AD-762 045

MECHANICAL PROPERTIES OF THERMAL BARRIER MATERIALS PROGRAM

GENERAL MOTORS CORP.

PREPARED FOR
NAVAL AIR SYSTEMS COMMAND

MARCH 1973

AD 762045

EDR 7786

Mechanical Properties Of Thermal Barrier Materials Program

Final Report

15 January 1972 to 15 February 1973

March 1973

By

K. E. Muszar
N. B. Edenborough

Prepared Under Contract N00019-72-C-0148
for
Naval Air Systems Command
Department of the Navy

"APPROVED FOR PUBLIC RELEASE. DISTRIBUTION UNLIMITED"

By

Detroit Diesel Allison Division
General Motors Corporation

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)*

Detroit Diesel Allison Division
General Motors Corporation; P. O. Box 894
Indianapolis, Indiana 46206

2a. REPORT SECURITY CLASSIFICATION
UNCLASSIFIED

2b. GROUP

3. REPORT TITLE

MECHANICAL PROPERTIES OF THERMAL BARRIER MATERIALS PROGRAM

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

Final Report (15 January 1972 to 15 February 1973)

5. AUTHOR(S) *(First name, middle initial, last name)*

K. E. Muszar and N. B. Edenborough

6. REPORT DATE
March 1973

7a. TOTAL NO. OF PAGES
66

7b. NO. OF REFS
3

8a. CONTRACT OR GRANT NO
N00019-72-C-0148

b. PROJECT NO.

c.

d.

9a. ORIGINATOR'S REPORT NUMBER(S)
EDR 7786

9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*

10. DISTRIBUTION STATEMENT

APPROVED FOR PUBLIC RELEASE
DISTRIBUTION UNLIMITED

11. SUPPLEMENTARY NOTES

12. SPONSORING MILITARY ACTIVITY

Naval Air Systems Command
Department of the Navy
Washington, D.C. 20360

13. ABSTRACT

Mechanical mixtures of 50 and 75 w/o Hastelloy X-ZrO_2 powders were arc plasma sprayed in a configuration suitable for fabrication of uniaxial tensile and ballistic impact test specimens. Specimens of each mixture of Hastelloy X-ZrO_2 were exposed to an inert environment for 10, 100, and 1000 hrs at 2200F and then tensile and ballistic impact tested. Another group of samples, exposed to a dynamic oxidation environment at 2125F for up to 16 hrs after being exposed to the inert environment for 10 hrs, were also uniaxial tensile and ballistic impact tested.

Results of the program established that exposure of both materials to the inert environment caused an increase in the uniaxial tensile strength of up to 100%. The increase being attributed to the sintering effect in the Hastelloy X phase. The dynamic oxidation exposures were found to have little effect on the tensile strength of the 50 w/o Hastelloy X-ZrO_2 material but did cause a 25% decrease in the tensile strength of the 75 w/o Hastelloy X-ZrO_2 material.

Room temperature ballistic impact tests were increased significantly on both materials as a result of the 2200F inert environment exposure. The 2100F ballistic impact properties of the Hastelloy X-ZrO_2 material experienced generally the same increase as was seen in the room temperature tests.

The dynamic oxidation exposures had no effect on the room temperature ballistic impact properties of the 75 w/o material but caused a 50% decrease in the property of the 50 w/o material.

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Thermal barrier						
Plasma spraying						
Zirconia						
Hastelloy X						
Tensile strength						
Ballistic impact						
Microstructure						
Fractography						

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FOREWORD

This final report describes the work completed at Detroit Diesel Allison (DDA) Division of General Motors Corporation during the period 15 January 1972 to 15 February 1973 on the "Mechanical Properties of Thermal Barrier Materials Program". This work was performed for the Department of the Navy, N.A.S.C. under Contract N00019-72-C-0148. K. E. Muszar, Senior Experimental Metallurgist, and Neville B. Edenborough, Section Chief, NDT-Ceramics, Materials Research, have contributed to the program. Technical support was furnished by Jack Cavanagh in the area of sample fabrication and Kenneth R. Cross in the area of high temperature inert atmosphere exposure. Dr. Marvin Herman, Chief, Materials Research, has acted as an advisor and consultant on the program.

ABSTRACT

Earlier work at Detroit Diesel Allison Division, General Motors Corporation, in the area of thermal barriers has shown the feasibility of using a graded approach whereby the thermal barrier is applied by arc plasma spraying mixtures of metal and ceramic and grading from a pure metal at the substrate surface to a pure ceramic as the outer layer of the thermal barrier. Thermal shock testing and ballistic impact testing of these graded thermal barriers has demonstrated the superiority of this approach compared to other methods of application of thermal barrier materials.

The objective of this program is to relate certain mechanical property changes of the component compositions of the graded thermal barrier to observed microstructural changes which occur as a function of exposure to specific high temperature environments.

Mechanical mixtures of 50 and 75 w/o Hastelloy X - ZrO_2 powders were arc plasma sprayed onto 0.030 inch diameter Hastelloy X tubing mandrel in a configuration suitable for fabrication of uniaxial tensile and ballistic impact test specimens. Specimens of each mixture of Hastelloy X-ZrO_2 were exposed to an inert environment for 10, 100, and 1000 hours at 2200°F and then tensile and ballistic impact tested. Another group of samples, exposed to a dynamic oxidation environment at 2125°F for up to 16 hours after being exposed to the inert environment for 10 hours, were also uniaxial tensile and ballistic impact tested. Uniaxial tensile and ballistic impact properties of the as sprayed materials were also determined.

Metallographic and scanning electron microscope examination were conducted on samples after testing to determine microstructural and fractographic characteristics of the materials. Electron microbeam X-ray analyses were conducted on selected samples to establish chemical element distribution in both the Hastelloy X and ZrO_2 phases.

Results of the program established that exposure of both materials to the inert environment caused an increase in the uniaxial tensile strength of up to 100%. The increase being attributed to the sintering effect in the Hastelloy X phase. The dynamic oxidation exposures were found to have little effect on the tensile strength of the 50 w/o Hastelloy X - ZrO_2 material but did cause a 25% decrease in the tensile strength of the 75 w/o Hastelloy X-ZrO_2 material.

Abstract (Cont'd)

Room temperature ballistic impact tests were increased significantly on both materials as a result of the 2200°F inert environment exposure. The 2100°F ballistic impact properties of the 75 w/o Hastelloy X - ZrO_2 material experienced generally the same increase as was seen in the room temperature tests, however, the 50 w/o material did not show as significant an increase at 2100°F test temperature as was seen in the room temperature tests.

The dynamic oxidation exposures had no effect on the room temperature ballistic impact properties of the 75 w/o material but caused a 50% decrease in the property of the 50 w/o material.

A precipitation of a secondary phase was observed in the Hastelloy X portion of the 50 w/o Hastelloy X - ZrO_2 material as a result of the dynamic oxidation exposure. The decrease in room temperature ballistic impact properties are thought to be related to this phase.

Chemical element segregation of Ca, Cr, and Si were noted in the ZrO_2 phase of both materials after exposure to the 2200°F inert environment, however, no correlation of this segregation with mechanical properties was found. No explanation of the mechanism of these segregations is presently known.

1.0 INTRODUCTION

1.1 General

This program was instituted to study certain mechanical properties of thermal barrier materials. Key items in the plan of study were as follows.

- Fabricate, by arc plasma spraying, test specimens using specific mixtures of Hastelloy X and zirconium dioxide (Hx-ZrO_2).
- Determine mechanical properties of the Hx-ZrO_2 specimens in both the as-sprayed condition and after exposure to high temperature thermal environments for times up to 1000 hrs.
- Evaluate metallographically the test samples to correlate changes in microstructural characteristics with changes in tested mechanical properties.

1.2 General Background and State of the Art

The use of ceramic thermal barriers to reduce the temperature of metallic components to a level where they retain good mechanical and chemical properties is not a new concept. Application of the concept to "real life" gas turbine components, however, has not been forthcoming. Some reasons for this are: (1) poor thermal shock resistance of the low thermal conductivity ceramic materials when applied directly to a metal substrate, (2) difficulties in obtaining a good bond between the ceramic material and the metallic substrate, and (3) the large difference in coefficient of expansion of ceramic materials compared to high temperature gas turbine alloys.

The ceramic coating investigated in this project is the result of several years of development effort at Detroit Diesel Allison.(1) The development effort in Reference 1 included, at first, three alternate approaches to fabrication. These approaches were: foamed ceramic held in a metal honeycomb sheath, hot pressed ceramic in metal honeycomb sheath, and plasma sprayed graded coating. Each technique had individual attributes and deficiencies. Plasma sprayed graded thermal barrier was ultimately selected as the best candidate because of survivability in thermal shock ballistic impact and erosion rig tests as well as ease of fabrication.

1.2 General Background and State of the Art (Cont'd)

The zirconia was selected as the best ceramic constituent by first performing a fairly exhaustive literature search. Two figures of merit were used for selection of the best candidate materials. These were; (1) thermal conductivity (the lower the conductivity the better thermal barrier) and (2) thermal shock figure of merit (the higher the better). From this data five materials were selected as prime candidates. These were: (1) Alumina, (2) Zirconia, (3) Mullite, (4) Spinel, and (5) Zircon. Preliminary screening tests were performed which showed that Zirconia was the best material for this particular application.

Three metal systems were tested. These were Ni + 5 w/o Al. (Metco 404), Ni + 20 w/o Chromium (Nichrome) and Ni-Mo-Cr (Hastelloy-X). The Hastelloy-X system was selected as the best of the three, although the differences were marginal.

The current project uses ballistic impact resistance and tensile strength as prime indicators of material degradation due to time/temperature effects. Tensile strength relates to thermal shock resistance by the thermal shock figure of merit equation:

$$R_2 = \frac{\sigma k}{E\alpha}$$

Where:

σ = tensile strength

k = thermal conductivity

E = Young's modulus

α = thermal expansion coefficient

The thermal conductivity has been shown experimentally to follow the law of mixtures. Young's modulus and the coefficient of thermal expansion may or may not completely follow the mixture law, but in any case should not vary appreciably since these properties are very similar in the two materials, as is shown in Table I. However, no obvious method of predicting strength in a mixture this complex exists. The strength of this type material is a function of individual strengths, strengths of the bonds between particles, and methods the stress is distributed among the constituents. Thus, strength is thought to be the most sensitive indicator of material degradation, as well as the one which will not remain stable, nor lend itself to prediction.

Table I

Comparison of

Physical and Mechanical Properties of Zirconia and Hastelloy X

	Zirconia(2)	Hastelloy-X (3)
Thermal Conductivity (BTU/ft-hr-°F)	1.0 - 1.2 (RT -1800°F)	5-16 (RT – 1800°F)
Young's Modulus (10^6 psi)	20 - 16 (RT – 1800°F)	28 - 18.5 (RT – 1800°F)
Coefficient of Thermal Expansion (10^{-6}/°F)	4.2 - 8.5 (RT – 2400°F)	7.7 - 9.2 (RT – 1800°F)
Tensile Strength (ksi)	20 - 12 (RT – 2200°F)	110 - 13 (RT – 1800°F)

1.3 Study Procedure

The following procedure was used to investigate the mechanical properties of the Hastelloy X (Hx)-ZrO_2 arc plasma sprayed materials under study.

Initially mixtures of Hx and ZrO_2 were arc plasma sprayed on 0.032 inch diameter by 0.006 inch wall Hx tubing in the rough shape of a standard 0.252 inch diameter tensile bar or as a 0.350 diameter rod for ballistic impact testing. These rough samples were then final machined to the appropriate test configurations. Representative samples of each arc plasma sprayed Hx-ZrO_2 composition were tested in the as-sprayed conditions. A second group of samples of each composition was loaded in a high temperature furnace and held at a temperature of 2200°F in a partial pressure (20-30 microns) of argon. Samples were removed from the furnace and tested after 10 hours, 100 hours and 1000 hours. A third group of samples were exposed to a dynamic oxidation environment at 2125°F and then tested.

Failed samples were examined using optical metallographic techniques to determine microstructural characteristics and with the scanning electron microscope to determine fracture characteristics and chemical changes of the constituent materials. Correlations between these microstructural characteristics and changes in the mechanical properties were then made. A flow chart of the investigational procedure is shown in Figure 1.

