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A SCANNING ELECTRON MICROSCOPE STUDY OF THE SURFACE
MORPHOLOGY OF TD-NiCr OXIDIZED AT 800° C TO 1200° C

by Carl E. Lowell
Lewis Research Center
Cleveland, Ohio
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ABSTRACT

Scanning electron microscopy was used to study the surface of oxides formed on TD-NiCr at 800⁰, 1000⁰, and 1200⁰ C for up to 64 hours. Abraded surfaces oxidized in air to form Cr₂O₃ which developed into large crystals suggesting vapor growth. Surfaces polished and oxidized had NiO on the surface except over grain boundaries and scratches which had Cr₂O₃ covering them.

Wire samples of TD-NiCr were oxidized at 1200⁰ C for up to 50 hours at pressures from 10⁻⁵ to 700 torr. Large crystals of Cr₂O₃ resulting from vaporization and condensation were observed at pressures of 10 torr and above. Humid air oxidation altered oxide morphology markedly.

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SUMMARY

Scanning electron microscopy was used to study the surface morphology of the oxides formed on TD-NiCr at temperatures of 800°, 1000°, and 1200° C and times up to 64 hours. The effects of two surface finishes were investigated. Surfaces abraded with 120 grit and then oxidized in air at atmospheric pressure grew an oxide layer which developed, after four hours at 800° C and one hour at 1000° C, large crystals of Cr_2O_3 . After 64 hours, the crystals had grown to about five micrometers (μM). The shape of the crystals suggested vapor growth. Surfaces polished through 0.5 μM diamond paste prior to oxidation oxidized differently over grain boundaries and scratches than over the rest of the surfaces. The bulk of the oxide was faceted NiO but showed little tendency toward the formation of large protruding crystals as the Cr_2O_3 did. At the grain boundaries, as at residual scratches, Cr_2O_3 grew at a much lower rate than the NiO. This gave the grain boundaries a deeply etched appearance. With time the NiO grew laterally to nearly cover over the Cr_2O_3 , although this growth was not completed even after 64 hours at 1000° C.

Five mil (0.0127 cm) diameter wire was heated at 1200° C at times up to 50 hours and at air pressures of from 10^{-5} to 700 torr. At 10^{-5} torr, the oxide formed on the surface of the wires was faceted but not protruding. As the pressure was increased above 10^{-4} torr large needle-like growths appeared. These resulted from the reflection of the volatile oxide species caused by collisions with air molecules. At 700 torr the volatility of the oxide was increased, but so

was the amount of reflection due to the higher density of the surrounding air. This caused the formation of numerous crystal growths on the wire, some of which extended as much as 0.02 centimeter outward.

INTRODUCTION

Much attention has been focused on TD-nickel chromium ($\text{Ni} + 20\% \text{Cr} + 2\% \text{ThO}_2$) (TD-NiCr) because of its high-temperature strength and reported good oxidation resistance (ref. 6). Unfortunately, some applications for TD-NiCr, e.g. gas turbine components and the space shuttle thermal protection system, include high velocity gas flow as well as high temperature. Under these conditions volatility of the oxide becomes an important part of the oxidation mechanism. Chromium oxide, Cr_2O_3 , a major constituent of scales formed on TD-NiCr, as well as on many other nickel and cobalt-base superalloys, is known to be volatile at high temperatures (refs. 1 to 3). It has been, therefore, anticipated and demonstrated (ref. 4) that the good oxidation resistance of TD-NiCr in a static furnace is degraded by flowing gas conditions.

Since volatility is primarily a surface reaction, the author felt that one approach to the understanding of this reaction was through a study of the surface morphology of oxidized specimens. Scanning Electron Microscopy (SEM) with its combination of high magnification and great depth of field is well suited for this type of study. This has been demonstrated in Ref. 5. The object of the present work was to evaluate the surface morphology of scales formed on oxidized TD-NiCr.

Two types of samples and oxidizing conditions were used. The first consisted of sheet specimens heated in a tube furnace. Since surface preparation has been found to affect the oxides formed in TD-NiCr (ref. 6), surface preparation was included as a variable here. Therefore, samples were polished on one side and abraded on another. These samples were oxidized in ambient air at 800°C and 1000°C to achieve minimum volatility.

The rest of the samples were in the form of 0.005" (0.013 cm) diameter wire. These samples were self-heated to 1200° C by passing current through them. The object of utilizing specimens of wire geometry was to increase the rate of volatilization without the necessity of providing high gas velocities. Fryburg had previously used this technique in his work on platinum oxidation (ref. 7). His work showed that the rate of loss of volatile platinum oxide was influenced by the ratio of the characteristic sample size, e.g. the diameter of a wire, to the mean free path of the oxidizing medium. As long as this ratio was less than unity the weight loss rate was linear with pressure. As the ratio exceeded unity the rate tended to stop increasing with pressure. Therefore, the smaller the sample size, the higher is the pressure at which the ratio of sample size to mean free path equals unity. Thus for small samples the limiting rate of volatilization in still air would be greater than that of larger samples. Such small samples would approach volatility rates of large samples oxidized by high velocity gases where the volatile oxides are swept away by the moving gas instead of being reflected back to the surface.

Materials and Preparation

TD-NiCr was obtained as 0.060" (0.15 cm) thick sheet from Fansteel Metallurgical Corporation and as 0.005" (0.013 cm) diameter wire from the Bendix Corporation under an NASA contract (ref. 8). The chemical analyses of the materials is shown in Table 1. Differences in the compositions are slight.

The sheet specimens were cut into 1/2" × 1/2" (1.3 cm × 1.3 cm) squares. One side of each sample was abraded with 120 grit SiC paper while the other side of each was metallographically polished through 0.5 μM diamond paste. The samples were ultrasonically cleaned and rinsed in methanol prior to oxidation. The wires were simply cut to length, ~6" (15 cm), and oxidized without further treatment.

