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Authors
Penisson, J.M.
Gronsky, R.

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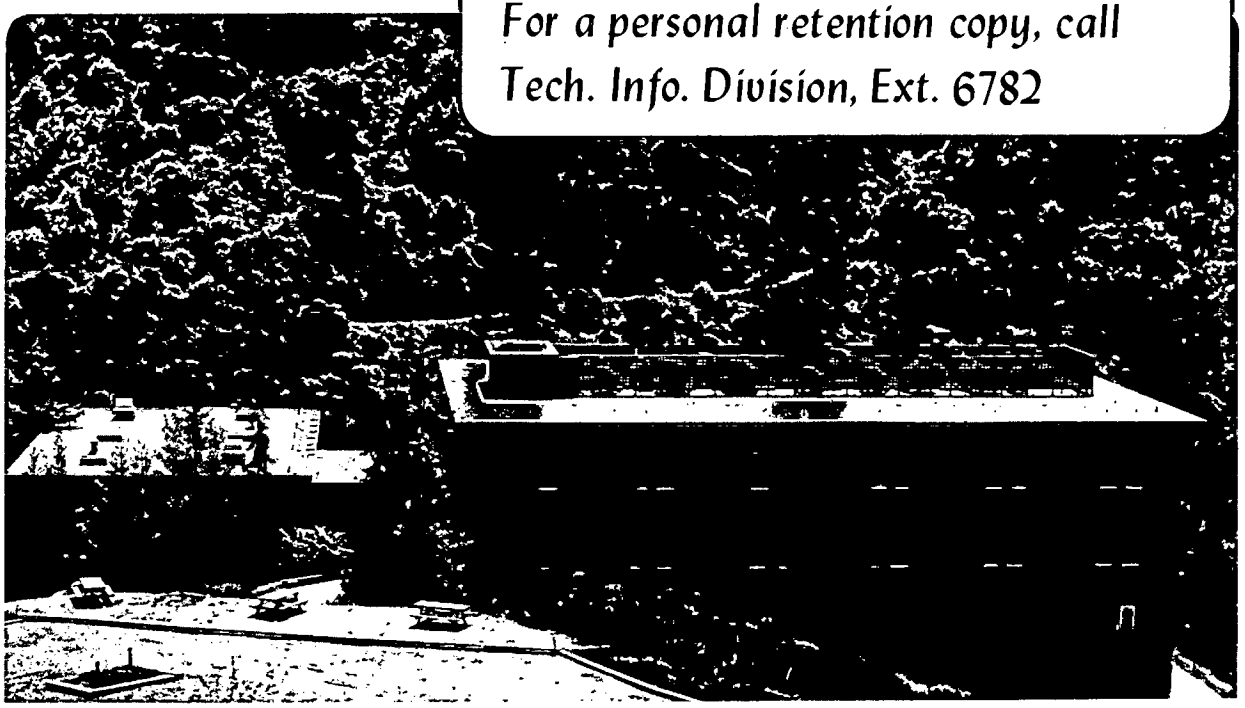

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EXPERIMENTAL STUDIES ON THE ATOMISTICS OF GRAIN BOUNDARY PRECIPITATION

J. M. Penisson and R. Gronsky

Materials and Molecular Research Division

Lawrence Berkeley Laboratory

University of California

Berkeley, CA 94720

Abstract

The incipient stages of precipitation at grain boundaries in Al-Zn alloys have been directly studied using a JEM 200CX ultrahigh resolution transmission electron microscope. At Scherzer defocus (1), the atomic positions delineated by intersecting 111 planes in these specimens are within the resolution limit of this machine. enabling grain boundary and interfacial structures to be analyzed at atomic resolution for particular zone axis orientations. Even at the earliest stages of precipitation, monolayer steps on interfacial facets are clearly revealed and support the operation of a ledge mechanism (2) from the onset of growth. Results are presented on the detailed crystallography of the nucleation event and the mechanisms by which grain boundary defects are incorpoated in precipitate growth processes. A description is also given of the optimum experimental conditions under which grain boundary reactions can be studied at atomic resolution.

