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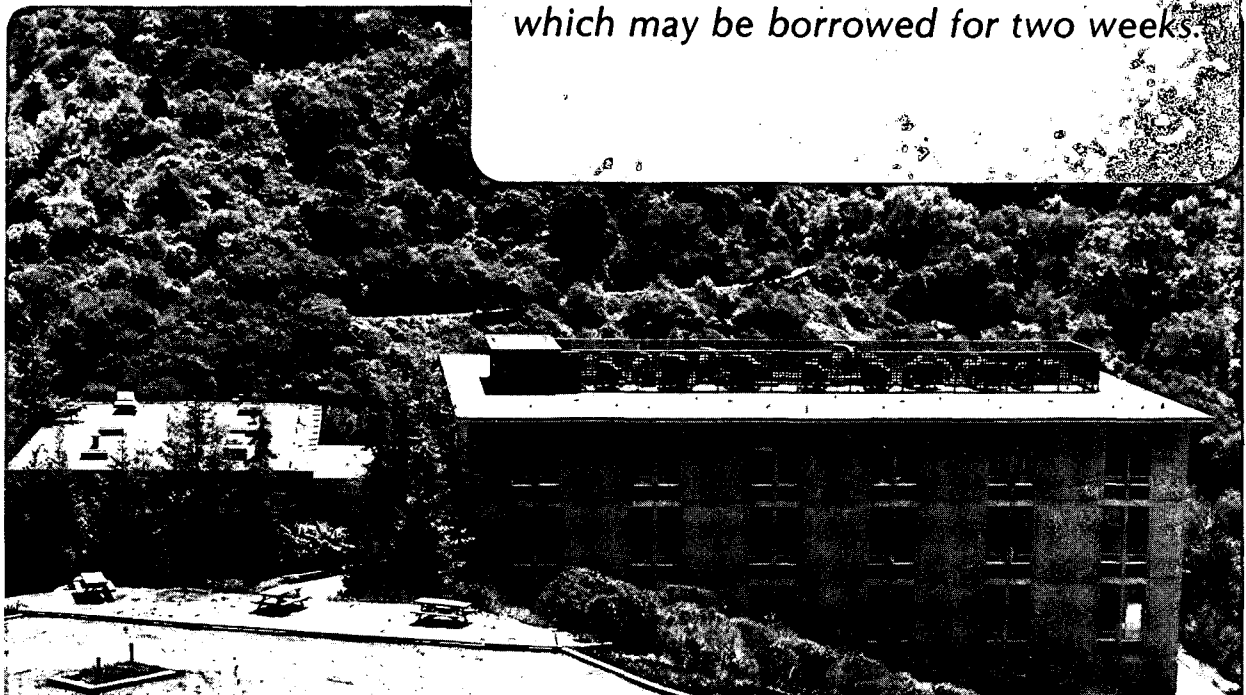
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April 1986

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EVOLUTION OF THE NICKEL/ZIRCONIA INTERFACE

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Abstract

The changes taking place at the nickel/zirconia interface during oxidation in air at 900 C were studied using analytical electron microscopy (AEM). The nickel oxide layer growing at the interface and the stabilizers used in zirconia interact, giving different interface morphologies.

## INTRODUCTION:

Preliminary studies on degradation of thermal barrier coatings have shown oxide products at the interface.<sup>1</sup> The interactions between the oxidation products of the bond coating and the ceramic coating are of importance in determining the degradation mechanisms of the coating. The present investigation involves studies on a model system, Ni/ZrO<sub>2</sub>. The modification of this interface during oxidation in air is relevant to actual thermal barrier systems where NiO is one of the oxidation products at the bond coat/zirconia interface.

## EXPERIMENTAL

Bulk samples, containing nickel particles dispersed in a zirconia matrix, were prepared by hot pressing mechanical mixtures of nickel and zirconia powders (about 10 vol% nickel). The zirconia powders were stabilized with three different stabilizers, to determine the effect of the nature of stabilizer on the interface reactions. The experimental details for sample preparation and further heat treatment are given in Table 1.

Analytical electron microscopy was used to establish the microstructural and microchemical changes taking place at the nickel/zirconia interface, as the oxidation progressed. The sample preparation for transmission electron microscopy (TEM) is especially important for metal/ceramic composites and conventional techniques always produce electron transparent foils with varying thickness of metal and ceramic near the thin edge. A modified thin foil preparation technique was therefore developed for obtaining a uniform thickness

across the metal/ceramic interface by minimal ion milling.<sup>2</sup> Specimens were examined in a Philips EM400 electron microscope at 120 kV. The microanalysis was carried out using energy dispersive x-ray spectroscopy.

