidification, it is possible that these final structures could have resulted from a two-stage process in that a simple structure is formed first by solidification, which is then transformed into a more complicated structure during further cooling in the solid state. The observed structural interrelations between metastable phases formed by rapid solidification and by martensitic transformations² indicate that this possibility perhaps does occur in some cases.

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A non-equilibrium hexagonal close-packed (h.c.p.) phase has been observed in Silver-Germanium (Ag-Ge) alloys containing 10–26 at.% Ge rapidly quenched from the liquid state.^{3, 4} X-ray examinations⁵ as well as electron-microscopic observations⁶ have provided evidence for heavy faulting in both the face-centred cubic (f.c.c.) and the h.c.p. structures in rapidly solidified Ag-Ge alloys. In particular, the alloy with 15 at.% Ge exhibits a highly irregular structure intermediate between the f.c.c. and h.c.p. phases. At this composition, a further non-equilibrium phase with a tetragonal structure ($a = 8.116 \text{ \AA}$, $c = 20.52 \text{ \AA}$) was derived from X-ray diffraction data.^{1, 7}

EXPERIMENTAL PROCEDURE

In this study, small quantities of a Ag-15 at.% Ge alloy were quenched by the gun technique from temperatures not less than 100°C above the liquidus on a copper substrate. Thin regions at the edges of the resulting foils were transparent to the electron beam without any further thinning procedures. The transmission electron-microscopic studies were conducted in JEOL 200 kV electron microscope.

RESULTS AND DISCUSSION

The microstructure of splat-cooled foils is inhomogeneous as a consequence of the successive solidification of numerous droplets which form the splat and of different thermal and mechanical effects during cooling of the foil in the solid state. The great advantage of transmission electron microscopy is the possibility to study individual grains even in fine-grained specimens (Fig. 1). A fine lamellar microstructure was evident in relatively large as well as in very small grains, the thickness of the lamellae varies considerably. The observed microstructure could be explained on the basis of profuse faulting, very fine twin lamellae or a lamellar mixture of phases with different structures.

The internal microstructure of the grains is quite analogous to the microstructure obtained by martensitic transformation in copper, silver and gold-base alloys when quenched from the β range in the solid state. In several of these alloys, the martensitic product consists of alternating lamellae of two phases with different stacking sequences.⁸ When martensitic transformations occur in thin foils, the martensitic crystallites can assume irregular shapes⁹ instead of the plate shape which is the usual morphology upon transformation of bulk material. Microstructures similar to those obtained in the Ag-Ge alloy have also been found in rapidly solidified Cu-Al

alloys.^{2, 10} In this case it was established that the alloy crystallized initially in the body-centred cubic (b.c.c.) high-temperature β phase. During cooling to room temperature in the solid state the β phase transformed martensitically into the same structures as if the alloy had been cooled from the β phase region in the solid state only.

Selected area electron diffraction of sufficiently large grains of the present Ag-Ge alloy yielded diffraction patterns of the type shown in Fig. 2. A high stacking-fault density is clearly evident from the intense broadening of the affected reflections in the direction normal to the plane of the stacking faults. A high density of randomly distributed stacking faults would result in the formation of continuous streaks. Periodically arranged stacking faults in a close-packed structure would produce distinct intensity maxima, the positions and intensity distribution of which are typical for the particular stacking sequence.

A close examination of the diffraction pattern in Fig. 2 shows the existence of reflections due to the f.c.c., the f.c.c. twin and the h.c.p. structure. A sketch of the corresponding reciprocal lattice section with the positions of these reflections has been given earlier.⁶ It should be noted that double diffraction effects have also to be taken into account for correct interpretation of the results. The occurrence of at least one additional long-period stacking structure can be derived from the pattern given in Fig. 2. An enlarged section of the same electron diffraction pattern is shown in Fig. 3. The set of nine distinct maxima occurring at equal intervals between the f.c.c. reflections would indicate the occurrence of a structure, whose periodicity is $10 d_{111}(\text{f.c.c.})$ in one direction parallel to $\{111\}_{(\text{f.c.c.})}$ coexisting with the f.c.c. and the metastable h.c.p. phase.^{3, 4} The superposition of the diffraction effects of different close-packed structures, double diffraction effects and the broadening of the reflections due to the randomly distributed stacking faults prevent comparison with calculated intensity distributions and hence the determination of the actual stacking order from the electron diffraction patterns obtained in this study. On the other hand, a tetragonal structure^{1, 7} whose a and c axes have been found to be approximately equal to $2a_a$ and $5a_a$ respectively has been derived from X-ray diffraction data for a splat-cooled Ag-Ge alloy of similar composition.

