Liquid-quenched Ag-Ge alloys; formation and evolution of metastable phases

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The formation and decomposition behaviour of metastable structures in liquid-quenched (LQ) Ag—Ge alloys was studied with X-ray diffraction, resistivity measurements and TEM techniques. Pure Ag and alloys containing 7, 10, 15, 20 and 22.5 at. % Ge were studied. Upon LQ, pure Ag and 7 and 10 at. % Ge alloys yield a single f c c phase; 15 and 20 at. % Ge alloys give a mixture of two metastable phases (f c c and h c p); and the Ag—22.5 at. % Ge alloy gives a metastable h c p phase. Also, the first evidence of an amorphous phase in as-LQ Ag—22.5 at. % Ge alloy is presented. It is shown that Ag-rich f c c phase can retain up to ∼ 20 at. % Ge in solid solution. Furthermore, stacking faults play an important role in the formation and decomposition of metastable phases in the Ag—Ge system.

1. Introduction

Ultrafast liquid quenching (LQ) of alloys has been studied for some years with a central goal of obtaining metastable states not achievable by bulk quenching. The simple eutectic Ag–Ge system has been examined extensively since the work of Duwez *et al.* [1] and Klement [2]. Using LQ, the terminal solid solubility of Ge in Ag has been extended from the maximum equilibrium value of 9.6 at. % to 13 ± 1 at. % Ge (all compositions are given in atomic percent). A metastable h c p phase occurs in LQ alloys containing 10 to 26 Ge [1, 2] (The equilibrium eutectic point is 25.9 at. % Ge at 615° C). Klement observed broadening of Debye–Scherrer reflections in the h c p phase containing 17 to 18 Ge, which he attributed to stacking faults [2]. This has been confirmed in some recent X-ray and TEM studies, where it was concluded that the metastable h c p phase occurs because of extensive faulting of the Ag–f c c solid solution [3,4]

The metastable h c p phase has been observed to be the sole product of LQ in the composition range 21 to 23 Ge [3, 6]. Its decomposition at 300° C into equilibrium f c c and Ge phases was

first studied by Klement [2]. A detailed calorimetric and metallographic study of the decomposition of the metastable h c p phase in Ag–23Ge has shown that the process takes place in two stages: a supersaturated f c c phase forms by profuse faulting in the h c p phase, followed by precipitation of Ge [6].

Due to the general inability to achieve reproducible LQ conditions, discrepancies in the composition ranges of metastable phases and their subsequent decomposition products are possible from one investigation to another. As will be seen later in this paper, discrepancies do in fact exist in the literature cited above. Based mainly on TEM, the present investigation aimed at a more comprehensive picture of the formation and decomposition of the metastable phases in the Ag–Ge system. Pure Ag and Ag–Ge alloys in the composition range 7 to 22.5 Ge were studied.

2. Experimental

Five Ag–Ge alloys, containing 7, 10, 15, 20 and 22.5 Ge were prepared from pure Ag and Ge (both 99.999% pure) by vacuum inert-gas arc melting. These alloys were then homogenized by

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inert-gas induction melting and quenched into water to minimize segregation.

About 50 to 100 mg samples were LQ using the gun technique [1]. The quenching temperatures were about 200°C above the melting point of the given alloy. The LQ foil varied in thickness from around 50 μm in the centre region, to thin edges which were suitable for direct TEM work without further preparation. The central region of the samples provided good continuous specimens for electrical resistivity measurements. An interruption method was employed to measure the resistance in 21°C acetone. A four-probe potentiometric technique was used. Fine flakes near edges ccould readily be used for X-ray powder diffraction studies. X-ray diffraction measurements were carried out using a 11.4 cm powder camera. A hot-stage was employed for ageing experiments carried out within the electron microscope.