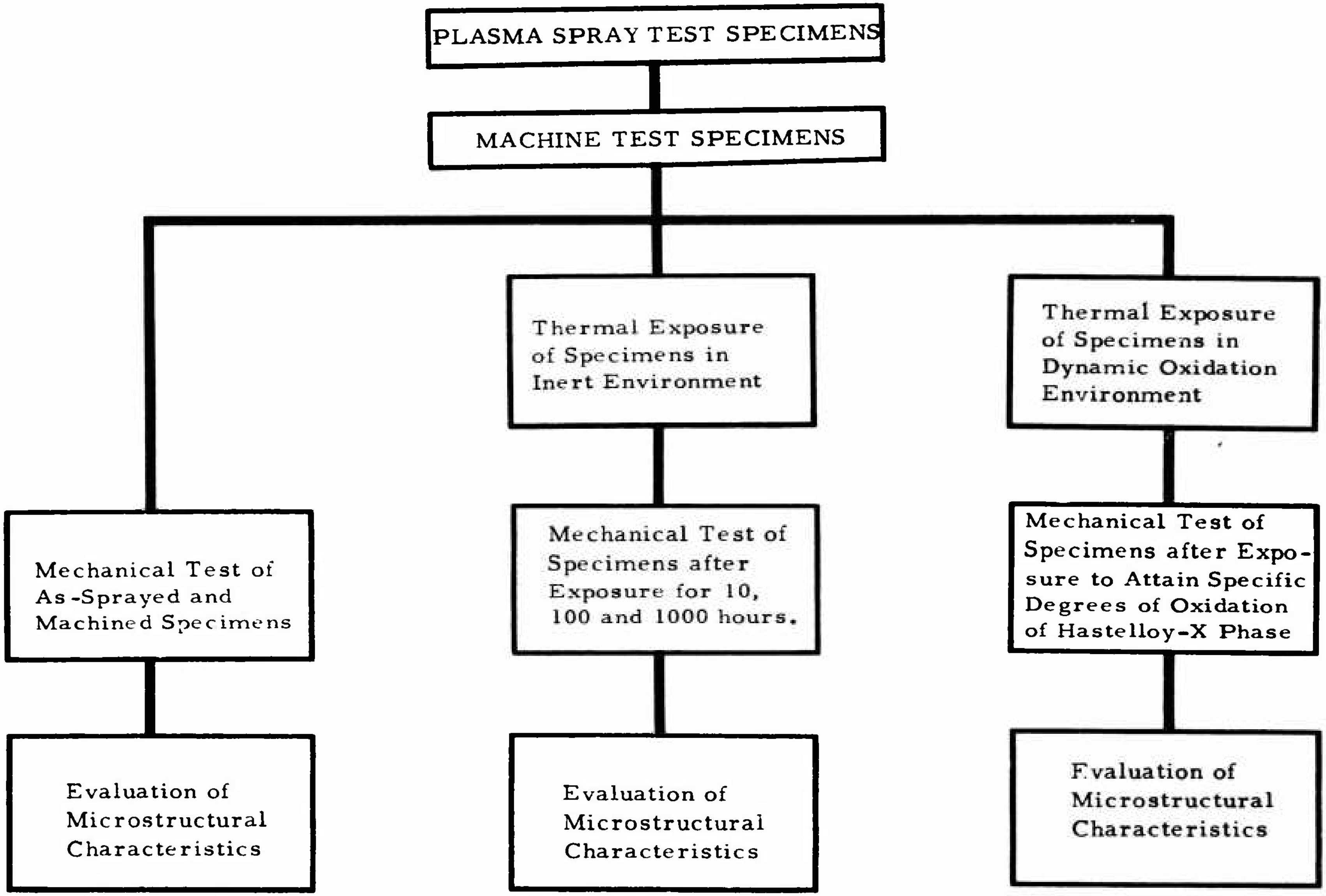


Figure 1. Flow Chart of Thermal Barrier Investigative Procedure

2.0 RESULTS

2.1 Fabrication of Test Specimen

The starting materials used in the fabrication of the test specimen for this program are shown in Table II. X-ray diffraction analysis of the ZrO_2 material revealed it to be c ZrO_2 with no detectable amounts of other crystallographic forms of ZrO_2 or foreign bodies being present. The X-ray diffraction analysis of the Hastelloy X powder disclosed only the nickel solid solution phase, typical of this alloy.

Scanning electron micrographs (SEM) of the starting powders are shown in Figures 2 and 3. No unusual features were noted in these materials.

The test specimen were fabricated by arc plasma spraying mechanical mixtures of the two components onto Hastelloy X hypodermic tubing. Plasma spraying was accomplished with a Plasmadyne SGG-1B unit using an argon/helium mixture as the carrier gas.

2.1.1 Uniaxial Tensile Specimens

Thirty-six uniaxial tensile samples were arc plasma sprayed on Hastelloy X tubing (0.030'' diameter x 0.006'' wall) to the configuration shown in Figure 4a. Twelve samples were sprayed from a starting mixture of 75 w/o Hastelloy X - 25 w/o ZrO_2, twelve samples from a starting mixture of 50 w/o Hastelloy X - 50 w/o ZrO_2 and twelve samples from a starting mixture of 25 w/o Hastelloy X 75 w/o ZrO_2. All of these samples were finish machined to the configuration shown in Figure 4b prior to testing or exposure to specific time-temperature environmental conditions.

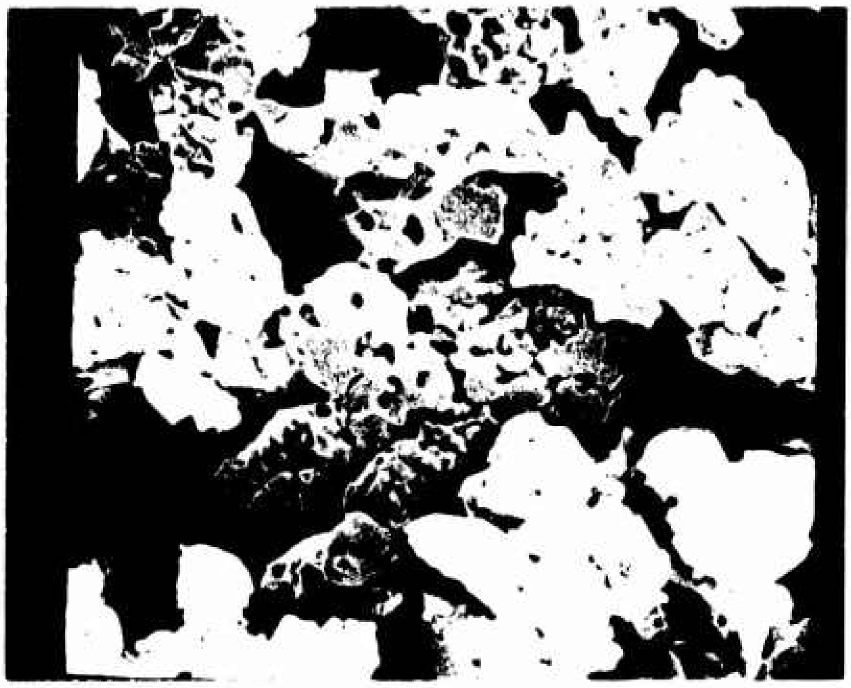
2.1.2 Ballistic Impact Specimens

Sixty ballistic impact specimens were arc plasma sprayed on Hastelloy X tubing (0.030'' diameter x 0.006'' wall) to a diameter of about 0.350 inch. Twenty specimens each were sprayed from starting mixtures of 75 w/o Hx - 25 w/o ZrO_2, 50 w/o Hx - 50 w/ZrO_2 and 25 w/o Hx - 75% ZrO_2. These specimens were final machined to a finish diameter of 0.300 inch prior to testing or exposure to specific time-temperature environmental conditions. Figure 4b shows a finish machined specimen.

Table II

Powder Materials Used for Plasma Spraying of Specimens

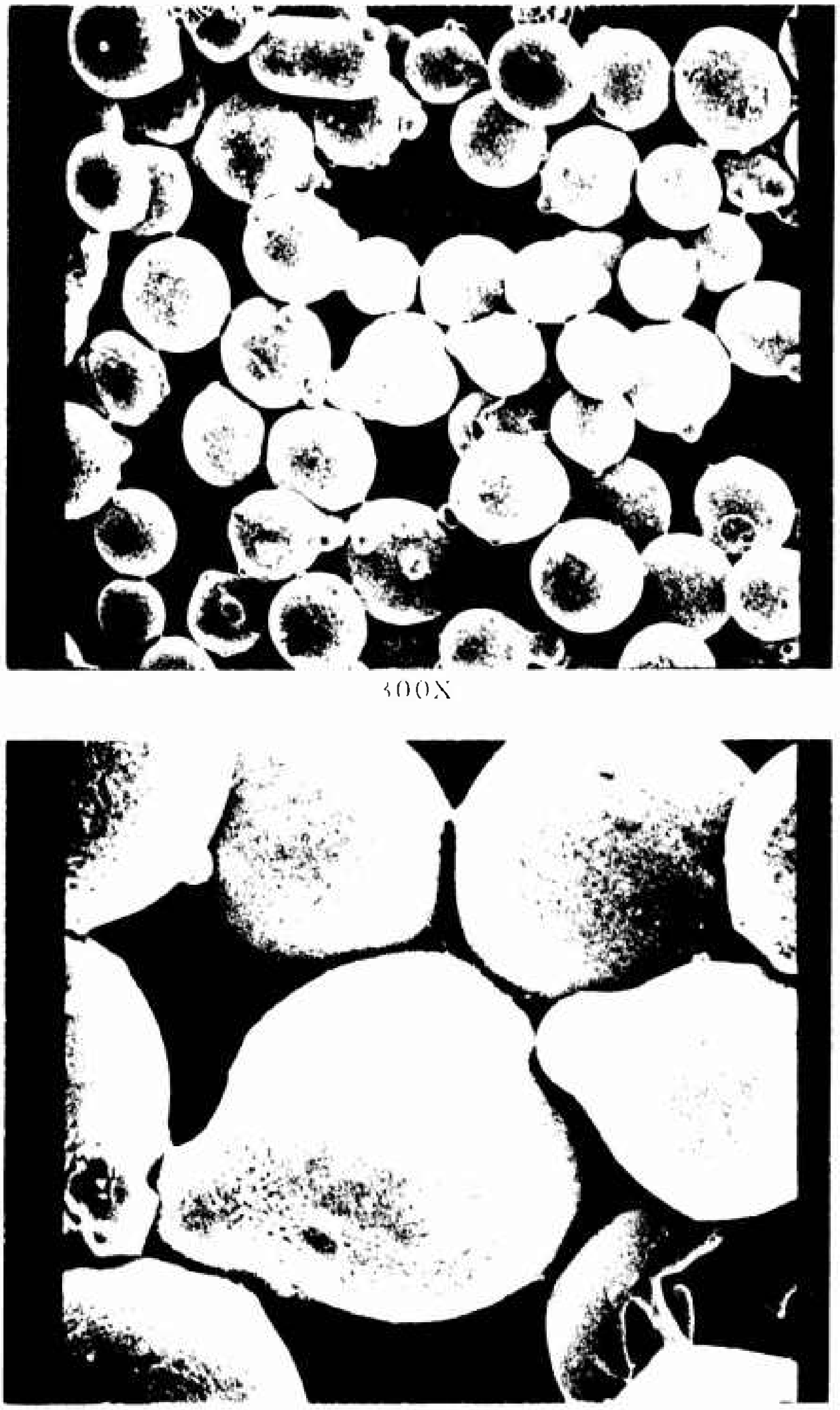
Material	Particle Size	Analysis	
Plasmalloy 327M (Plasmadyne Corp)	+200 mesh (20% max)	ZrO_2+HFO_2	91.5% min.
Zirconium Dioxide	-325 mesh (25% max)	CaO	4.5-5.5%
	-200 + 325 mesh (Bal)	Al_2O_3	0.60% max
		MgO	0.90% max
		TiO_2	0.40% max
		SiO_2	0.80% max
		Fe_3O_4	0.30% max
Hastelloy X (Stellite Div., Cabot Corp.)	-200 + 325 mesh	Cr - 21.49	
		W - 0.57	
Heat Number 69-49-A		Fe - 19.78	
		C - 0.085	
		Si - 0.71	
		Co - 2.13	
		Mo - 8.57	
		P - 0.019	
		S - 0.004	
		Ni - Balance	



300X

1000X

Figure 2. Original ZrO_2 powder in the as-received condition.



300X

1000X

Figure 3. Original Hastelloy X powder in the as-received condition.