Introduction

It is well known that grain boundaries dominate heterogeneous solid-solid nucleation in a wide variety of alloy systems, yet the specific mechanisms by which these reactions occur is not fully understood. The causal distinction between active and passive sites for formation of a new phase, even along regions of the same grain boundary, is not only difficult to detect (3), but also nearly impossible to predict. Many of these deficiencies in understanding grain boundary precipitation obviously stem from a lack of spatial resolution in experimental studies. Problems with complete descriptions of both nucleation and the detailed mechanisms of growth in fact rely upon a knowledge of the atomistics involved and the requirements this places upon experimental precision are extremely strict.

However, the development of electron-optical instrumentation has now advanced to the point where atomic resolution imaging is at least feasible (4), if not routine. The present study is based upon an application of transmission electron

microscopy at the highest levels of spatial resolution to characterize and understand the atomistics of grain boundary precipitation. Since this is a relatively new technique, extra care has also been taken in establishing the experimental conditions required for optimum results. An aluminum-zinc binary alloy was chosen for this study chiefly to minimize specimen-induced problems due to preparation and conventional analyses, as well as to maintain contact with the closely allied studies of this system (5).

Experimental Procedures

The Al-Zn alloy used in this research was determined by wet chemical analysis to contain 20.3wt% Zn after processing into sheet form. Specimens were aged for 10 minutes at 180°C and thinned in a nitric acid-methanol electrolyte at -27°C.

The microscope used in this investigation was a JEOL JEM 200CX equipped with a top-entry ultrahigh resolution goniometer stage (requiring 2.3mm diameter specimens) and high brightness LaB_6 gun. Operating conditions included an accelerating potential of 200kV, use of a biaxial tilt ($\pm$ 10°C) specimen cartridge, and condenser system settings to maintain a beam convergence angle of less than 3 milliradians. The filament (provided by JEOL) was driven at relatively low bias voltage in a slightly undersaturated condition, drawing a maximum beam current of 30 microamps. This enables photographic exposures to be recorded on Kodak 4489 film within a 4 second duration at 850,000X direct magnification. Most micrographs were recorded in the 270,000X to 530,000X magnification range and all were accompanied by their corresponding electron diffraction patterns from the specimen. Because of the limited tilt range of the high resolution stage, the search for suitably thin regions of the foil which contained a grain boundary and reaction product in an appropriate orientation proved most time-consuming. Nevertheless contamination of the specimen during this time remained negligible.

During high resolution imaging every attempt was made to include within the photographed area a portion of the thinnest edge of the specimen. This region was then used during subsequent optical diffraction analysis to determine the optical transfer characteristics of the objective lens as illustrated in Fig. 1.

Once the optical conditions of the lens are determined in this way, the specimen area of interest is recorded and analyzed as shown in Fig. 2. Measurements of the diffraction disc diameters (Fig. 2(a)) yield the beam convergence angle directly. The diffraction condition is brought as near to symmetrical as possible for one grain (or both if possible) and the image (Fig. 2(b)) is recorded in a through-focus series. The optimum image is then chosen according to its optical diffractogram (Fig. 2(c)). A detailed description of these procedures is provided in reference 6.

Experimental Results

The micrograph in Fig. 3 is a detail of an image recorded at 180nm underfocus. Although at this defocus value there were numerous gaps in the transfer function, the regular periodicities of the lattice have been clearly resolved. The orientation of the precipitate in the lower portion of the image was more favorable for crossed-fringe detail, while the matrix in the upper portion of the image shows only one of its (111) spatial periodicities in contrast. The interface is at the growth front of the emerging particle, nucleated at a grain boundary and indicated by diffraction data to be the rhombohedrally-distorted Zn-rich phase. On the basis of the differences in contrast of the two phases determined by a through focus series (1), a dashed line has been superimposed over the interface which is nearly edge-on over the segment seen here. It is clear that the interface consists of extended planar portions of close-packed planes from the precipitate phase. Furthermore the ledges between these planar portions (see large arrow) again parallel another set of close-packed planes in the precipitate.

