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MICROSTRUCTURAL CHANGES IN (Mg) PSZ DURING AGING AT 1000°C

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DURING AGING AT 1000°C

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May 1986

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MICROSTRUCTURAL CHANGES IN (Mg) PSZ DURING AGING AT 1000°C

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A (Mg) Partially-Stabilized Zirconia aged for various times at 1000°C has been characterized by transmission electron microscopy and correlated with earlier fracture property measurements. The most important microstructural features in terms of explaining an observed deterioration in both rupture strength and fracture toughness are a grain boundary phase (0) rich in Mg and Si with orthorhombic crystal structure (probably an olivine) and a glassy phase which progressively precipitates preferentially at interphase interfaces. A loss in rupture strength is attributed to formation of a glassy film on the boundaries between the (0) phase and the ZrO<sub>2</sub> matrix. Similarly, the development of a continuous glassy film at the interfaces between monoclinic particles and the matrix can account for the decrease in fracture toughness. Results obtained by conventional imaging, high resolution and analytical electron microscopy will be given to support the conclusions.

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## 1. INTRODUCTION

Partially-stabilized-zirconia (PSZ) is one of a class of new materials based on  $ZrO_2$  (Zirconia-toughened ceramics, ZTC's) that has received considerable attention in the last decade because of their high strength and potential for engineering applications in severe operating conditions (see ref. [1-3] for comprehensive reports of recent work). They appear to offer great flexibility in that they exhibit a range of properties that, in principle, can be matched to specific applications (Claussen, ref. [2] p. 325). The properties are not achieved routinely and depend on careful control of composition, processing variables, and heat treatments. The promise of ZTC's is however clouded by concern that some of them may have an Achilles Heel, namely a lack of long term phase and structural stability at high temperature. This aspect, in spite of its importance, has been the subject of relatively little study. Investigations have been conducted on the changes in microstructure and mechanical properties that occur during high temperature aging of PSZ's both above and below the eutectoid. With increasing time at temperature in the range 1400-1500°C, a large drop in properties is observed as coarsening of the tetragonal (t) precipitates causes them to lose coherency and transform to the monoclinic (m) phase during cooling [4,5]. Below 1400°C, a eutectoid decomposition occurs whereby the cubic (c)  $ZrO_2$  matrix transforms to (t)  $ZrO_2$  + MgO and subsequently to (m) $ZrO_2$  + MgO during further cooling [6,7] again with concomitant deterioration in properties. At 1200°C and below, the latter reaction occurs directly. According to the results of Hanninck [8], both increases and decreases in the mechanical properties occur during aging at 1100°C depending on the alloy composition and aging time.

Farmer et al [9] also studied decomposition reactions in (Mg) PSZ and showed a variety of products formed with a marked dependence on the prior thermal history. They found the predominant reaction at 1100°C to be the formation of a cellular structure of m-ZrO<sub>2</sub> and MgO at the grain boundaries. Butler and Heuer [10] also emphasized the importance of the structure of the boundary regions on mechanical and other properties. They observed two cubic phases and an associated glassy phase forming at grain boundaries during aging of a (Ca,Mg) PSZ at 1400°C. One of the cubic phases resulted from migration of the grain boundary in a manner reminiscent of diffusion-induced grain-boundary migration. Rühle et al [11] found a crystalline grain boundary phase of MgSiO<sub>4</sub> containing Fe, Ca, Si and Al impurities in (Mg) PSZ.

Recently, two of the present authors have shown [12] that significant reductions in fracture strength and fracture toughness occur in a (Mg) PSZ during relatively short term exposures at 1000°C. A drop in K<sub>IC</sub> from an initial value of 9 MPa m<sup>1/2</sup> to 6.4 MPa m<sup>1/2</sup> was measured after 96 hours with an intermediate value of 6.7 after 48 h. A concomitant change in the room temperature fracture strength from 500 to 400 to 355 MPa was also found. A detailed microstructural characterization of these samples has now been performed, using a variety of TEM techniques, to investigate the origin of this property degradation.

## 2. EXPERIMENTAL PROCEDURE

TEM specimens were made from the three bars (A, B and C aged for 0, 48 and 96 h respectively) of a commercial 3.6 w/o (Mg) PSZ supplied by Feldmühle, W. Germany which was used in the earlier study. The material had a density of 5.75 g.cm<sup>-3</sup>, a porosity of 1.5 v/o, and a grain size of about 50 μm. Initially, the material contained volume fractions of the cubic (c),

tetragonal (t) and monoclinic (m) phases in the ratio 34 : 35 : 31. Disc samples were ground, ion milled and coated with carbon using standard practice.

Most of the observations were carried out at 300 kV on a Philips EM 430, but the X-ray microanalysis was performed at 100 kV on a JEOL 100CX analytical microscope (AEM) equipped with an EDAX X-ray energy dispersive spectrometer. The size of the probe used for the analysis depended on the size of the region examined, 100 seconds counting intervals were used, and foil thickness giving good count rates were selected. A quantitative analysis was not attempted; instead the ratios of the peak heights of the Mg K, Si K and Zr L lines were used as a rough measure of the relative compositions of the various phases examined. In addition to peaks originating from Mg, Si, Fe and Zr, peaks corresponding to Cu and Zn, were also observed. These are attributed to excitation of the specimen holder.

### 3. RESULTS

#### 3.1 General observations

A detailed comparison of the gross microstructural features of samples A, B and C revealed that with the exception of the (t)/(m) ratio no significant changes had occurred during aging. In each case the microstructure consisted of large homogeneous regions of (c)  $ZrO_2$  containing a distribution of (t) and (m) precipitates typical of PSZ's. Interspersed with these regions were, however, large heterogeneous areas containing a distribution of grains of another phase as shown in Fig. 1. This phase had a much greater transparency to electrons making it particularly easy to survey at low magnifications. Observation was also aided by the propagation of bend contours through the grains during large angle tilting of the specimen. The grains were often elongated and occasionally the long grains themselves contained transverse grain boundaries (see Fig.



1). This suggested that they had nucleated and grown on prior (c)  $ZrO_2$  grain boundaries, with growth along these boundaries occasionally leading to impingement and coalescence. This picture was confirmed by the observation of a number of triangular-shaped grains of the new phase which had clearly formed at triple points of (c)  $ZrO_2$  grains. An example is shown in fig. 2. Diffraction patterns from the new phase and the three surrounding (c)  $ZrO_2$  grains, confirmed this interpretation.

The initial electron diffraction patterns indicated the g.b. phase has cubic symmetry. However, application of convergent beam diffraction showed unambiguously that in fact it has orthorhombic symmetry as shown in fig. 3. The conventional diffraction pattern indicated a 4-fold crystal symmetry characteristic of a cubic or tetragonal structure, whereas the whole CBD pattern and HOLZ lines clearly show only two mirror planes which together with the lattice parameter obtained from the First Order Laue Zone ring identify it as orthorhombic. Patterns from many zone axes were obtained but it has not been possible to identify this (0) phase by comparison with ASTM cards. Porter and Heuer [7] also reported observing an orthorhombic phase in (Mg) PSZ but in their case the phase was present as finely dispersed precipitates making further analysis extremely difficult.