## RESULTS AND DISCUSSION

### As Hot-Pressed Samples:

TEM specimens from as-hot-pressed samples were examined to determine the nature of the original metal/ceramic interface. Fig. 1a shows a conventional bright field micrograph of a nickel grain surrounded by zirconia grains. All the boundaries are sharp and show fringes when tilted in the electron beam, similar to grain boundaries in single phase materials. Fig. 1b shows a lattice image near one of the grain boundaries in 1a. The 111 atomic planes of zirconia continue right up to the metal/ceramic boundary. A lattice image of nickel could not be obtained because the nickel metal had been heavily deformed during hot pressing and also because astigmatism, due to the magnetic nature of nickel, is quite difficult to correct. However, the experimental results are sufficient to conclude that there is no interfacial reaction during hot pressing at a resolution of less than a nanometer.

### Samples Oxidized in Air at 900 C

Fig. 2 shows the development of a nickel oxide (NiO) layer at the nickel/zirconia interface after oxidation of the hot-pressed Ni/ZrO<sub>2</sub> composites. The zirconia was stabilized with yttria (8 wt%). The presence of NiO is established using micro-diffraction and EDXS (Inset

top left, Fig. 2). There is no change in composition of zirconia near the interface. The interface between NiO and  $ZrO_2$  ( $Y_2O_3$ ) is sharp, and no interaction between any components is seen.

A similar interface in a specimen prepared using calcia stabilized zirconia is shown in Fig. 3. Now a banded layer has developed at the NiO/ $ZrO_2$  interface, all around the nickel grain. Microdiffraction, using a 50nm probe, shows this region to be twinned, monoclinic zirconia (inset top left, Fig. 3). Also, the superimposed EDX spectra taken from the twinned zirconia and the neighboring zirconia (inset bottom left, Fig. 3) matrix show that the twinned region is depleted in calcia. Thus the growth of NiO during oxidation has led to CaO depletion from the adjacent  $ZrO_2$ . Microcracking is seen at the twinned monoclinic zirconia layer. This could result from the volume expansion (3-5%) associated with the transformation of the Zirconia from the tetragonal to monoclinic phase, as a result of the CaO extraction.

In the case of magnesia stabilized zirconia (Fig. 4) it is possible to detect magnesium in the EDX spectrum taken from the NiO layer, indicating extensive dissolution of MgO in NiO. As a result, the adjacent zirconia grains are completely transformed to monoclinic zirconia.

All these observations can be understood simply on the basis of the phase relationship between NiO and the stabilizers used. Yttria is insoluble in NiO<sup>3</sup>; CaO is partially soluble in NiO<sup>4</sup>; MgO is completely miscible with NiO.<sup>5</sup> The amount of stabilizer dissolved in

NiO depends on the solubility at the oxidation temperature; hence one sees only a narrow band of transformed zirconia in calcia stabilized zirconia, whereas the spatial extent of transformation in magnesia stabilized zirconia is quite large. The volume expansion associated with tetragonal to monoclinic transformation causes micro-cracking which is the initial stage of interface degradation. These results thus indicate that yttria stabilized zirconia will show no chemical interface degradation resulting from chemical interactions. A detailed analysis of these results will be reported in the near future.

**ACKNOWLEDGMENT:**

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3. "Phase Diagrams for Ceramists", Eds. E. M. Levin and H. F. McMurdie, Pub. The American Ceramic Society, 121 (1975).
4. Ibid., Eds. E. M. Levin, C. R. Robins and H. F. McMurdie, p. 102 (1964).
5. Ibid, p. 110 (1964).