Another boundary-nucleated particle is shown in Fig. 4, also in an edge-on configuration. Here the precipitate phase is close to pure Zn in overall composition, and the larger fringe spacings within the particle are representative of the basal-plane stacking frequency. Small arrows mark the positions of clearly defined ledges in the low-index pole regions of the interface. Each of these ledges is only a single lattice spacing in height and separated again by extended portions of the low-index precipitate planes. As the interface changes orientation to a higher index facet, the spacing between these ledges decreases until they extend again along the orthogonal low-index front. The lattice fringes in the adjoining matrix grain comprise the image of a single set of close-packed planes which are slightly misoriented with respect to the corresponding fringes within the precipitate. However, since the diffraction conditions were not sufficient to produce greater structural detail in the matrix, no conclusions can be drawn about the nature of atomic matching at the interphase boundary.

An early-stage event is shown imaged at lattice resolution in Fig. 5. Here again the limited tilting range of the ultrahigh resolution goniometer prevented the formation of a structural image; instead only a one-dimensional periodicity is revealed. The dark band running horizontally through this image is the Pendellosung contrast (1) of a steeply-inclined grain boundary separating regions of different interplanar spacing. From the persistent through-focus behavior of this type of image feature, and the relative dimensions of fringe spacings, this micrograph most probably represents a Zn-rich region on the upper portion of the boundary (arrowed). It occurs only over the regions of the boundary with the low-index orientation seen here, and the maximum height of the Zn layer is ~ 2nm. The upper grain is so far removed from a favorable diffraction condition that it is imaged only as phase contrast noise.

Discussion

The enhanced resolution in microstructural analysis attained in this study has revealed some of the finest crystallographic aspects of transformation phenomena. The microledge structure clearly revealed in Figs. 3 and 4 is a striking example of the dominant influence (2) of crystallography on interface formation and/or propagation. It is particularly evident that low-index orientations seek broad planar configurations with minimum deviation in the form of ledges. Also where they do form, ledges tend to assume well-defined orientations themselves often in parallel arrays on the atomic scale.

The distinctions between the precipitate-matrix interfaces shown in Figs. 3 and 4 might also be attributed to the differences in composition between the Zn-rich particles imaged here. At higher Zn concentration, the effects of crystallography were apparently less severe, allowing the development of a smoother curvature at the interphase interface. By contrast, all of the lower-Zn particles imaged in this study were more sharply faceted along crystallographic indices.

Observations similar to those shown in Fig. 5 were reported earlier (1) but not at this level of resolution. In fact, the outstanding performance of the microscope (Fig. 1) during this study lends more support to the atomistic interpretation of this result as a simple wetting of the boundary plane, again strongly influenced by the orientation of the boundary, prior to sustained growth. The most encouraging aspect of this result is that the new phase could be identified by its image contrast to below 2nm scale. Further experiments are currently underway to extend the resolution of these studies by optical processing and computer simulation.