PROCEDURE

The sheet samples were oxidized in a resistance heated tube furnace at 800⁰ C and 1000⁰ C. The times of exposure were 15 seconds, 1 minute, 4 minutes, 16 minutes, 1 hour, 4 hours, 16 hours, and 64 hours.

Wires, mounted in a vacuum bell jar, were heated by passing current through them. The temperature was measured by an optical pyrometer. Both transmission and emissivity corrections were made. The temperature of oxidation was 1200⁰ C while the times were up to 50 hours. The pressures were varied from 10⁻⁵ to 700 torr.

After oxidation some samples were examined by X-ray diffraction (XRD) and all were coated with a vapor deposit of Au-40% Pd to act as a conducting layer. Surface observations were then made with a scanning electron microscope (SEM) operated at 25 kV. A few samples were also analyzed with an electron microprobe.

RESULTS AND DISCUSSION

Sheet Samples - Polished Surfaces

In the initial stages of oxidation, both Nickel Oxide (NiO) and Cr₂O₃ form on the polished surface of TD-NiCr (ref. 6). Figure 1, which shows the oxide morphology after one minute at 800⁰ C, reveals that the oxides start to grow in patches. The oxides then spread laterally. After 15 minutes at 800⁰ C, the NiO has covered most of the surface, see Fig. 2(a). However, the grain boundaries appear to be covered only by Cr₂O₃ as can be seen by the electron microprobe pictures in 2(b) and 2(c).

By one hour at 800⁰ C the NiO has become faceted (fig. 3). In addition, both scratches and grain boundaries appear alike, i.e., they both appear to be covered only by Cr₂O₃ which must be a thinner scale as these two features are deeply recessed beneath the level of the NiO. At longer times and higher temperatures the oxides continue to grow, but even after 64 hours at 1000⁰ C, the grain boundaries are not completely overgrown with NiO (see fig. 4). The 1000⁰ C sample is used to show

long term oxidation; the initial stages are the same as those of 800° C. Figure 4 also shows even greater faceting of the NiO. This could be evidence of volatilization, but it is more likely due only to preferred growth directions in NiO.

Sheet Samples - Abraded Surfaces

At the start of oxidation (~one minute at 800° C), Cr_2O_3 grows without changing the surface morphology (fig. 5). X-ray diffraction confirmed that Cr_2O_3 was the only oxide. After four hours at 800° C small, ~one micrometer (μM), crystals of Cr_2O_3 appear on the surface (fig. 6). These crystals continue to grow, reaching ~5 μM by 64 hours at 800° C and little, if any, larger after 64 hours at 1000° C (fig. 7). Once again, as in the case of polished samples, the sequence at 1000° C was the same as at 800° C. In contrast to the NiO of Figs. 3 and 4, the Cr_2O_3 crystals of Fig. 7 stick high above the surface with minimal contact with the surface scale. This morphology is strongly indicative of vapor growth. This would be a result of CrO_3 vapor leaving the oxide scale and then condensing. This condensate would then become the site of continued condensation. That this should take place at temperatures as low as 800° C is surprising, but this had been indicated by the weight gain curves of Ref. 6. These data show no net weight gain after a few hours of exposure even though oxides continue to form and metal is consumed.

It should not be inferred from these results that polishing the samples to form NiO on the surface would eliminate the loss of chromium via the vapor. Reference 6 shows that chromium may still be lost through the NiO due to the solubility of Cr in NiO at elevated temperatures. This has been further born out by further investigations (proposed NASA Technical Note: Mach 1 Oxidation of TD Nickel Chromium at 1204° C (2200° F)). Here, high gas velocity (Mach 1) oxidation tests showed that electropolishing in order to favor the formation of NiO was of little or no value in altering measured oxidation rates.

Wire Samples

Low pressure (10^{-4} torr) oxidation, in the range where the mean free path is much greater than the sample ($\sim 200\times$), was expected to result in none of the condensations seen above. This was the case (fig. 8). The oxidized wires are relatively smooth although the high magnification picture of 8(b) shows a rather porous oxide layer. This layer was solely Cr_2O_3 .

At 10 torr, where the mean free path is somewhat smaller than the sample size ($\sim 20\times$), condensation would be expected from the work of Fryburg on platinum oxidation (ref. 7). Condensation is noted (fig. 9). It takes the form of needle-like growths forming perpendicularly to the surface and large oxide crystals on the surface. That the oxide is Cr_2O_3 was determined both by X-ray diffraction and by electron probe (fig. 9(c)).

At 700 torr (where the sample size is $1400\times$ the mean free path) the needles are themselves highly faceted (see fig. 10). They appear to be composed of many crystal platelets.

At the same pressure, with humid air (relative humidity $\sim 30\%$) as the oxidizing medium, the needle appears to be more massive (fig. 11). In addition, small filaments are observed growing from the surface. This morphology may be due to the enhanced volatility of Cr_2O_3 in the presence of water vapor. This increased volatility has been observed earlier by Caplan and Cohen (ref. 2). The cause of the increase has been assumed to be the formation of chromium hydroxide and the magnitude of the effect has been calculated by Kohl and Stearns (ref. 1).

SUMMARY OF RESULTS

The results of this investigation of the morphology of TD-NiCr oxidized in air at 800°C to 1200°C may be summarized as follows:

1. Abraded surfaces oxidized to Cr_2O_3 which volatilizes and recondenses to form large (up to $5\ \mu\text{M}$) crystals on the surface. The volatility is noticeable at temperatures as low as 800°C .

2. Polished surfaces oxidize so that NiO is the scale found except over scratches and grain boundaries where Cr_2O_3 is found exclusively. Little or no evidence was found for NiO volatility up to 1000°C .

