

Crystallization embrittlement of Ni-Si-B alloys

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Changes in the mechanical properties, and in particular the loss of ductility, have been examined during the crystallization of a series of Ni-Si-B amorphous alloys and an Ni-Fe-Si-B alloy. In all cases crystallization takes place by the formation of large numbers of small crystals and at some stage during the crystallization process embrittlement occurs. The geometrical characteristics of the crystal phases, and the mechanical properties of the crystalline and amorphous components are assessed in an attempt to define the factors leading to embrittlement. Sensitivity to embrittlement does not seem to be related to the particular phase nature, geometry nor distribution of the crystals formed. Rather, the mechanical properties of the crystals seem to be the determining factors. Hard and brittle crystals lead to alloy embrittlement; soft, ductile crystals can lead to enhanced toughness of the alloys.

1. Introduction

The embrittlement taking place during crystallization of amorphous metallic alloys is one of the most important characteristics limiting application of these materials. Both attempts at consolidation of amorphous powders or tapes, generally by warm consolidation, and coating techniques, for example laser deposition, will benefit from an improved understanding of the factors controlling crystallization and embrittlement. Embrittlement, in particular, is poorly understood with some alloys showing extreme sensitivity while others may be only mildly affected.

A number of changes have been postulated as responsible for the embrittlement of amorphous alloys during heat treatment. This embrittlement may occur, according to the alloy system, before or during crystallization. Several studies have attempted to relate such embrittlement to the structure of the first crystalline phase forming and to the incipient atomic groupings which may precede crystallization. Inoue *et al.* [1], for example, found that nickel-base and palladium-base amorphous alloys remained ductile even after formation of the first fcc crystalline phase; cobalt-base alloys embrittled immediately after the formation of the first crystalline phase, which had a cph

structure; iron-base alloys, however, embrittled even before the formation of any crystalline phase. Embrittlement during crystallization was associated with the appearance of phases which did not have the fcc structure. Embrittlement prior to crystallization was not completely understood and was attributed to the atomic reorganization taking place which produced some form of pre-crystallization, non-fcc structures. In a similar way, Lewis *et al.* [2] found that Fe-Ni-B alloys which crystallized by the initial formation of an fcc phase remained ductile even after first crystallization, whilst those Fe-Ni-B alloys which transformed initially to a bcc phase embrittled even before crystallization and remained brittle on initial crystallization. The reasons for embrittlement prior to crystallization are, however, more complex as suggested by subsequent work [3] on Co-Fe-B alloys which remained ductile until crystallization began both when fcc and bcc phases were the initial structures. It has been proposed that such embrittlement in the amorphous state may be related to structural relaxation involving changes in the free volume or the local state of order [4, 5].

Several different reasons have been proposed to explain the embrittlement effect of crystalline

particles in a still-amorphous matrix. For example the formation of phosphorus particles or cobalt-boride particles has been claimed as responsible for easy crack propagation or nucleation [6]. On the other hand, the addition of finely dispersed carbide particles has been described as enhancing ductility by inducing a transition from intense slip on a limited number of shear bands to homogeneous, wavy slip [7]. Alternatively, it has been postulated that embrittlement may be the result of a change in the amorphous matrix properties following depletion or enrichment during crystallization [8, 9]. More recently, it has been suggested that the mechanical behaviour during crystallization can be related to the mechanical properties of the crystals formed [10] – hard particles can lead to interface void formation whilst soft particles can diminish stress concentrations and enhance ductility. This work examines the mechanical property changes taking place during the crystallization of a series of amorphous alloys whereby a number of different crystal phases are formed, of different geometries, distributions and mechanical properties. In this way it should be possible to identify the factors leading to the mechanical property changes.

2. Experimental procedure

The procedures adopted for alloy and amorphous tape preparation have been detailed before [11]. Briefly, the desired alloy compositions were prepared by melting together mixtures of elemental powders, and tapes were prepared by melt-spinning onto a copper roller. Three alloys in the ternary Ni–Si–B system were studied: Ni_{77.5}Si_{7.5}B₁₅, designated alloy D; Ni_{74.5}Si_{8.5}B₁₇, designated alloy E; Ni₇₀Si₁₀B₂₀, designated alloy F. In addition, an iron-containing alloy, designated L, was prepared by replacement of some of the nickel in alloy D. This alloy, (Ni_{0.4}Fe_{0.6})_{77.5}Si_{7.5}B₁₅, was chosen in an attempt to study different phase formation within one material. Thus at low temperatures, a bcc form of iron (ferrite) might crystallize, whilst at higher temperatures the fcc form (austenite) might be obtained.

Heat treatments of pieces of alloy tapes were carried out in salt baths. Following heat treatment, the microhardness was measured on polished tape surfaces using a Vickers microhardness tester with a load of 100 g; these measurements were always made on the side of the tape which had contacted the melt-spin roller. Ductility was determined by

bending small pieces of tape between the plattens of a micrometer and noting the separation at fracture. The strain (Σ) was estimated using the formula $\Sigma = t/(D - t)$ where t is the tape thickness, about 30 μm , and D the platten separation.