Acknowledgements

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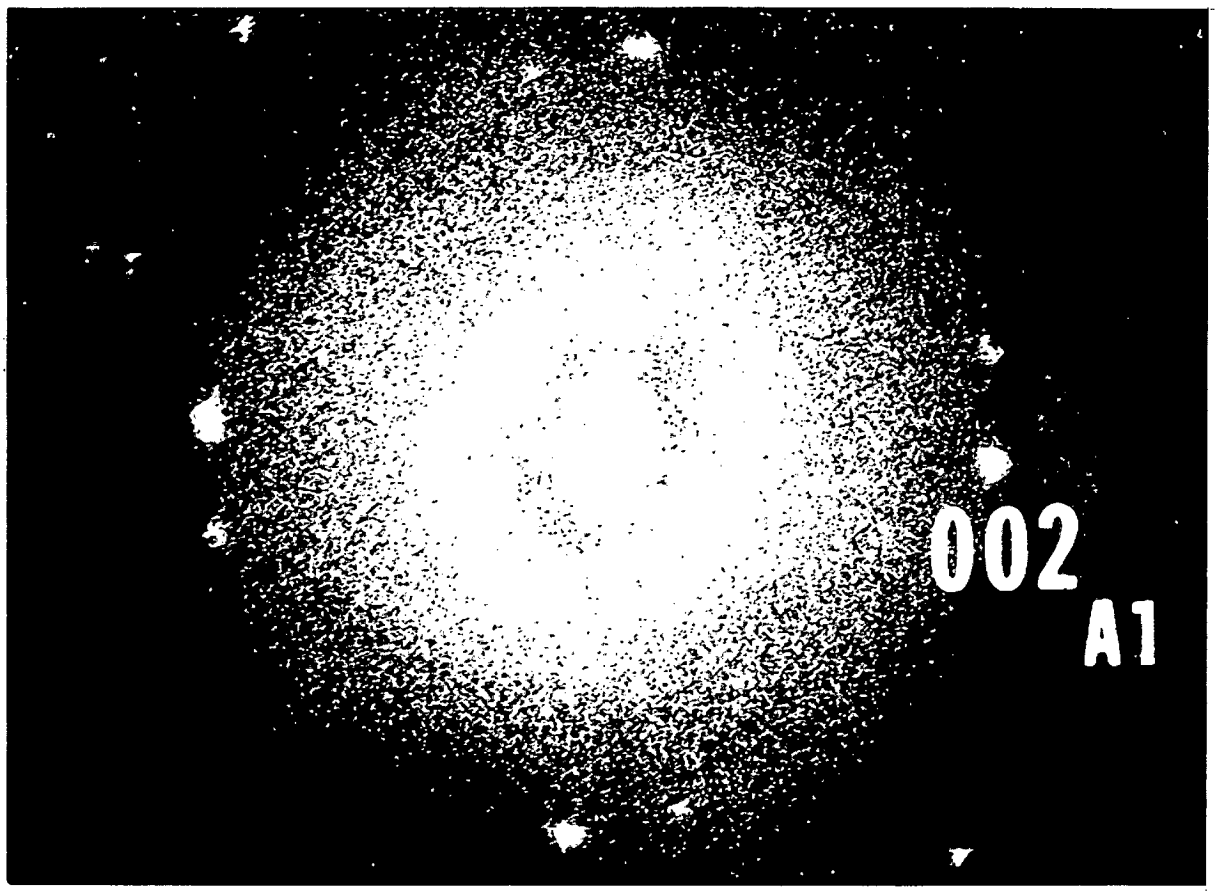

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Fig. 1 - Optical diffractogram of a high resolution image recorded at Scherzer defocus (4). The specimen area contained a small angle tilt boundary about the [100] zone axis reflected in the pattern of spots here. Note that the halo produced by an amorphous contamination layer is continuous out to spatial periodicities of 0.2nm, demonstrating the excellent point-to-point resolution of the microscope.

