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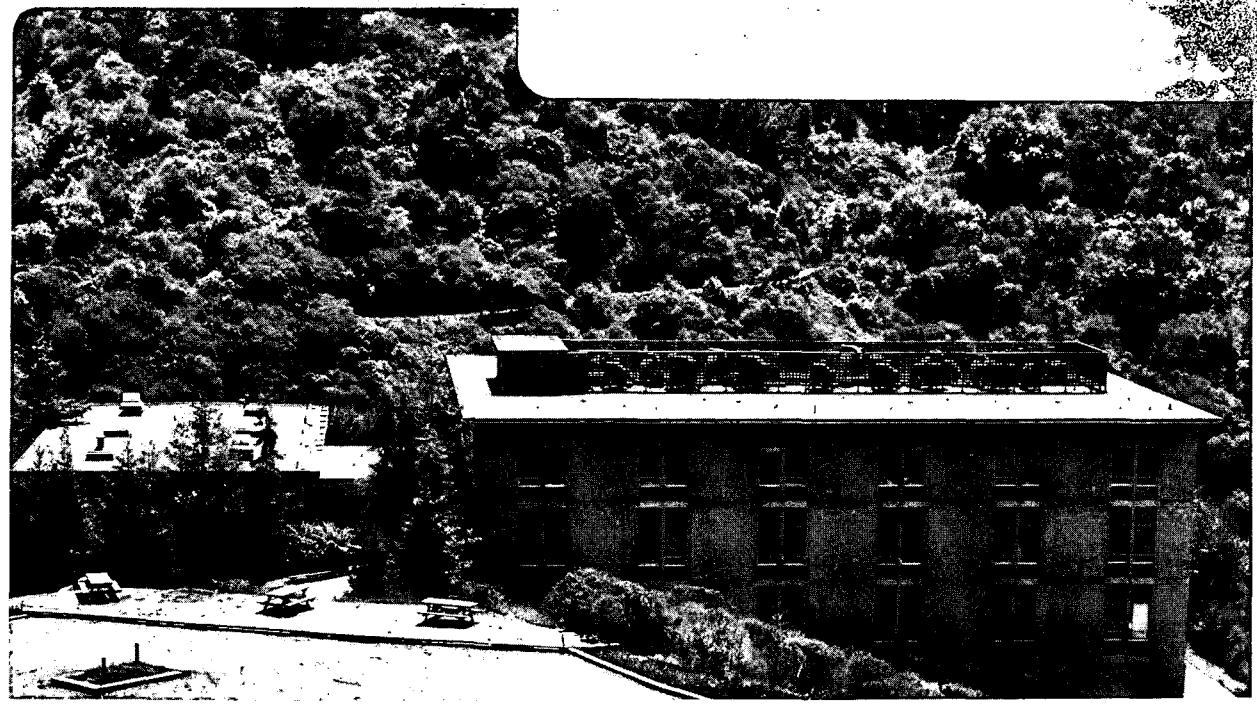
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DEGRADATION IN A THERMAL BARRIER COATING

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Abstract

The failure of a thermal barrier coating (TBC) involves cracking and spalling of the ceramic layer, primarily brought about by bond-coat oxidation during operation. The present investigation focuses on the microstructural and microchemical changes in a TBC, oxidized in air for 1 and 10hrs at 900°C. The zirconia coating shows a gradual increase in the amount of monoclinic phase with time at temperature. The bond-coat layer shows substantial aluminum depletion in the region adjacent to the ceramic. This aluminum forms an oxide layer (Al_2O_3) at the interface. However, nickel oxide (NiO) is also found to be another important oxidation product. The relevance of these observations to the degradation observed in TBC's is discussed.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under contract No. DE-AC03-76SF00098.

INTRODUCTION:

Thermal barrier coatings (TBC's) have been considered for application in turbines and jet engines since the 1970's.^{1,2} Their positive features, including high thermal impedance,² high temperature stability, corrosion resistance, and ease of fabrication with plasma spray-guns, have led to extensive research aimed at producing TBC's with increased reliability and performance. One major part of the research has involved understanding mechanical degradation^{3,4} when the TBC's are subjected to elevated temperatures (as high as 1200 - 1300 C) in aggressive atmospheres. This degradation involves delamination and spalling of the coating. Coating failure can result from factors such as thermal expansion mismatch stresses associated with thermal cycling, microstructural changes in the ceramic coating during exposure to elevated temperatures, or debonding between the ceramic and the bond coating due to oxidation of the bond coat.⁴ Few investigations have included a detailed characterization of microstructural and microchemical changes taking place at the ceramic coat/bond coat/substrate interfaces.^{3,5} The studies mostly involved optical metallography (OM) and scanning electron microscopy (SEM), and the oxidation products were identified using energy dispersive x-ray spectroscopy (EDXS) in the SEM.

Stecura⁵ studied the degradation of thermally cycled TBC's. He reported that interdiffusion of alloying elements between bond coat and substrate, and oxidation of bond coat at the bond coat/ceramic interface led to cracking and failure. Miller⁴ reported that pre-oxidized samples failed in a single heating cycle, indicating that oxidation contributes to degradation. The empirical oxidation-based model predicting the lifetime of a TBC, developed by Miller, incorporates a time-at-temperature component together with a cycle-frequency component. The time-at-temperature component would include all thermally activated processes, such as diffusion, phase transformation, plastic deformation, and oxidation. Understanding of each of these processes is vital to the development of better TBC's.