3. Results and discussion
3.1. Lattice parameter data
A single fcc phase was found in LQ pure Ag and in alloys containing 7 and 10 Ge. In the 15 and 20 Ge alloys, a mixture of fcc and hcp phases was detected, the hcp phase being more prominent in the 20 Ge alloy. Fig. 1 shows the lattice parameter versus Ge content for the Ag-rich fcc phase. Also shown are LQ data available in the literature [2] and data for solid quenching. The lattice parameter of the LQ pure Ag in the present study agrees with that of pure bulk Ag [7], and a straight line is obtained up to 20 Ge, indicating enhanced solubility well beyond the 13 ± 1 Ge reported by Klement [2]. It should be noted that
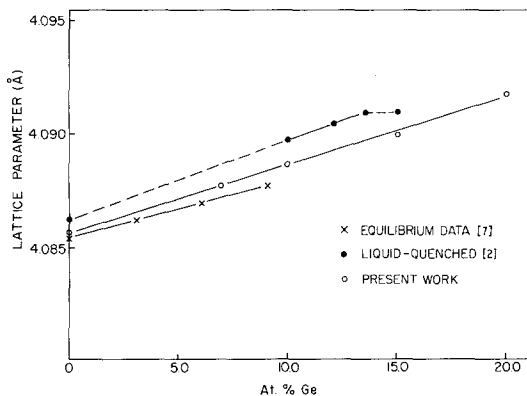
Klement's value of lattice parameter for pure Ag is significantly higher than for both bulk Ag [7] and for the present results.

These lattice parameter results, as well as some TEM findings, to be given later, indicate that the LQ rates for the present study exceed those reported previously. It thus appears, based upon the present lattice parameter results, that at least 20 Ge can be retained in the fcc solid solution. Consistent with this conclusion, Kirchner et al. [7], in their investigation of decomposition of the metastable hcp phase in LQ Ag–23 Ge, found that the hcp phase transforms first into a supersaturated fcc phase before decomposing into the Ge and the equilibrium fcc phases.

The c/a value for the metastable hcp phase in the Ag–20 Ge alloy is determined in this study to be 1.4. The Ag–22.5 Ge alloy essentially contains a single hcp phase (only one weak fcc reflection was detected which could have resulted from faulting). In this case, however, computation of lattice parameters and c/a values was not possible due to excessive line-broadening for the high-angle reflections.
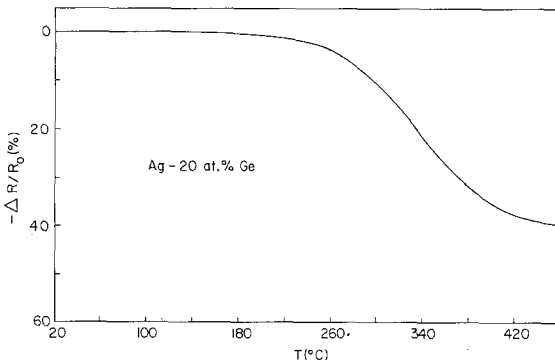
Figure 2 Isochronal annealing curve for LQ Ag–20 Ge.

3.2. Isochronal annealing
In order to determine an appropriate temperature for isothermal ageing of the metastable hcp phase, a LQ 20 Ge alloy was heated isochronally from 20 to 450°C. Fig. 2 shows percentage change in resistivity plotted versus temperature. Only one broad stage is obtained, with a resistivity drop of about 20% between 300 and 400°C. To give adequate ageing rates, an ageing temperature of 350°C was chosen for the subsequent isothermal experiments.

Figure 1 Lattice parameter versus Ge content for the Ag-rich fcc phase.

3.3. Isothermal ageing

Isothermal decomposition of the LQ Ag–Ge alloys was studied at 350°C. The two f c c alloys, 7 and 10 Ge, decomposed into two phases, a solid solution f c c phase and Ge. In the case of two-phase f c c–h c p, obtained with the 15 and 20 Ge alloys, three resultant phases were found even after long ageing times (∼40 h at 350°C): f c c solid solution, h c p and Ge phases. The lattice parameter of the f c c phase showed a monotonic decrease with ageing time for four alloys, 7, 10, 15 and 20 Ge. For the 20 Ge alloy, the c/a ratio of the h c p phase changed from 1.4, in the as-LQ condition, to 1.6 following 16 h at 350°C. Thus, precipitation in the two-phase alloys appears to follow the sequence: metastable f c c and h c p phases transforming to f c c (lower solubility) + h c p (lower solubility) + Ge.