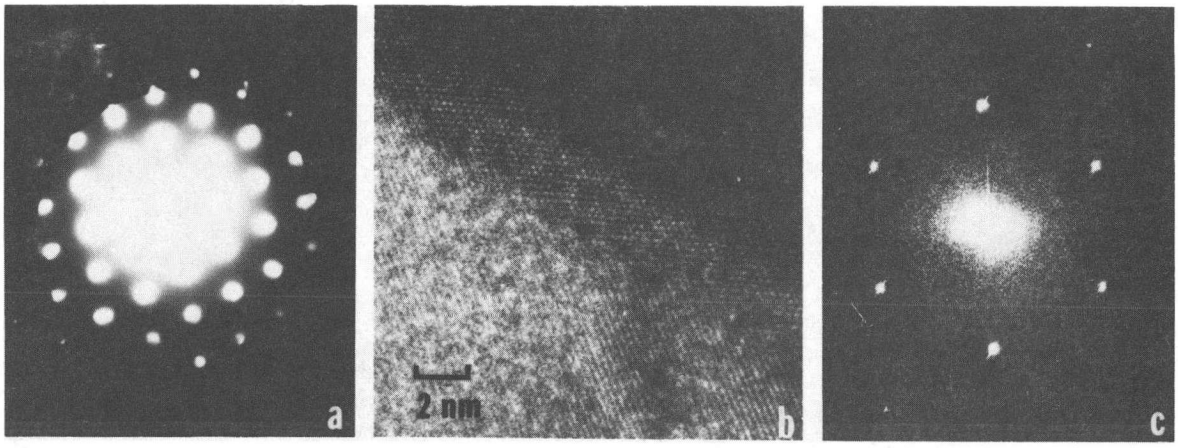

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Fig. 2 - High resolution imaging and analysis scheme used in this study. The electron diffraction pattern (a) recorded with superimposed aperture shadow indicates the diffraction conditions of the interface region imaged in (b). The optical transform (c) shows that all 111 and the (002) planes of one grain were resolved. Spot streaking is a shape factor effect from the boundary.