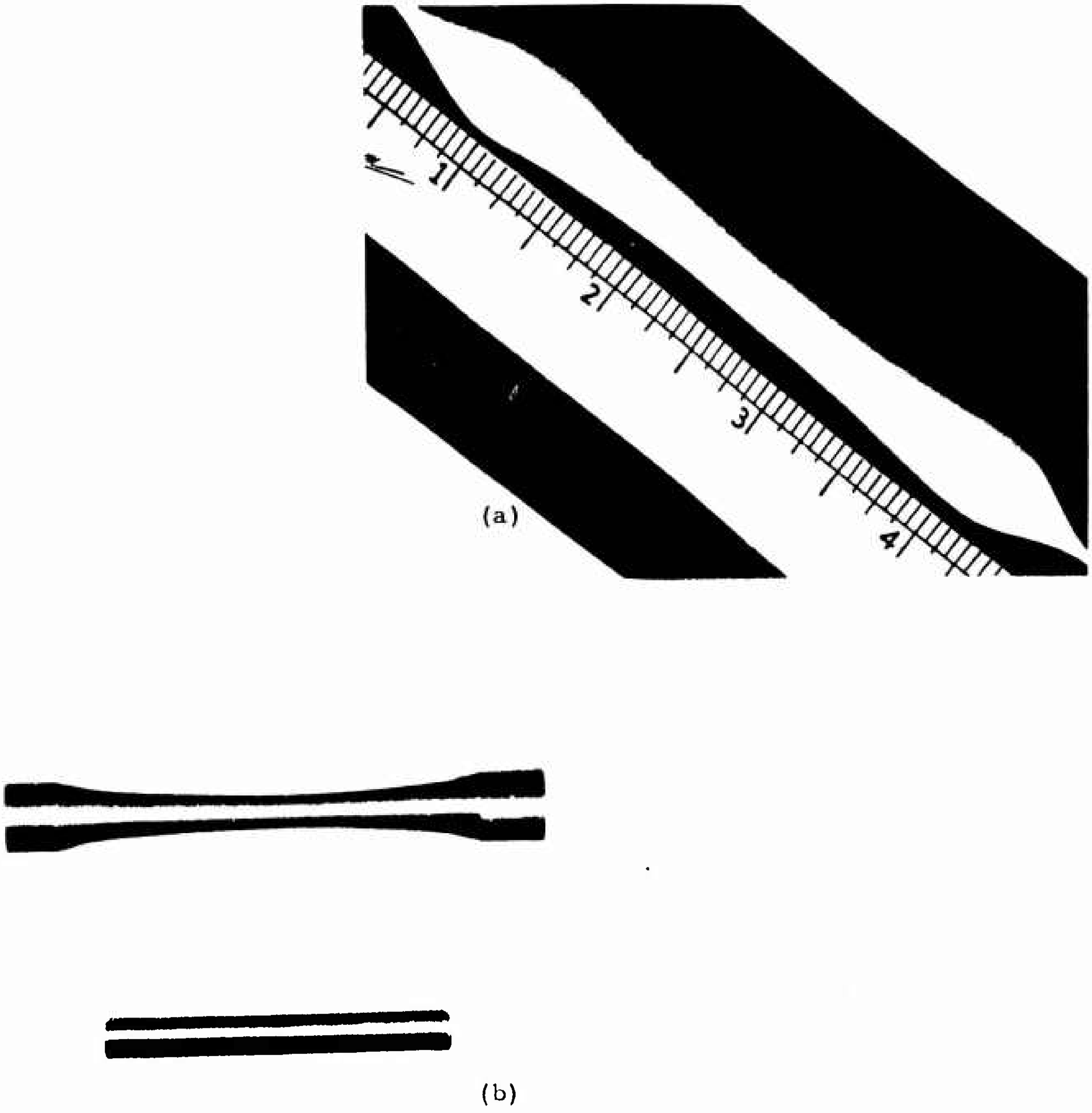


Figure 4. Typical as-sprayed tensile specimen (a) and machined arc plasma sprayed uniaxial tensile and ballistic impact test specimens (b). (Magn. 1X)

2.2 High Temperature Environmental Exposure

2.2.1 Inert Atmosphere Exposure

A Brew Corporation, Model 942 high temperature vacuum furnace, modified to allow a through-put of argon so that a partial pressure of 20 to 30 microns could be maintained at 2200°F, was used for this phase of the program. Specimens were exposed for either 10, 100, or 1000 hours in this unit and then tested to determine the effect of the exposure on the tensile and ballistic impact properties of the particular material.

2.2.2 Dynamic Oxidation Exposure

A natural gas-oxygen burner was set up to allow exposure of some test specimens to an oxidizing environment prior to tensile and ballistic impact testing to determine the effect of this exposure on these particular properties. Two levels of oxidation were chosen to be evaluated, based on the total time in the flame at 2100-2150°F. The first group of samples were exposed for 7 hours and the second group was exposed for 16 hours.

2.3 Volume Fraction Determination

Quantitative metallographic examination studies were conducted on representative specimens of the 25, 50 and 75 weight percent Hastelloy X materials in the as-sprayed condition, as well as after inert atmosphere exposure at 2200°F for 10 and 100 hours. The volume percent of Hastelloy X was determined by measuring the area percentage of Hastelloy X in metallographically polished specimens, in the longitudinal and transverse direction of the plasma sprayed bars. Five area percentages were obtained for each specimen on a Metals Research Limited Model QTM Quantimet Image Analyzer. The results of this analysis in Table III show that the intended 25 and 50 weight percent Hastelloy X materials were actually the same composition, nominally 50 w/o, with a measured volume percent Hastelloy X of 39-48, compared to a 41 volume percent value calculated for a 50 weight percent Hastelloy X-ZrO_2 material. Since the materials are the same composition, they are referred to as 50 w/o Hastelloy X, Group A and Group B, in the remainder of this report.

The 75 w/o Hastelloy X material was found to have a volume percent ranging from 74 to 80, compared to a 67 volume percent calculated for a 75 weight percent Hastelloy X. Although the volume percent measurements indicate a weight percent somewhat higher, this material is referred to as 75 w/o Hastelloy X in the remainder of the report.

Table III

Hastelloy X Volume Percentage Measurements on Plasma Sprayed Hastelloy X-ZrO$_2$ Materials

		Measured Volume Percent					
		Hastelloy X					
Material	Condition	1	2	3	4	5	Avg
25 w/o Hastelloy X	As Sprayed	42	40	38	42	32	39
(Transverse)	2200F - 10 hr	38	42	38	40	52	42
	2200F - 100 hr	44	44	48	40	44	44
	As-Sprayed	46	49	53	48	45	48
(Longitudinal)	2200F - 10 hr	40	41	48	52	56	47
	2200F - 100 hr	52	46	48	47	43	47
		(Calculated from w/o)					(19)
50 w/o Hastelloy X	As Sprayed	45	50	40	46	40	44
(Transverse)	2200F - 10 hr	38	39	40	47	38	40
	2200F - 100 hr	48	42	48	36	46	44
	As Sprayed	44	47	36	43	39	42
(Longitudinal)	2200F - 10 hr	44	44	42	41	40	42
	2200F - 100 hr	38	41	44	50	49	44
		(Calculated from w/o)					(41)
75 w/o Hastelloy X	As Sprayed	77	74	76	74	70	74
(Transverse)	2200F-10 hr	74	76	74	82	83	78
	2200F - 100 hr	78	78	82	75	80	79
	As Sprayed	72	78	78	76	80	77
(Longitudinal)	2200F - 10 hr	80	78	82	81	80	80
	2200F - 100 hr	80	81	76	79	77	79
		(Calculated from w/o)					(67)

2.3 Mechanical Testing

Machined specimens of the 50 and 75 w/o Hastelloy X compositions were evaluated for room temperature tensile properties and ballistic impact resistance at room temperature and 2100°F. These properties were evaluated in three conditions:

(1) as sprayed
(2) after inert atmosphere exposure and
(3) after oxidizing atmosphere exposure.

2.3.1 Uniaxial Tensile Properties

Room temperature tensile strength tests were conducted on specimens machined to an hourglass configuration with a test diameter of 0.250 inch. Split conical grips were used to load the specimens through a pin and clevis system to facilitate testing of low ductility materials. All testing was performed at a crosshead speed of 0.01 inch per minute. The tensile properties obtained are shown in Table IV and Figure 5.

- 50 w/o Hastelloy X

Examination of the average tensile strength data in Figure 5 and Table IV shows that the 10-100 hours inert exposure at 2200°F accomplished a strengthening of the material over the as-sprayed condition; however longer times to 1000 hours at the same temperature, resulted in a lower increase in tensile strength. The initial strengthening was probably due to a sintering and densification effect in the material.

The 2125°F - 7 hour exposure of this material to a dynamic oxidation environment (after a 10 hour - 2200°F inert atmosphere treatment) resulted in a slight tensile strength increase. However, after 16 hours exposure to the oxidation environment the material had in one case lost strength to a level nearly the same as as-sprayed material, while the other sample showed a slight loss of tensile strength.

- 75 w/o Hastelloy X

The data shows a 100% increase in tensile strength, over the as-sprayed condition was realized from the 2200°F - 10 hour inert exposure. It also shows that increased exposure time, to 100 hours, seems to cause a decrease in the tensile strength from the 10 hour level. The specimens which were treated

Table IV

Room Temperature Tensile Strength of Plasma Sprayed Hastelloy X - ZrO_2 Materials

		Tensile Strength - ksi					
			2200F-Inert Exposure			2125F-Oxidation Exposure**	
Hastelloy X w/o		As-Sprayed	10Hr	100Hr	1000Hr	7 Hr	16 Hr
50(Group A)		19.2	31.1	28.9	21.4	35.0	17.9
		18.5	31.8	25.8	21.4	39.3	31.3
	Av.	18.9	31.5	27.9	21.4	37.2	24.6
50(Group B)		17.9	27.8	31.6	27.9	--	--
		19.2	30.6	35.6	*	--	--
	Av.	18.6	29.2	33.6	27.9	--	--
75		40.1	78.6	71.7	*	76.4	55.4
		39.4	78.3	68.9	*	57.7	59.8
	Av.	39.8	78.5	70.3		67.1	57.6

* Severely distorted on removal from furnace therefore not tested.

** All specimens pretreated 10 hours at 2200°F in inert atmosphere.

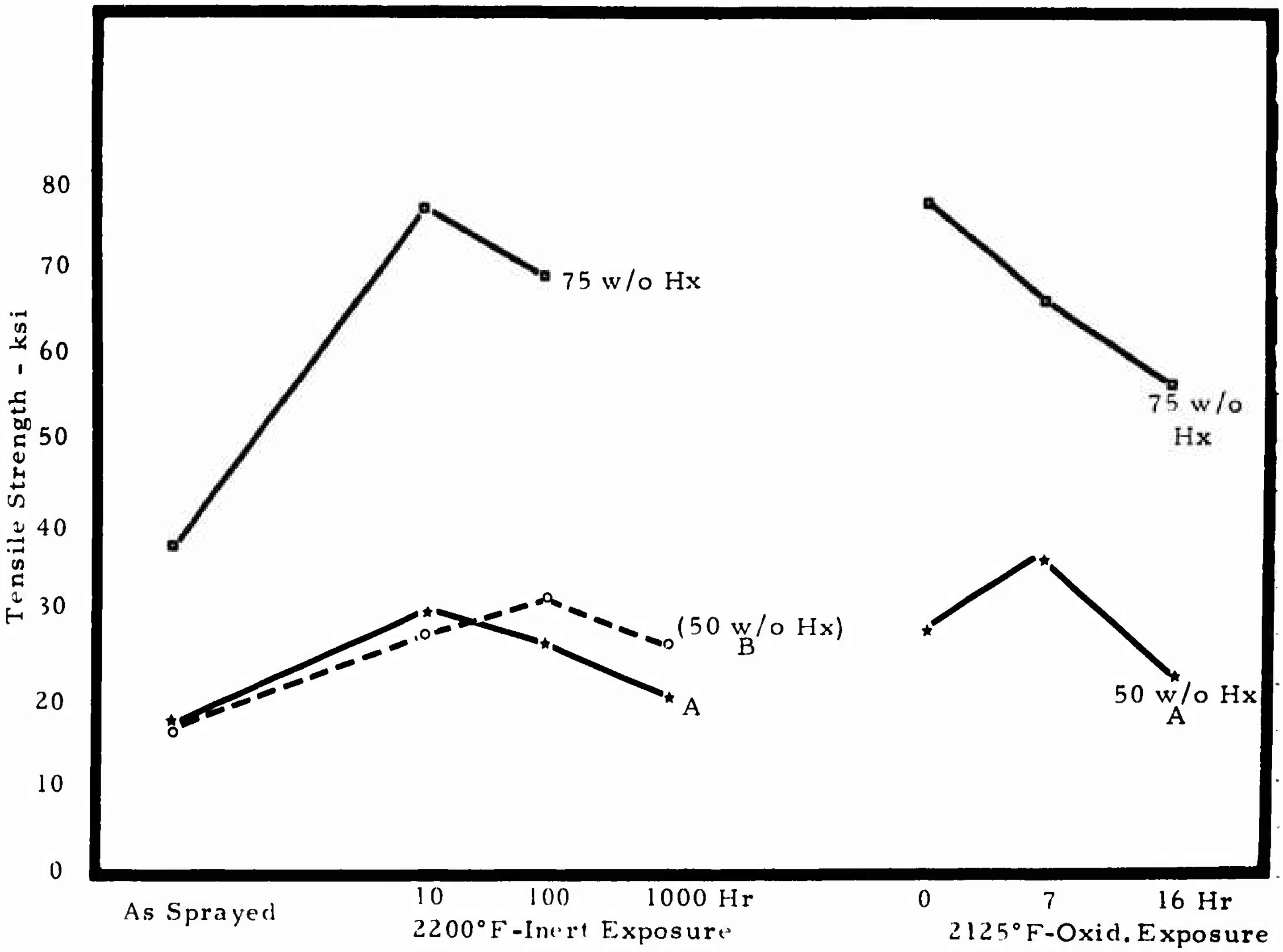


Figure 5. Room temperature tensile strength of plasma sprayed Hastelloy X-ZrO_2 Materials.

- 75 w/o Hastelloy X (Cont'd)

for 1000 hours were found to be so badly distorted when they were removed from the furnace that they were unusable for testing.

After exposure to an oxidizing environment for seven hours at 2125°F two specimens were tested. One of the specimens showed only a slight (2000 psi) strength decrease from the initial 2200°F - 10 hr inert exposure condition, while the other exhibited a much greater decrease (21,000 psi).

A 16 hour exposure to an oxidizing environment at 2125°F caused a further decrease in strength to a level 45% higher than the as-sprayed material.

2.3.2 Ballistic Impact Behavior

Ballistic impact tests were conducted at RT and 2100°F on 50 and 75 w/o Hastelloy X-ZrO_2 specimens machined to a 0.300 inch diameter. The two inch long specimens were supported as cantilever beams during the test. Each specimen was subjected to 4-6 impacts of constant energy level along an axial line. Lines of different energy level impacts were made at 120° intervals around the bar circumference. The elevated temperature test specimens were heated to 2100°F by a butane-air torch and the specimen temperature monitored by a Thermo-Dot infrared pyrometer.