Kirchner *et al.* studied the decomposition of the single metastable h c p phase in Ag–23 Ge [6]. They found a two-stage decomposition process over a temperature interval from about 240 to 400°C and proposed the following decomposition sequence:

Below 280°C:
metastable h c p phase $\xrightarrow{\text{faulting}}$ a new supersaturated f c c phase

Above 320°C:
supersaturated f c c phase $\longrightarrow$ f c c solid solution + Ge

Our TEM observations on LQ Ag–22.5 Ge, which forms a single h c p phase on LQ, qualitatively support the above decomposition processes.

3.4. Stacking faults and phase transformations in Ag–Ge alloys

It is well established that stacking faults play an important role in the formation and decomposition of the metastable h c p phase in Ag–Ge alloys [4, 5]. Due to the low stacking fault energy for pure Ag, the faulting probability for the Ag–Ge alloys should be very high. Barrett has suggested that there should be a high faulting tendency for supersaturated phases within a two-phase region where close-packed structures coexist [8]. Indeed, profuse faulting has been noted in LQ Ag–Ge alloys [3–5].

*SAD = Selected area diffraction.

Using X-ray line shape analysis, Ramachandrarao *et al.* [4] have determined the faulting probabilities for a number of LQ Ag–Ge alloys. Their findings can be summarized as follows: (a) for pure Ag and f c c Ag–7 Ge, X-ray line broadening is due mainly to small domain size, (b) Two-phase, f c c–h c p, LQ alloys containing 9 to 22 Ge display profuse faulting in both phases, (c) the single h c p phase (Ag–22 Ge) shows both growth and deformation faulting.

While Ramachandrarao *et al.* have attributed X-ray line broadening in LQ pure Ag and Ag–7 Ge to a domain-size effect [4], Furrer *et al.* observed profuse faulting in the same alloys [5], these two observations being in contradiction. The reason that Ramachandrarao *et al.* did not detect a peak shift (which would have arisen from faulting) from X-ray reflections can be explained if mixed faulting (intrinsic and extrinsic) occurs. It has been shown that intrinsic and extrinsic faults give equal and opposite peak shifts [9]. Observations of Furrer *et al.* [5] support this interpretation.

In the present investigation, LQ specimens of pure Ag and Ag–Ge alloys containing 7, 10, 20 and 22.5 Ge were examined by TEM. Specimens of LQ 10, 20 and 22.5 Ge alloys were isothermally aged *in situ* in the hot-stage. Due to the very small grain size of the LQ material, SAD* patterns usually contained superimposing reflections from a number of grains, and therefore it was difficult to carry out quantitative analyses of the faults. The results of the TEM study are given in the following.

3.5. TEM
3.5.1. Pure Ag and low-Ge f c c alloys
The LQ specimens of pure Ag displayed both existing stacking faults (probably growth faults) and faults arising from dislocation motion and interactions likely due to thermal stresses. It is to be noted that this contradicts the interpretation of Ramachandrarao *et al.*, who attributed the observed X-ray line-broadening effects to small domain size [4]. The as-LQ structure for both 7 and 10 Ge alloys was characterized by small grains with heavy faulting. Fig. 3a shows a typical as-LQ microstructure of Ag–10 Ge. Generally, the faults run across the grains. In some areas the structure is lamellar and bears a close resemblance to martensitic products.
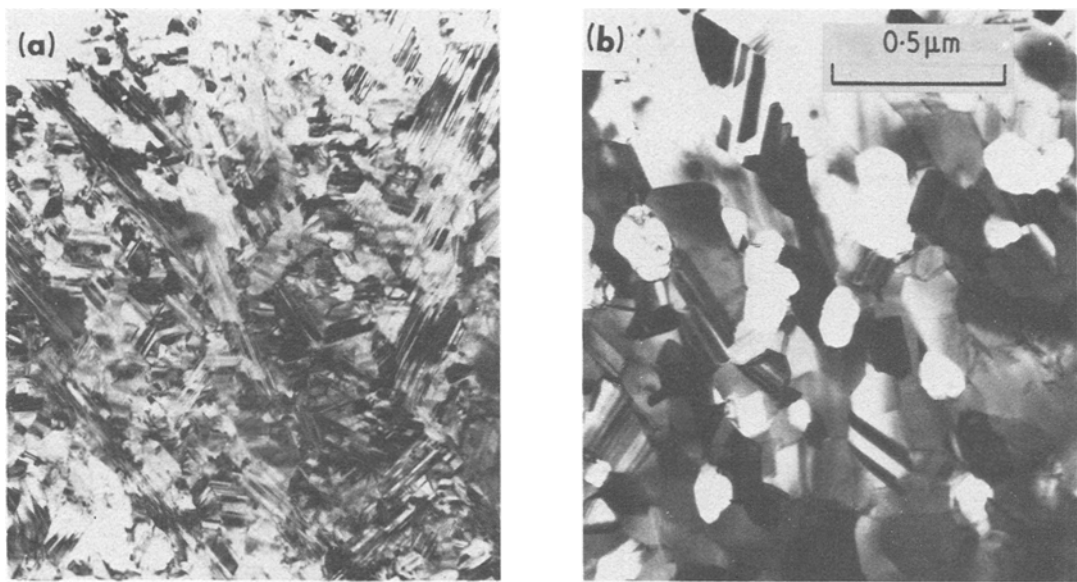
Figure 3 Isothermal ageing of LQ Ag–10 Ge: (a) as LQ, (b) 5 min at 350° C.