The present communication reports an examination of the changes taking place in a thermal barrier coating exposed to oxidizing atmospheres at 900°C. The identification of oxidation products at the bond coat/ceramic interface and the characterization of the microstructural changes in the ceramic coating are two important aspects of this study.

EXPERIMENTAL:

The TBC's examined had been prepared for zirconia coated diesel engine cylinder heads,* by plasma spraying. The spraying conditions were selected according to the specificatins outlined in Metco[†] sheet

*Plasmatech Inc., Torrence, CA 90501

†Metco Inc., 1101 Prospect, Westbury, Long Island, NY 11590

no. 202NS. The TBC consisted of a 200-300 μm of zirconia coating on a 50-100 μm bond coat layer; the substrate was cast-iron. The composition of these coatings is given in Table I. Some of the samples were heated in air at 900°C for 1 and for 10 hours to study the changes taking place at the bond coat/ceramic interface. These samples will be referred to henceforth as oxidized samples. The test temperature of 900°C was chosen to accelerate strongly the oxidation phenomena occurring at the bond-coat/zirconia interface. It is believed that these phenomena can be common to TBC's that experience lower temperatures (diesel engines) as well as TBC's that operate at much higher temperatures (gas turbines), and hence this investigation focuses on those phenomena. The effects of phase changes in the substrate on degradation are specific to the particular applications, and hence are not studied.

The as-sprayed and the oxidized samples were characterized using optical metallography (OM), x-ray diffractometry (XRD) and scanning and transmission electron microscopy (SEM, TEM). This made it possible to resolve the overall microstructural changes, changes in the phase composition of zirconia, as well as microstructural and microchemical changes using energy dispersive x-ray spectroscopy (EDXS), near the bond coat/zirconia interface. The details of the equipment used and the operating conditions are listed in Table II.

Specimen Preparation: After oxidation in air, specimens were cut from the flat sections of the cylinder head, and ultrasonically cleaned using acetone and ethanol (both electronic grade). X-ray

diffractometry was then carried out to determine qualitatively the phase changes in the ceramic coating. Optical, as well as scanning and transmission electron microscopy, were carried out on the cross-sections. For this purpose, the zirconia faces of two pieces were glued together using 'DEVCON 2 ton epoxy'[†] and cross-sections were prepared. The procedure described by Bravman et al⁶ for making cross sectional TEM specimens was modified for obtaining uniformly thin TEM samples from TBC's. The procedure is described in detail elsewhere.⁷

Optical metallography was used to determine overall changes. SEM in combination with energy dispersive x-ray spectroscopy (EDXS), was used to establish compositional changes across the bond coat layer, and analytical electron microscopy was used to identify the oxidation products at the bond-coat/zirconia interface.

RESULTS AND DISCUSSION:

X-ray Diffractometry: The changes in the phase composition of the ceramic were evaluated using x-ray diffraction. The superimposed traces near the (111) and (400) zirconia reflections show that the amount of monoclinic phase increased with time at 900°C (Figs. 1a and b). The analysis of (400) peak (Fig. 1b) requires quantitative deconvolution due to the superposition of the tetragonal and cubic zirconia reflections, which was not carried out. However, qualitative estimates indicated that the amount of tetragonal phase was decreasing.

[†]Devcon Corporation, Danvers, MA 01923

Also, the shifts of both (111) and (400) peaks indicated that the composition of the tetragonal and cubic phases was changing.

Optical Metallography:

The edges of cross-sectional samples made from TBC's oxidized for 1 and 10hrs, seen in fig. 2, illustrate the extent of oxidation that an uncoated sample would undergo. They also show how degradation of the remaining TBC's accelerated if part of the ceramic coating were to spall off. The arrows indicate regions where the oxidation from the edge has propagated beneath the bond coat, leading to degradation of the substrate.

The other, and perhaps more important part of the optical metallography consisted of examining the ceramic coating in polarized light. It was possible to identify subsurface features in this mode of illumination as seen in Figs. 3 (a,b). Fig. 3 shows a pair of images of oxidized samples taken from the same region with normal and with polarized light. The features marked by arrows in the polarized light image extend below the surface, and the contrast could be caused by cracks, or by the variation in phase composition between different regions. The actual image is multi-colored, and the arrowed regions in Fig. 3b show different colors. The regions near the bond coat/ceramic interface show a greenish color and the ones within the ceramic show reddish colors. It is therefore plausible that the inhomogeneities within the ceramic coating near the interface are chemically different

in nature than the ones within the ceramic coating. Also, the greenish regions appear only in the oxidized samples, indicating that these inhomogeneities are associated with bond coat oxidation products.

Electron Microscopy: TEM samples were prepared from as-made and from oxidized (10 hrs at 900°C) samples. The thinned regions of bond coat and zirconia could be identified by examining the thinned samples using an optical microscope.