3. Wire samples oxidized to Cr_2O_3 only, at 1200°C . The Cr_2O_3 was volatile but the rate of recondensation varied with pressure (see fig. 12) as follows:

(a) At 10^{-4} torr (MFP $\sim 200\times$ sample size) no recondensation occurs.

(b) At 10 torr (MFP $\sim 1/20$ sample size) recondensation is just observable.

(c) At 700 (MFP $\sim 1/1400$ sample size) recondensation is extensive.

(d) Humid air alters the morphology of the recondensed oxide considerably and may enhance volatility of Cr_2O_3 .

CONCLUDING REMARKS

The above observations of oxide morphologies allow a few deductions about the formation and volatilization of the oxides formed on TD-NiCr. As in Ref. 6, the formation of the oxide has been shown to be dependent on surface preparation prior to oxidation. NiO forms on polished surfaces, but not over worked areas, grain boundaries or scratches. On the latter sites only Cr_2O_3 forms. Since these sites have high concentrations of dislocations, perhaps the exclusive formation of Cr_2O_3 is due to enhanced diffusion of Cr in the metal.

While little if any evidence of volatilization of NiO was found, the volatility of Cr_2O_3 (no doubt via CrO_3) can be easily deduced from these studies. A surprising feature of the volatility is that it occurs to such an extent as to be detectable at temperatures as low as 800°C . Also, the volatility is affected by the presence of moisture. These observations would seem to indicate when TD-NiCr is oxidized by flowing gases, at temperature above about 800°C , loss of material by vapor transport could be a problem.

REFERENCES

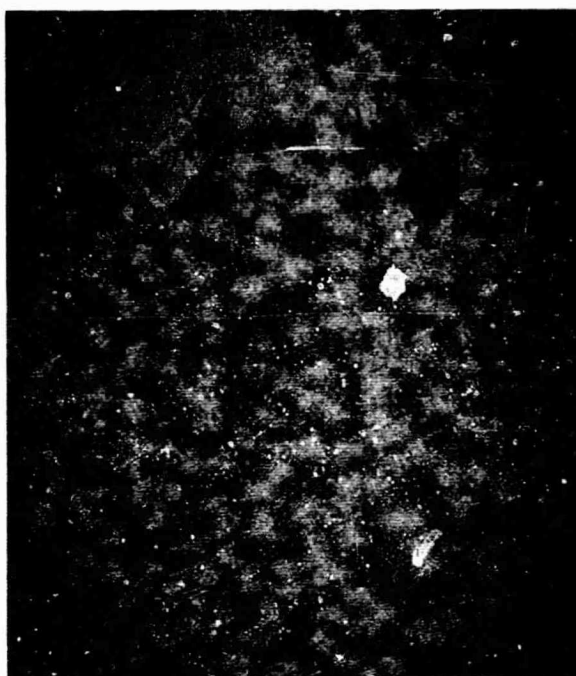
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**Table 1. - Chemical Analysis
of As Received TD-NiCr
Weight Per Cent**

Element	Sheet	Wire
Cr	21.71	21.85
Th	2.19	2.2
O	0.37	N.A. *
Ni	Bal.	Bal.
Fe	0.003	N.A.
Si	0.001	N.A.
N	0.131	N.A.
C	0.008	0.01
S	0.010	0.006

***Not analyzed.**

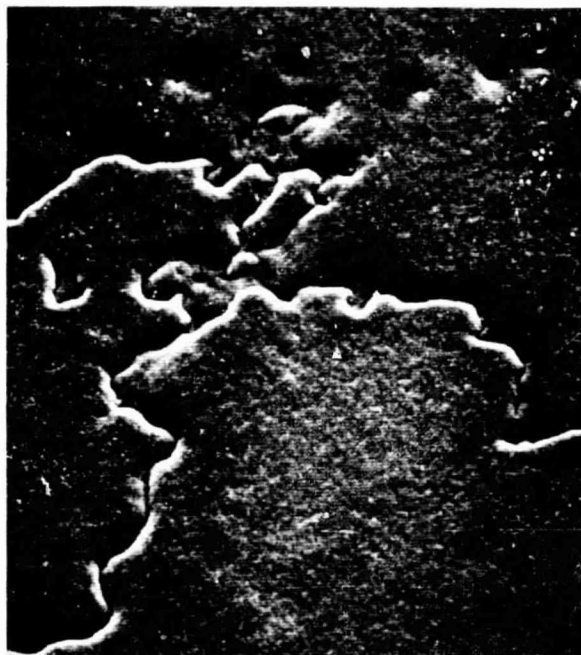
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1000 X
45° Tilt

Figure 1
The Initial Stages of Oxidation of
Polished TDNiCr - one minute at 800° C,
760 Torr.

A.
1000 X 45° Tilt



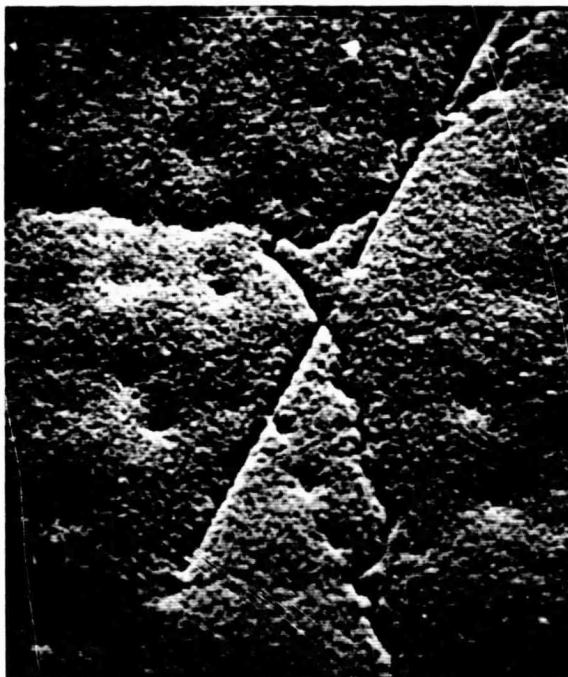
B.
1000 X Secondary Electron
Image, Probe



C.
1000 X Probe
Cr K α Image

Figure 2
Identification of Grand Boundary Oxide on TDNiCr Oxidized for 15 Minutes
at 800° C, 760 Torr.