Structural changes taking place during crystallization were studied by transmission electron microscopy using, principally, a Philips 300 microscope. Mechanisms of embrittlement were examined in detail by studying thin foils of suitably heat-treated materials which were gently deformed after foil preparation in order to induce cracking. In this way crack morphology changes within the amorphous matrix, and interactions between the cracks and crystals present in the foil, can be identified.

3. Results

3.1. Structural changes during crystallization

The mechanisms by which crystallization takes place have previously been described in detail [12]. A brief summary of the processes and the phases formed is given here. Alloy D crystallizes by growth on pre-existing nuclei leading to the formation of butterfly-shaped crystals of the orthorhombic Ni₃B phase (Fig. 1). When about 40 to 50% of the material has crystallized a eutectic transformation begins which leads to full crystallization of the material. The orthorhombic crystals are complex in both structure and morphology (Fig. 2), containing large numbers of faults and showing fine speckling indicative of phase decom-

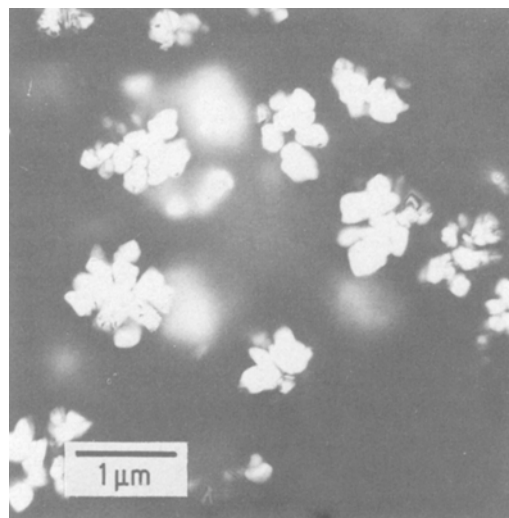


Figure 1 Crystals of the orthorhombic Ni₃B-type phase formed on annealing alloy D.