As prepared TBC's: The zirconia coating showed very complex microstructures. Some regions exhibited columnar grains, Fig. 4a, their long direction perpendicular to the interface. Micro-diffraction of these grains gave patterns mostly consistent with the tetragonal zirconia phase. However, a few grains also gave patterns consistent with a monoclinic phase, Fig. 4. The columnar grain regions alternated with regions with equiaxed grains, (Fig. 4). EDXS, using probes large enough to include about ten grains, showed no difference in yttrium content between the two regions. This, and the fact that these two regions alternated throughout the ceramic layer, indicates that the difference in grain morphology results mainly from local differences in thermal history associated with plasma spraying, and not from changes in chemical composition.

No segregation of any one element was detected, and no oxidation products were found in the bond coat, at the interface between bond coat and zirconia for the as-prepared TBC's.

Oxidized TBC's: (10hrs at 900°C): The cross-sectional TEM samples made from oxidized TBC's were examined to identify the changes in microstructure and chemistry near the metal/ceramic interface and in the zirconia coating.

Structural changes near the interface: Fig. 5a and b show adjoining regions at the interface between the bond coat and the ceramic. The bright field image in Fig. 5a shows an alumina region, as confirmed by its EDXS pattern and by the selected area diffraction pattern. The ring pattern obtained in selected area diffraction shows that the grain size of the Al_2O_3 is very small. It was not possible to get a single crystal pattern using even the smallest available probe size, i.e. 50 nm. The grain size is therefore smaller than 50 nm. EDXS patterns taken with a 100 nm probe placed at various positions in the adjoining bond coat grain showed aluminum depletion (see Fig. 5a). It can therefore be concluded that aluminum diffuses out of the bond coat during oxidation to form Al_2O_3 . Fig. 5b shows another region only a few tens of nms away, where a grain showed only nickel in the EDXS (inset). A microdiffraction pattern (inset) from this grain, using a probe of 65 nm in diameter, showed two superimposed $\langle 110 \rangle$ diffraction patterns. All the other reflections can be explained as arising from multiple diffraction.⁸ The ratios of interplanar spacings of the two patterns agree with the corresponding ratios in Ni and NiO. Also the dark field image obtained using the 200 reflection of NiO lit up the whole grain. These two observations indicate that there are, in fact, two grains (one Ni and the other NiO) superimposed in the electron

beam. It is possible that a film of NiO had formed on top of a Ni grain; however, it is difficult to explain the presence of pure Ni grains in the bond coat alloy. It is possible that the bond coat was inhomogeneous.

Careful examination of all the thin area at the interface between the bond coat and zirconia did not reveal other oxides.

Microstructural Changes in Zirconia

The changes occurring at 900°C in the zirconia layers are quite involved, due to the complexity of the original microstructure. The observation from XRD that the volume fraction of monoclinic phase is increasing with time-at-temperature is substantiated by the larger fraction of monoclinic grains in the oxidized sample. It is possible that grains low in yttria content underwent this transformation, producing monoclinic zirconia.⁹ Some regions also showed microcracking between the microtwinned columnar grains. This cracking may have resulted from the volume change during the tetragonal-to-monoclinic transformation. These processes, however, do not seem to play a major role in the degradation of the TBC because the cracking responsible for spalling always initiated at the bond-coat/zirconia interface. The thermal expansion mismatch between the bond coat and the zirconia coating and also between the bond coat and the substrate would not contribute to the stresses at the interface because of the static nature of the test (temperature constant).

It is therefore safe to conclude that, during a static test, nucleation of oxidation products at the bond coat interface is a major reason for the degradation of the TBC.

An oxidation based model developed for predicting the life-time of the TBC should incorporate the oxidation behavior of the bond coat and the nature of the oxidation products. Different oxidation products have different associated volume increases thus resulting in different strains at the interface. Also, the chemical interaction of these oxidation products with the zirconia coatings have not been addressed before. Investigations in this laboratory have indicated that the interactions between oxide products and stabilizers used in zirconia may lead to cracking.¹⁰

SUMMARY:

The examination of the thermal barrier coating, oxidized at 900°C, has revealed a number of changes occurring in the ceramic as well as at the interfaces within the TBC. The zirconia coating has a complex morphology, with alternating layers of columnar and equiaxed grains. The as-sprayed zirconia is largely tetragonal. It transforms slowly to monoclinic zirconia during exposure to elevated temperature in air. But even though some micro-cracking was seen, no large scale cracking in zirconia coating was noticed. Polarized light microscopy showed presence of inhomogeneities at the interface between bond coat and zirconia in oxidized samples, indicating formation of bond-coat oxidation products. These oxidation products were identified as NiO

and Al_2O_3 . Alumina was formed by removal of aluminum from the bond coat, whereas nickel oxide seems to grow by diffusion of oxygen through the nickel oxide. These two products may represent the initial stage in the degradation of TBC during prolonged exposure to elevated temperatures.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under contract No. DE-AC03-76SF00098.

