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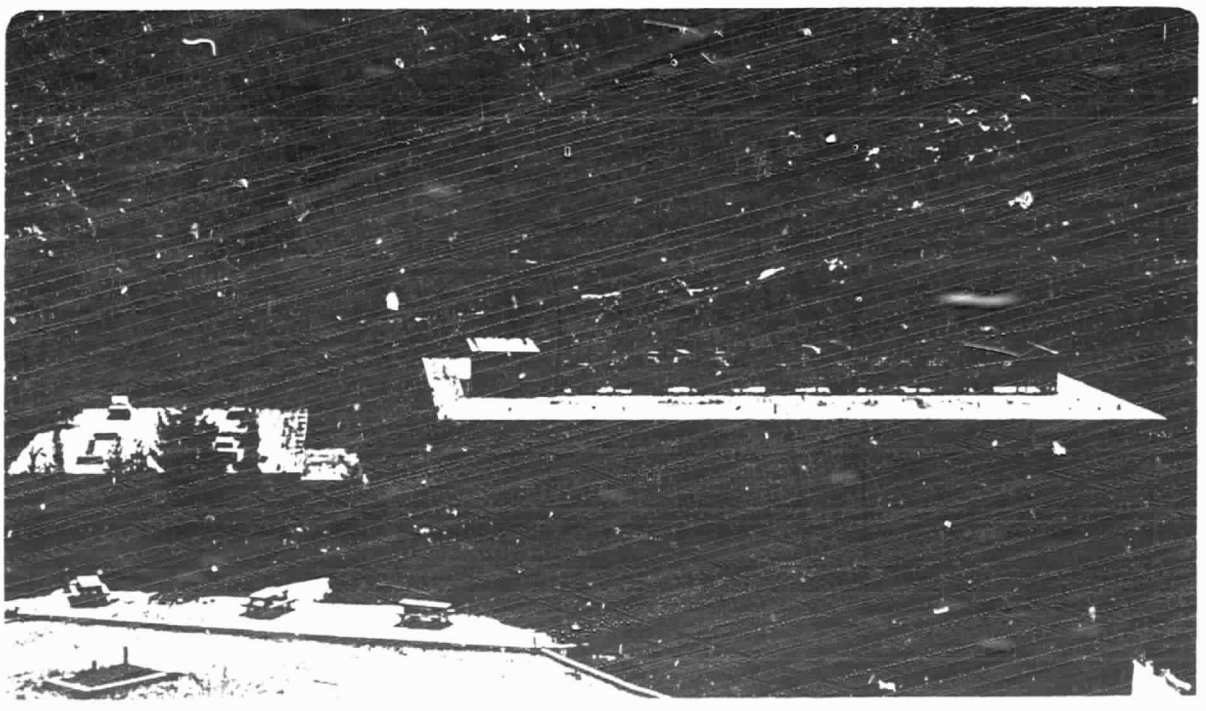
April 1986



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ABSTRACT

The degradation mechanism in thermal barrier coating system subjected to prolonged heating in air as well as to thermal cycling was studied. Bond coat oxidation was found to be the most important reason for degradation. The oxidation produced NiO as well as Al_2O_3 in one set of samples, but the variation in initial coating structure made it difficult to resolve systematic differences between isothermally heated and thermally cycled samples. However, the contribution to degradation from changes in substrate compostion seemed less in the cycled sample.

I. INTRODUCTION

Thermal barrier coatings (TBC's) have been developed for high temperature gas turbine application since the 70's.[1,2] The generally accepted thermal barrier system consists of a 'bond-coat' layer of Ni, Cr, Al, Y alloy on the substrate covered by a ceramic layer, usually ZrO_2 with stabilizers (such as yttria or magnesia). The ceramic layer establishes a temperature gradient, thus making it possible to use higher surface operating temperatures. The bond coat serves as an oxidation resistant coating and as a buffer between the ceramic layer and mechanically dissimilar substrate. A failure in such a system consists of spallation and subsequent removal of the ceramic layer.[3] Recent studies have shown that the oxidation of the bond coat is largely responsible for the degradation.[3,4] It is therefore important to determine the nature of the products produced at the bond coat/ceramic interface in oxidizing environment. The stresses at the interface will depend on whether the TBC is being subjected to prolonged or to cyclic heating. This paper reports on the identification of the oxidation products at the interface and on the differences in the interface microstructure and chemistry in TBC's subjected to prolonged heating and to thermal cycling.