The projectiles in the ballistic impact test were Daisy X-tra Special Steel "BB" shot, 0.175 inch in diameter and weighing 0.361 gram. These projectiles were fired from a bench mounted Crossman air rifle pressurized with argon gas. An impact energy-gas pressure calibration was established by measuring the projectile velocity with an Autron Model T 333 Ballistic Chronograph and computing the impact energy from $K.E. = \frac{mv^2}{2}$. Impact energies ranging from 0.5 inch-pound to 7.0 foot-pounds are possible with this apparatus. A visual/binocular (30X) examination supplement by a fluorescent penetrant inspection (FPI) in questionable cases was the basis for judgment of the presence of cracks at any energy level. The results of the room temperature impact tests, given in Table V and Figure 6, show an increase in the ballistic impact cracking threshold energy from ~1 ft lb as-sprayed to the 5-6 ft-lb level after inert atmosphere exposures at 2200°F for 10-1000 hours. The 50 and 75 w/o Hastelloy X materials showed similar values at a given exposure condition.

Table V

Room Temperature Ballistic Impact Test Results on Plasma Sprayed Hastelloy X-ZrO_2

	Number Cracked/Number Impacts								
Energy Level (ft-lbs)	0.5	1.0	1.25	1.5	2.0	3.0	4.0	5.0	6.0
50 w/o Hastelloy X (Group A)									
As-sprayed	0/6	0/6	1/6	1/4*	2/2*	---	---	---	---
Inert 2200F-10 hr	0/6	0/6	0/6	0/6	0/4	0/4	0/4	0/4	---
Inert 2200F-100 hr	0/6	0/6	0/6	0/6	0/4	0/4	1/2*	---	---
Inert 2200F-1000 hr	---	---	---	---	0/5	0/5	0/5	0/5	1/4*
**Oxid. 2125F-7hr	---	---	---	---	0/2	1/2*	---	---	---
**Oxid. 2125F-16 hr	---	---	---	---	1/2*	---	---	---	---
50 w/o Hastelloy X (Group B)									
As-sprayed	0/6	1/6	0/4	1/4*	3/3*	---	---	---	---
Inert 2200F-10 hr	0/6	0/6	0/6	0/6	0/4	0/4	0/4	1/2*	---
Inert 2200F-100 hr	0/6	---	0/5	0/5	0/4	0/4	0/4	0/4	---
Inert 2200F-1000 hr	---	---	---	---	0/5	0/5	0/5	1/5	2/5
75 w/o Hastelloy X									
As-sprayed	0/6	0/6	0/6	5/5	---	---	---	---	---
Inert 2200F-10 hr	0/6	0/6	0/6	0/4	0/4	0/4	0/4	0/4	---
Inert 2200F-100 hr	0/6	0/6	0/6	0/4	0/4	0/4	0/4	0/4	---
Inert 2200F-1000 hr	---	---	---	---	---	---	---	---	---
**Oxid. 2125F-7 hr	---	---	---	---	0/2	0/2	0/2	---	0/2
**Oxid. 2125F-16 hr	---	---	---	---	0/2	0/2	0/2	---	0/2

* Specimen broke in two on last impact - no additional impacts possible.

** Specimens pre-treated 2200F-10 hr in inert atmosphere prior to oxidizing exposure.

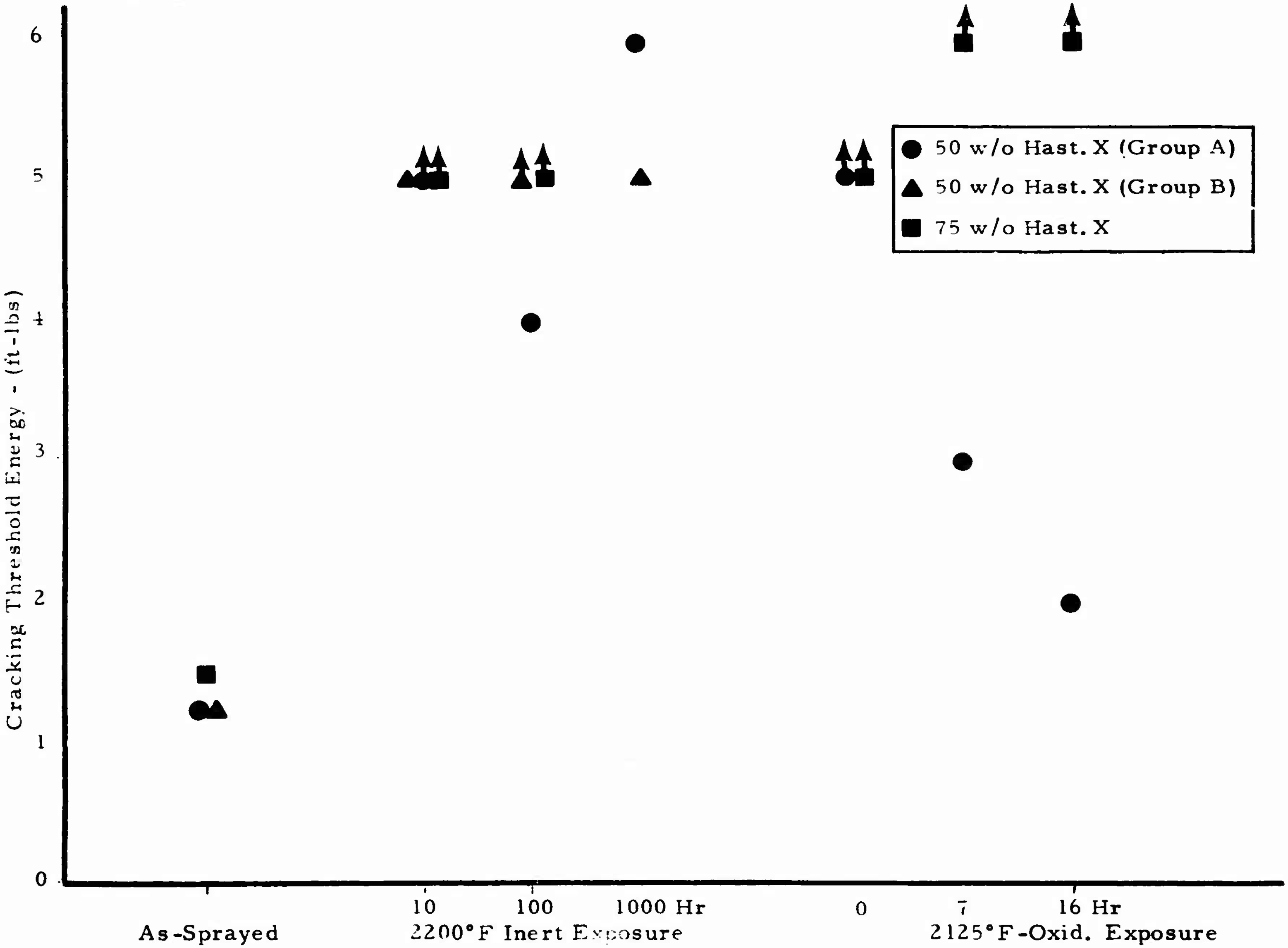


Figure 6. Room temperature ballistic impact test results plasma sprayed Hastelloy X-ZrO_2.

2.3.2 Ballistic Impact Behavior (Cont'd)

Exposure to 2125°F dynamic oxidation lowered the impact cracking threshold level from the 5-6 ft-lb range down to 2-3 ft-lbs for the 50 w/o Hastelloy X material. Longer oxidizing exposures produced a greater degree of degradation. The specimens failed across the full cross section and examination of this fracture surface disclosed a green discoloration found in the tensile specimens. This is most likely evidence of oxygen penetration at ZrO_2-Hx interfaces resulting in oxidation of the Hx phase at particle surfaces.

The 75 w/o Hastelloy X material did not show impact property degradation due to the oxidizing environment exposure up to 16 hours at 2125°F. The elevated temperature (2100°F) ballistic impact test results are shown in Table VI and Figure 7. The elevated temperature impact energy values were generally lower than the room temperature values but showed the same trend in that exposure to inert atmosphere at 2200°F for 10-100 hours improved the impact properties over the as-sprayed condition, but to a lesser degree. The 75 w/o Hastelloy X material showed a marked superiority over the 50 w/o material by a factor of 2.0-2.5. A typical specimen after 2100°F ballistic impact testing is shown in Figure 8.

2.4 Metallographic Studies

Optical metallography was used to correlate microstructures with mechanical properties, as they are influenced by the composition and thermal exposure environment conditions of the plasma sprayed Hastelloy X-ZrO_2 materials.

2.4.1 50 w/o Hastelloy X-ZrO_2

Figures 9 through 15 show the typical microstructure of the 50 w/o Hastelloy X-ZrO_2 material in the as-sprayed condition and after 10, 100, and 1000 hours inert environment exposure at 2200°F. The microstructure of the material after 10, 100 and 1000 hours exposure can be seen to be nearly identical. The metallic component is single phase with no carbide particles noted in either the as-sprayed or the exposed material. However, a fine laminar oxide phase, found in the as-sprayed material, was not present after exposure to the 2200°F environment. Examination of the specimens after oxidation exposures at 2125°F for 7 or 16 hours disclosed no appreciable loss of material by spalling, however, an increase in the cross section size due to oxidation of the Hastelloy X phase was observed.

Table VI

Elevated Temperature (2100°F) Ballistic Impact Test Results on Plasma Sprayed Hastelloy X-ZrO_2

	Number Cracked/Number Impacts				
Energy Level (ft-lbs)	1.0	2.0	3.0	4.0	5.0
50 w/o Hastelloy X (Group A)					
As-sprayed	5/5	9/9	4/4	---	---
Inert 2200F-10 hr	4/5	9/9	4/4	---	---
Inert 2200F-100 hr	0/5	9/9	5/5	---	---
50 w/o Hastelloy X (Group B)					
As-sprayed	5/5	9/9	4/4	---	---
Inert 2200F-10 hr	0/5	5/9	3/4	---	---
Inert 2200F-100 hr	0/5	9/9	8/8	---	---
75 w/o Hastelloy X					
As-sprayed	0/5	9/9	8/8	---	---
Inert 2200F-10 hr	0/5	0/8	0/8	1/4	1/4
Inert 2200F-100 hr	0/4	0/9	0/9	0/4	3/4

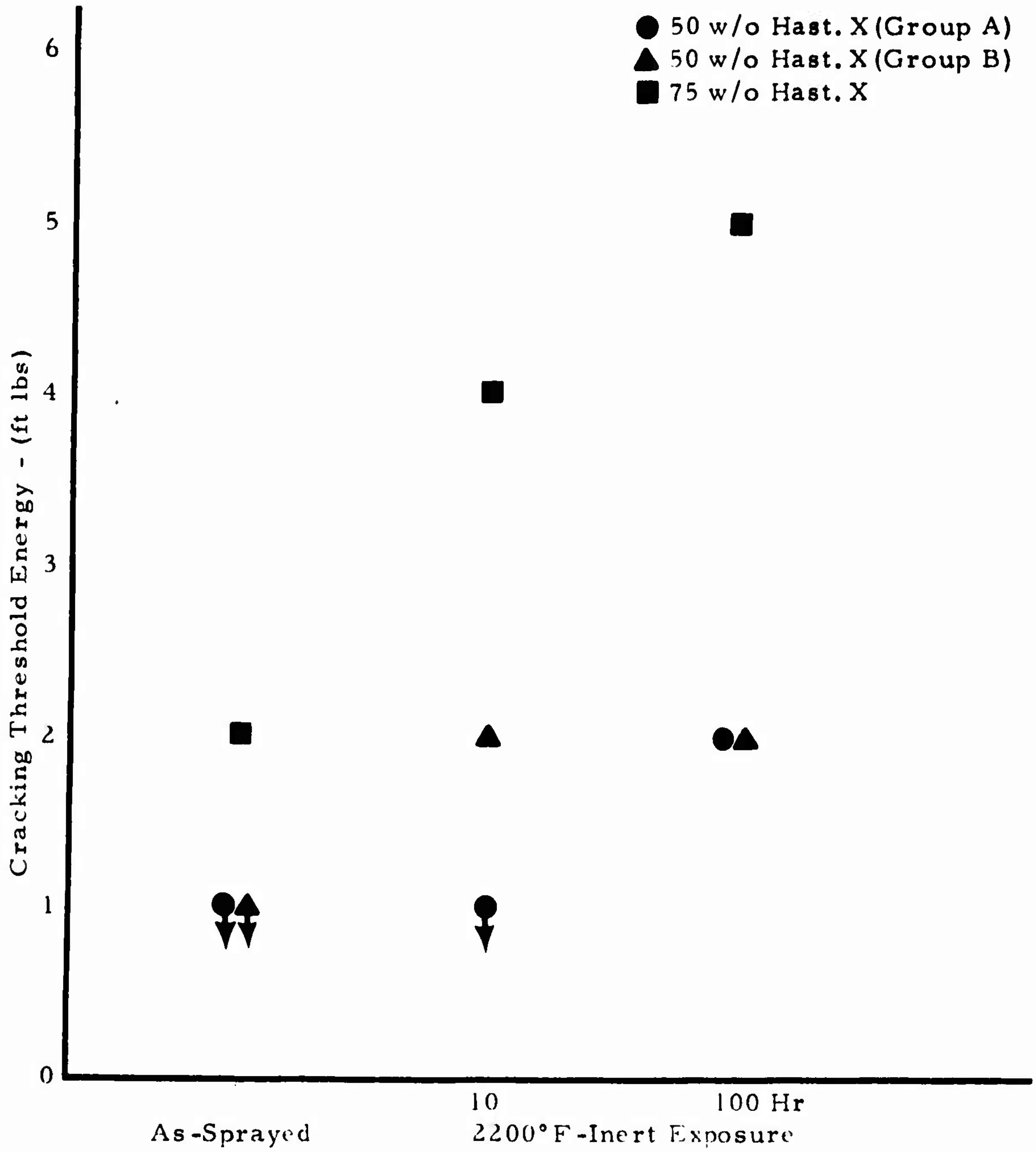


Figure 7. Elevated temperature (2100°F) ballistic impact test results plasma sprayed Hast. X-ZrO_2