The ageing behaviour of both 7 and 10 Ge alloys was identical. Upon isothermal ageing at 350° C, the supersaturated f c c phase starts to decompose. Ge precipitates, which show a very light contrast, can be clearly seen in Fig. 3b, which is for ageing the Ag–10 Ge specimen for 5 min at 350° C. Because of the small grain size it is difficult to determine whether Ge nucleates at the grain boundaries or within the matrix.

Thus, for both pure Ag and low Ge f c c alloys, heavy faulting occurs in LQ specimens and stacking faults appear to be of mixed character.

3.5.2. Ag–20 Ge alloy

This composition yields a predominant h c p phase and a minor f c c phase upon LQ. The as-LQ microstructure consists of a heavily faulted structure (Fig. 4a). The SAD pattern in the as-LQ state showed mainly prominent h c p reflections. Heavy streaking of certain h c p reflections in the *L*-direction in reciprocal lattice was also observed. This observation is in agreement with that of Furrer *et al.* [5].

The early stages of isothermal decomposition of Ag–20 Ge at 350° C are shown in Fig. 4b, c and d. It can be seen from Fig. 4b (5 min at 350° C) and Fig. 4c (15 min at 350° C) that nucleation of Ge occurs within the matrix as well as at grain boundaries. The SAD pattern after ageing 15 min showed streaked h c p reflections with superim-

posed rings arising from precipitation of Ge. The Ge precipitates develop with time. This is shown in Fig. 4d (25 min at 350° C). Because profuse faulting persists even after longer ageing times, it appears, as also concluded from isothermal annealing data in Section 3.3, that Ge precipitates from both the h c p and f c c metastable phases.

3.5.3. Ag–22.5 Ge alloy

This alloy gives a h c p metastable single phase on LQ. No evidence of faulting is noted in the as-LQ condition. Small isolated areas of the LQ foil also showed the presence of an amorphous phase. This is the first evidence of an amorphous phase in the Ag–Ge system, however, despite repeated efforts, it was not possible to obtain a uniform amorphous phase. Fig. 5 shows the amorphous-to-crystalline transition. Fig. 5a is the SAD pattern from an amorphous region of the foil, showing only a weak diffuse ring, characteristic of amorphous solids. Upon heating to 350° C, the amorphous structure begins to crystallize rapidly. The crystallized structure is shown in Fig. 5b after 2 min at 350° C, the corresponding SAD pattern being shown in Fig. 5c. It consists of spotty rings typical of a fine grain crystalline material. This crystalline phase could not be identified as Ge or any of the metastable phases.