Experimental Procedure

Specimens for optical metallography (OM), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) were prepared from two sets of TBC's. One set consisted of TBC's prepared for the cylinder head in a diesel engine*; the other was a TBC under development at the NASA- Lewis Research Center, Ohio. The first set was subjected to oxidation in air at 900°C for 1 and 10 hours. A sample in the second set was oxidized at 1100°C for 10 hours and an other one was cycled ten times, each cycle consisting of 1 hour at 1100°C in air, followed by rapid cooling to room temperature.

Both the as-received and the oxidized samples were prepared for cross-sectional microscopy (OM, SEM and TEM) by a technique described elsewhere.[5] An AMR 1000 SEM, fitted with a KEVEX system was used for scanning electron microscopy, and a Philips EM400 with EDAX was used for analytical electron microscopy (AEM).

RESULTS AND DISCUSSION

The results on the first set of TBC's have been reported earlier.[6] One of the figures is reproduced for the sake of completeness. Only results relating to changes at the interface between bond coat and zirconia are presented here.

Fig. 1 is an SEM micrograph showing the bond-coat portion of a TBC that was oxidized for 10 hours at 900°C in air. The EDX spectra were taken using a raster mode, with the raster covering

* Plasma Tech. Inc., Torrence, CA

approximately a 5-8 m square area. This gave information on the average compositional changes in the bond-coat as a function of distance from the ceramic layer. The three spectra included in Fig. 1 show definite aluminum depletion in the bond coat near the interface. The reduction in the Al peak intensity is noticeable, whereas a Cr-peak intensity variation could not be detected. One can therefore conclude that aluminum diffuses out of the bond coat to form an oxide layer (alumina) at the ZrO_2/alloy interface. Also, because there is no variation in chromium peak intensity, one would expect the major constituent of the oxide layer developed at the interface to be alumina. Cross-sectional TEM samples made from the same specimen provided additional information.

Figs. 2a and b show the two oxidation products detected at the bond-coat/zirconia interface. This sample was oxidized at 900 °C for 10 hours. Microdiffraction and EDXS established that the oxidation products were alumina (Al_2O_3, Fig. 2a) and nickel oxide (NiO, Fig. 2b). The bond-coat grains surrounding the alumina were found to be depleted in aluminum (see EDX spectrum, top right, 2a). Thus aluminum diffused out of the bond-coat grains to form alumina at the ceramic/metal alloy interface. Further oxidation of the bond-coat grains should then produce oxide products other than alumina. The microdiffraction pattern in Fig. 2b resulted from both nickel and nickel oxide grains superimposed in the electron beam, as confirmed by the EDX

spectrum. Thus, nickel oxide can be one of the oxidation products at the interface. It is possible that the Ni, Cr, Al, Y bond coat was not homogeneous in composition, so that unalloyed nickel grains were present near the interface, leading to NiO formation.

These observations indicate that the oxidation products at the interface are not alumina grains alone; other oxidation products may be produced depending on the homogeneity of the bond- coat and on the aluminum concentration in bond-coat grains near the interface.