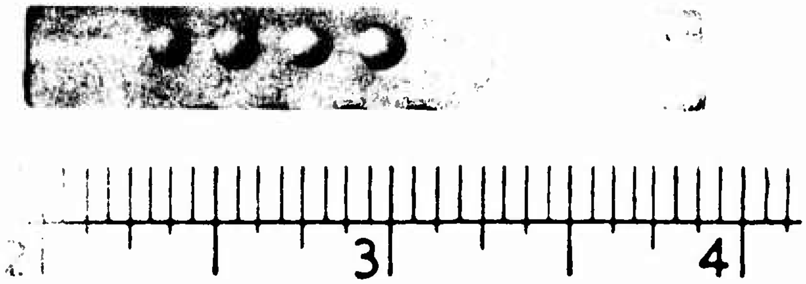
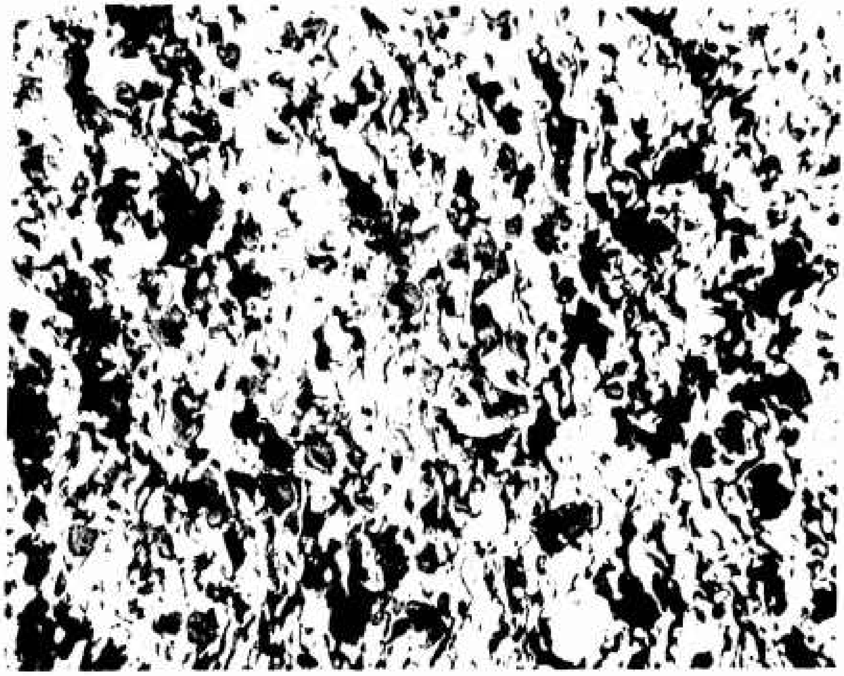


Figure 8. Ballistic impact specimen of 50 w/o Hastelloy X-ZrO_2 (Group A) after 3.0 ft-lb impact testing at 2100°F.

100X



500X

Figure 9. 50 w/o Hastelloy X-ZrO_2 (Group A) material in the as-sprayed condition.

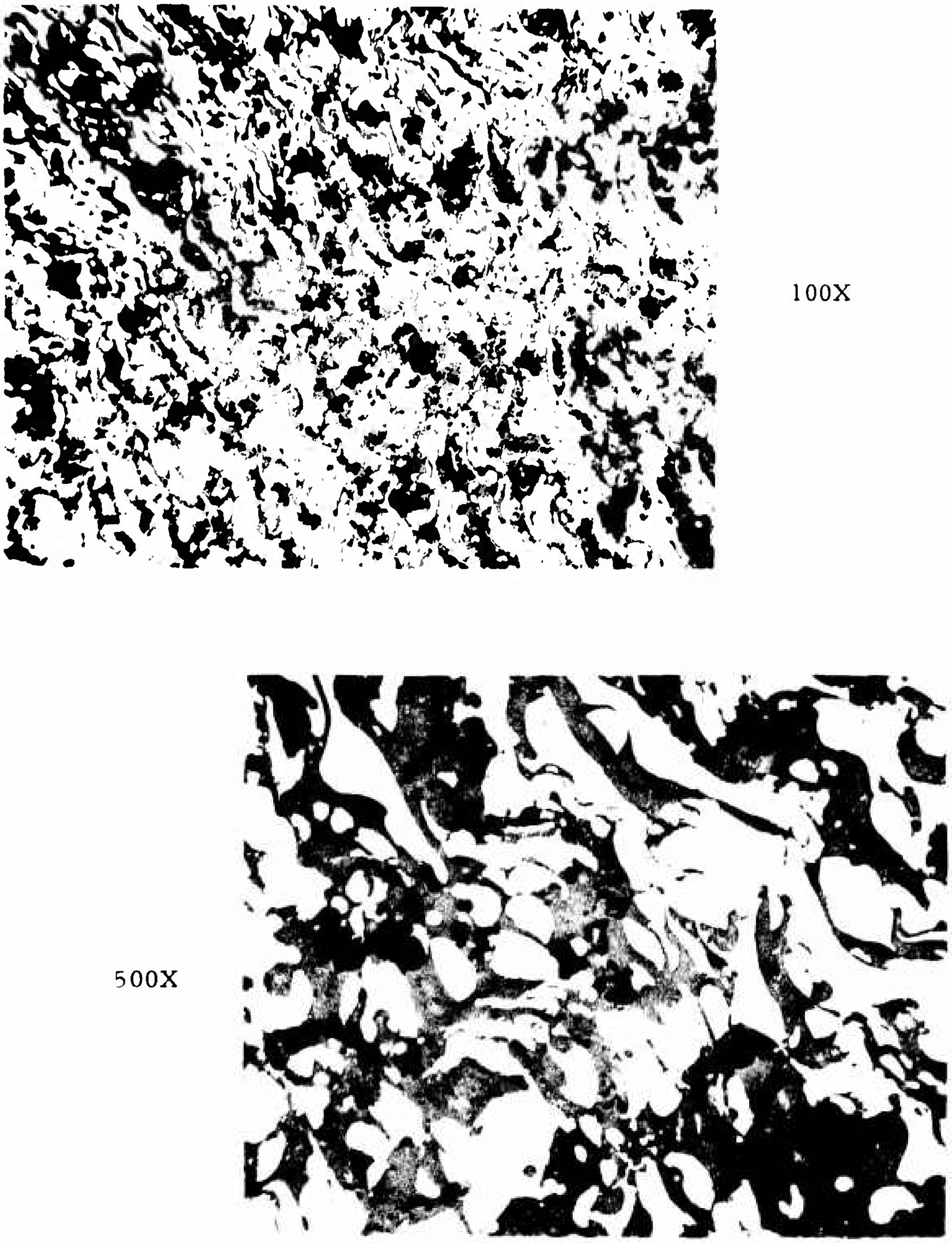
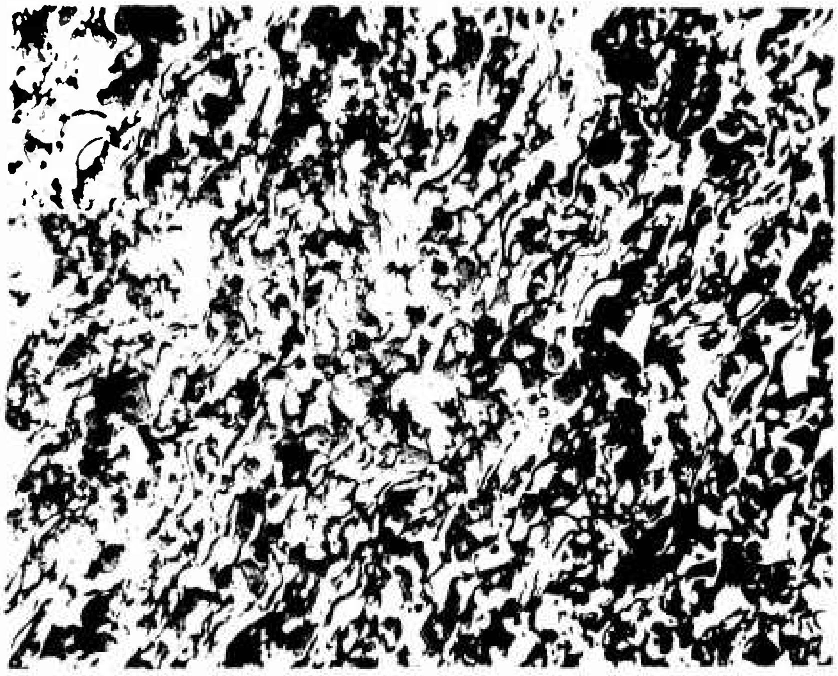


Figure 10. 50 w/o Hastelloy X-ZrO_2 (Group B) material in the as-sprayed condition.

100X



500X

Figure 11. 50 w/o Hastelloy X-ZrO_2 (Group A) material after exposure for 10 hours at 2200°F in an inert environment. Disappearance of fine laminar phase is the only noticeable change found.

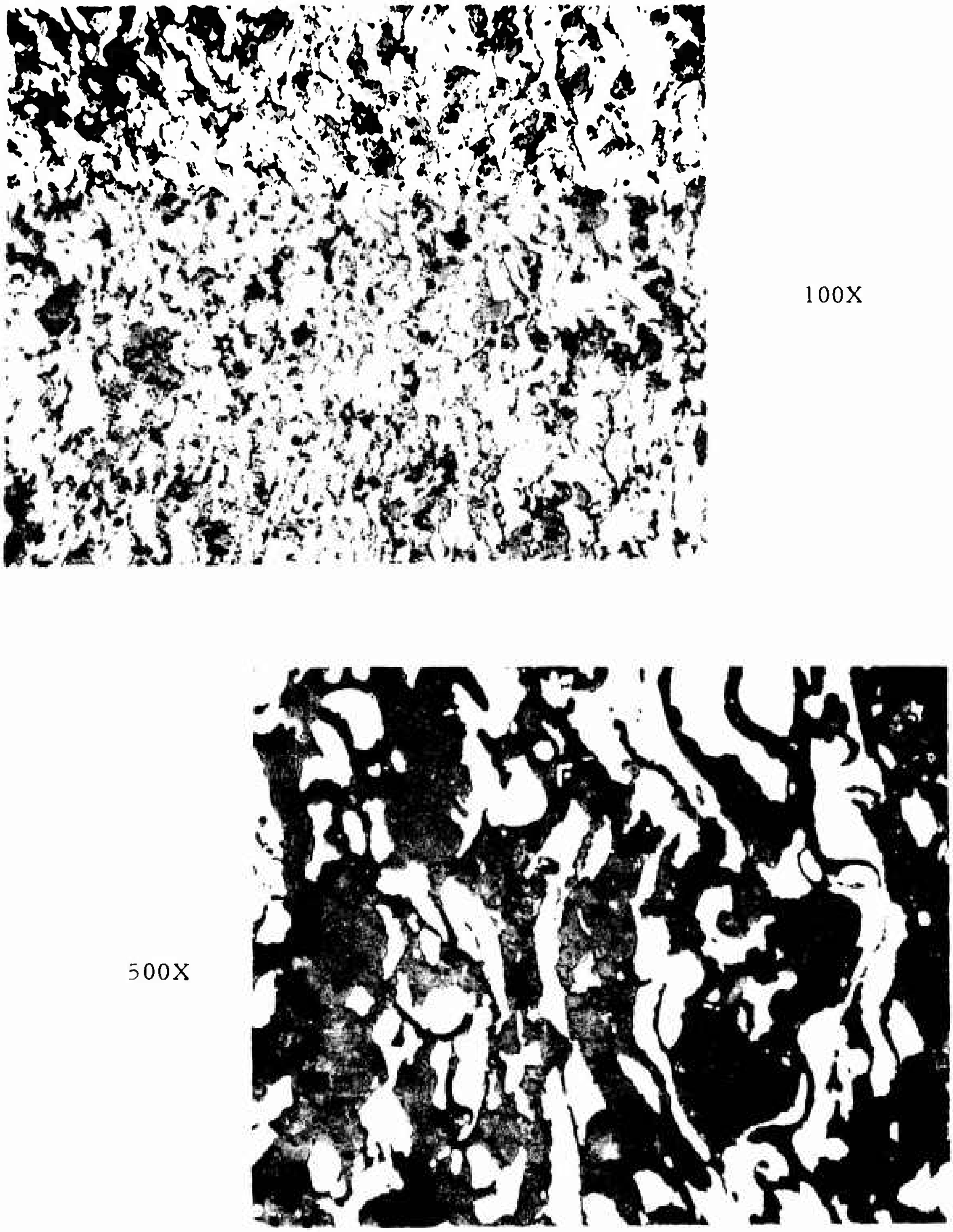


Figure 12. 50 w/o Hastelloy X-ZrO_2 (Group B) material after exposure for 10 hours at 2200°F in an inert environment.