In addition to the (0) grains, the uniformity of the microstructure was disturbed by the occasional presence of pockets of a glassy phase. These were usually found adjacent to (0) grains, or around holes which could have originated from the preferential thinning of (0) grains. An example of such a region is shown in the dark field image of fig. 4 which was recorded by placing the objective aperture over a segment of the diffuse ring characteristic of diffraction patterns from non-crystalline materials.

In one instance, a glassy region entirely surrounding an (0) phase was found suggesting a close connection between the two phases. To examine this point further, the AEM was used to obtain semi-quantitative analyses of the various phase compositions.

### 3.2 Analytical electron microscopy

A comparison of the relative compositions of the (0) grains, glassy phase pockets and (c)  $ZrO_2$  matrix was obtained from analyses on specimens A and C. Typical spectra are given in fig. 5 and the results of all the analyses are summarized in Table I. They represent the average of five spectra recorded from different regions of the same specimen. No systematic changes in the compositions of the three phases due to aging was detectable, since the variations from region to region in the same sample were as large as the differences between the samples.

It is apparent from the results that relative to the matrix both the (0) and glassy phases are richer in Mg and Si. However the observed large Zr peaks in both the (0) grains and glass may have originated from excitation of the nearby matrix since in one measurement on an (0) grain only Mg and Si was detected. In this instance the ratio of Si to Mg was also 1:1. It is also seen that almost all the Fe in the material is concentrated in the glass phase.

The absence of gross microstructural or microchemical differences between the samples (A-C) led to a search for more subtle changes which is described next.

### 3.3 Higher resolution observations

Examination at higher magnifications revealed the presence of a "bubble-like" phase (x) that was precipitated from the (0) grains in amounts that increased with aging time at  $1000^\circ C$  (i.e. from A to C). This feature was also observed

but to a lesser extent, throughout the matrix together with apparently related tube-like features (or stringers) which exhibited identical contrast behavior. Of particular significance was the fact that this (x) phase precipitated preferentially at interphase boundaries.

The bubble-like contrast is illustrated in the through-focus series in fig. 6. As in the well-documented case of gas bubbles or voids, the precipitates are virtually invisible at focus (fig. 6b) and display distinctive contrast differences in the under (fig. 6a) and over - (fig. 6c) focused conditions. It should be emphasized that the observations were conducted at 300 kV and that these features were present at the outset. Electron-beam-induced changes in the structure of the (0) grains did take place slowly over the course of long periods of viewing but these were over and above the features described here.

Stereopairs of micrographs taken from the same region showed the (x) precipitates are distributed throughout the foil thickness and are not a surface artifact. The stereo-pair, one half of which is shown in fig. 7, clearly showed that while the (x) phase has precipitated uniformly throughout the (0) grain interiors it precipitates preferentially at the (0) grain/(c)  $ZrO_2$  matrix interfaces and the monoclinic precipitate (m)/ (c) matrix interfaces. In the latter case, the individual (x) precipitates were seen to be associated with the large multiply-twinned particles, e.g. X in fig. 7. They have nucleated at the triple points where several twin variants meet. In other instances the precipitation is in the form of a continuous or semicontinuous film (e.g. at Y and Z) and appears to envelope an (m) or (t) particle in the matrix. Another striking example of the precipitation at twin/matrix interfaces is given in fig. 8; in this case from the unaged specimen A showing that the effects are present (but to a much smaller extent) in the as-prepared material.

Since these features represented the only observed progressive change in microstructure in the three samples, attention was concentrated on establishing the nature of the (x) phase by studying both the (0) grains and the matrix.

In the (0) grains the (x) precipitates were readily identified as a glassy phase. The diffraction pattern of a particularly thin grain showed both diffraction spots and diffuse rings. Fig. 9, which is a dark field imaged formed from part of the ring, revealed that the diffuse intensity originates from the (x) precipitates. Similar attempts to repeat this experiment on the matrix to image the stringers were unsuccessful because the diffuse scattering from the small amount of glass was completely masked by the much greater diffracted intensity originating from scattering in the (c), (t) and (m) phases. It was, however, possible to show the existence of a continuous glassy phase at the interphase boundaries between the (0) grains and the matrix as shown in fig. 10.

Although the stringers in the matrix could not be imaged directly using the diffuse scattering method, it was always observed that they exhibited identical imaging characteristics as the (0) grain/matrix interphase glassy film. This is also illustrated in fig. 10 which was taken with an objective lens defocus of  $3\mu\text{m}$ . Earlier work on glassy regions in ceramic materials has shown that the strong dark contrast bounded by the Fresnel fringes is characteristic of a glassy film [14]. The micrograph also clearly shows the continuous nature of the film around the transformed (m) grain.

Several attempts were made to image the glass pockets in the matrix directly using high resolution structure imaging. In many cases a stringer exhibited an amorphous structure at some defocus settings and fringe contrast at another.

This can be understood if the glass pocket only extends partially through the foil thickness. An example in which the non-crystalline structure was observed at all defocus settings over the range  $\pm 48$  nm in five 24 nm steps is shown in fig. 11.

#### 4. DISCUSSION

The two microstructural features that appear to be related to the deterioration in fracture toughness and strength at 1000°C are the grain boundary phase with orthorhombic symmetry and the glassy phase distributed inhomogeneously throughout the material. Many workers, most recently Butler and Heuer [10], have emphasized the importance of grain boundary regions in ceramic alloys. Not only do critical processes occur there which aid initial consolidation but the subsequent properties and structural integrity also strongly depend on the residual phases formed on cooling. Large orthorhombic grains at (c) zirconia boundaries have not been observed previously, although Porter and Heuer [7] have shown that fine scale matrix precipitation is associated with extra diffraction spots with orthorhombic symmetry. These workers have also reported observing Forsterite, another phase with orthorhombic crystal structure, but no details were given.

From the observed close connection between the (0) grains and pockets of glassy phase material it is reasonable to conclude that the grains crystallize from the glass during cooling. This is consistent with other observations where large monoclinic (m) or cubic (c) zones nucleated in the (c)  $ZrO_2$  grain boundaries, often with an associated glassy phase. It appears that many different types of grain boundary phase may form; the actual ones presumably depending on the precise alloy composition and the prior thermal history.

Attempts to positively identify the (0) phase are continuing. The microanalyses to date show it to be rich in Mg and Si, and the orthorhombic

structure suggests that it is likely to be of the olivine type. However, the appearance of the grains is quite different to that reported earlier (compare, fig. 1 with fig. 4 of ref. [11]).

The mechanical property measurements show that the presence of the (0) grains in the (Mg)  $ZrO_2$  does not have a deleterious effect at ambient temperatures. However, in the material aged at  $1000^{\circ}C$ , the observed precipitation of a glassy film in the (0) grain/matrix interfaces can be expected to lead to a significant deterioration in the fracture strength. A graphic illustration of this point is shown in fig. 12 where a long crack is seen propagating through the foil. Regardless of whether the crack was present in the bulk sample, or introduced during specimen thinning or handling, it is clearly seen to follow a path that links one (0) grain with the next. Evidently, the elongated (0) grain morphology and a completely wetted interface with the matrix has provided an easy course for the crack to follow. Similar easy crack propagation has been observed in a (Mg) PSZ containing a thick continuous (m) phase in the grain boundaries.