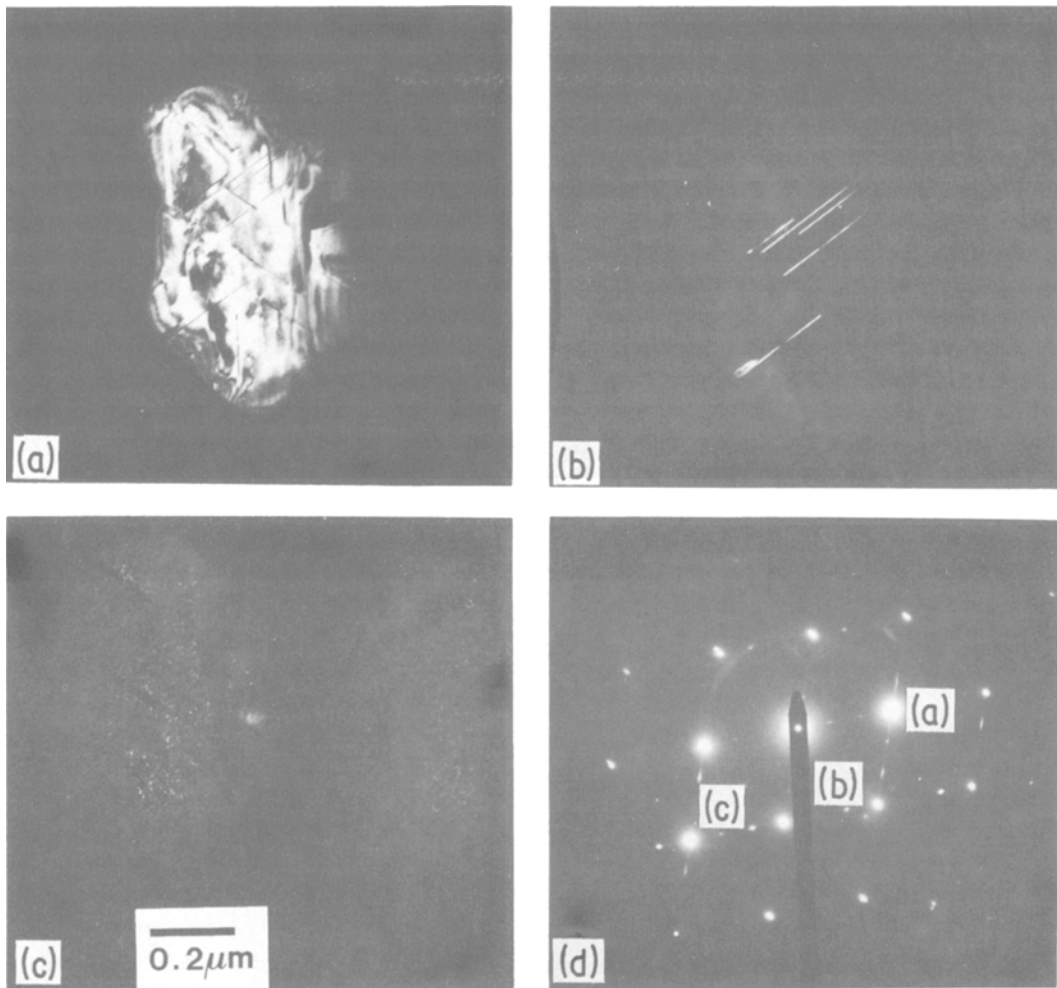


Figure 2 Detailed structure of an orthorhombic Ni_3B phase in alloy D after partial crystallization: (a) dark-field image using a diffraction spot of the Ni_3B structure; (b) dark field with faults of one orientation in strong contrast; (c) dark-field image showing fine speckling which indicates precipitation within the Ni_3B structure; (d) diffraction pattern showing also the diffraction intensities used to obtain the previous images.

position within the crystal. Alloy E crystallizes by the diffusion-controlled formation and growth of crystals, leading once again to the formation of crystals of the orthorhombic Ni_3B -type phase (Fig. 3). The crystals formed are still irregular in shape and contain many faults. At about 75% crystallization a eutectic forms. Alloy F crystallizes by the formation and growth of numerous crystals (Fig. 4), which have a structure intermediate between that of orthorhombic Ni_3B and fcc Ni_{23}B_6 . There is again indication of decomposition of the crystal structure taking place after initial formation, see Fig. 5. It is possible that initial crystallization leads to the orthorhombic structure and the subsequent decomposition tends

towards the complex cubic structure. After about 90% crystallization a second phase nucleates and further transformation takes place by eutectic growth. Alloy L transformed by the homogenous nucleation of nearly spherical crystals having a bcc structure (ferrite) (Fig. 6). Over the complete range of temperatures examined, 350 to 500°C, the material crystallized in this way with no evidence of a change to the fcc structure (austenite) at higher temperature.

3.2. Hardness and ductility changes during crystallization

Hardness changes taking place during the crystallization of alloys D and F at 450°C are shown in

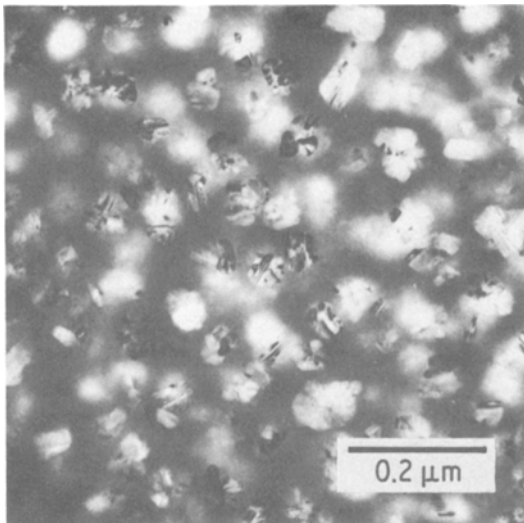


Figure 3 Crystals of the orthorhombic Ni₃B-type phase formed on annealing alloy E.

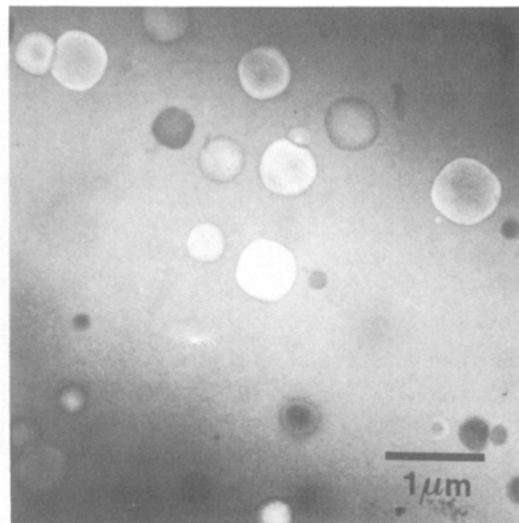


Figure 4 Crystals of orthorhombic Ni₃B-type phase formed in alloy F.