Figs. 6a, b and c illustrate the isothermal decomposition of the metastable h c p phase in Ag–

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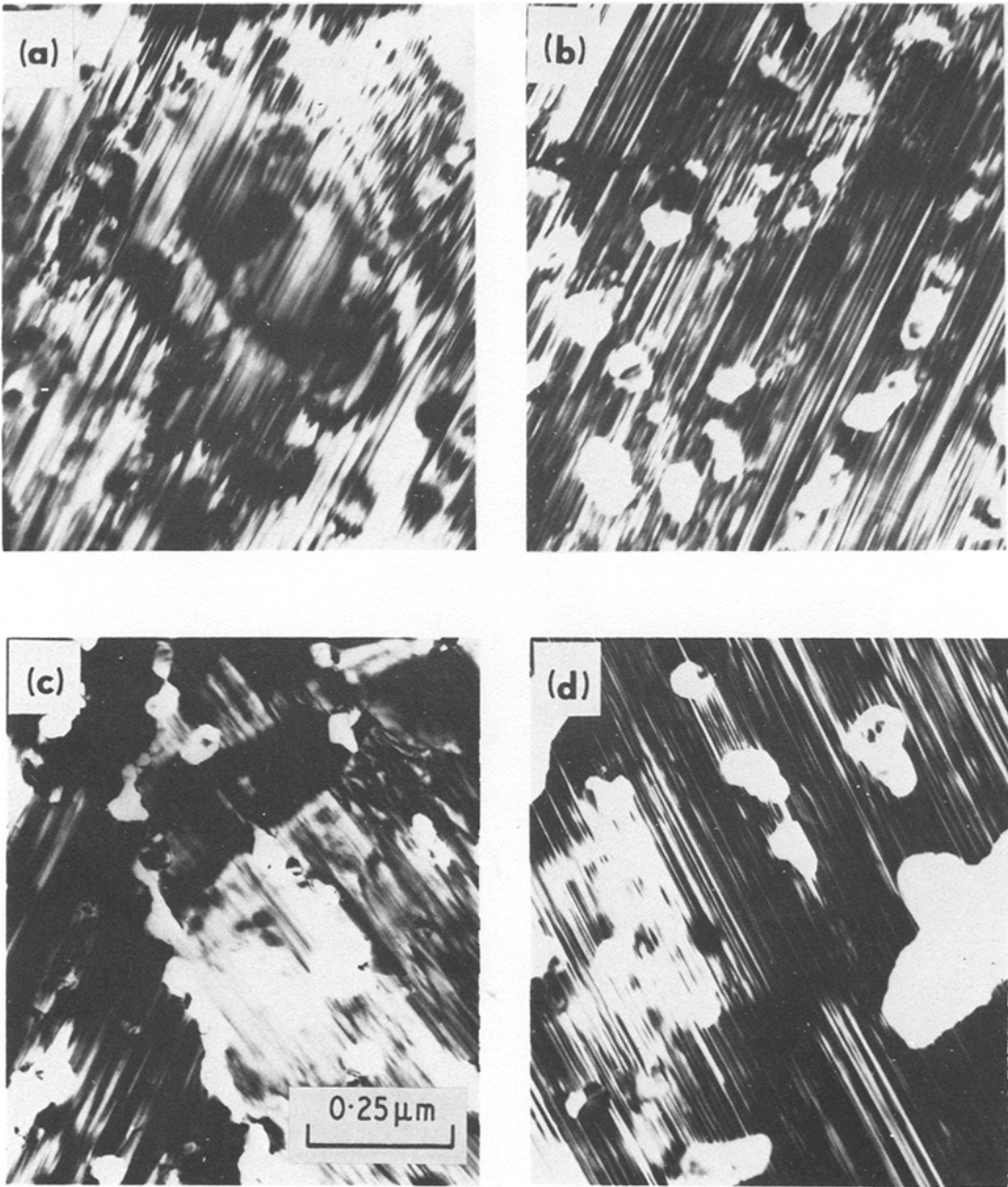
Figure 4 Isothermal ageing of LQ Ag–20 Ge at 350° C: (a) as LQ, (b) 5 min, (c) 15 min, (d) 25 min.