The only microstructural difference between the three specimens, A, B and C was in the amounts of glassy phase precipitated in the (0) grains, matrix and the interphase boundaries. For the case of (m) particle/(c) matrix interfaces this difference can be seen by comparing fig. 8 (specimen A) with fig. 10 and fig. 13 (specimen C). With no aging at  $1000^{\circ}C$  a small amount of glass is already present concentrated in pockets at the twin boundary/matrix interfaces of a particle that has already undergone the (t) $\rightarrow$ (m) transition (X). After aging for 96 h at  $1000^{\circ}C$ , the glassy films are (1) present in much larger quantities and (2) often in continuous or semi-continuous films around the precipitate particles (see fig. 10 and 13). Fig. 10 also shows that the interphase (0)/(c) film is continuous.

The drop in fracture toughness during aging may be related to the amounts and distribution of glass precipitated in the (c) matrix. It is well known that the toughness is a function of the volume fraction of (t) precipitates since crack propagation is inhibited by the stresses set up by the transformation of the (t) to (m) phase. However, it is also well documented that (t) particles spontaneously transform to the (m) symmetry either when a critical size is exceeded, or when they lose coherency. In considering mechanisms whereby a strained coherent precipitated can lose coherency, decohesion at the particle/matrix interface by the precipitation of a glassy film is clearly one of the simplest. Thus, the progressive growth of such films during aging at 1000°C will lead to a significant reduction in the (t) volume fraction and a concomitant loss in fracture toughness. Preferential formation of the glass at the interfaces is favored presumably because the energy of the system is lowered as the coherency strains are relaxed.

Since the above interpretation hinges on establishing a correspondence between the (x) precipitates in the (0) phase with the stringers in the matrix and both with a glassy phase, we conclude by reviewing the experimental evidence and considering related research.

Both the (x) precipitates and stringers exhibit identical absorption contrast behavior in a through-focus series and as shown by Ruhle et al [14] the bright and dark line contrast is a characteristic of a glassy film. Although it was not possible to obtain dark field images from the stringers by using the diffuse scattered intensity, the technique was successful in identifying the (x) precipitates in (0) grains and the interface film, as a glassy phase. Finally, the high resolution structure image of the (c) matrix provided direct evidence for the presence of pockets of glassy phase. It is important to reiterate these

points since in early studies features that bear a close resemblance to the stringers have been observed and interpreted differently. For example, Hannink [8] in a study of the decomposition of (c)  $ZrO_2$  into (t)  $ZrO_2$  and  $MgO$  observed the formation of Mg-rich pipes. The pipes bear a resemblance to the stringers but they form on a much coarser scale.

Secondly when in-focus images of the stringers are formed they sometimes show the same contrast as the microcracks which form at particle/matrix interfaces in  $ZrO_2$ . Of course, in sufficiently thin areas of the foil the stringers, if large enough in size, may become microcracks if the ion-thinning preferentially etches the glassy phase. In thick regions of the foil, distinguishing between small stringers containing a glass composed of low atomic number elements and microcracks becomes more difficult. However, the strong internal contrast exhibited for example in figs. 8 and 13 is not usually observed from a crack. Also microcracks obviously cannot completely envelope the particle as does the glassy film, and the precipitation of a string of discrete particles in the interface, as seen for example in fig. 6 and 7 can not be explained as cracks.

In the absence of a more detailed knowledge of the material chemistry and prior history, the origin of the glass precipitation can only be speculated on. One possibility is that the initial processing steps left the (c)  $ZrO_2$  matrix and the (0) phase supersaturated in Mg and Si even at  $1000^\circ C$ . Assuming sluggish kinetics, slow precipitation of a  $MgO$ ,  $SiO_2$  glass could occur over the course of 100 hrs. An equivalent but alternate view is that Mg and Si segregation at the interphase interfaces occurs leading to conditions favorable for a glassy phase to form [15]. One problem with this is the question of how likely it is that the (0) phase and (c) matrix would both have the appropriate solid



solubilities for Si and Mg and supersaturations for the glass to precipitate to about the same extent.

## 5. CONCLUSIONS

1. A deterioration in the fracture properties of a (Mg) PSZ that occurs during aging at 1000°C has its origin in an unstable microstructure that progressively precipitates a glassy phase, principally at interphase interfaces.

2. The decrease in fracture strength is also related to the presence of a Mg, Si-rich grain boundary phase with orthorhombic crystal structure. Glassy films precipitating on its long interfaces with the matrix  $ZrO_2$  provide easy paths for cracks to run.

3. Glass precipitation at the (t) particle/(c) interfaces cause the particles to lose coherency and spontaneously transform to the (m) phase, with attendant decrease in fracture toughness.

## 6. ACKNOWLEDGEMENTS

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TABLE 1

Ratios of X-ray peak heights for various phases in (Mg) PSZ

REGION ANALYZED	SPECIMEN A MgK : SiK : ZrL : FeK	SPECIMEN C MgK SiK ZrL FeK
(O) GRAINS	1 : 1 : 3 : Tr <sup>+</sup>	1 : 1 : 1 : Tr
GLASS POCKET*		1 : 2.5 : 6 : 12
MATRIX ZrO <sub>2</sub>	1 : 2 : 18 : Tr	1 : 2 : 12: Tr
+TRACE		

\* Argon peaks were also observed in these spectra providing confirmation that argon ions are incorporated into the glass structure during thinning [13].

## 8. FIGURE CAPTIONS

Fig. 1. Bright field micrograph of elongated grains of (0) phase in matrix of  $ZrO_2$ . Note the high transparency of (0) grains to electrons, the distinctive bend contours, and the boundaries (arrowed).

Fig. 2. (0) phase formed at  $ZrO_2$  grain boundary triple point and spreading along adjacent boundaries.

Fig. 3. Convergent beam diffraction pattern taken from an (0) grain showing a mirror symmetry plane of whole pattern and HOLZ rings.

Fig. 4. Large pocket of a glassy phase, A, imaged in dark field using part of the diffuse rings shown in the inset diffraction pattern. The objective aperture was too large to exclude all the diffracted beams emanating from the matrix, thus scattered intensity is observed from some of these regions too (e.g. B).

Fig. 5. Representative x-ray spectra from micro-analyses of (a) the (0) phase; (b) a glass pocket; and (c) the  $ZrO_2$  matrix. Considerable variations in the relative peak heights were found in the analyses of (0) grains.

Fig. 6. Through-focus series of a region containing fine precipitates of the glass A and continuous films B. Typical bubble/void Fresnel fringe contrast is exhibited by both features A and B.

Fig. 7. One half of an underfocussed stereo pair showing individual particles (X) at twin boundaries strings of precipitates (Y) and continuous films (Z) at interfaces.

Fig. 8. Micrograph showing strong contrast exhibited in overfocussed image of continuous (A) and semicontinuous (B) films of glass precipitated at the (m)/(c) interfaces.