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FIGURES:

- Fig. 1: Diffractometer scans on the TBC's showing the (111) and (400) peaks. The amount of monoclinic phase increases with time at 900^oC and the composition of the tetragonal and cubic phases is changing as seen by the peak shift.
- Fig. 2: Optical micrograph highlighting the protective nature of TBC's (a) 1 hr at 900^oC in air has produced an oxide layer 0.25 mm thick, on the uncoated surface. Arrows indicate oxidation underneath the bond coat. (b) 10 hrs at 900^oC leads to extensive oxidation but the coated surface is still protected. Oxidation underneath the bond coat shows detrimental effects of exposed edges and ceramic coating spall-off.
- Fig. 3: Optical micrograph of an oxidized TBC in (a) Normal and (b) Polarized light. The arrow within zirconia indicates region showing reddish color and the arrows near the interface indicate region showing greenish color under polarized light.
- Fig. 4: Microstructure of the ceramic coating in the TBC (a) Columnar grains adjacent to the monoclinic grains as inferred from the micro-diffraction pattern (inset)
(b) Equiaxed grains. Both columnar and equiaxed grains gave diffraction patterns consistent with tetragonal zirconia. Their yttria content was also similar, (see microdiffraction pattern in 'B' and EDX spectra showing same yttrium peak intensity).
- Fig. 5: Bright field images showing two oxidation products at the bond coat/zirconia interface. (a) Alumina region as confirmed by the diffraction pattern and EDXS. The surrounding bond coat grains are depleted in aluminum (b) Nickel oxide grain grown on top of a nickel grain.

Table I

Composition of the Coatings

Bond Coat Ni-15.5wt%, Cr-6.4wt%, Al-0.1wt.%Y

Zirconia ZrO_2 -8 wt% Y_2O_3

Table II

Equipment Used

<u>Equipment</u>	<u>Operating Conditions</u>	<u>Remarks</u>
Siemens Kristaloflex X-ray Diffractometer	40 KV, 30 mA Slits 1° , 1° , 1° , 0.15° , 0.15° Scan Step Counting Time	0.05° 20 sec
AMR 1000 SEM	30KV	Secondary Electron Mode and EDXS
Philips EM4400* TEM with EDAX	120 kV	Microdiffraction and EDXS

*Permission from Dr. A. Marshall to use the EM400 in CMR, Stanford University, is gratefully acknowledged.