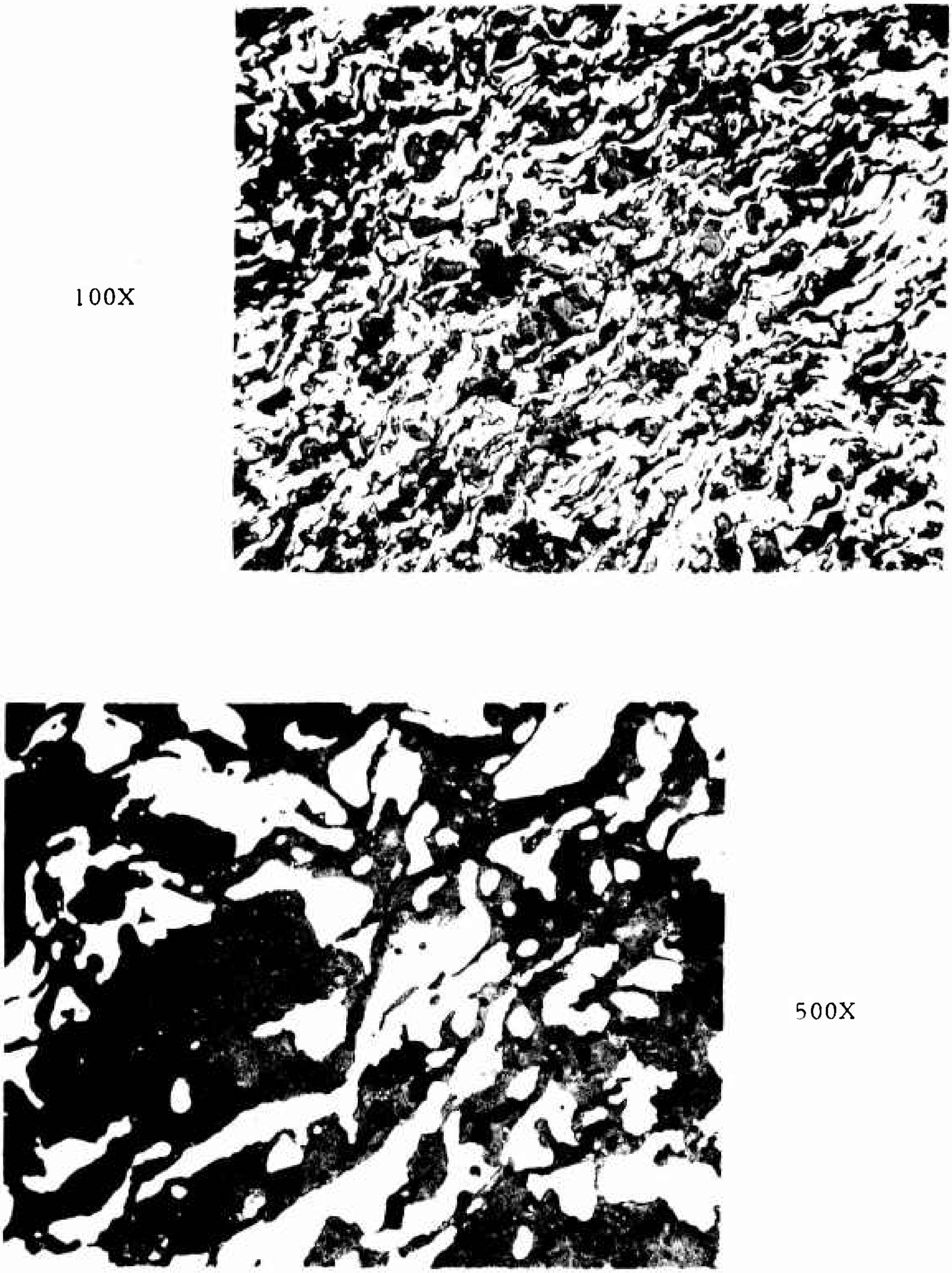


Figure 13. 50 w/o Hastelloy X-ZrO$_2$ (Group A) material after exposure for 100 hours at 2200°F in an inert environment. No noticeable change has occurred from the 10 hour exposed material.

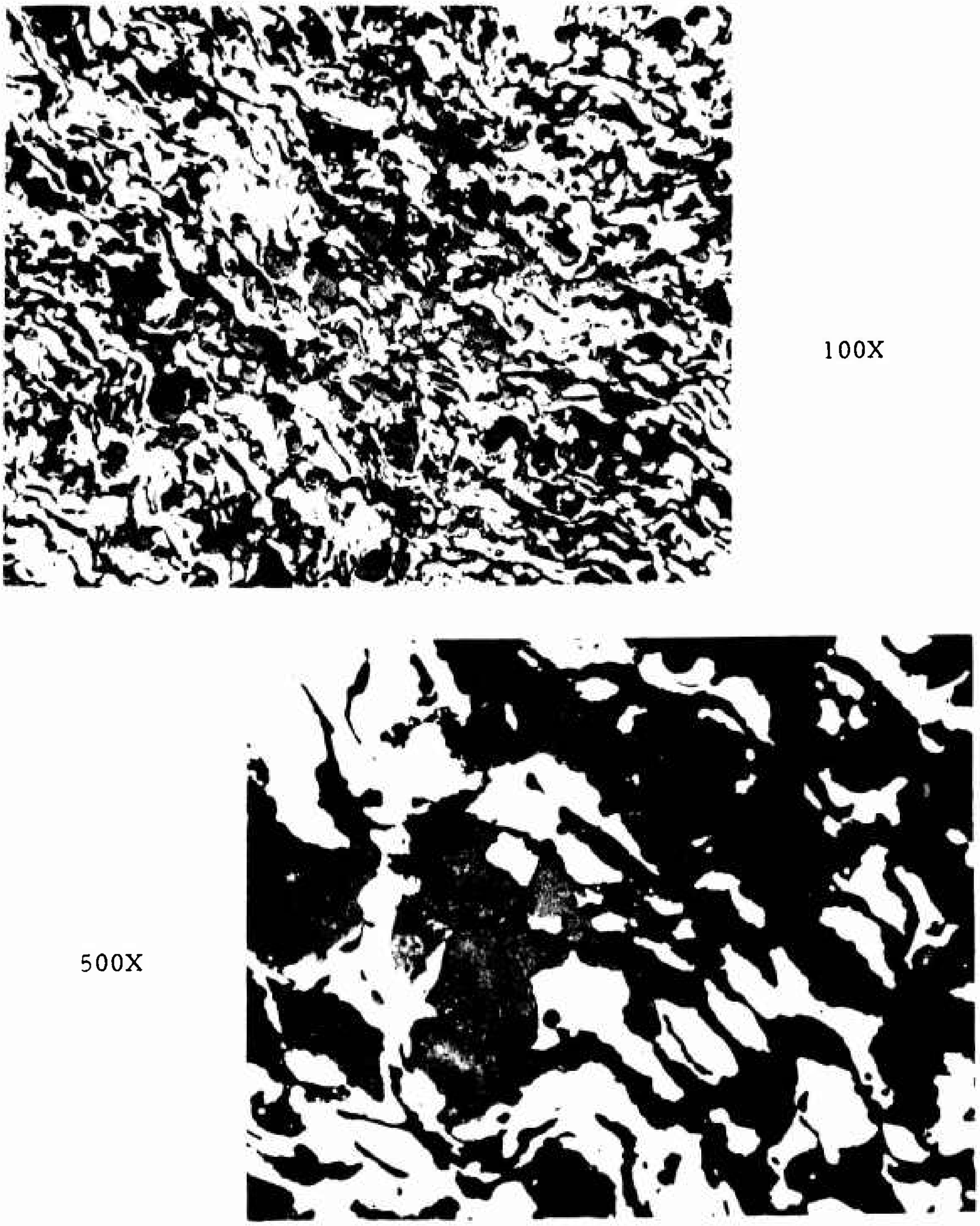


Figure 14. 50 w/o Hastelloy X-ZrO_2 (Group B) material after exposure for 100 hours at 2200°F in an inert environment.

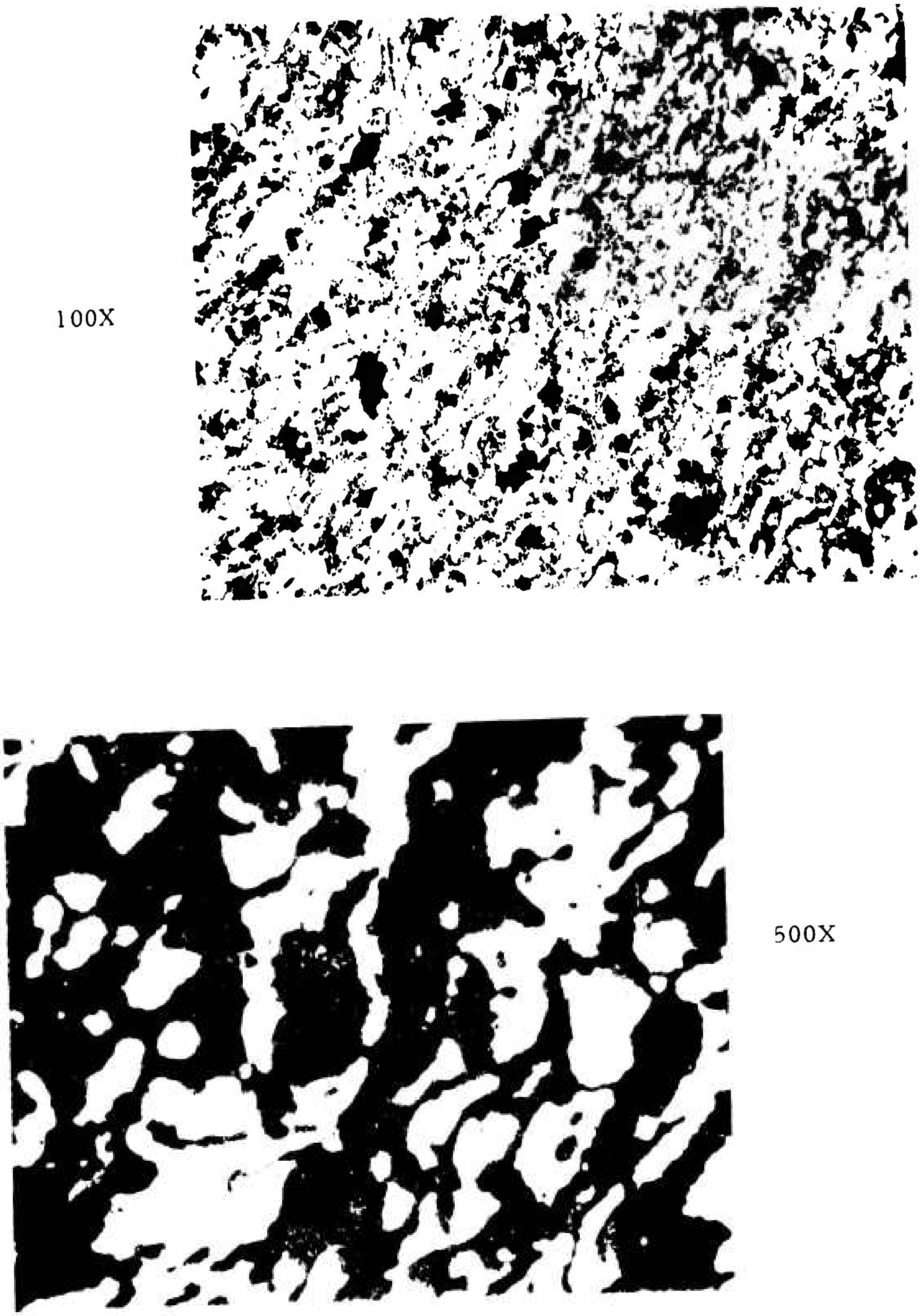


Figure 15. 50 w/o Hastelloy X-ZrO_2 (Group A) material after exposure for 1000 hours at 2200°F in an inert environment.

2.4.1 50 w/o Hastelloy X-ZrO_2 (Cont'd)

The microstructures of the tensile specimens exposed to the dynamic oxidation environment for 7 hours are shown in Figures 16 and 17. Examination of these microstructures show evidence of some surface oxidation but nothing which would be considered catastrophic. A second phase was found to be precipitating non-uniformly through the cross section of the Hastelloy X material after this exposure. A slight gradation of the ZrO_2 through the cross section was also observed. This ZrO_2 gradation may have been caused by the constantly varying specimen diameter during arc plasma spraying. Subsequent electron microbeam X-ray analysis (Section 2.5) characterized the precipitating phase as having a high Cr and Mo content when compared to the Hastelloy X matrix.