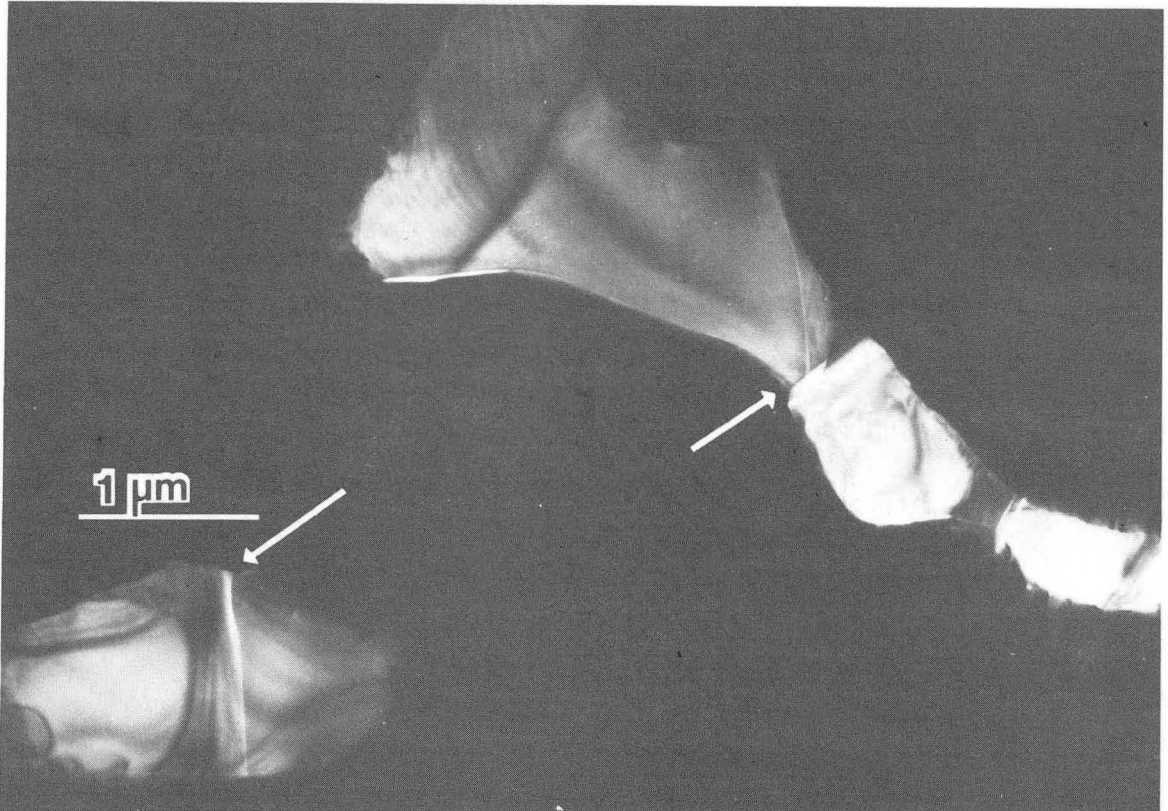
Fig. 9 Dark field image of (X) precipitates formed with diffuse scattered intensity.

Fig. 10. Overfocussed image of glassy films at the (0) grain/ $ZrO_2$  interface (x) and around monoclinic particle (Y) showing similarity of contrast behavior.

Fig. 11. High resolution image of the interface between a twinned monoclinic particle (M) and the cubic matrix (C). Note the regions (arrowed) exhibiting contrast characteristic of a glassy phase. No lattice fringes were observed in these regions throughout a  $\sim 48$  nm five exposure series.

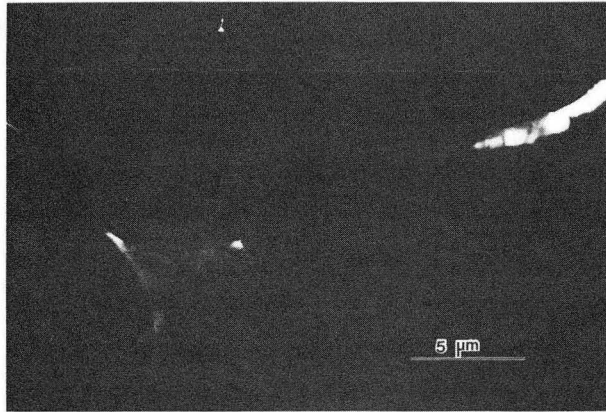
Fig. 12. Low magnification micrograph showing how a propagating (Z) crack follows a path that links up the (0) grains.

Fig. 13. Underfocussed image showing extensive glass film precipitation around monoclinic particles.