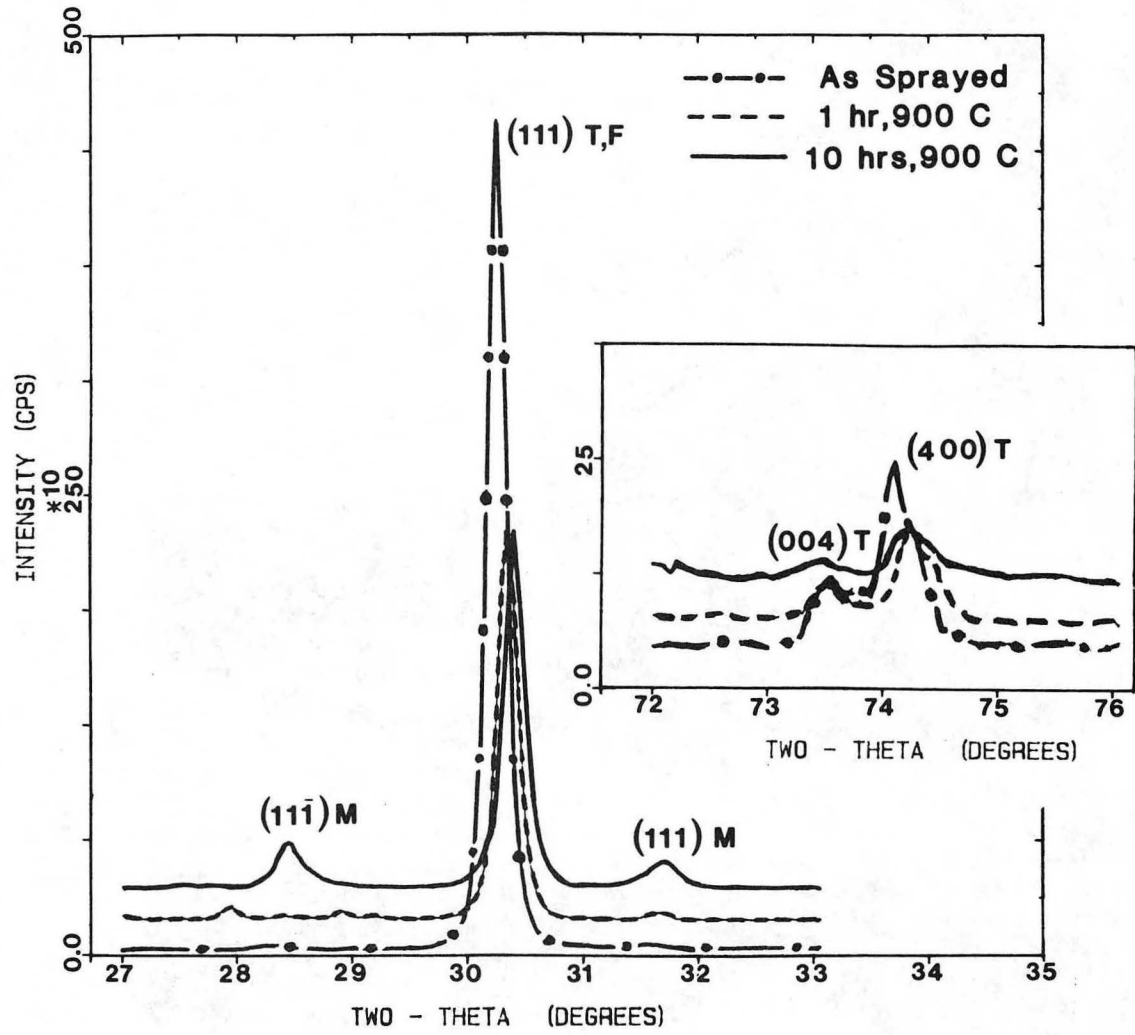


Fig. 1

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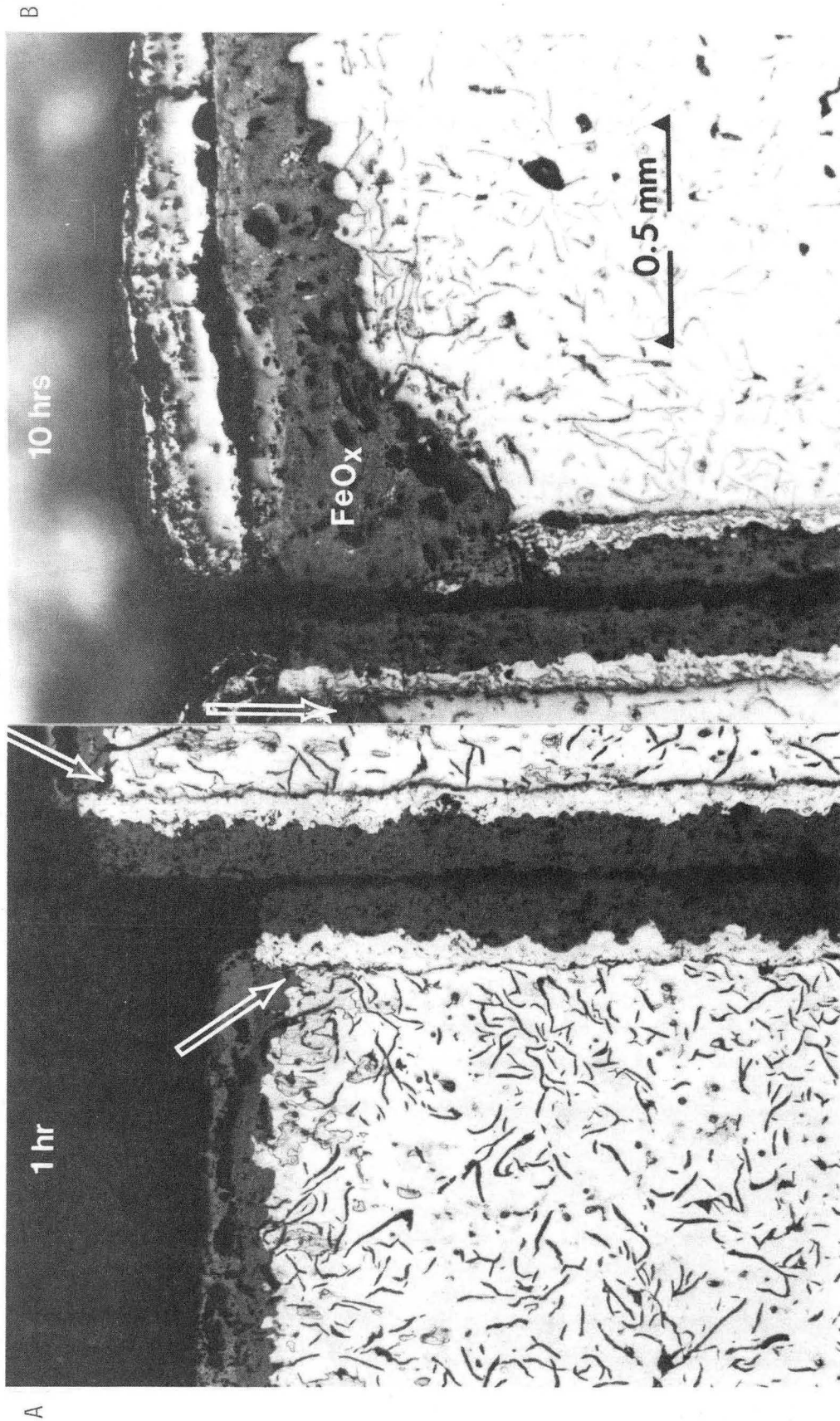