Figs. 3a, b and c show optical micrographs from the second set of samples. Fig. 3a shows the cross-section of the as-sprayed sample; Fig. 3b the cross-section of the sample oxidized in air at 1100 ^{o}C for 10 hours (isothermal); and Fig. 3c the cross-section of the sample cycled 10 times (cycled). Each cycle consisted of 1 hour at 1100 ^{o}C in air, followed by rapid cooling to room temperature. The difference in interface morphology in the isothermal (Fig. 3b) and cycled samples (Fig. 3c) is evident in these micrographs. Extensive bond-coat oxidation has led to formation of oxides in both cases; however, the oxide layer has penetrated up to the substrate/bond coat interface only for the isothermal sample (arrows in Fig. 3b).

The oxidation products in both the isothermal and cycled samples were characterized using SEM (AMR 1000) attached with a KEVEX microanalysis system. Figs. 4a and 4b and Table I show the variation in composition as a function of position in these

two samples. The quantitative estimates of the bulk bond coat, and substrate compositions were in reasonably good agreement with the reported compositions (± 5% error).

The isothermal sample showed oxidation of the substrate as well as of the bond coat. Microanalysis at position 1.1 (Fig. 4a and Table 1) shows the elemental composition of the oxide layer developed at the bond coat/ceramic interface. If it is assumed that all elements formed oxides, then the composition comes out to be 75 mol%Al_2O_3, 16.8 mol % Cr_2O_3 and 8.2 mol % NiO. Alumina is thus a major constituent of the oxide layer at the interface. Aluminum depletion from the bond-coat also was observed in this sample. However, even the bond-coat grains at the center of the layer were depleted in aluminum (position 1.2, Fig. 4a). This indicates that some bond coat oxidation took place during the fabrication (plasma spraying) itself. Extensive oxidation of the substrate also had occurred during fabrication. Microanalysis at position 1.3, Fig 4a shows all elements of the substrate with enrichment in Al and Cr. The substrate has oxidized in this region to form Al_2O_3 and Cr_2O_3. The substrate showed aluminum depletion (see compositions at positions 1.4, 1.5 and 1.6). It would be difficult to say if this depletion would also occur in the absence of the observed substrate oxidation. The cycled sample showed very similar compositional changes, the only difference being the absence of aluminum depletion in the substrate near the bond coat/substrate interface (see compositions at positions 2.1 and 2.2, Fig. 4b).

It is difficult to establish, with certainty, the differences between the isothermal and the thermally cycled samples at this time, since some oxidation took place during the fabrication itself, and the starting microstructures were quite different. The results so far point out the importance of controlling the initial microstructure of the TBC for reliable performance. Experiments on microstructure-controlled specimens are currently in progress and will be reported in the future.

ACKNOWLEDGMENT

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Table I

Compositional Variation in

Isothermally heated and Cycled TBC's

POSITION	Ni	Cr	Al	Co	Ti	LOCATION
Fig. 4a		wt %				
1.1	23.71	34.62	79.77	-	-	ZrO_2 /b.c interface
1.2	82.47	17.08	2.75	-	-	Center of b.c.
1.3	43.69	29.04	26.92	13.15	7.01	Center of oxidized sub.
1.4	67.85	12.58	4.12	15.28	3.47	Substrate near b.c./sub. interface
1.5	70.10	10.07	5.70	14.24	4.49	Substrate 20 μm away
1.6	67.8	11.32	7.66	15.03	4.11	Substrate 50 μm away
Fig. 4 b						
2.1	73.06	9.55	6.41	10.82	5.36	Substrate near b.c./sub. interface
2.2	73.21	8.54	6.87	11.22	5.73	Substrate 40 μm away
Nominal Compositions						
Bond Coat	88.05	15.6	6.35	-	-	
Substrate	63.00	9.0	5.00	15.00	5.0	and 3 % Mo not analyzed

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LIST OF FIGURES

FIG 1. Changes in the bond-coat aluminum concentration with distance from the bond-coat/zirconia interface. Zirconia is to the right and the substrate is to the left of the bond-coat. The EDX spectra show aluminum depletion near the bond-coat/zirconia interface.