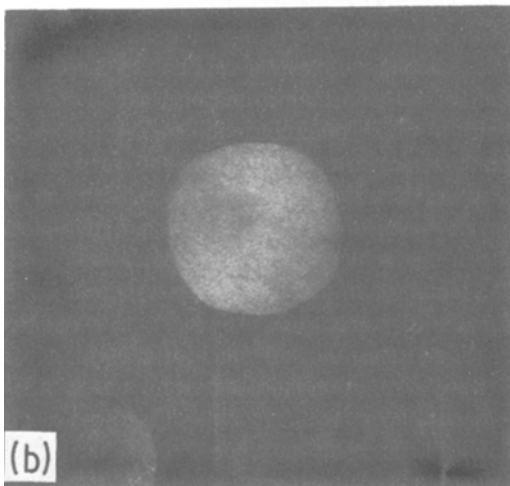
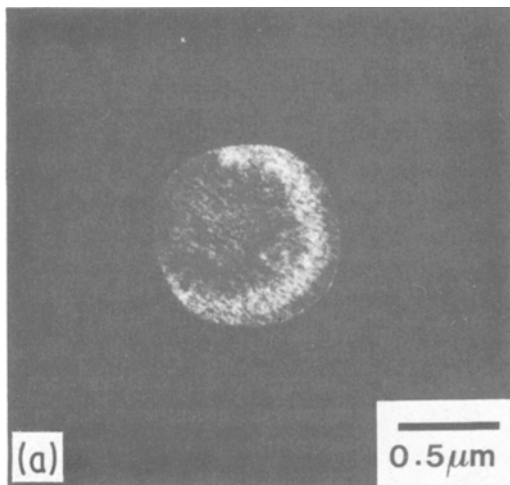
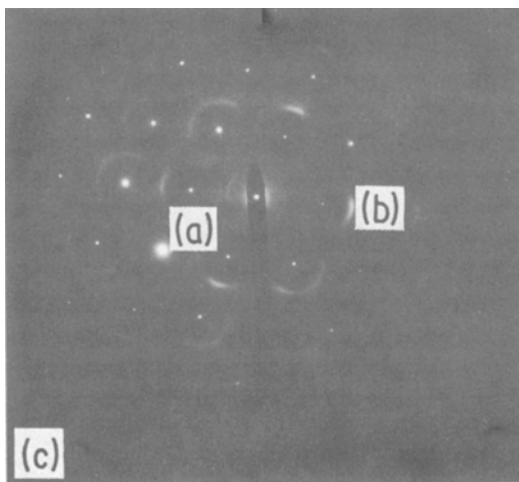


Fig. 7. Fig. 8 compares the embrittlement of these two alloys, at a range of temperatures, with the kinetics of crystallization. In Fig. 7 the beginning of crystallization, the appearance of the second phase and eutectic structure, and completion of crystallization are indicated. For alloy D a significant hardness increase occurs at very short annealing times, before crystallization. (It should be noted that for this alloy, crystal nuclei are quenched in during rapid solidification and it is not possible to define an absolute start to crys-

Figure 5 Detailed structure of a crystal in alloy F: (a) dark-field image on Ni₃B spot; (b) dark-field image using a diffraction arc produced by fine-scale decomposition of the Ni₃B structure; (c) diffraction pattern.



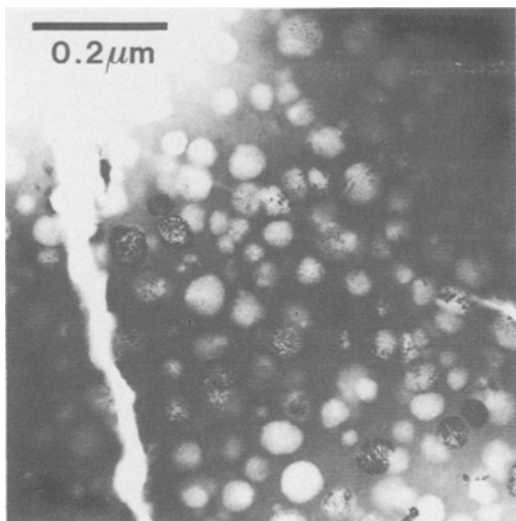


Figure 6 Crystals of bcc phase formed in alloy L during crystallization.

tallization). The start of crystallization is taken as the time when a small amount of crystallinity, a few per cent, has formed. This alloy retains about the same hardness during the first stage of crystallization and shows a large hardness increase near the end of crystallization, corresponding to the appearance of the eutectic. At much longer annealing times the material softens. Alloy F

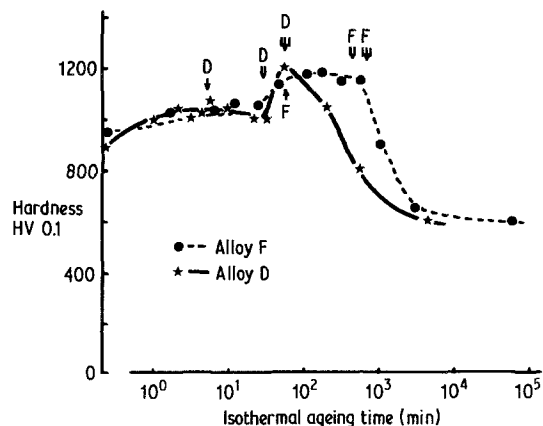


Figure 7 Hardness changes on annealing amorphous alloys D and F at 450°C. The arrows indicate the times at which first crystallization (↓), appearance of the eutectic structure (⊥), and final crystallization (⊚) take place.

behaves similarly in showing a hardness increase after very short annealing times, but now shows an additional sharp increase in hardness apparently just before crystallization. During crystallization there is little change in hardness, even as the eutectic phase appears and crystallization is completed. At very long annealing times the hardness again falls. The hardness variations of alloy D were similar to those shown by the other alloys studied.