Table 1

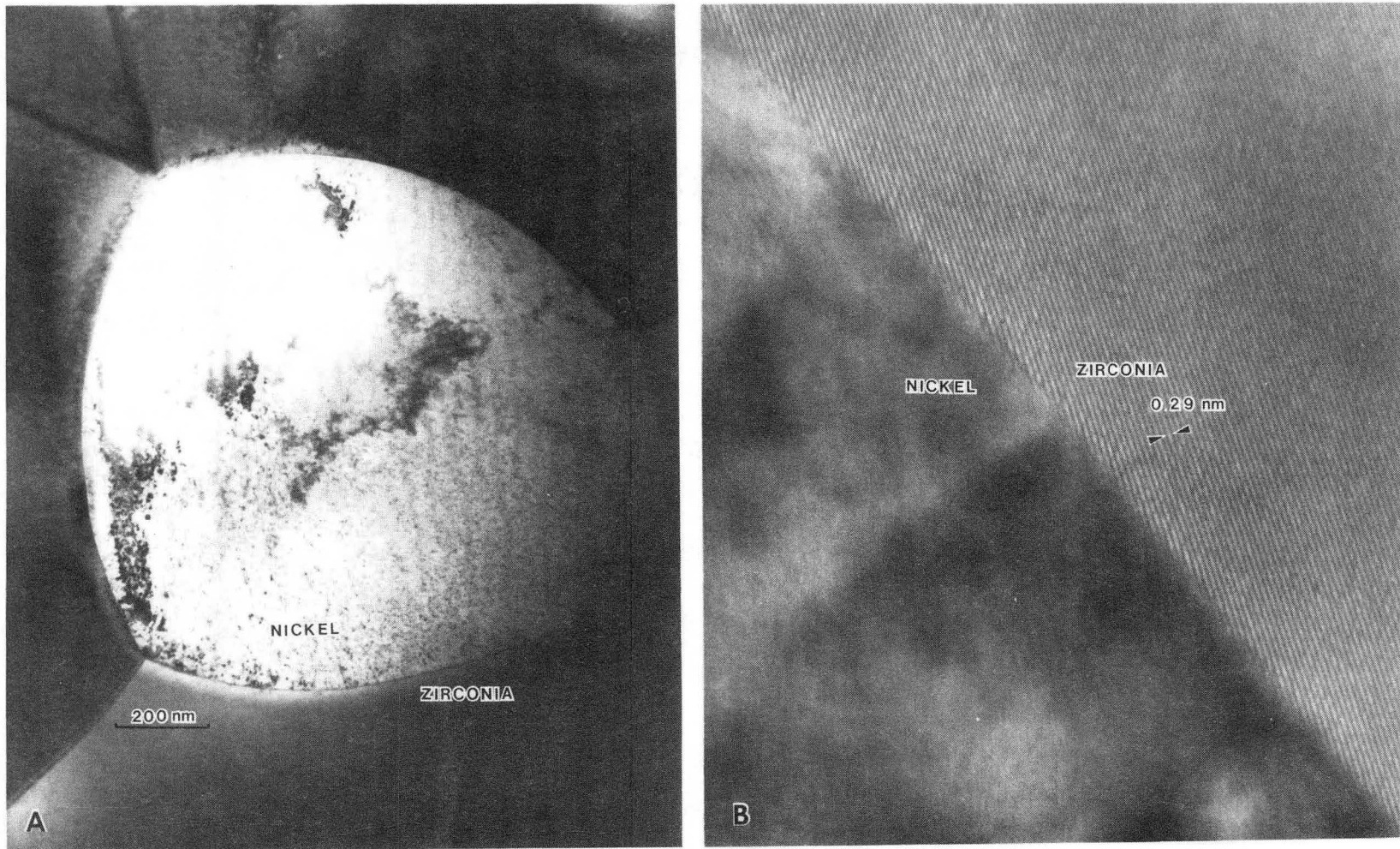
NICKEL-ZIRCONIA SAMPLES

No.	Composition*	Hot Pressing Conditions	Heat Treatment
1	ZrO <sub>2</sub> + 8 wt% Y <sub>2</sub> O <sub>3</sub>	1300 C	1 and 10 hrs
2	ZrO <sub>2</sub> + 5.5 wt% CaO	1 hr	at
3	ZrO <sub>2</sub> + 22 wt% MgO	41.4 MPa	900 C in air

\*All Samples contained 10 vol% nickel powder

## LIST OF FIGURES

- Figure 1: (A) Nickel grain in zirconia (with 11-3 mol% Calcia) in as hot-pressed sample. (B) Lattice image of the nickel/zirconia boundary. The interface shows no evidence of chemical interactions.
- Figure 2: Growth of NiO, after oxidation, at the nickel/zirconia (yttria stabilized) interface. No interfacial reaction at the NiO/ZrO<sub>2</sub> (Y<sub>2</sub>O<sub>3</sub>) interface is seen.
- Figure 3: Interfacial reaction at NiO ZrO<sub>2</sub> (Calcium Stabilized) interface. A thin band of zirconia has transformed to monoclinic zirconia (inset microdiffraction pattern, top left). The superimposed EDX spectrum (bottom left) shows Ca depletion from the twinned region.
- Figure 4: Interfacial reaction in magnesia stabilized zirconia. Extensive dissolution of MgO in NiO is in evidence. (see inset B). Adjacent zirconia grain shows almost no MgO (inset A).