2.4.2 75 w/o Hastelloy X-ZrO_2

The microstructures of 75 w/o Hastelloy X-ZrO_2 material in the as-sprayed condition, as well as after 10 and 100 hours at 2200°F in an inert atmosphere, are shown in Figures 18 through 20. Quantitative metallographic analysis (Table III) had shown that this material had an actual composition of 74-80 w/o Hastelloy X. Examination of the microstructure of the as-sprayed material, Figure 18, discloses the presence of two types of non-metallic phases, the larger blocky material and a very fine laminar material. The very fine material was later identified by electron microbeam X-ray analysis (Section 2.5) to be rich in silicon and chromium; while the blocky phase was identified as the ZrO_2 material. After exposure at 2200°F, Figures 19 and 20, the ZrO_2 material was seen to change to a two phase structure material, while the fine laminar Si-Cr rich phase spheroidized into very small particles. This same effect was noted for both the 10 and 100 hour exposures.

The microstructures of specimens exposed to 2200°F for 10 hours in an inert environment, followed by a dynamic oxidation exposure at 2125°F for 7 and 16 hours, are shown in Figures 21 and 22, respectively. No change in microstructure due to the dynamic oxidation exposure was observed, in contrast to the behavior of the 50 w/o Hastelloy X-ZrO_2 material.

2.4.3 Microstructure Discussion

In order to explain the difference in behavior of the two materials when exposed to the oxidizing environment, i.e., precipitation of a secondary phase in the Hastelloy X, a series of critical experiments was conducted. The purpose of these experiments was to establish whether the precipitation was

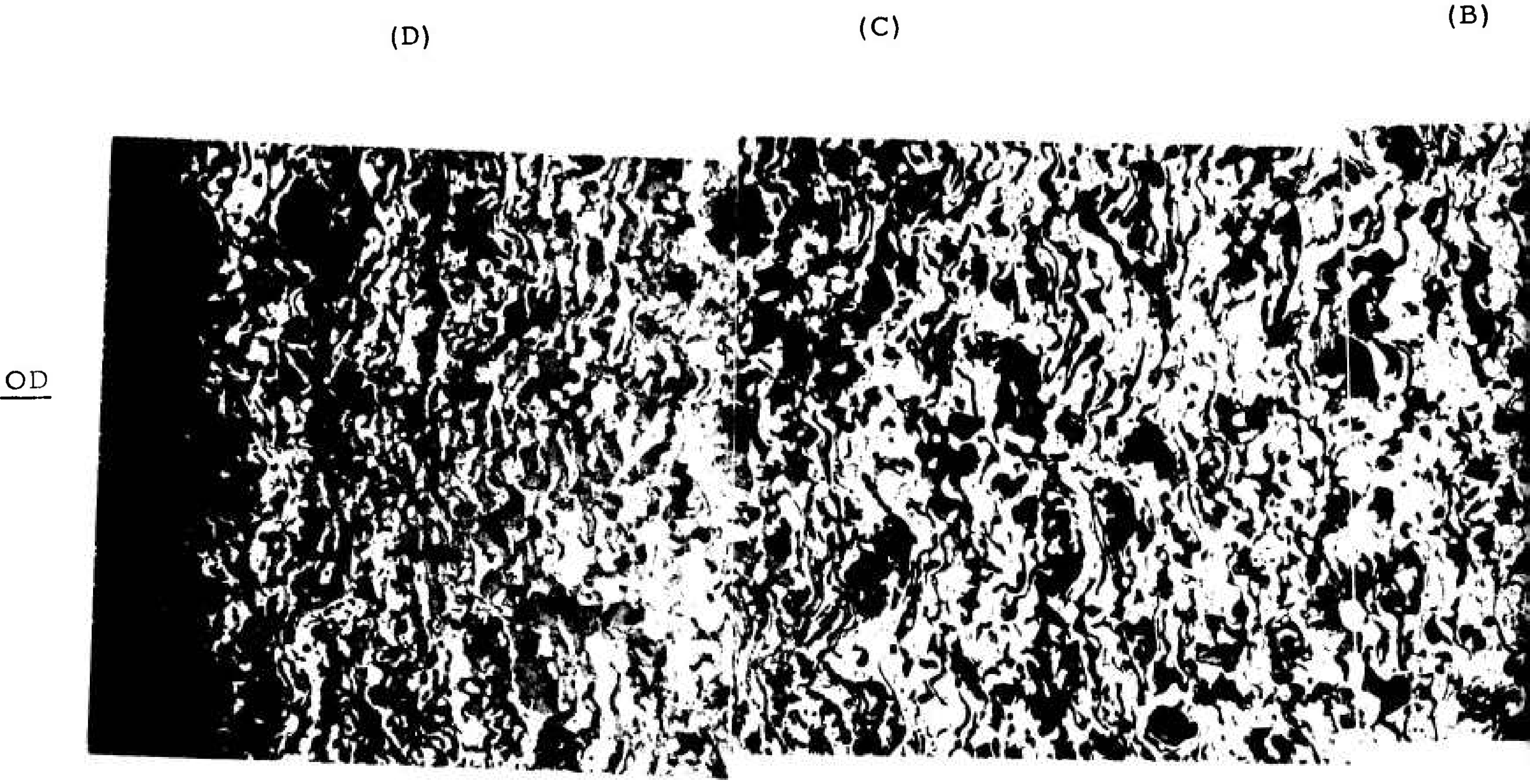
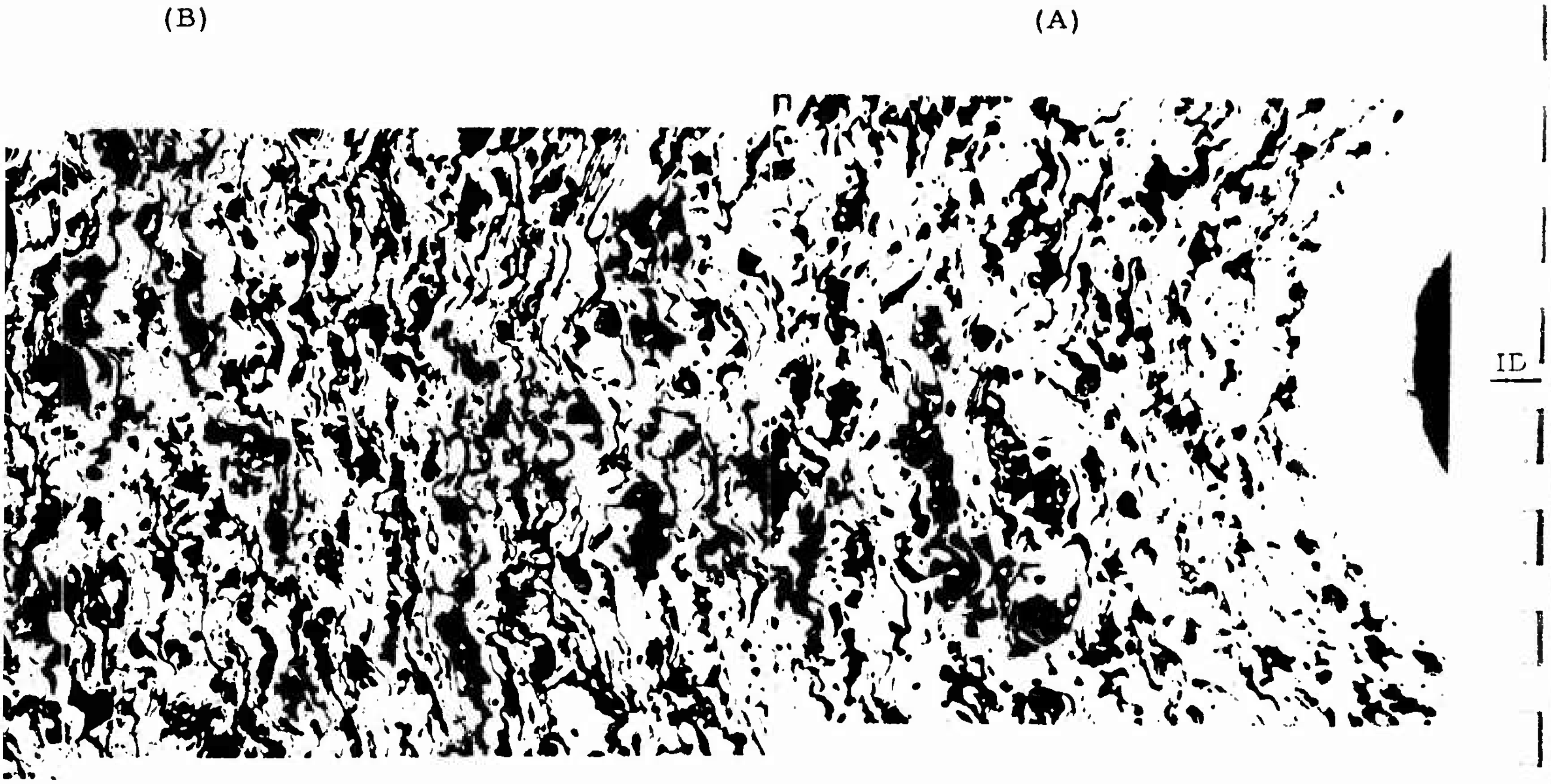
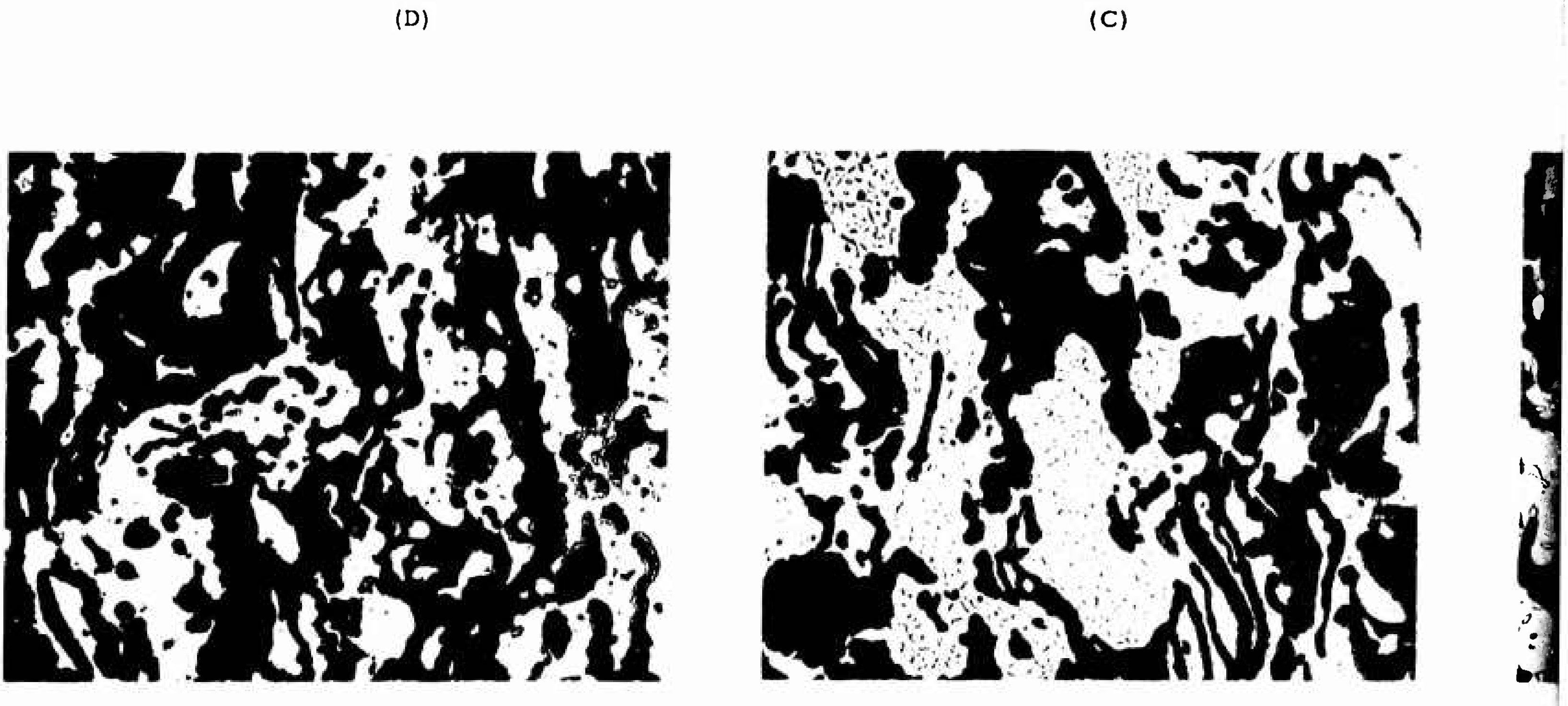


Figure 16. 50 w/o Hastelloy X-ZrO_2 (Group A) material after exposure for 10 hours at 2200°F for 7 hours at 2125°F. (Magn. 100X)