Fig. 2A and 2B

XBB 850-8249A

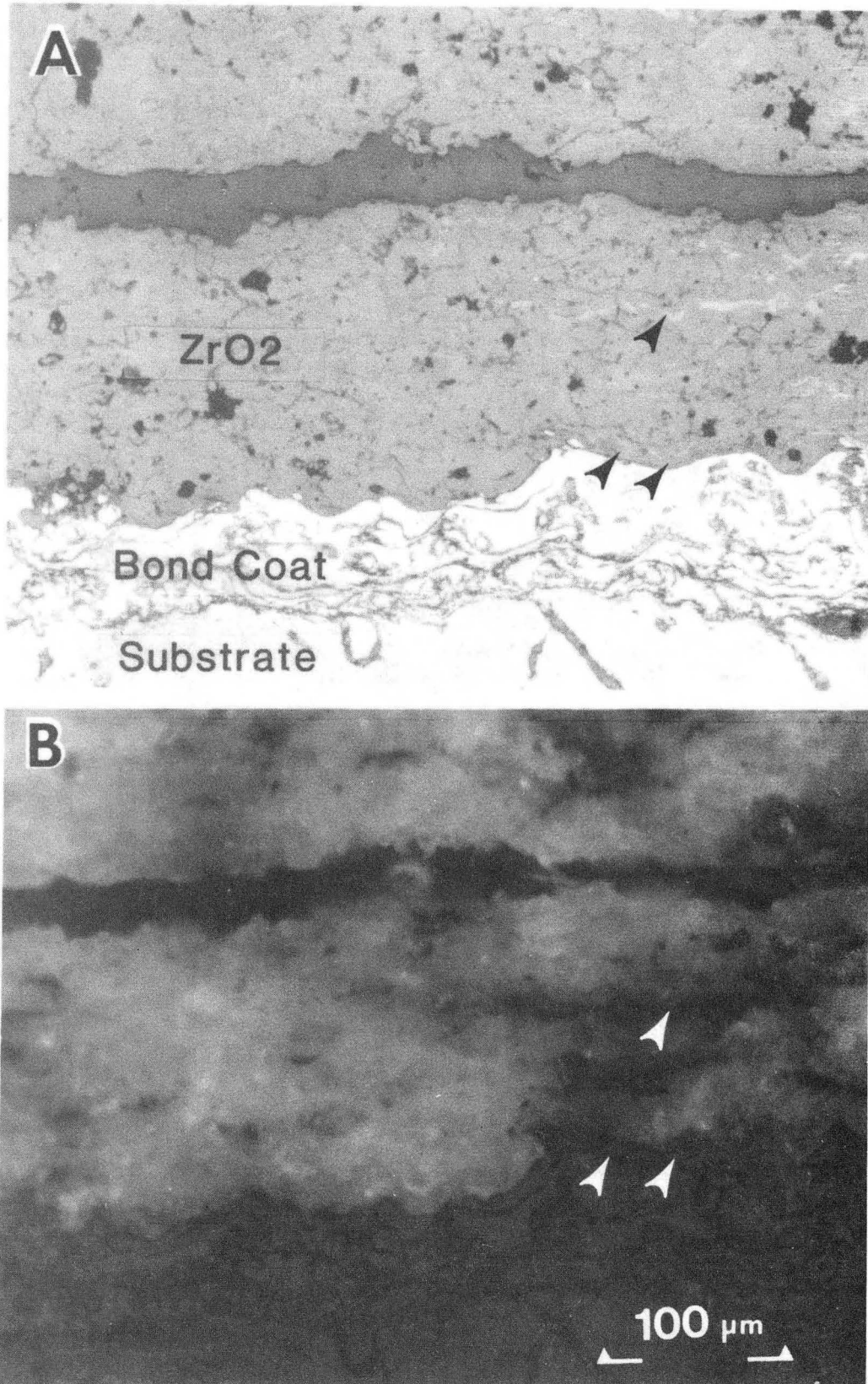