2-6-11

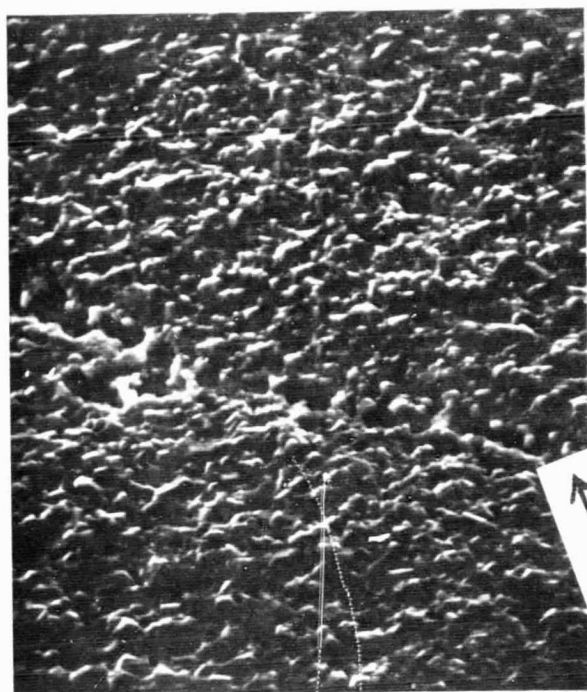


A.
1000 X 2-6 μ M 45° Tilt
Diamond Scratches



B.
10,000 X 2-6 μ M Scratch
45° Tilt

Figure 3
Similarity of Oxidation of Grain Boundaries and Scratches on Polished TDNiCr -
One Hour at 800° C

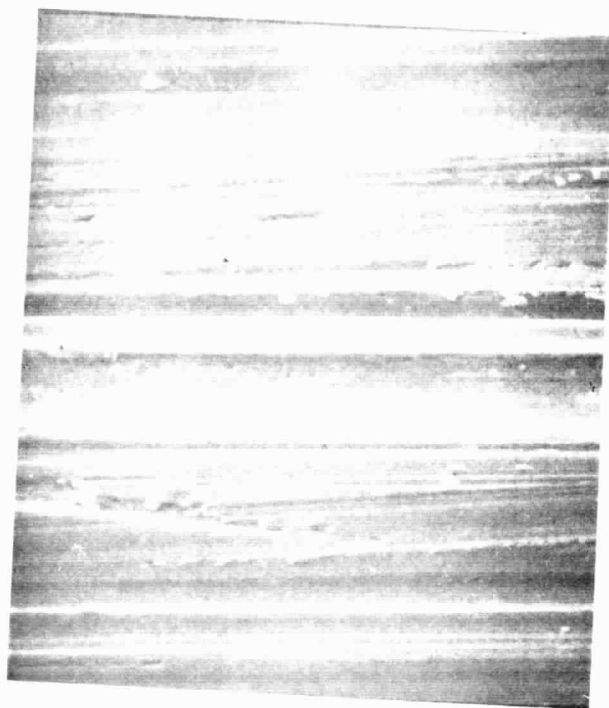


A.
1000 X 45° Tilt



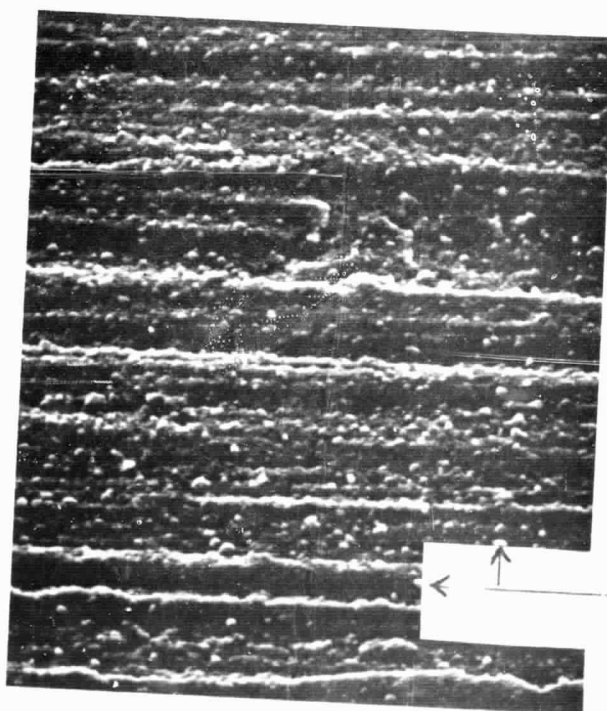
B.
10,000 X 45° Tilt

Figure 4
Faceting of NiO Formed on Polished TDNiCr - 64 Hours at 1000° C, 760 Torr.