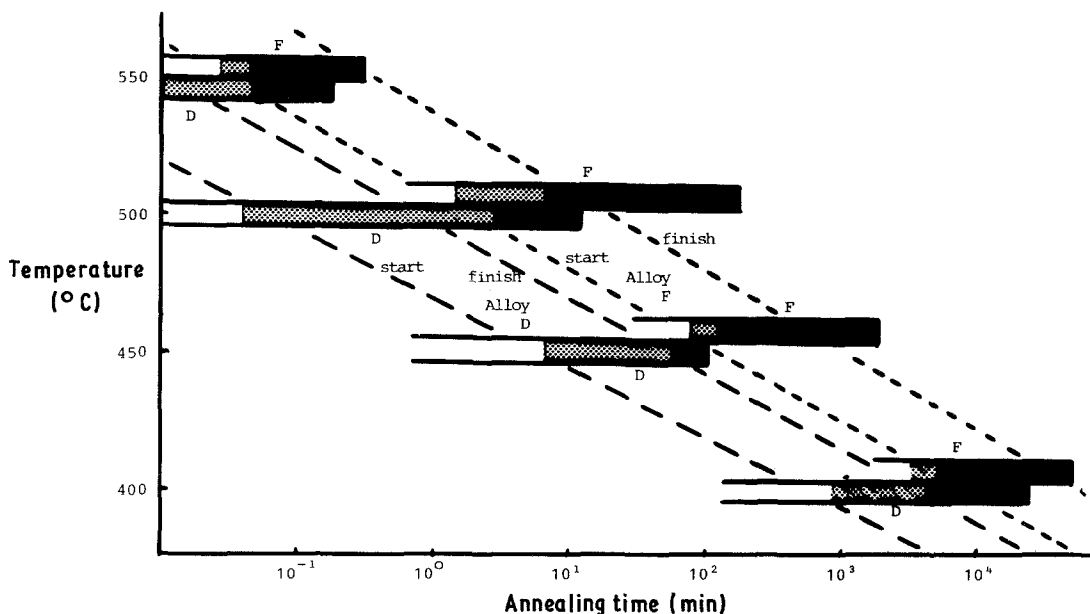


Figure 8 Changes in bend ductility and crystallization kinetics of alloys D and F with annealing temperature. The dashed lines indicate the start and finish of crystallization as a function of temperature. The horizontal bars represent the ductility observed: open – ductility greater than about 3%; hatched – ductility in the range 3 to 1%; closed – ductility less than about 1%.

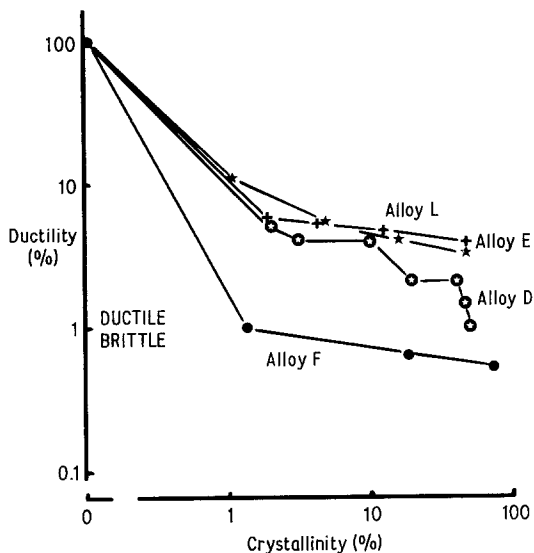


Figure 9 Ductility of the four alloys tested as a function of the amount of crystalline material present. Alloy F embrittles immediately a small amount of crystallinity appears. The other alloys remain relatively ductile as crystallization takes place. Alloy D becomes brittle as the eutectic transformation completes crystallization.

Fig. 8 shows that alloy D gradually becomes less ductile, at each of the temperatures, as crystallization occurs. Total embrittlement, for simplicity considered here as ductility less than the elastic strain at first deformation, say about 1%, occurs only when crystallization approaches completion. In fact, for some of the annealing temperatures, according to the embrittlement criterion adopted, this material hardly became brittle. Alloy F, on the other hand, very rapidly loses ductility as the first crystals form and almost immediately becomes brittle. Alloys E and L behaved similarly to D (except that alloy D embrittled when the eutectic structure formed). The changes in fracture strain are shown in detail in Fig. 9, where the ductilities of each alloy are related to the fraction crystallized.