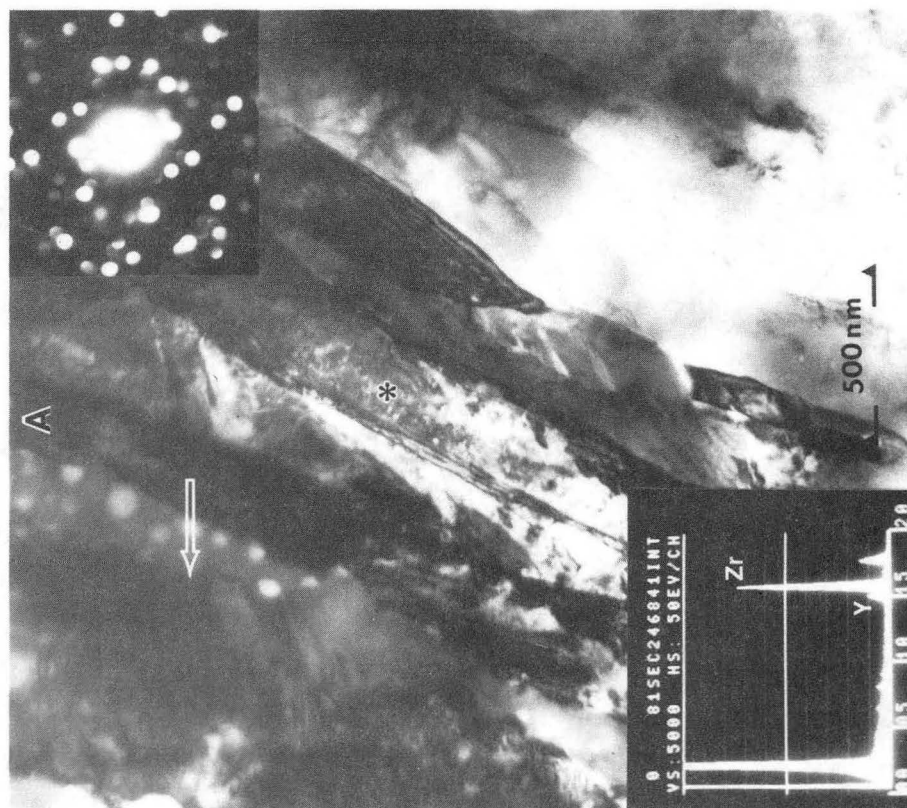
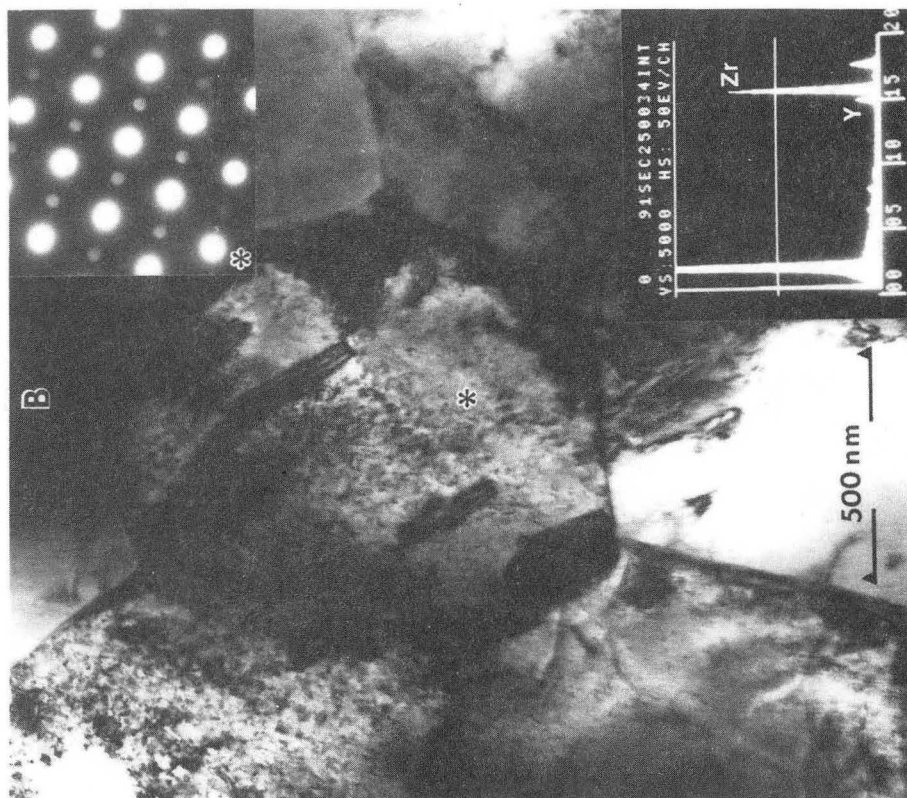