Long-period stacking structures occur in Cu, Ag and Au-base alloys at concentrations with about the same electron-to-atom ratios on extremely rapid solidification as well as on martensitic transformation induced by rapid cooling in the solid state, and are also occasionally found in the stable

state as well.² In particular, a long-period stacking structure consisting of ten layers has been observed as a stable phase in the system Au-Mg near the composition Au₃Mg.^{11, 12} Since in rapidly solidified alloys, structures with long-period stacking sequences are very unlikely to have formed directly from the melt, they could well be the result of martensitic transformation of a metastable b.c.c. phase, which would have crystallized from the melt first. Further support for this conclusion may be derived from the observation that splat-cooled metals and alloys usually have a low dislocation density and are practically free of twins.¹³ Even in alloys, where the stacking fault energy is very small, *e.g.*, in the α phase of the Cu-Al system at high Al contents, the fault density is considerably lower than in the present Ag-15 at.% Ge alloy.¹⁰

On the basis of the present electron-microscopic study it seems probable that solidification of a metastable β phase which transforms martensitically immediately afterwards is the mode of formation of the observed structures in the Ag-Ge alloy. This is not meant to imply that all lattice defects observed in the present study should stem exclusively from the occurrence and mode of martensitic transformation. Since the stacking fault energy is considerably decreased with increasing solute content in most noble metal alloys, the occurrence of stacking faults would not be unexpected in metastable phases of this type. The predominance of growth faults has often been found in the h.c.p. Ag-Ge phase.⁶ They are most probably due to the rapid solidification mechanism. Plastic deformation due to thermal strains during further cooling in the solid state may be the cause for the formation of deformation faults. This would also explain the occasional observation of faults which originate at a grain boundary, but do not extend across the entire grain. Under certain contrast conditions, dislocations terminating the thin lamellae can be observed within the grains (Fig. 1).

In spite of these possible sources of plastic deformation and of growth faulting in the present Ag-Ge foils, it is most improbable that these defects, which could have been introduced by the splat formation as such, should all be restricted to essentially one slip system in each crystallite. This feature, however, is characteristic of martensitic transformations and lends support to the conclusion that a metastable β phase is formed first upon solidification, which is subsequently transformed into a more stable phase martensitically. It would be desirable to obtain more direct evidence of the occurrence of a metastable β phase by its retention in the splat-cooled samples as found in other noble metal-based alloys.² But its stability against further martensitic