FIG 2a. Alumina grains at the bond-coat/zirconia interface in a TBC heated isothermally at 900 °C for 10 hrs. The EDX spectrum (top left) and the diffraction pattern (bottom right) established the grains to be alumina. The adjoining bond-coat grains are depleted in aluminum (EDX spectrum, top right).

FIG 2b. Nickel oxide grain at the bond-coat/zirconia interface. The composite diffraction pattern is due to Ni and NiO grains superimposed in the electron beam.

FIG 3. Optical micrographs showing differences in morphology of the as sprayed (1), isothermally heated (2), and cycled (3) TBC's. The arrows in (2) and (3) point to regions where substrate oxidation has occurred.

FIG 4. SEM micrographs of isothermally heated (A) and cycled (B) TBC's. The results of microanalyses at positions 1.1 through 1.5 and 2.1 and 2.2 are presented in Table I.

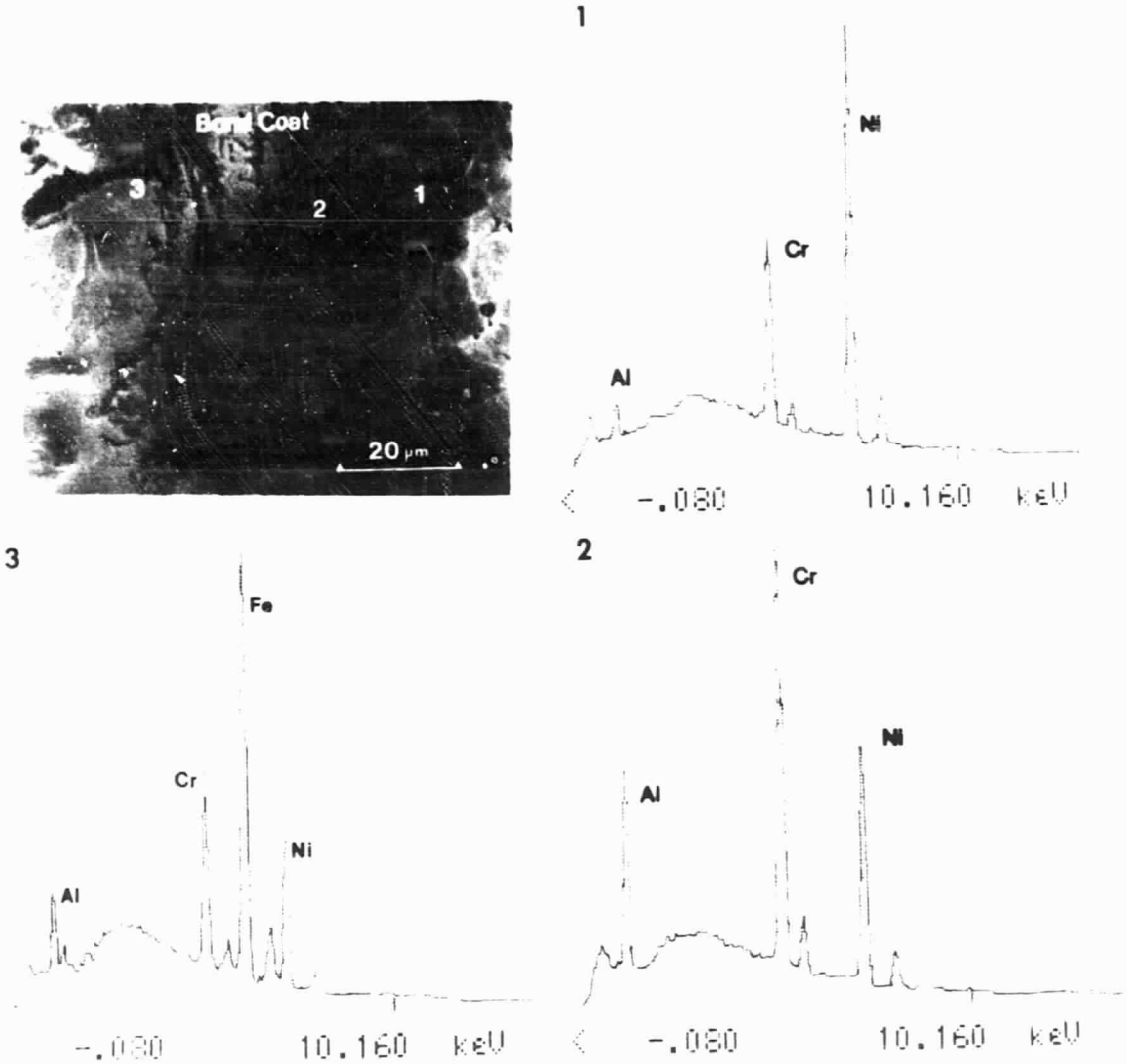

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Fig. 1