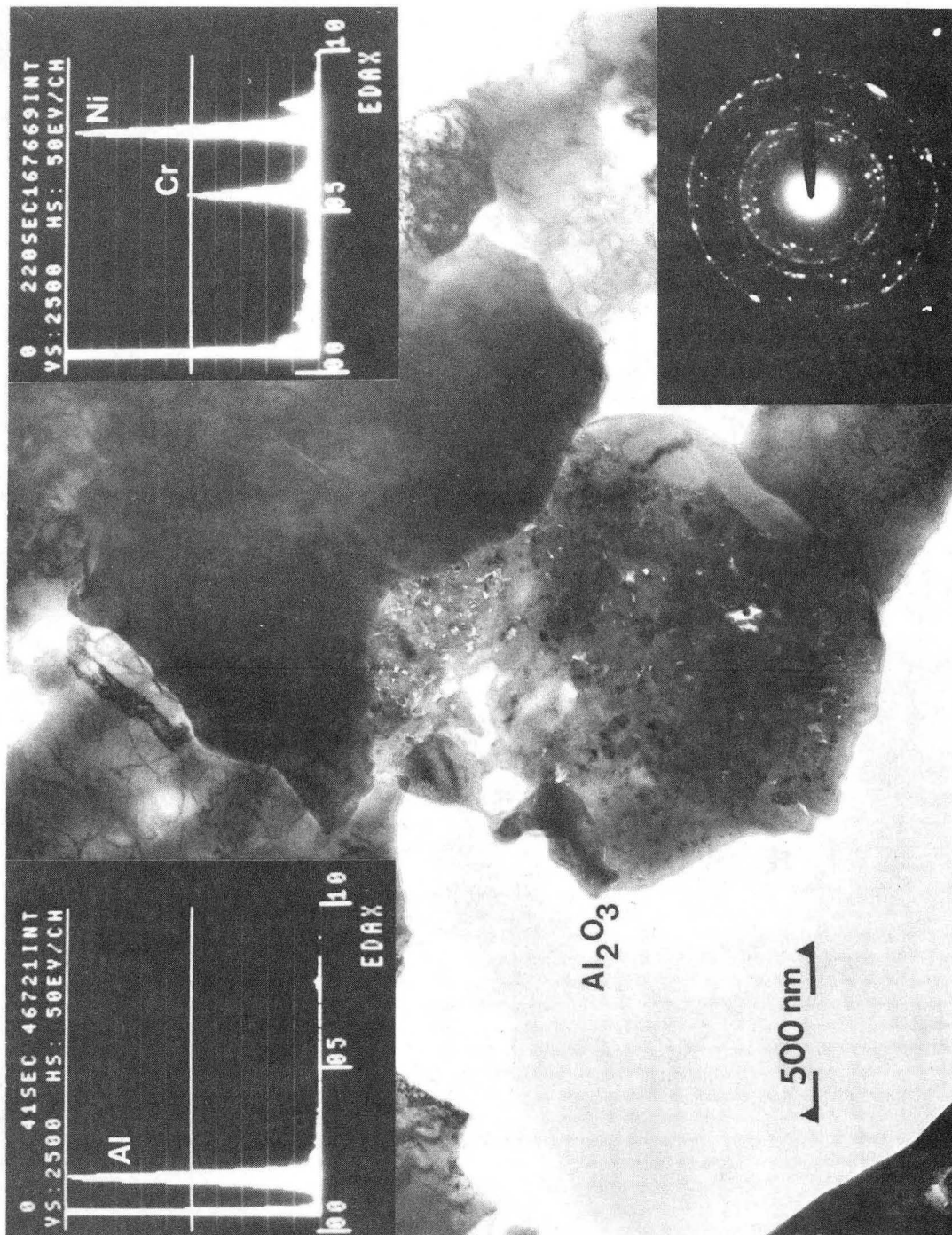
Fig. 3A and 3B

XBB 850-10129



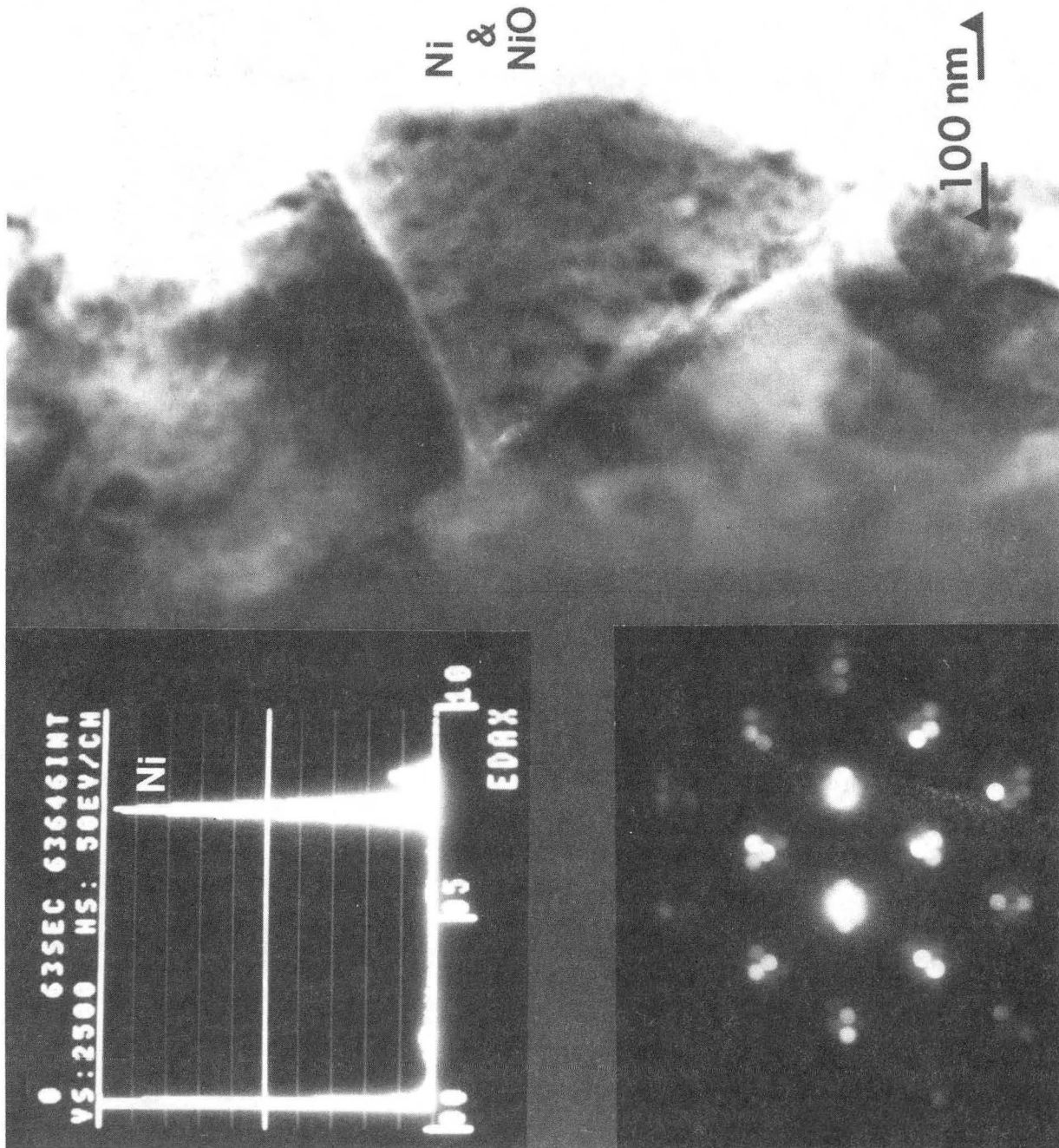
XBB 850-10170

Fig. 4A and 4B



XBB 850-8255

Fig. 5A



XBB 850-8252

Fig. 5B

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