3.3. Crack morphologies

Fig. 10 shows the tip portion of a crack in a specimen of partially crystallized alloy D. The characteristic oscillatory nature of the crack should be noted, and also the large extent of the plastic shearing zone ahead of the tip itself. Both these features were identical at cracks in fully amorphous specimens and can be taken as characteristics of the ductile nature of the amorphous state. In Fig. 11 a crack may be seen which connects a large

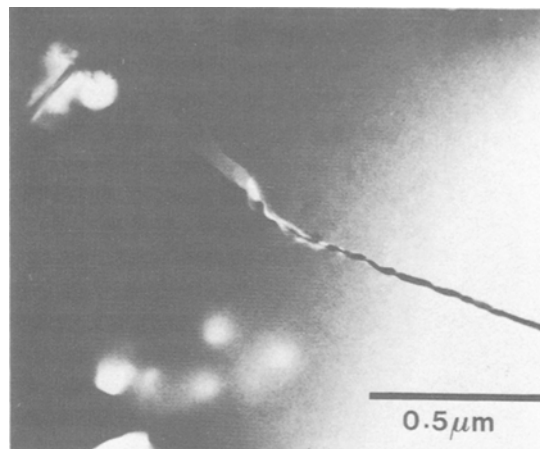


Figure 10 Crack morphology in a thin foil of partially crystallized alloy D. Note the slight undulations of crack direction and the large extent of plastic crack tip zone.

number of crystals in about 50% crystallized alloy D. The crack direction changes between each crystal and it may be seen that the soft crystals act to blunt the crack tip.

Fig. 12 shows a similar crack in a partly crystallized foil of alloy E. Similar characteristics, namely oscillation and extensive plastic tip deformation zone, can be distinguished. It is by no means obvious that the small crystals present cause significant disturbance of the crack, perhaps because the crystal size is small as is the volume fraction crystallized.

Cracks in foils of alloy F are shown in Figs. 13, 14 and 15. In Fig. 13 it may be seen that, despite the brittleness of this material, the same crack oscillation and extensive crack tip shear occur. Figs. 14 and 15 in addition show that the cracks are not deviated, blunted, or stopped by the crystals present. In Fig. 14 the crystal has broken in two pieces with some signs of deformation of the crystal. In Fig. 15 the crack appears to have passed along the interface between the crystal and the amorphous matrix. It has not been possible from these observations to establish the location of crack nuclei within bulk material: cracks within thin foils start at corners around penetrating holes. Clearly, however, the crystals in alloy F do not impede crack growth.

A crack within alloy L has previously been shown in Fig. 6. In this alloy, as within alloy D, the soft crystals act to blunt and slightly deviate the crack during propagation.

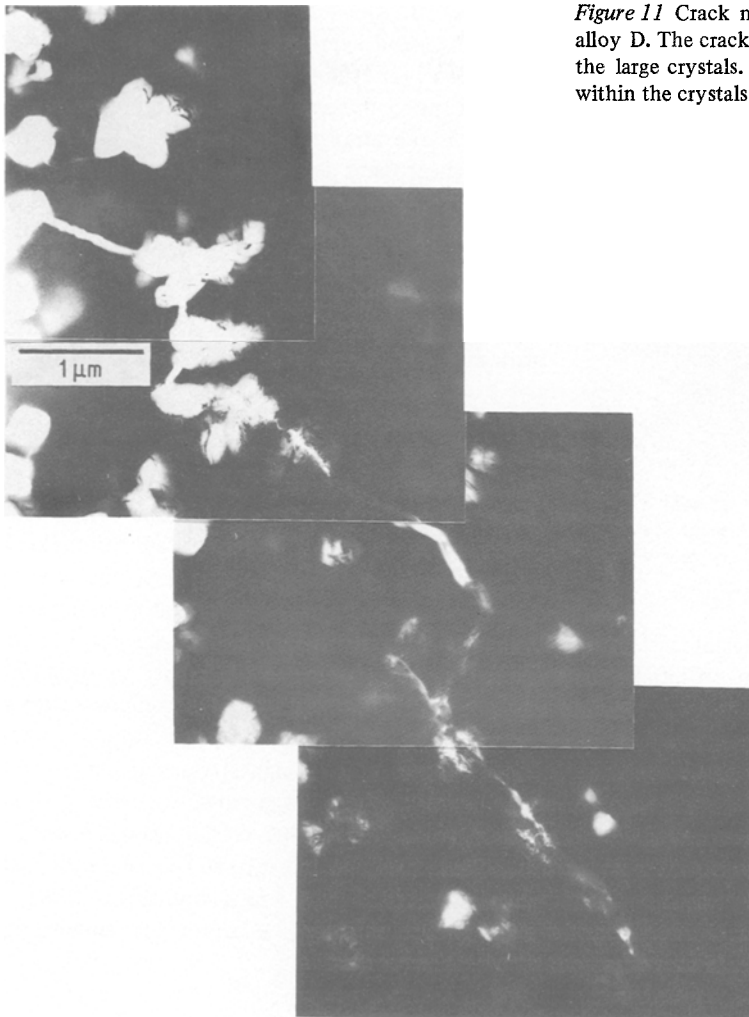


Figure 11 Crack morphology in almost fully crystallized alloy D. The crack follows a highly deviated path between the large crystals. Extensive deformation has taken place within the crystals.