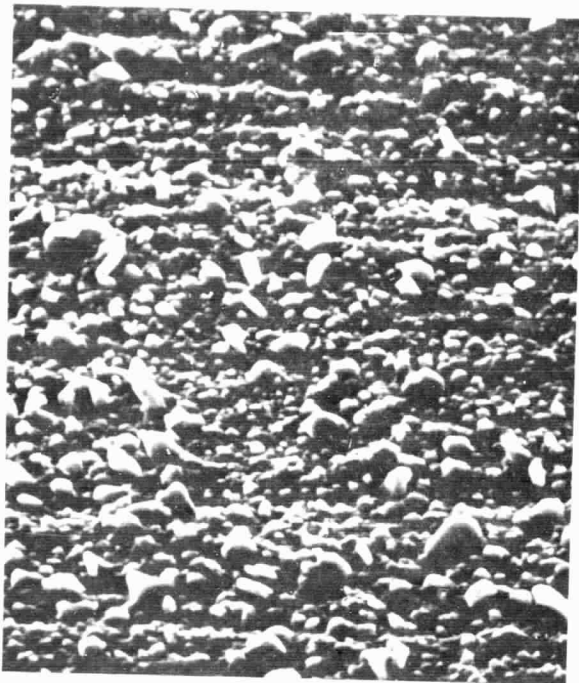
1000 X 45° Tilt

Figure 5
Early Stages of Oxidation on Abraded TDNiCr - One Minute at 800° C,
760 Torr.



1000 X 45° Tilt

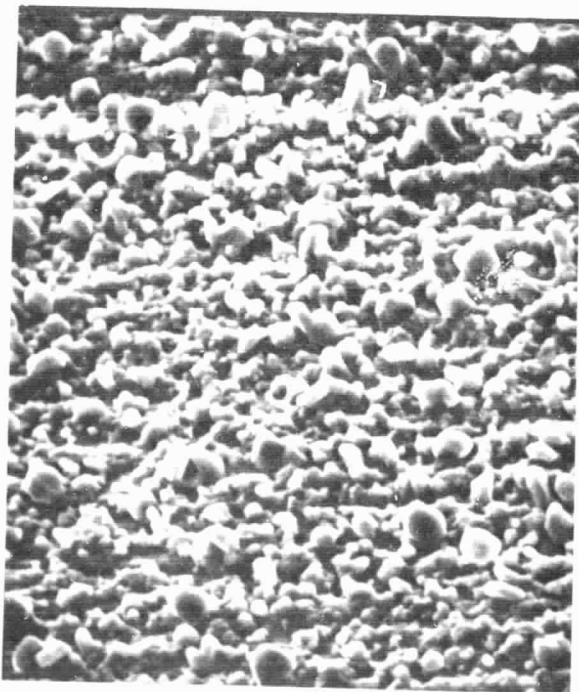
Figure 6
Crystal Formation of Cr_2O_3 on Abraded TDNiCr - 4 Hours at 800° C,
760 Torr.