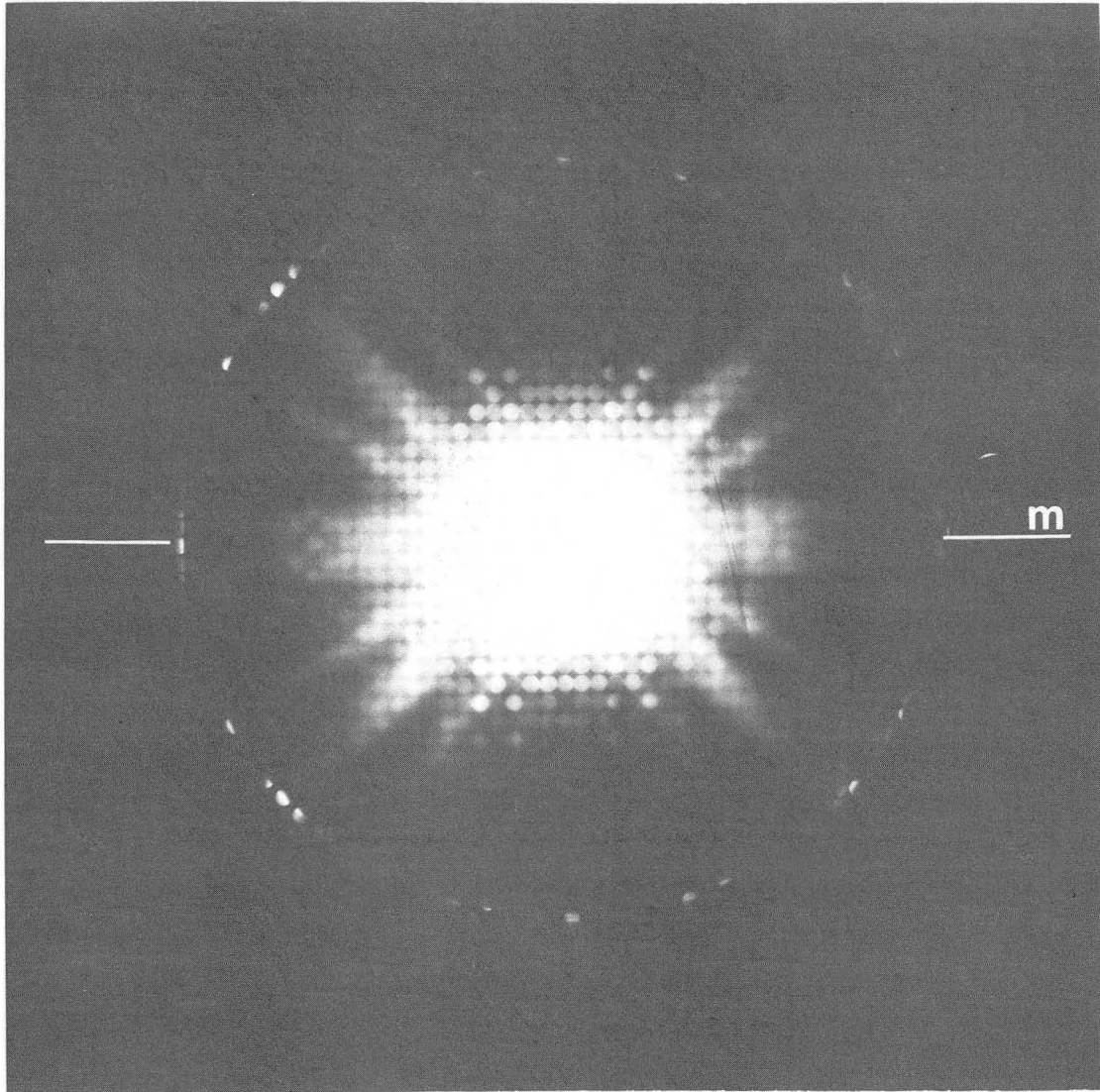
XBB 864-3471

Fig. 1



XBB 864-3472

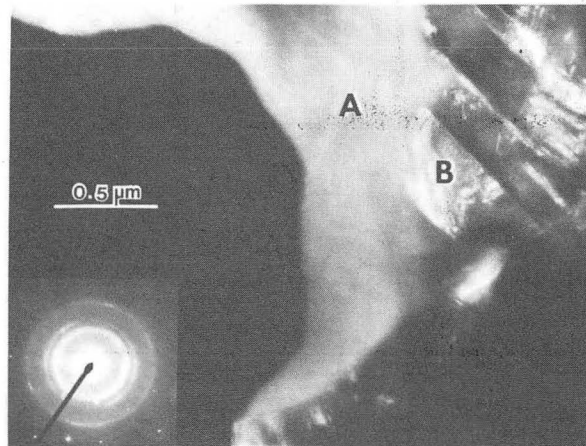
Fig. 2



XBB 864-3473

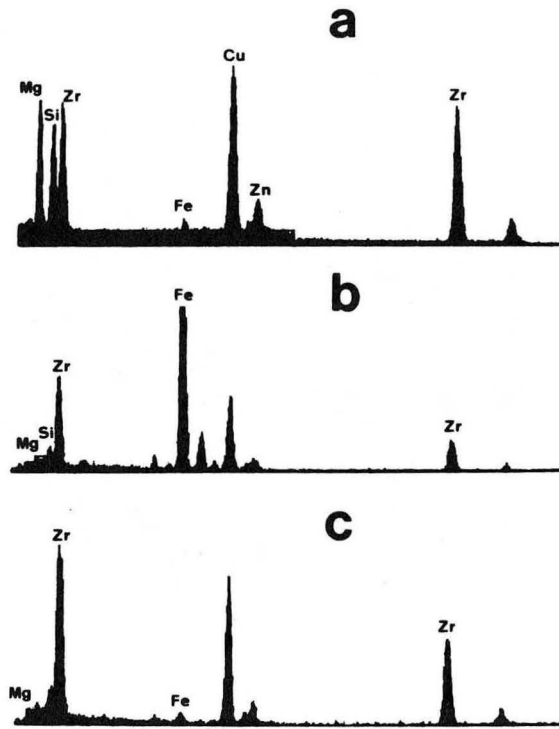
Fig. 3





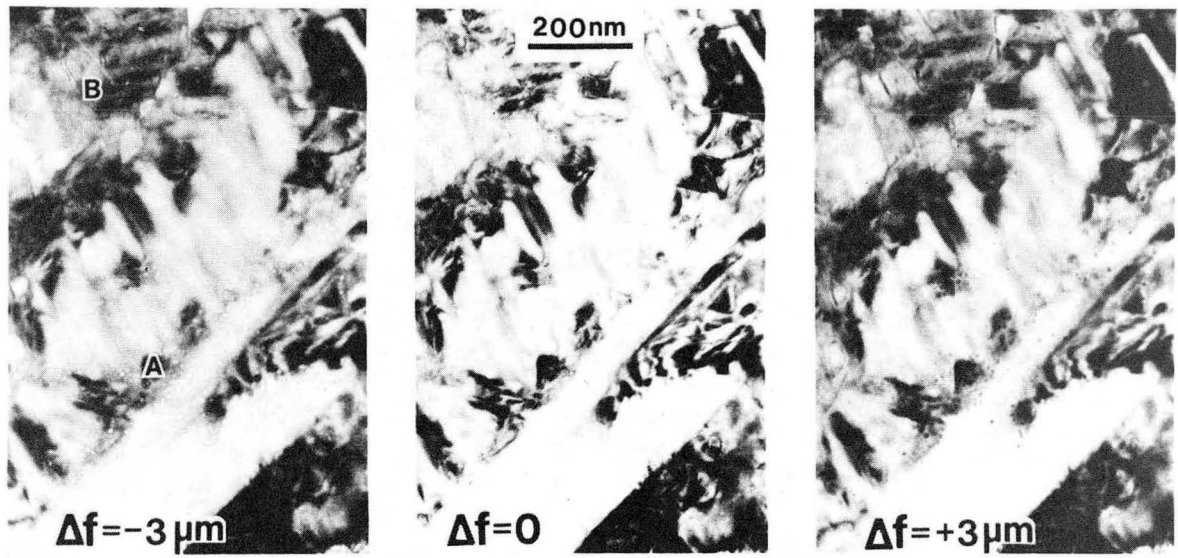
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Fig. 4



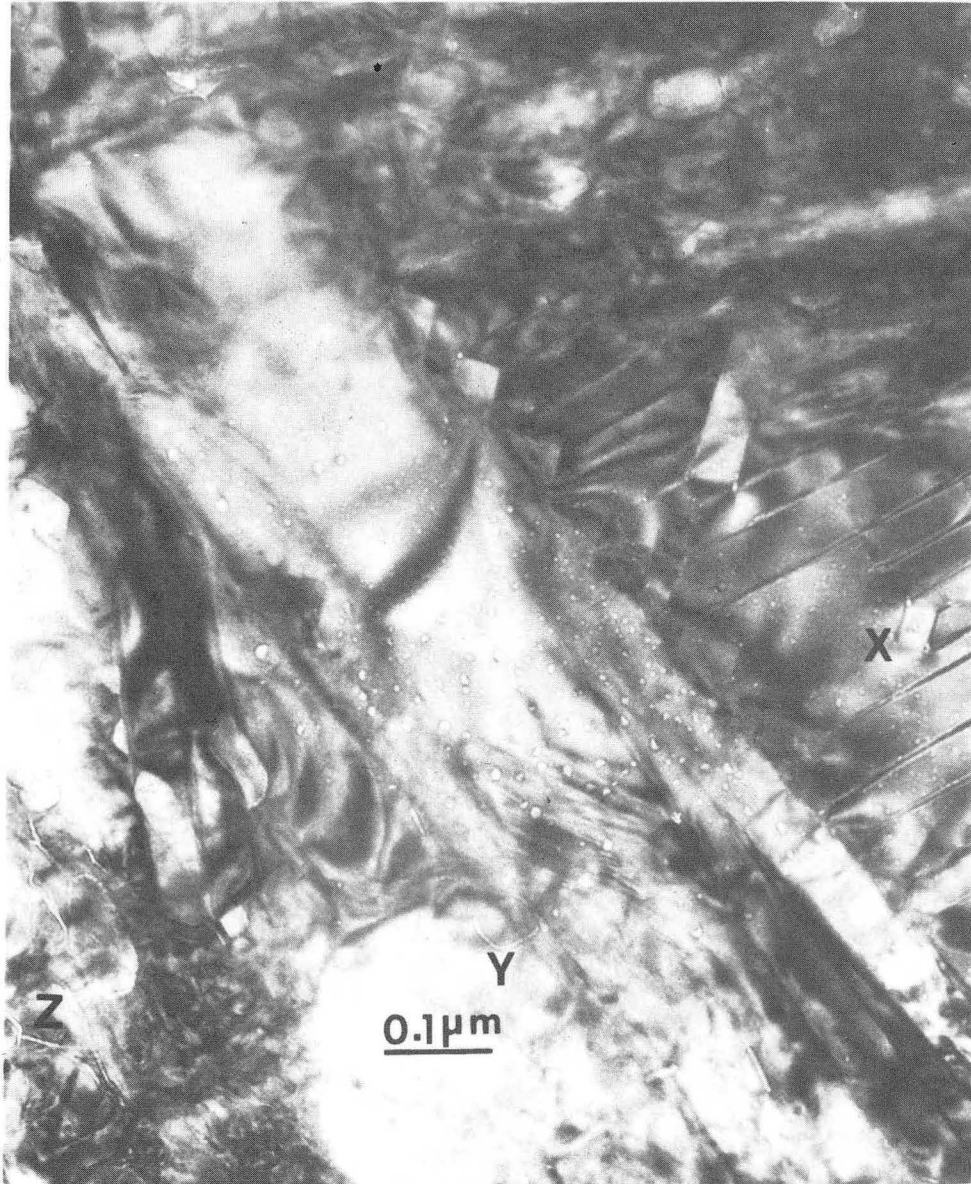
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Fig. 5