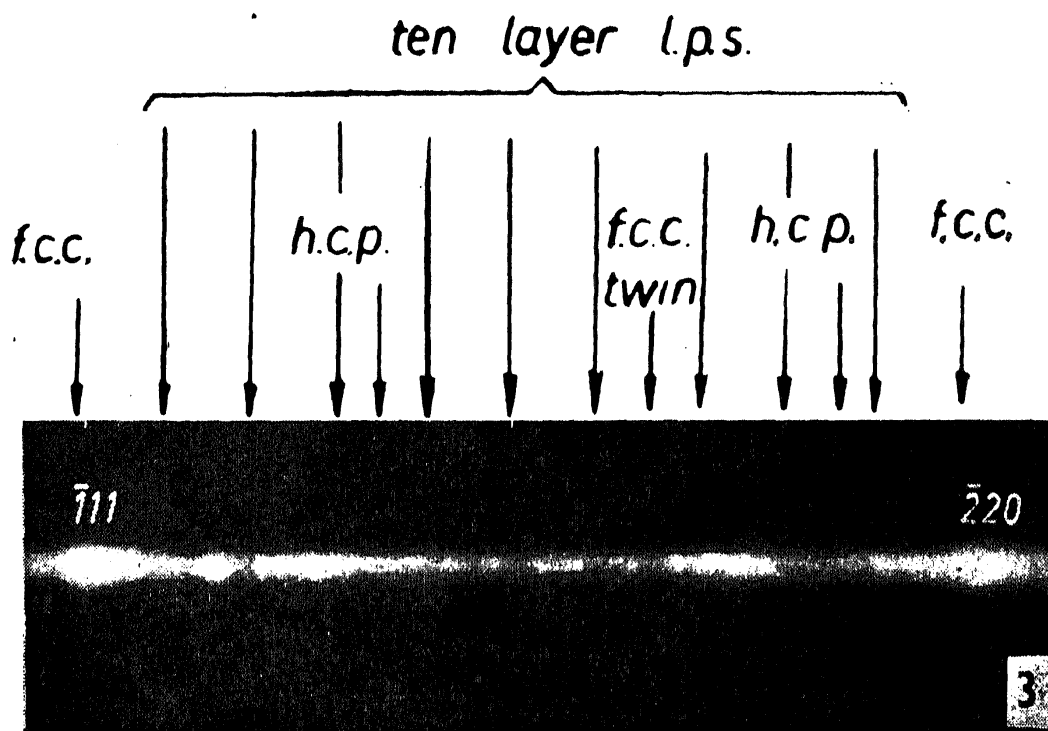
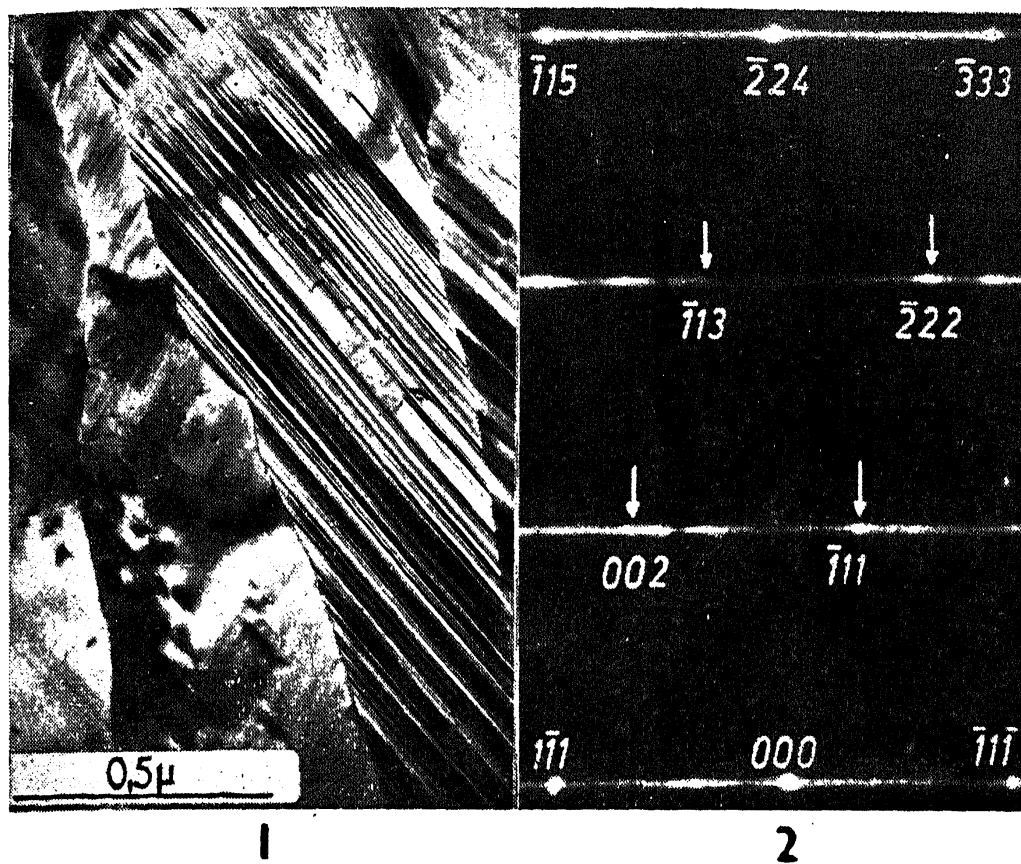


FIG. 1. Transmission electron micrograph, showing lamellar microstructure in a Ag-15 at.% Ge alloy rapidly quenched from the melt.

FIG. 2. Electron diffraction pattern from a rapidly solidified Ag-15 at.% Ge alloy [reciprocal lattice plane (110) for the f.c.c. or (100) for the h.c.p. phase]. The f.c.c. reflections have been indexed.

FIG. 3. Enlargement of a section of Fig. 2, showing distinct intensity maxima due to the different stacking variants.

transformation appears to be too low. This is not surprising because silver forms no stable β phase with any of the group IVA metals.

REFERENCES

1. Anantharaman, T. R. and Suryanarayana, C. *J. Mat. Sci.*, 1971, **6**, 1111.
2. Warlimont, H. and Furrer, P. *Fizika*, Suppl. 2, 1970, **2**, 26.
3. Duwez, P., Willens, R. H. and Klement, W. *J. Appl. Phys.*, 1960, **31**, 1136.
4. Klement, W. .. *J. Inst. Met.*, 1961, **90**, 27.
5. Ramachandrarao, P. and Anantharaman, T. R. *Phil. Mag.*, 1969, **20**, 201.
6. Furrer, P., Anantharaman, T. R. and Warlimont, H. *Ibid.* 1970, **21**, 873.
7. Ramachandrarao, P. .. *Ph.D. Thesis*, Banaras Hindu University, Varanasi, 1968.
8. Delacy, L. .. *Phys. Stat. Sol.*, 1968, **25**, 697.
9. Hull, D. .. *Phil. Mag.*, 1962, **7**, 537.
10. Furrer, P. and Warlimont, H. To be published.
11. Burkhardt, K. and Schubert, K. *Z. Metallkde.*, 1965, **56**, 864.
12. Sato, H. and Toth, R. S. .. *J. Phys. Chem. Solids*, 1968, **29**, 2015.
13. Willens, R. H. .. *Proc. Fifth International Meeting for Electron Microscopy*. Academic Press, New York, 1962, **1**, EE-6.