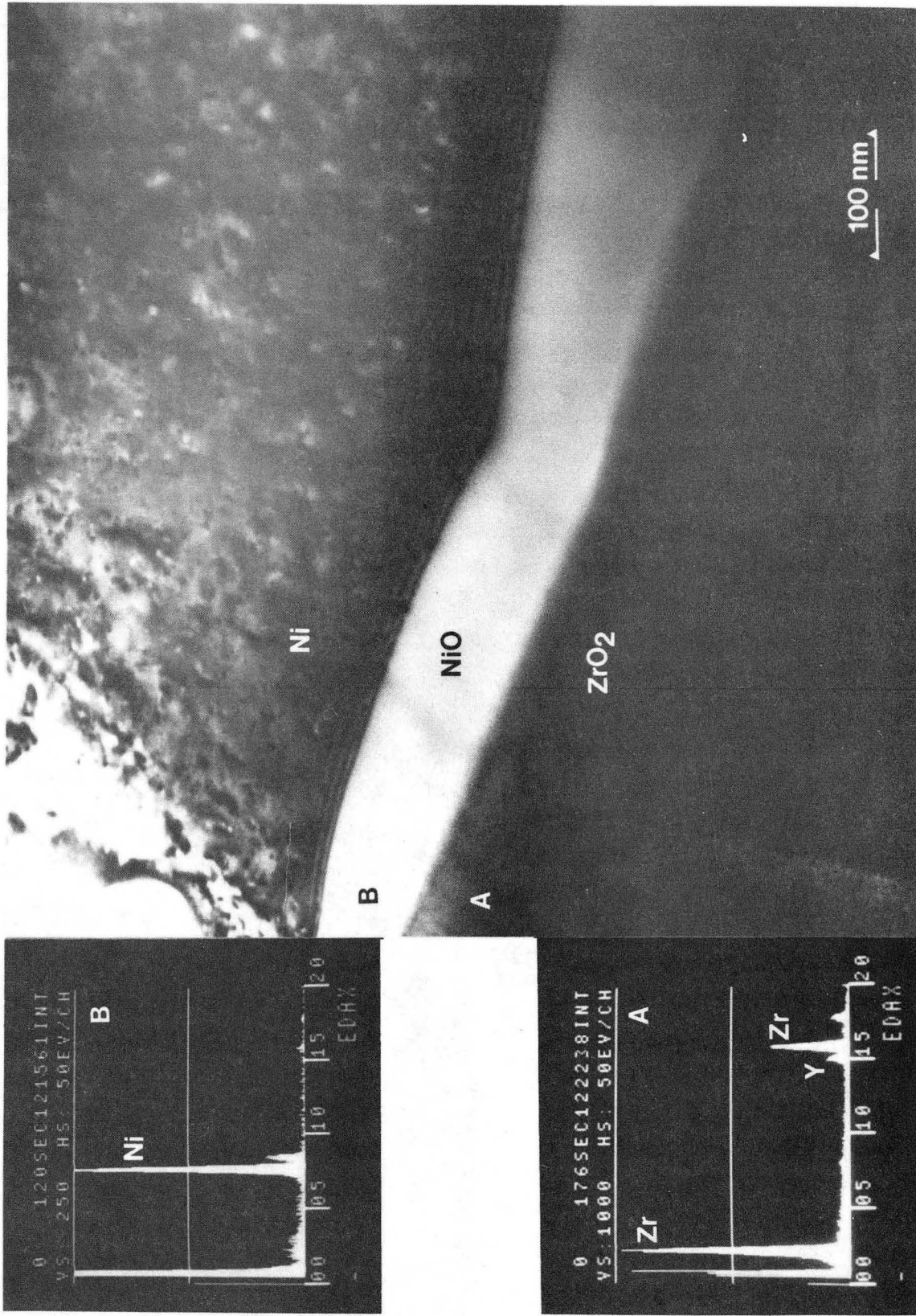


(A) NICKEL GRAIN IN ZIRCONIA (WITH 11.3 MOL% CALCIA) MATRIX IN AS HOT-PRESSED SAMPLE.