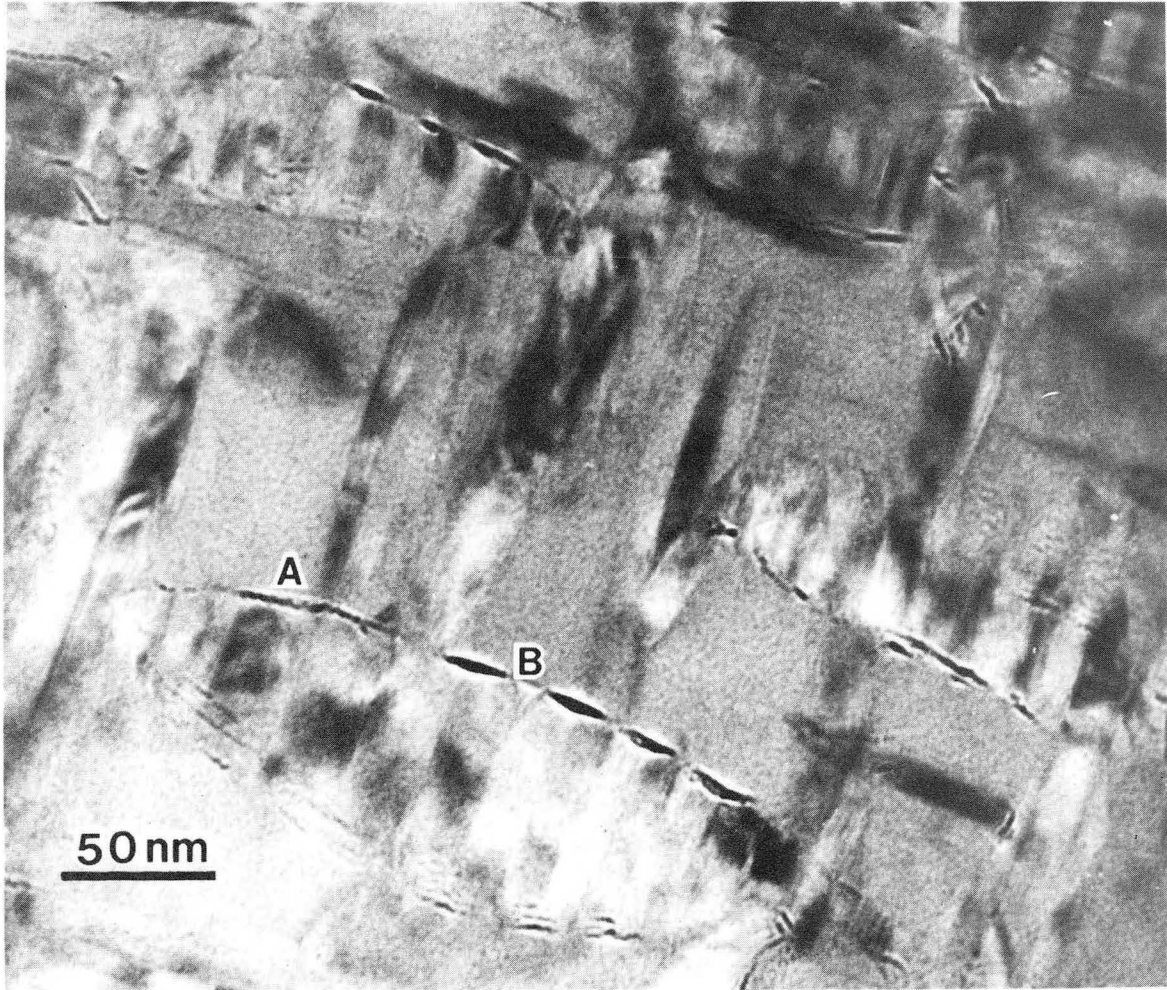
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Fig. 6