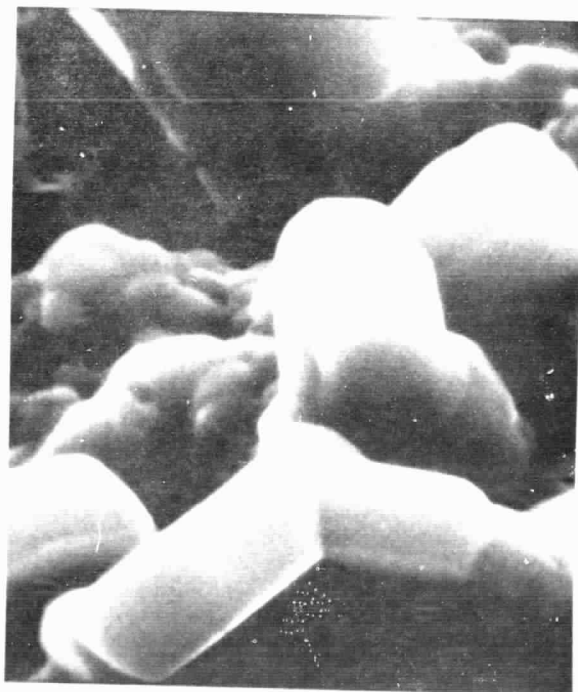
A.
1000 X 800° C 45° Tilt



B.
10,000 X 800° C 45° Tilt



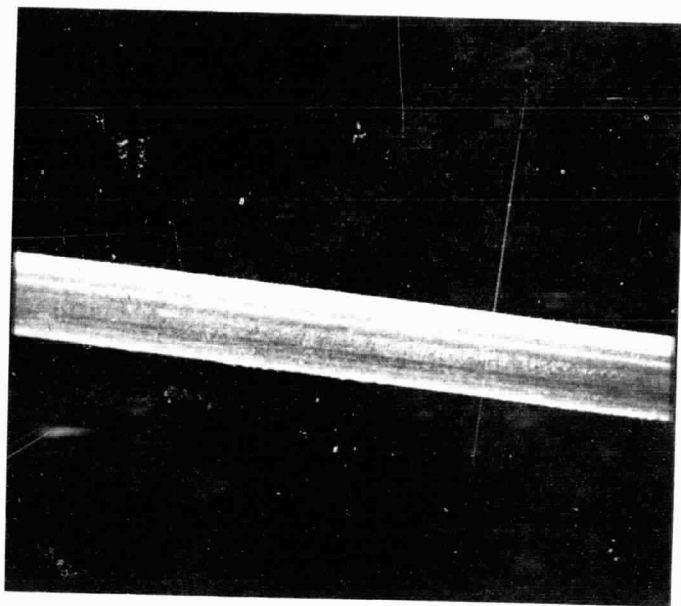
C.
1000 X 1000° C 45° Tilt



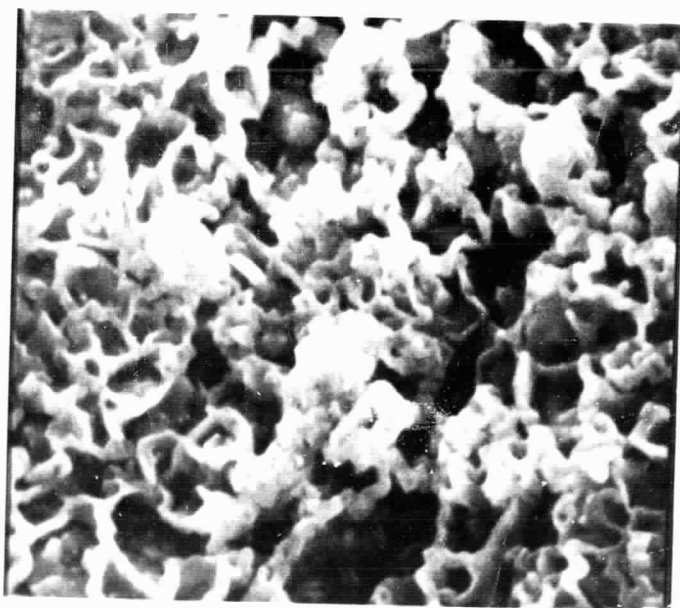
D.
10,000 X 1000° C 45° Tilt

Figure 7.
Crystal Growth of Cr_2O_3 on Abraided TDNiCr - 64 Hours, 760 Torr.

E-6411



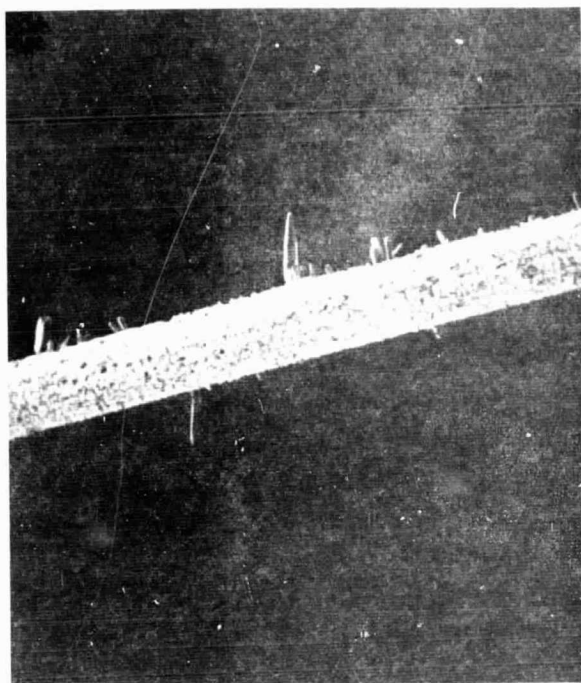
A.
100 X



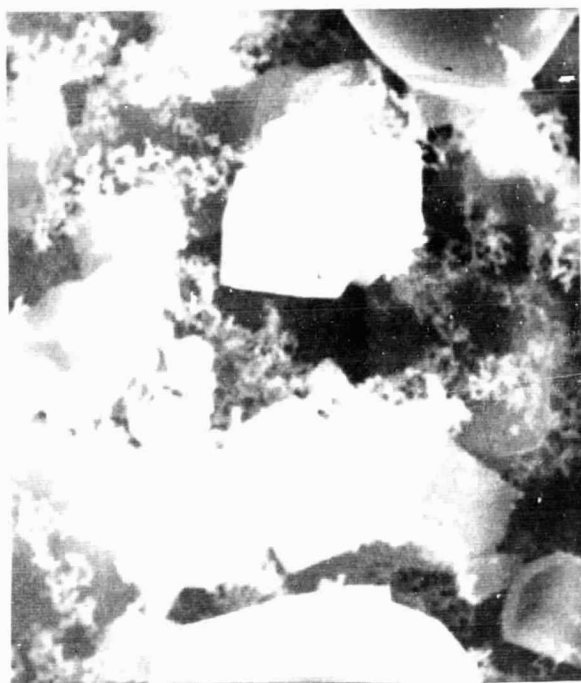
B.
10,000 X

Figure 8
Oxidation of TDNiCr Wire Without Vapor Grown Crystals of Cr_2O_3 -
 10^{-4} Torr - 50 Hours - 1200°C

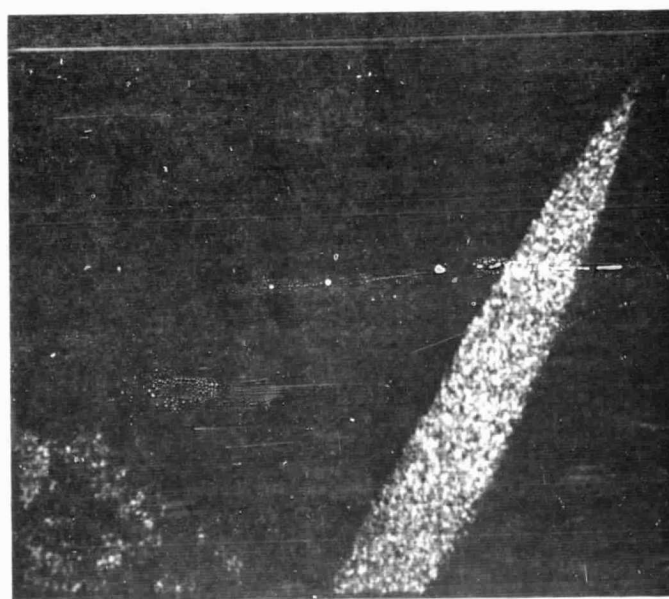
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A.
100 X