4. Discussion

The present series of experiments has studied the changes in hardness, ductility and crack morphology during crystallization of amorphous alloys where crystals of orthorhombic Ni_3B -type phase of differing compositions and mechanical properties form, and where a bcc, iron-based phase forms. Within one of the alloys (alloy F) the crystals appear to be very hard, resisting deformation, and brittle (note the very high hardness of this alloy, Fig. 7, when the material is nearly completely crystallized, and the limited extent of deformation and ductility of the crystals in Fig. 14). Within the other three alloys the crystals formed are relatively soft and capable of significant deformation (note the constancy of hardness in Fig. 7 as crystals form in alloy D, and the faults, bend contours and dislocations in the

crystals formed, see Fig. 11, for example). The similarity of the mechanical characteristics of the crystals formed in alloys D, E and L imply that these factors are important in controlling the crack morphologies and the ductility of the partially crystallized material, and that the specific phase nature of the crystal, *per se*, has no effect.

It is clear from the hardness data of Fig. 7 that significant changes take place in the amorphous state before any crystallization occurs. It seems likely that such changes may continue to occur in the amorphous matrix even as crystals form. The extent of this change appears to be small for alloy D (Fig. 7) where the hardness appears to reach a near constant value before appreciable crystallization. However, for alloy F there appears to be a significant change in the amorphous structure just before crystallization (as seen by the

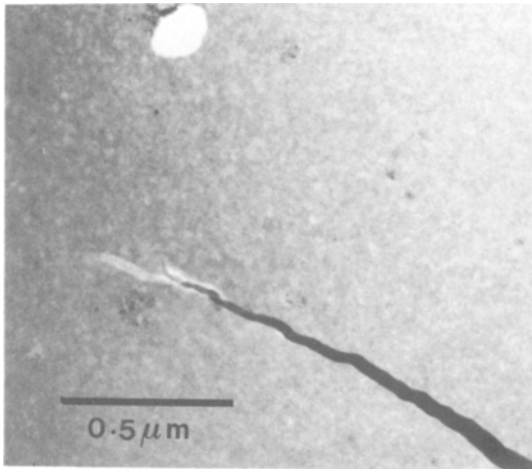


Figure 12 Crack morphology in partially crystallized alloy E. Extensive crack tip plasticity may be seen. The crack appears to pass by the side of small crystals without obvious interaction.

hardness increase just before crystallization in Fig. 7). Nevertheless, the similarity of crack and tip morphology within the amorphous matrix, both when in the as-cast, fully amorphous state and when partly crystallized implies that it is not cracking of the amorphous material itself that induces embrittlement. Cracking appears to take place in a similar manner in fully amorphous material and in the amorphous matrix of a partly crystallized material.

The influence of a foreign particle (crystal) within an amorphous matrix may be considered

in terms of the effect on deformation, crack nucleation and crack propagation. A crystal of almost any mechanical nature should be capable of interrupting the intense shear band propagation typical of the amorphous state. The change from intense shear band deformation to more homogeneous, wavy shear has been observed both when very hard [7] and very soft [10] crystals are introduced. The hard crystal will act as a more-or-less elastic barrier, impeding deformation and leading to stress concentration. This stress concentration can ultimately cause particle cracking, if the particle is brittle, or particle-matrix decohesion, if the interface is relatively incoherent. The soft crystal, on the other hand, will deform, dispersing thereby the intense, localized shear into a larger volume. Deformation zone "blunting" thereby occurs, limiting stress concentration. Hard, brittle particles may, therefore, be considered as more likely sources of crack nucleation, while soft, ductile particles will be only weak sources for nucleation. Similar arguments apply to the influence of brittle or ductile particles on crack propagation. The brittle crystal can oppose crack propagation, but the high stresses generated will subsequently fracture the particle, or lead to particle-matrix interface decohesion. The soft ductile crystal will readily deform at the tip of a propagating crack, leading to crack blunting, crack tip stress reduction, and to the crack slowing or stopping.