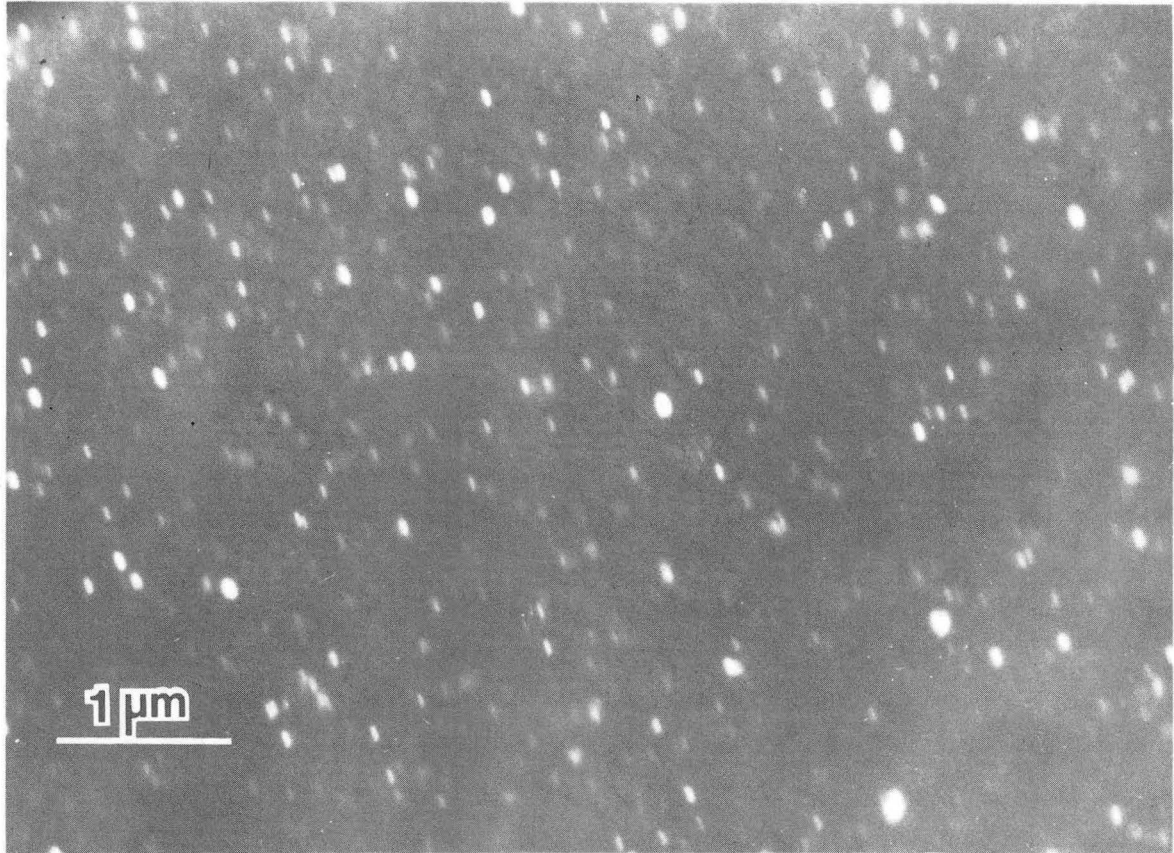
XBB 864-3476

Fig. 7



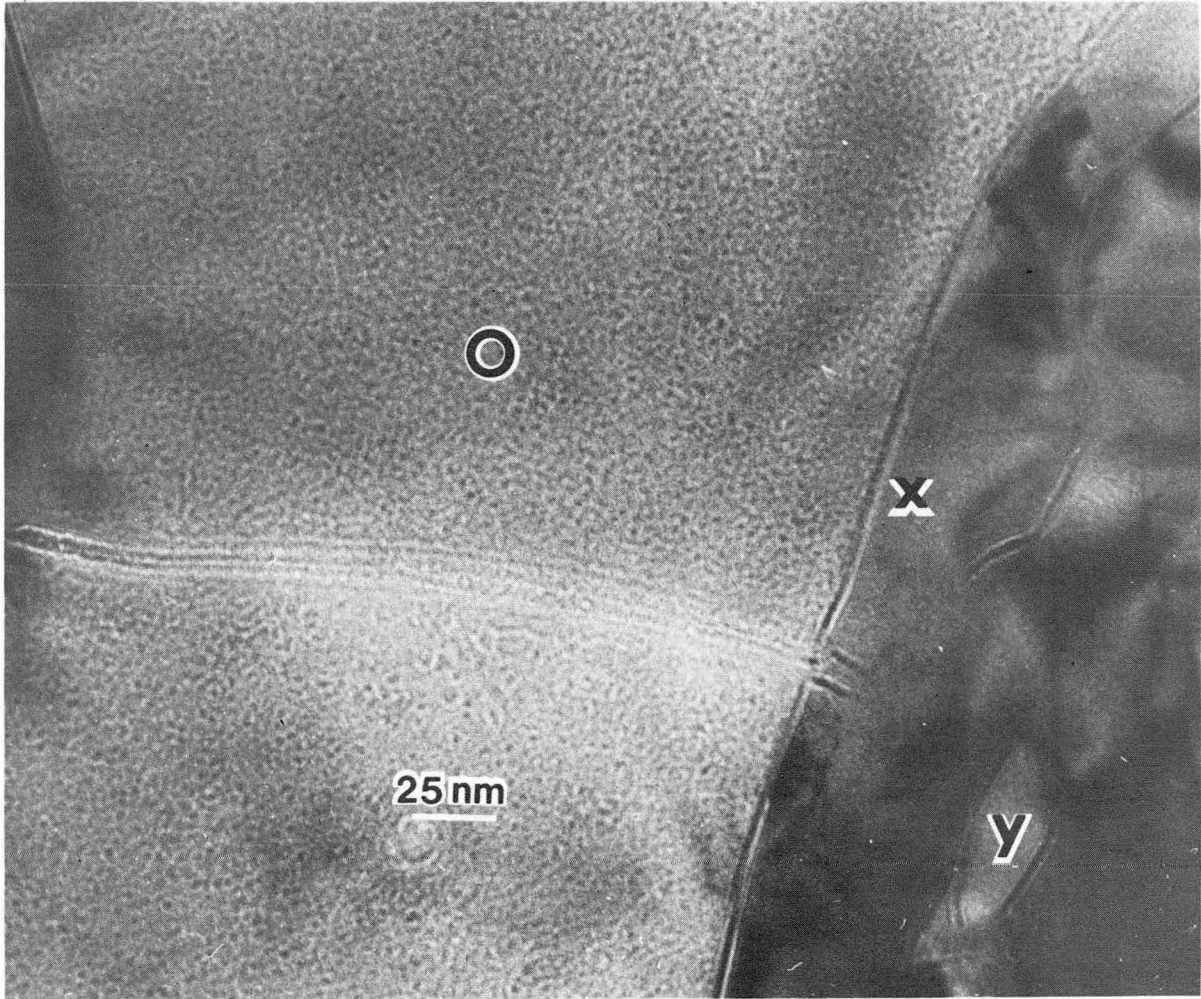
XBB 864-3477

Fig. 8



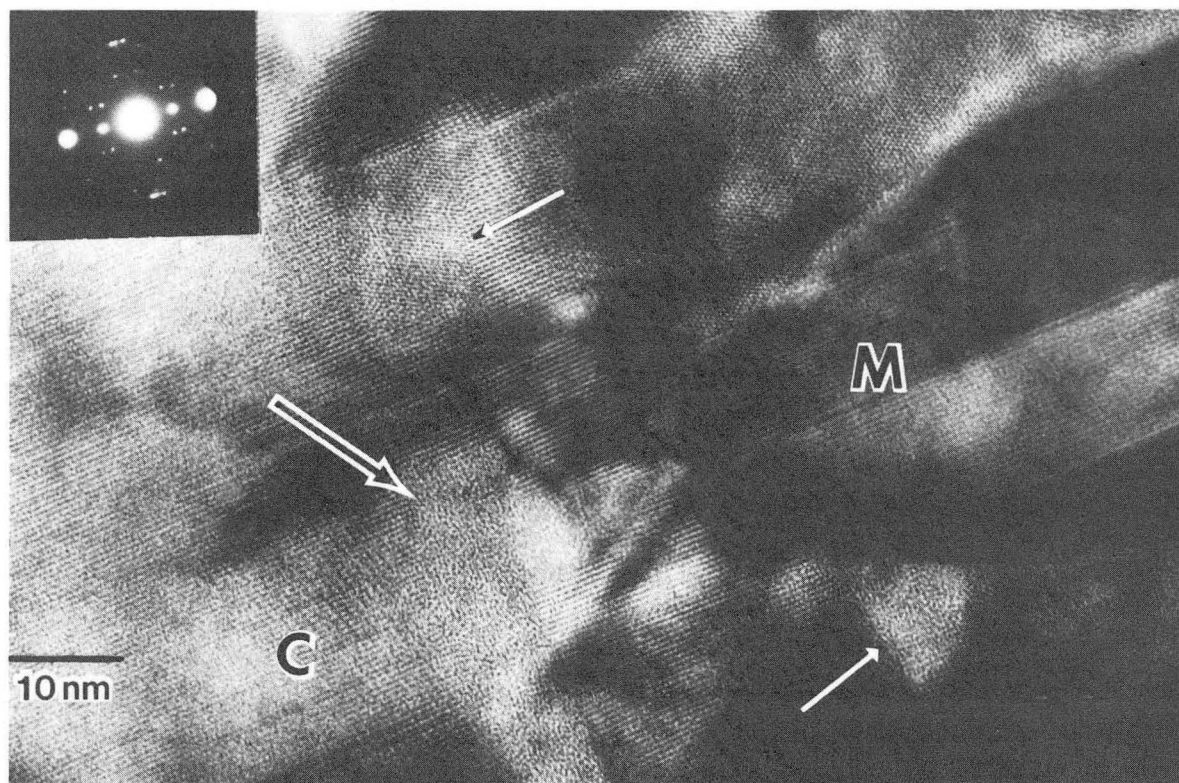
XBB 864-3478

Fig. 9



XBB 864-3479