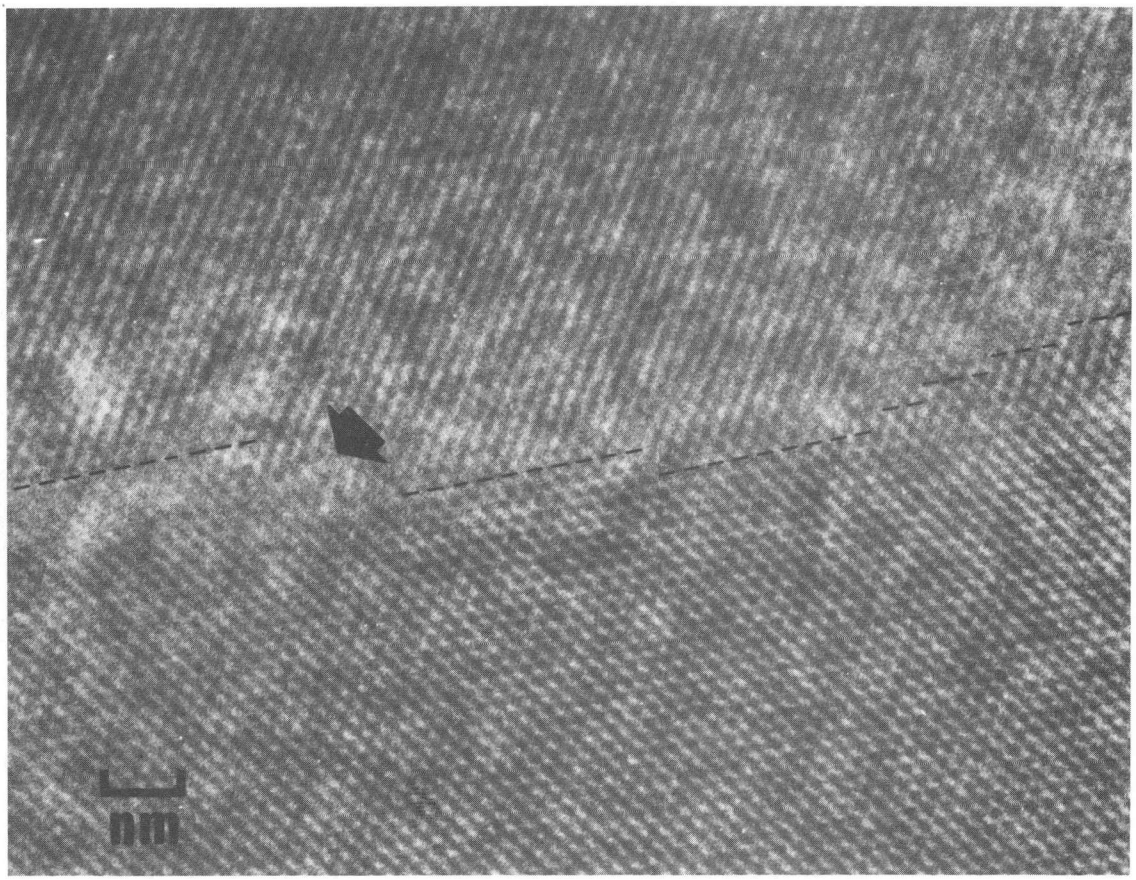

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Fig. 3 - High resolution image of a grain boundary-nucleated precipitate (bottom)/ matrix (top) interface. Atomic detail of interfacial structure is highlighted along with the location of the interface determined from an extended through-focus series.

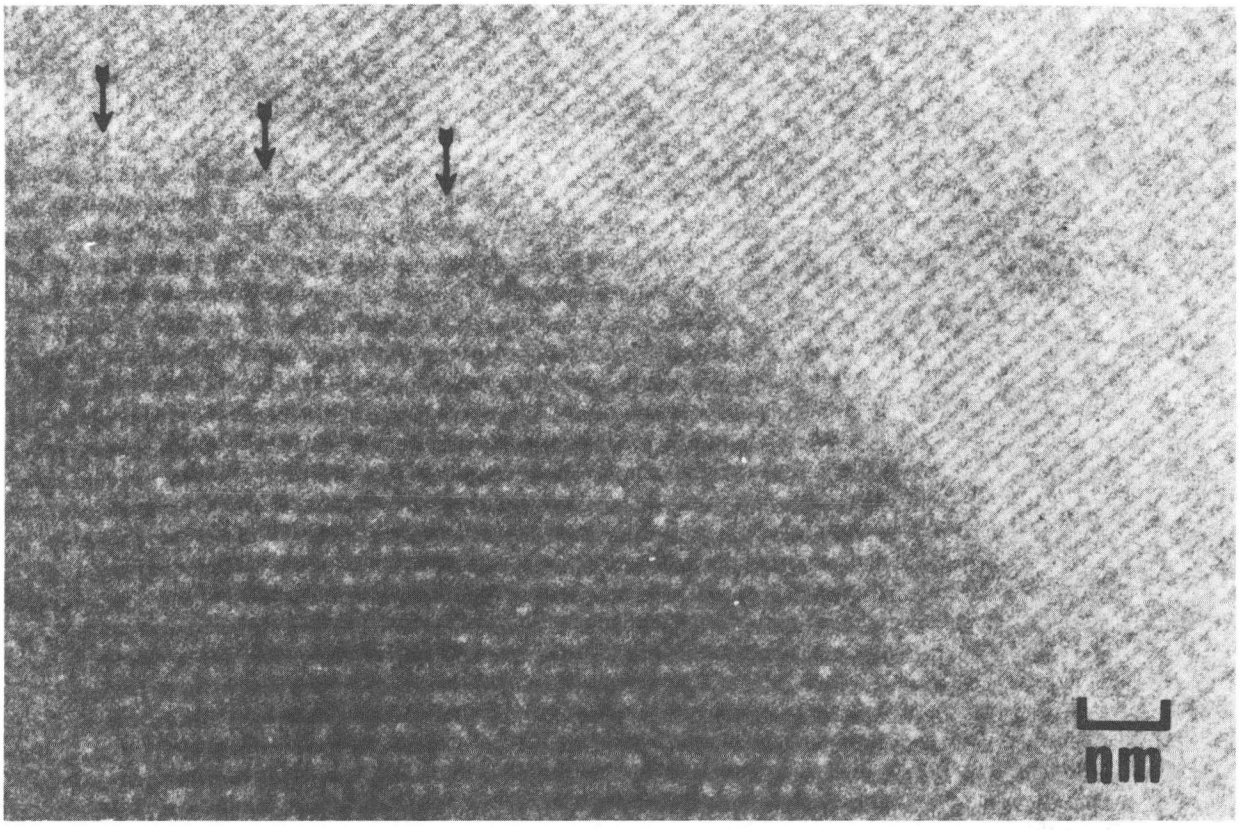

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Fig. 4 - High resolution image of a high-Zn boundary-nucleated precipitate (bottom) in contact with matrix (top). Arrows mark single atomic layer ledges in low-index interfacial region. The precipitate image contrast suggests that it has reached equilibrium composition.