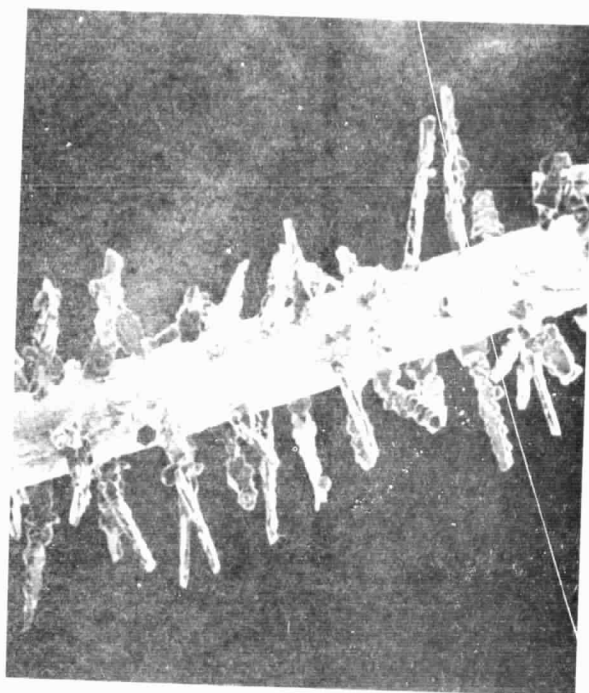
B.
10,000 X



C.
Probe Scan, Cr K α 500 X

Figure 9
Appearance and Identification of Vapor Grown Crystals on TDNiCr
10 Torr - 1200° C - 24 Hours

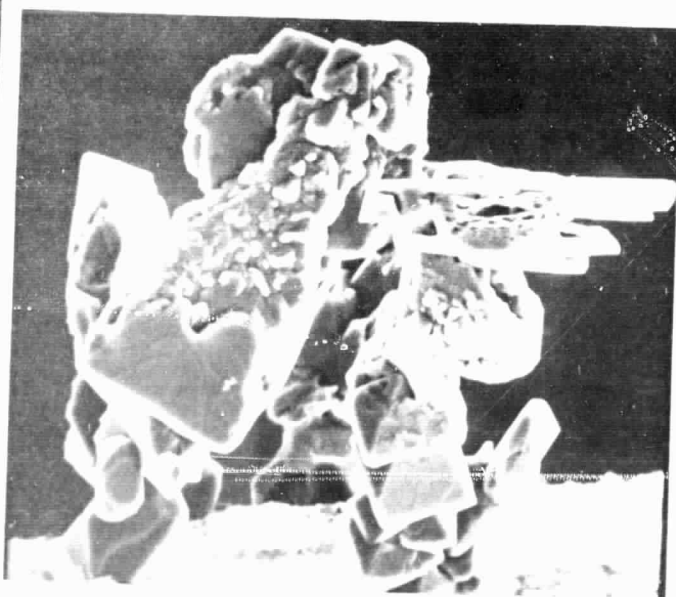
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A.
100 X



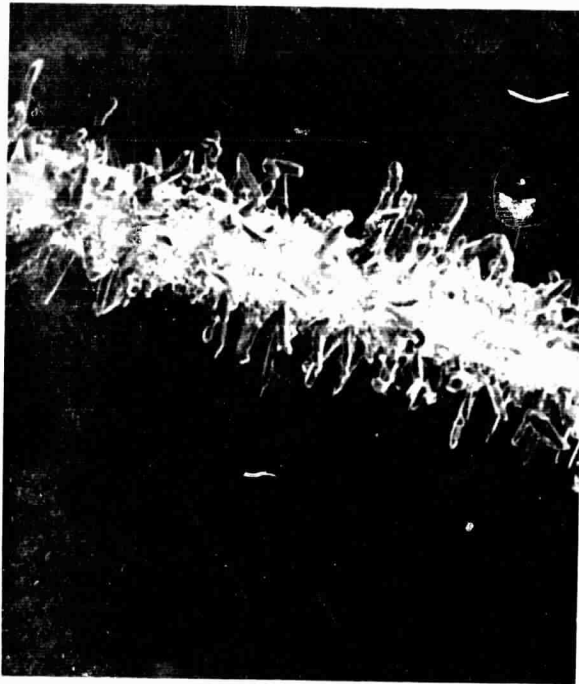
B.
300 X



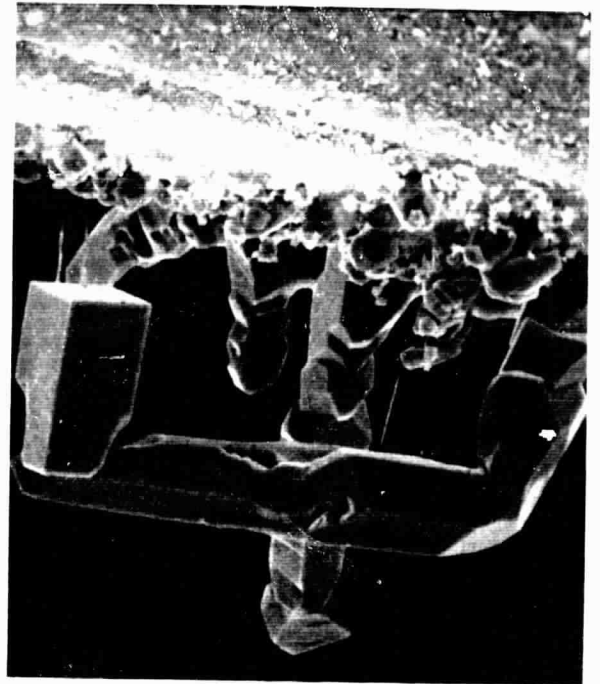
C.
750 X

Figure 10
Extensive Growth of Cr_2O_3 Crystals From the Vapor on TDNiCr Wire
700 Torr - 1200°C - 24 Hours