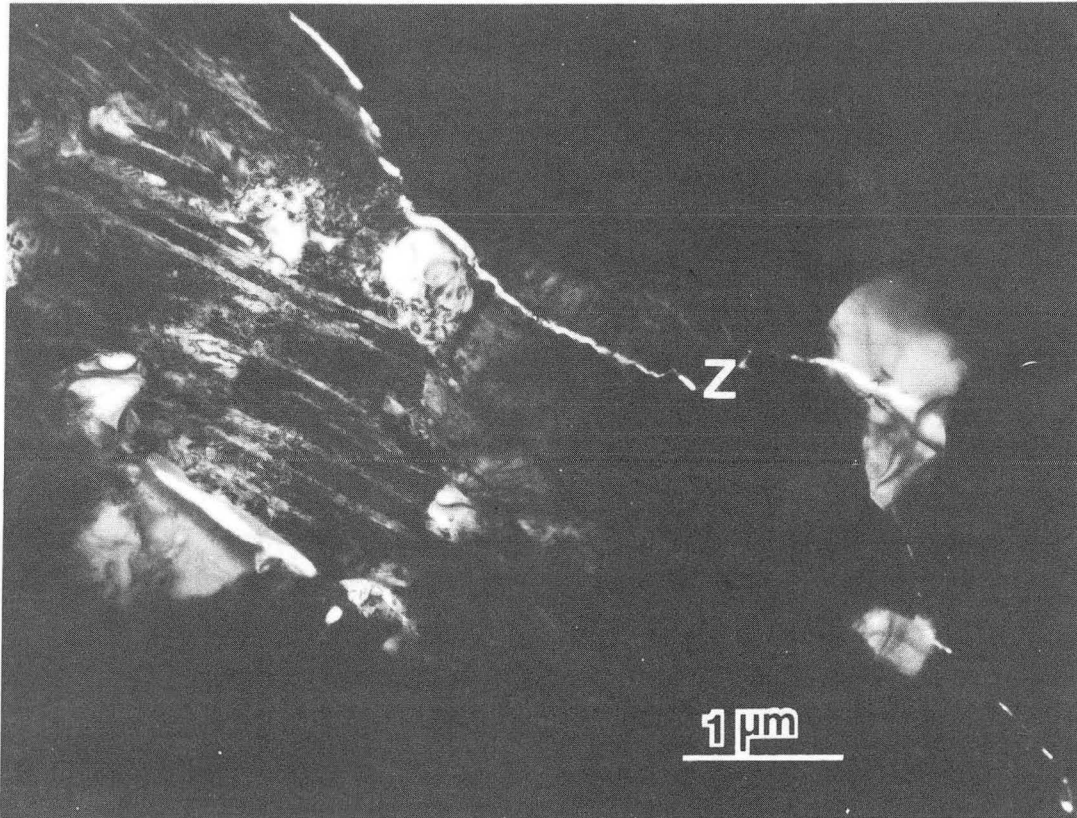
Fig. 10



XBB 864-3480

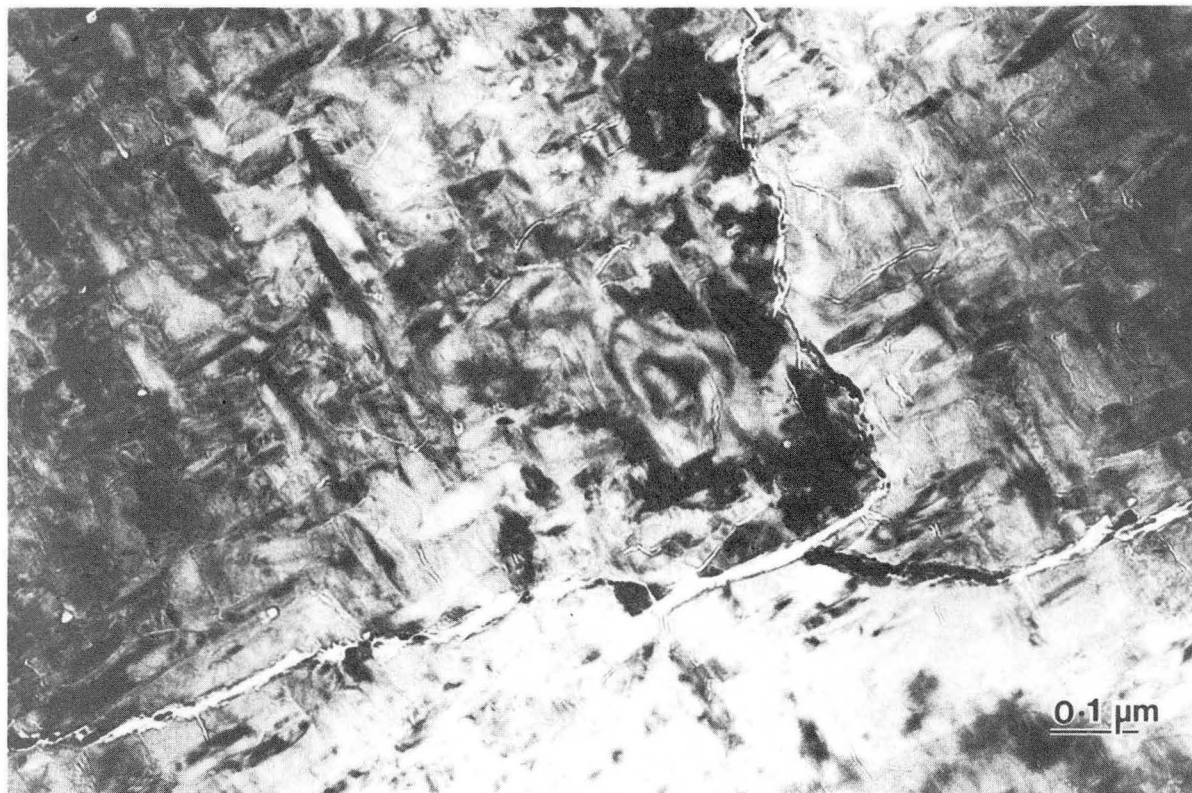
Fig. 11





XBB 864-3481

Fig. 12



XBB 864-3482

Fig. 13

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