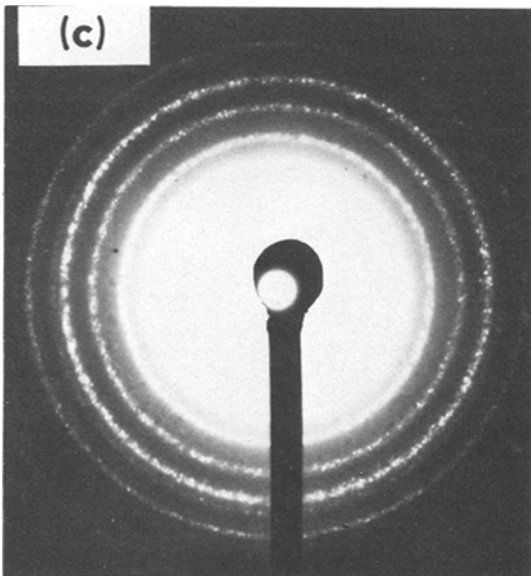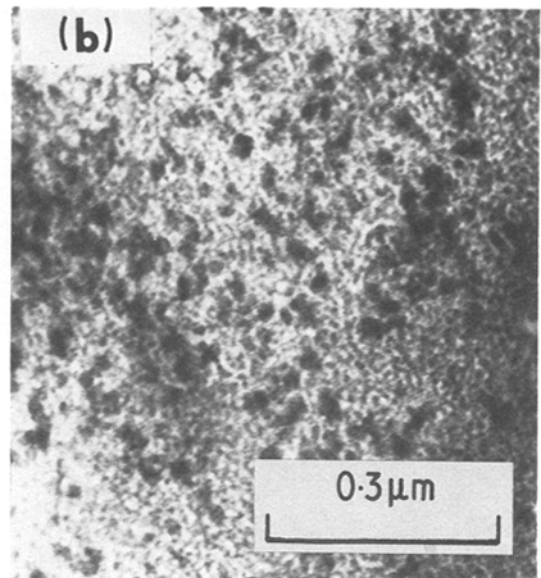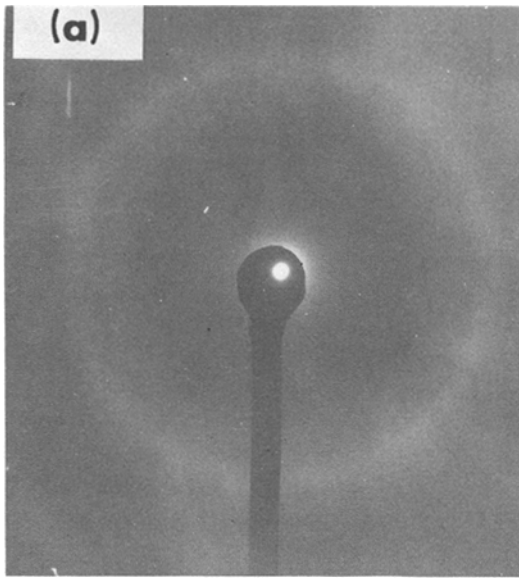
Figure 5 Amorphous to crystalline transition in LQ Ag–22.5 Ge: (a) SAD as LQ (b) 2 min at 350° C, (c) SAD of (b).