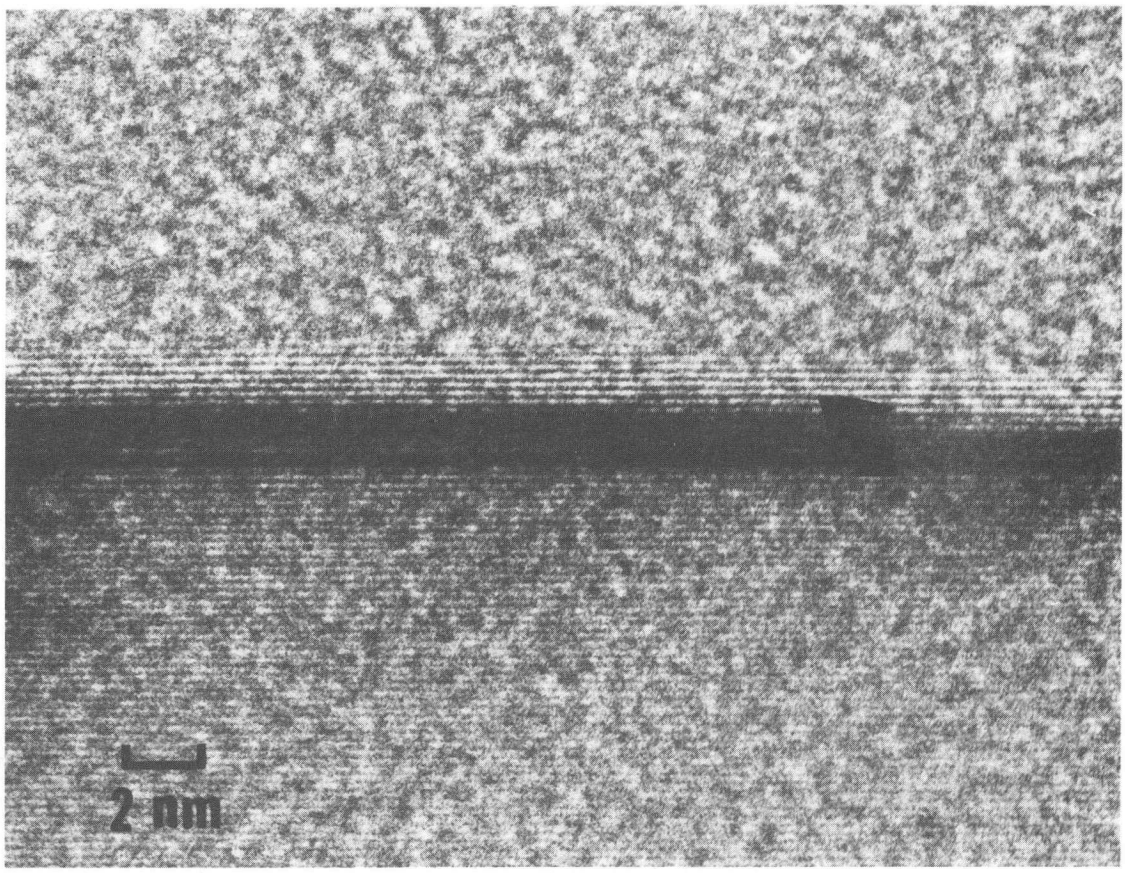

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Fig. 5 - High resolution image of grain boundary region which reveals a 2nm layer of Zn-rich phase (arrowed) along the low index pole orientations of the boundary plane. The upper grain shows only background contrast due to its unfavorable diffraction conditions.

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