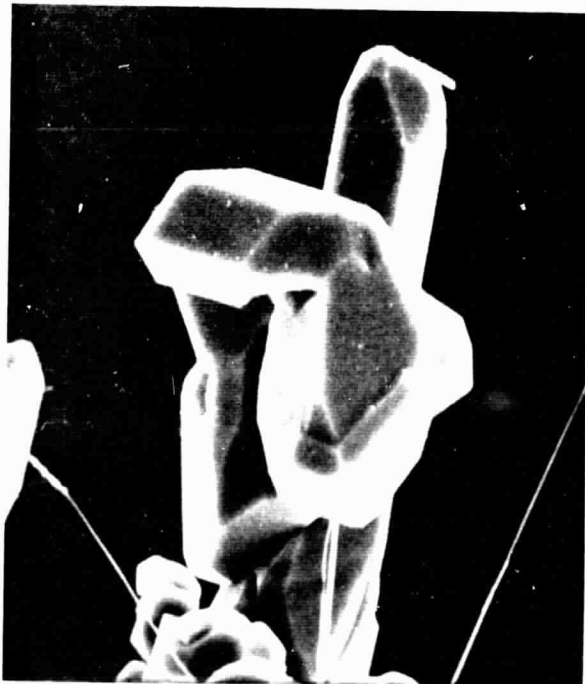
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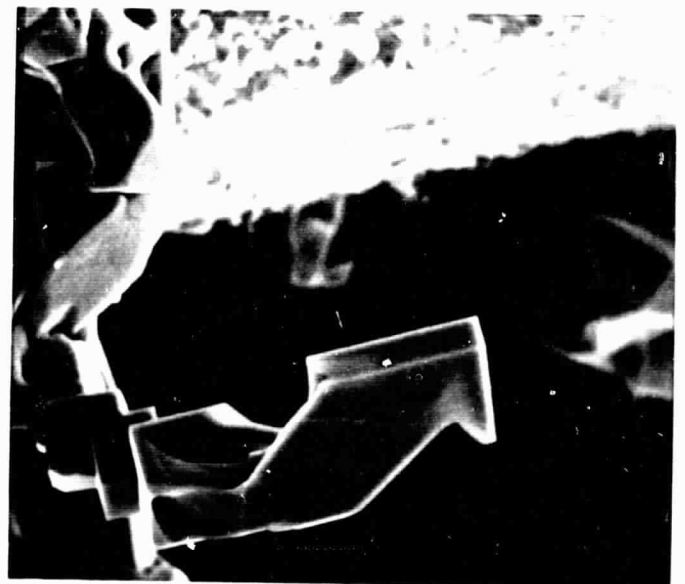
A.
100 X



B.
600 X



C.
1500 X



D.
1000 X

Figure 11
Effect of Moisture on the Vapor Growth of Cr₂O₃ Crystals on TDMiCr
700 Torr Wet Air - 1200° C - 6 Hours

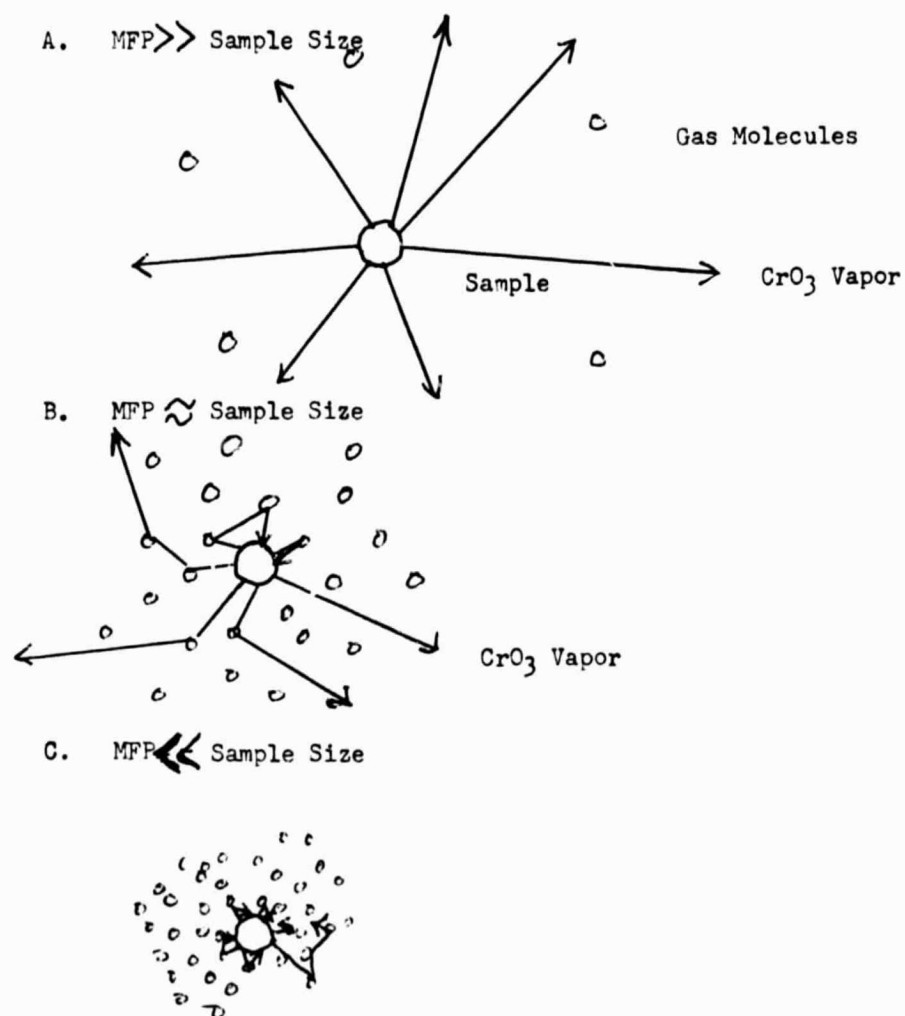


Figure 12
The Effect of Mean Free Path on Volatilization