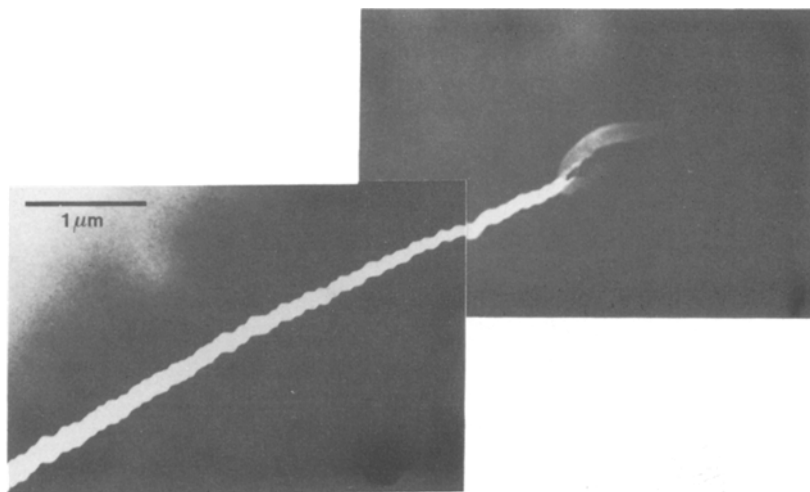


Figure 13 Crack morphology in slightly crystallized alloy F. The undulations in crack surface, and the large crack-tip plasticity are evident.

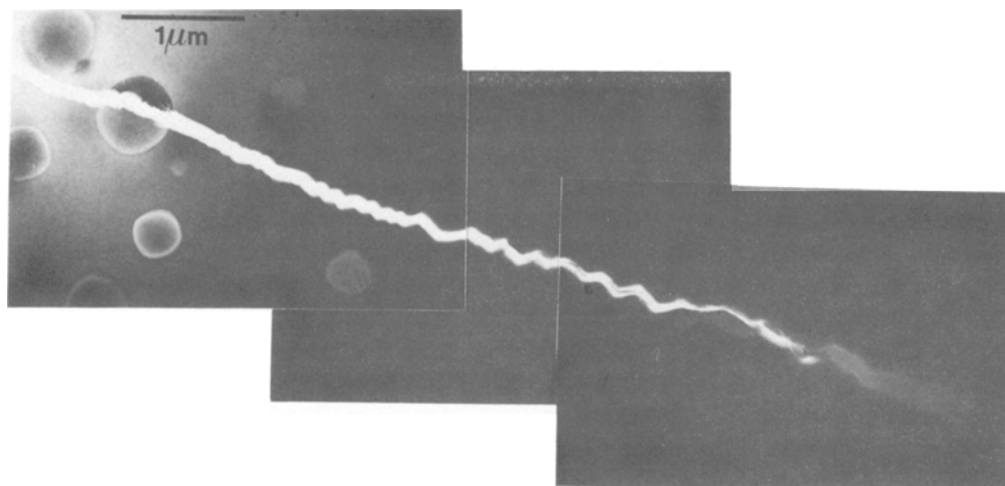


Figure 14 Crack morphology in partially crystallized alloy F. The crack still undulates, with a large plastic zone ahead of the tip. One crystal has broken in two with no sign of significant deformation.

5. Conclusions

1. The changes in hardness and bend ductility of a series of Ni–Si–B amorphous alloys on annealing to crystallize depend on a number of factors, including changes in the amorphous matrix itself and the type of crystal produced.

2. Hardness increased on initial annealing of the present amorphous alloys before any crystallization began. For one of the alloys, a significant further hardness increase occurred just prior to, or during early crystallization. As crystallization of this alloy continued to completion, the hardness maintained this high value. For the other alloys studied, the crystal phases formed were relatively soft and there was no sudden hardness increase at, or immediately before crystallization. One of these

alloys subsequently hardened when a fine-scale eutectic structure formed.

3. One of the alloys studied embrittled immediately when crystallization began, whilst the other alloys remained ductile until near full crystallization. Based on the morphological examination of cracks within thin foils of these materials it appears that it is the mechanical properties of the crystal phase and the integrity of the crystal amorphous–matrix interface that controls embrittlement. Soft, well-adhered crystals are effective at stopping intense shear and crack propagation, whilst hard or poorly adhered crystals act as crack nucleators and do not delay crack propagation. The crystalline nature of the phase that forms and changes in the amorphous matrix itself do not appear to play an important role in causing embrittlement of these alloys.

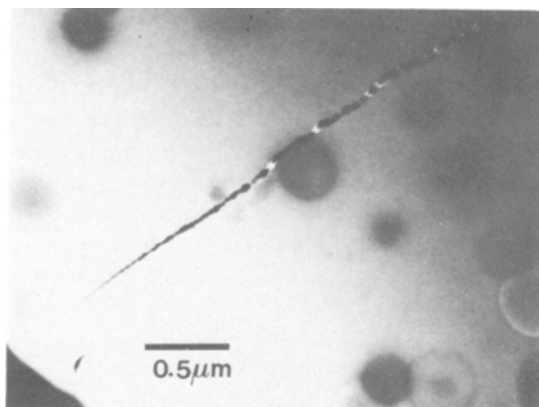


Figure 15 Crack–crystal interaction in partially crystallized alloy F. The crack has apparently caused decohesion of the crystal–matrix interface.

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