to fault profusely. This was followed by the appearance of very small Ge precipitates in the matrix and at grain boundaries. Fig. 6b shows the microstructure after 3 min at 350° C; considerable faulting in the matrix and the presence of Ge precipitates are clearly visible. The inserts in Figs. 6b and c show the evolving SAD shape of the diffraction spot marked by an arrow in Fig. 6a. This developing streaking is due to faulting of the metastable h c p phase. After 5 min of ageing the streaking is further enhanced (Fig. 6c), and Ge precipitates grow and become visible. At this stage, spotty rings from the Ge phase could also be detected on SAD patterns.

The above decomposition sequence for the single metastable h c p phase is in agreement with the results of Kirchner et al. [6], i.e. the metastable h c p phase first transforms into a supersaturated f c c phase by profuse faulting, followed by the precipitation of Ge from the f c c phase.

4. Conclusions
(1) The first evidence for the occurrence of a metastable amorphous phase was found in the Ag–Ge system: in Ag–22.5 Ge.
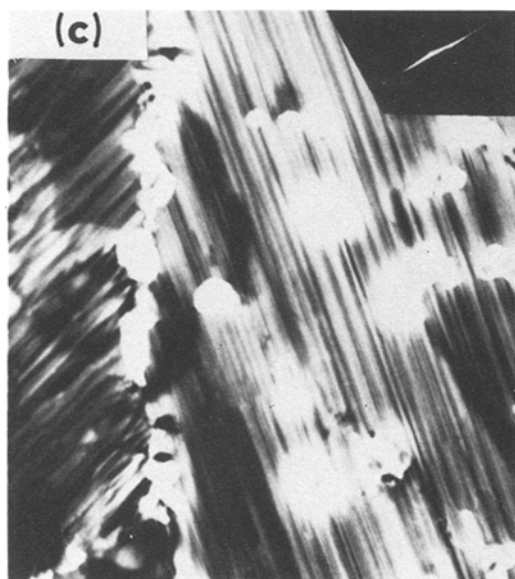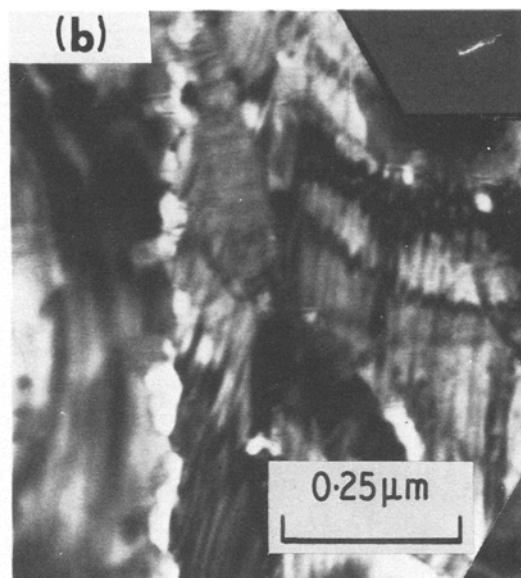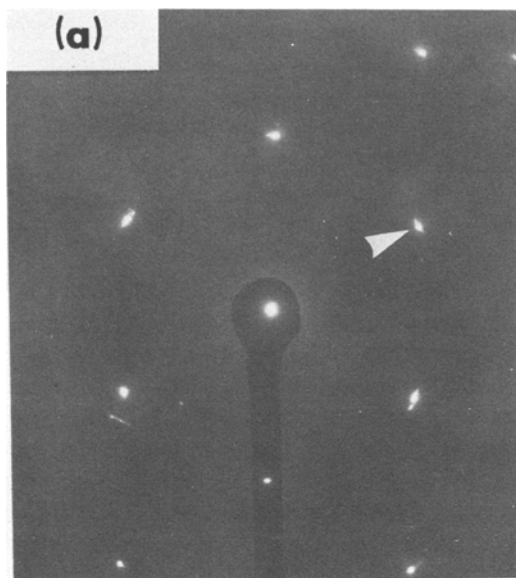
22.5 Ge at 350° C. Fig. 6a is SAD pattern from the as-LQ foil, the pattern being representative of a h c p structure with a {0 0 1} orientation. It should be noted that no faulting was observed in the as-LQ structure, this being further substantiated by the fact that the diffraction spots in Fig. 6a show no streaking. When the temperature of this specimen was raised 350° C, the h c p phase began

Figure 6 Isothermal decomposition of the metastable h c p phase in LQ Ag–22.5 Ge: (a) SAD as LQ, (b) 3 min at 350°C, (c) 5 min at 350°C.

decomposition proposed by Kirchner *et al.* [6] is valid for the decomposition of LQ metastable h c p phase in Ag–22.5 Ge.

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(2) It has been shown that on LQ, the Ag-rich f c c phase can retain up to approximately 20 at.% Ge in solid solution.

(3) It has been confirmed by TEM examination that LQ pure Ag, as well as low-Ge alloys (7 and 10 Ge), have heavily faulted as-LQ structures.

(4) It has been verified that the mechanism of