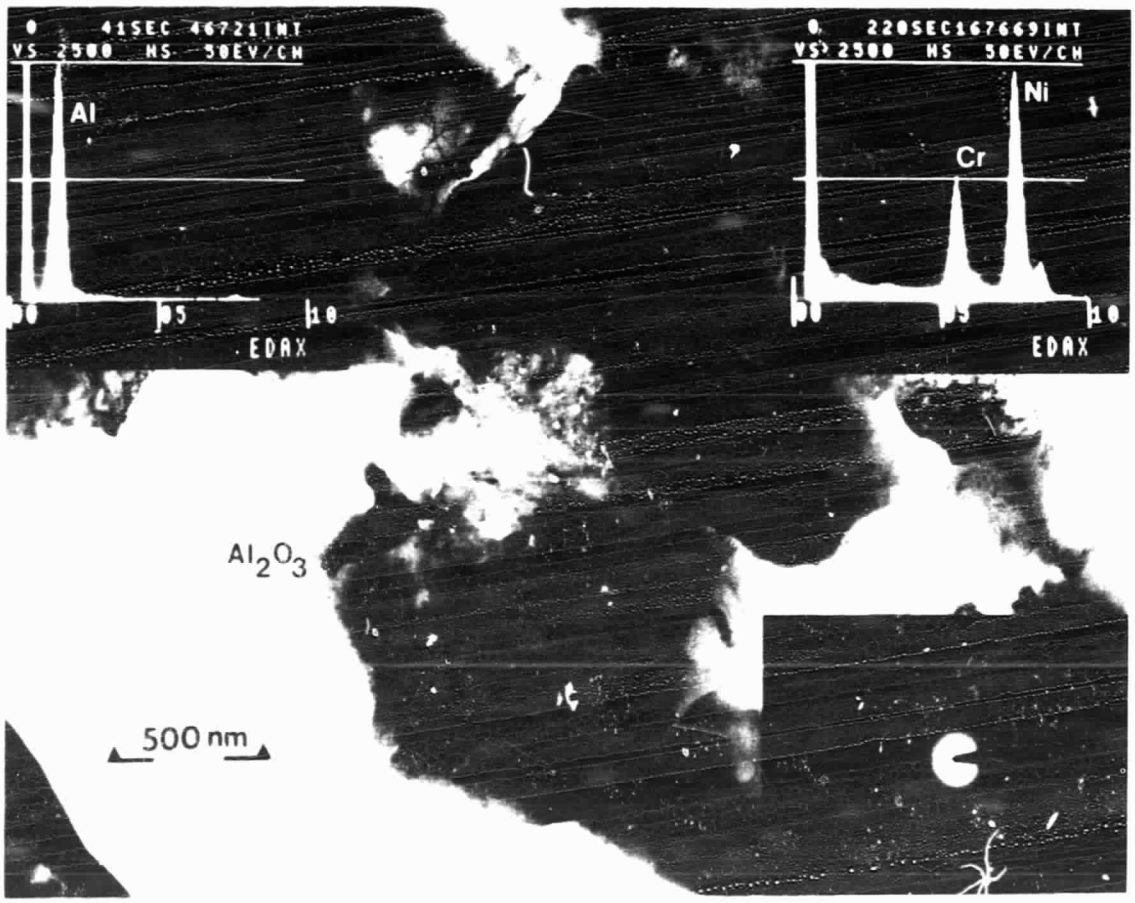

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Fig. 2a

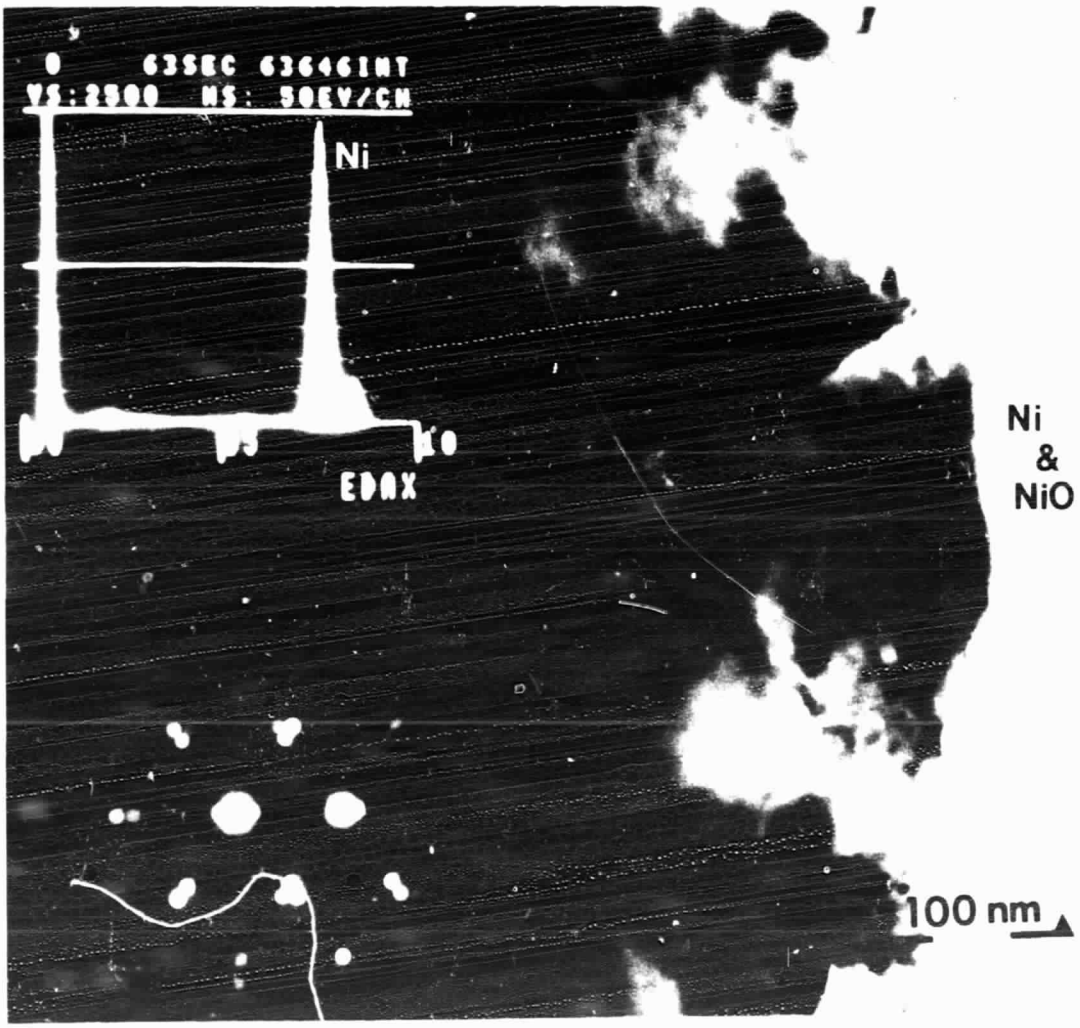

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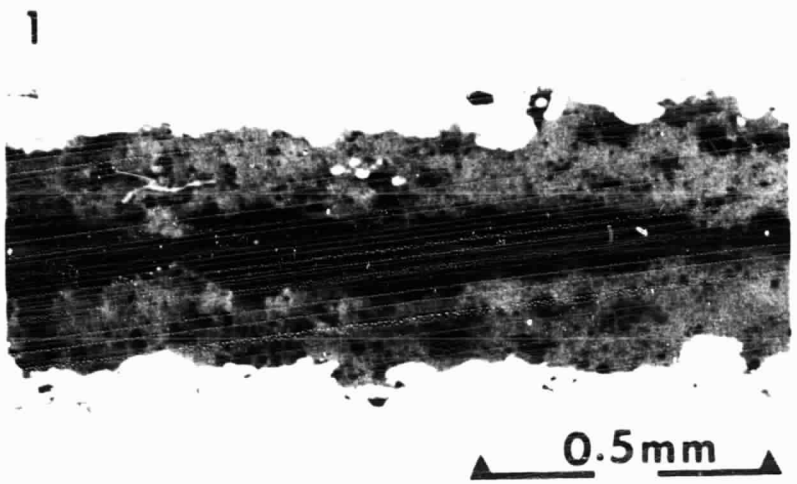
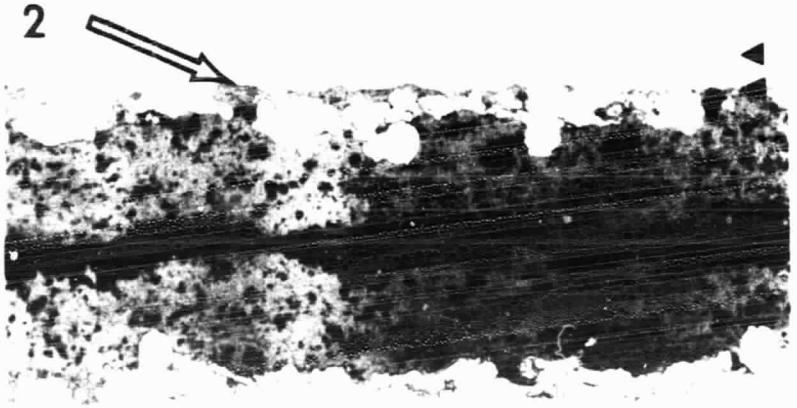
Fig. 2b