FIG. 1

(B) HIGH RESOLUTION LATTICE IMAGE OF THE OUTLINED REGION OF THE NICKEL-ZIRCONIA BOUNDARY. THIS INTERFACE IS SEEN TO BE ATOMICALLY SHARP.

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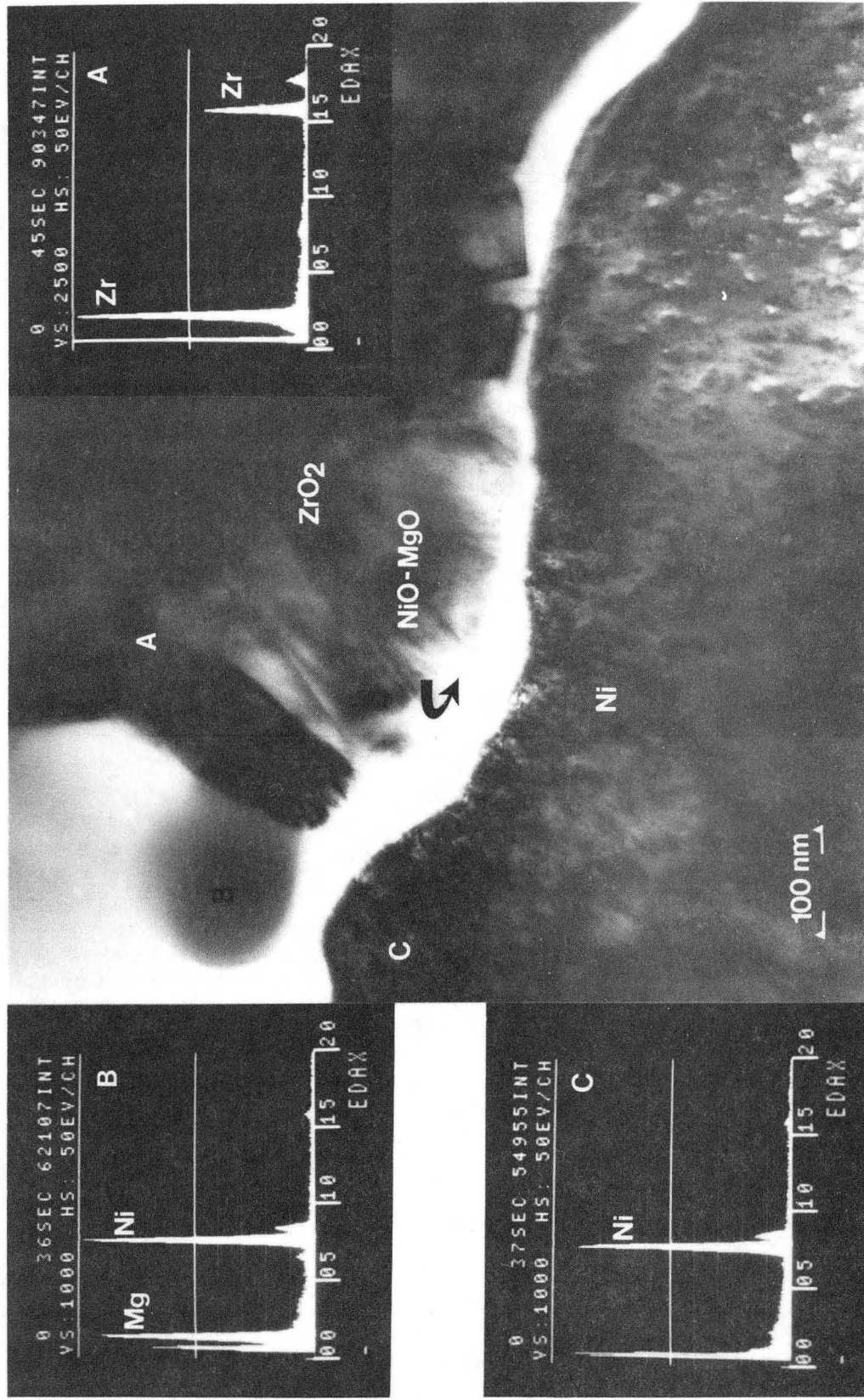
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Fig. 2



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Fig. 3



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Fig. 4

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