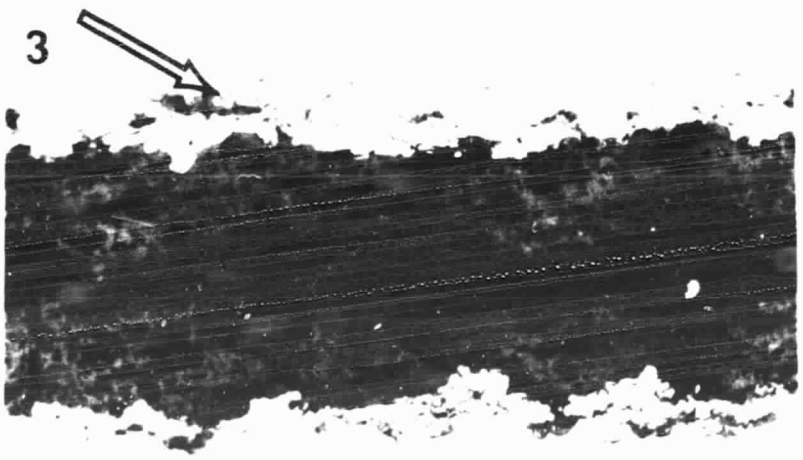


AS SPRAYED



STATIC

10 hrs, 1100 C



CYCLED

10, 1 hr Cycles

1100 C

XBB 861-374

Fig. 3

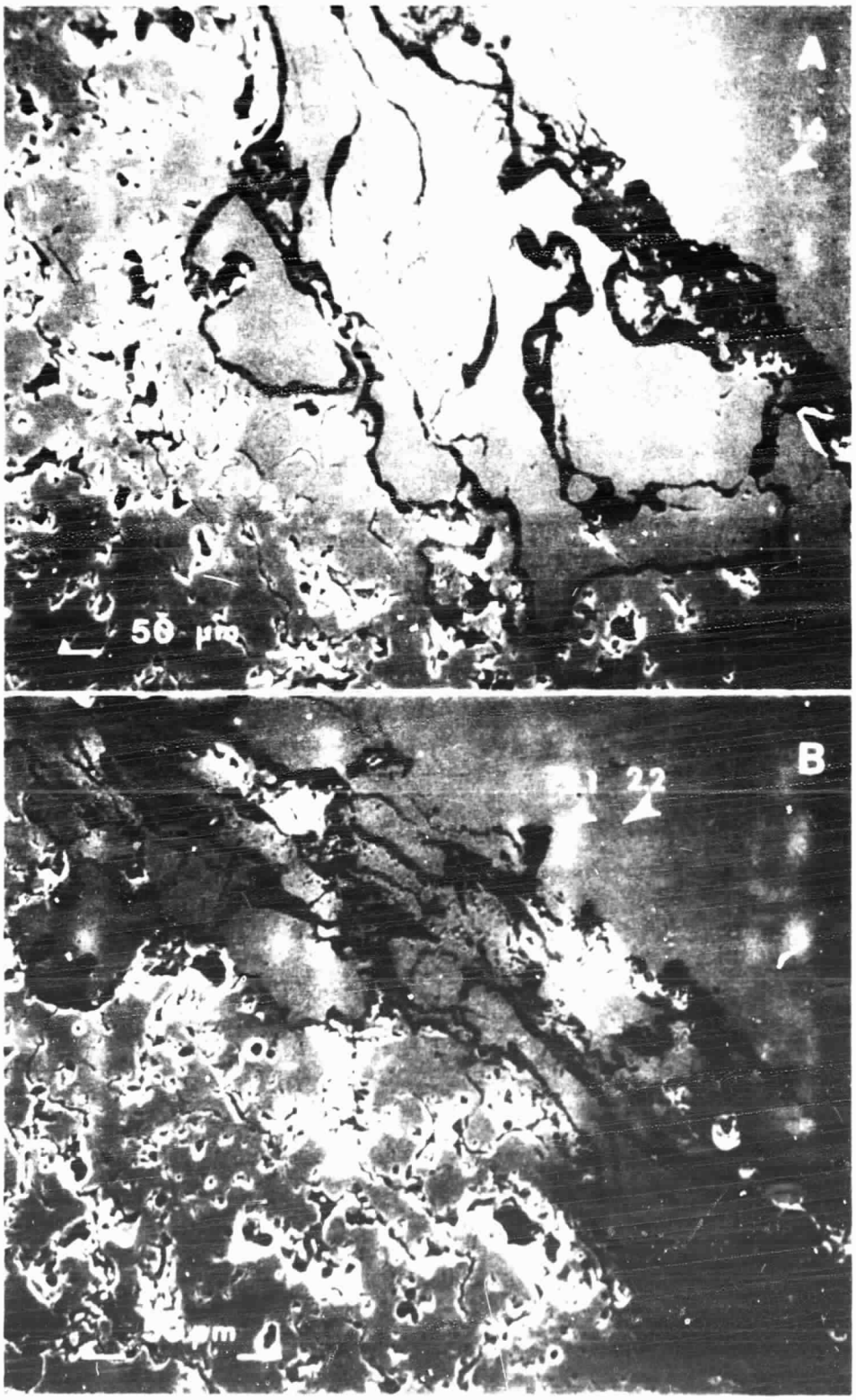


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Fig. 4

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