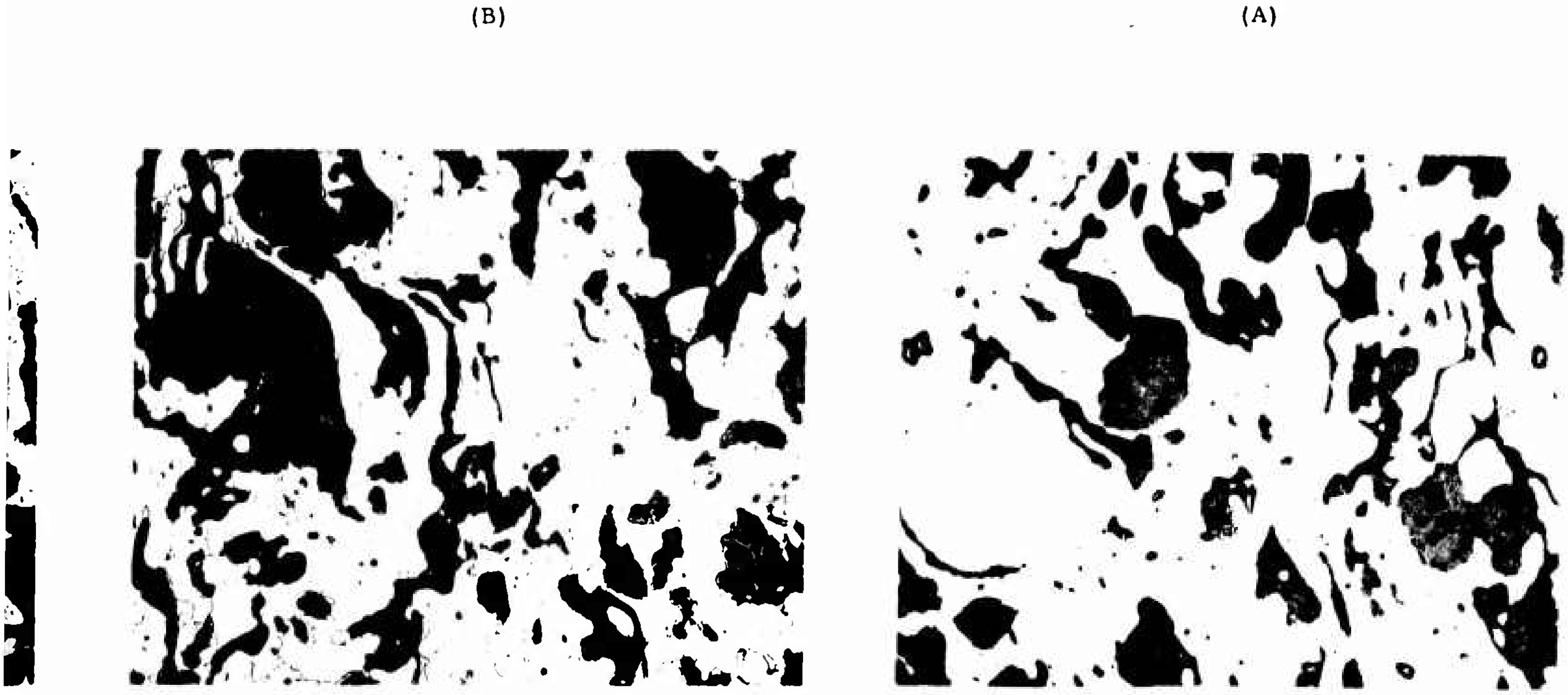


ours at 2200°F in an inert environment followed by exposure to a dynamic oxidizing environment
agn. 100X) Etchant: Kalling's Reagent


(D)

(C)

Figure 17. 50 w/o Hastelloy X-ZrO$_2$ (Group A) material after exposure for 10 hours at 2200°F in
7 hours at 2125°F. These photomicrographs show in detail the structures observed in



(B) (A)

at 2200°F in an inert environment followed by exposure to a dynamic oxidizing environment for
observed in the corresponding areas of Figure 16. Etchant: Kalling's Reagent (Magn: 500X)

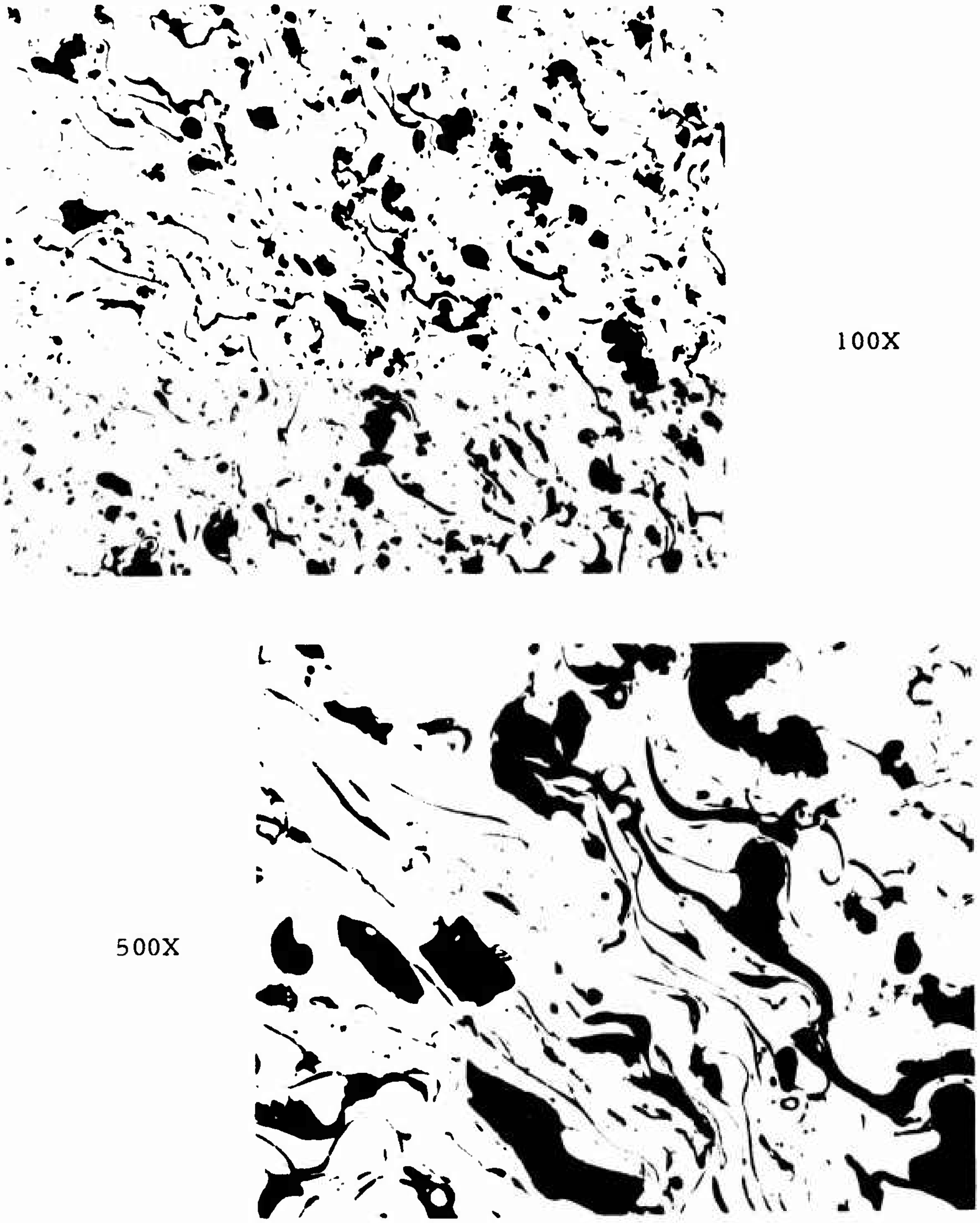
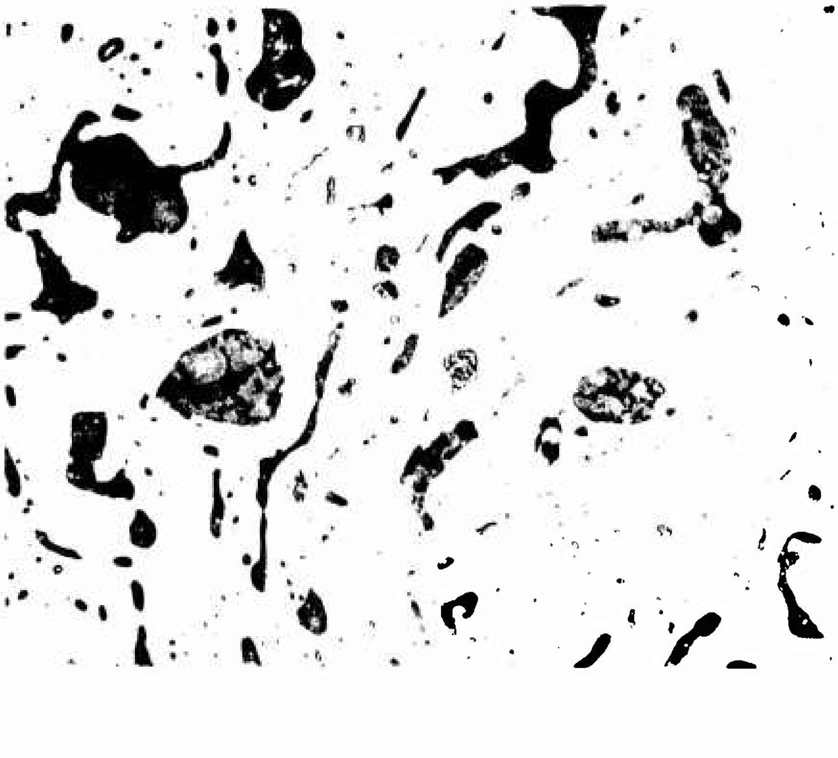


Figure 18. 75 w/o Hastelloy X-ZrO_2 material in the as-sprayed condition.

100X



500X

Figure 19. 75 w/o Hastelloy X-ZrO_2 material after exposure for 10 hrs at 2200°F in an inert environment. The spheroidization of the very fine laminar phase and the change in the ZrO_2 particles to a two-phase material should be noted.

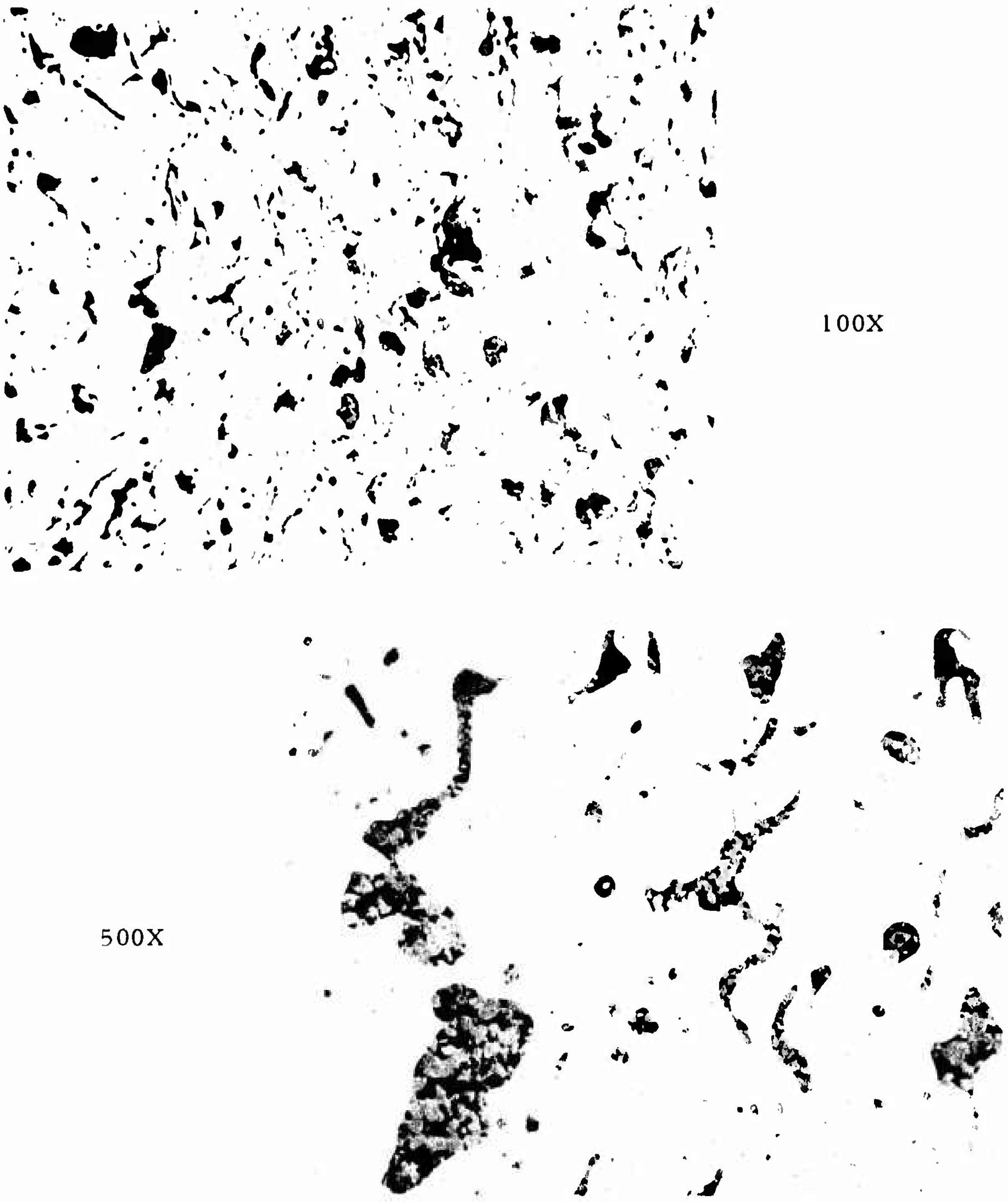
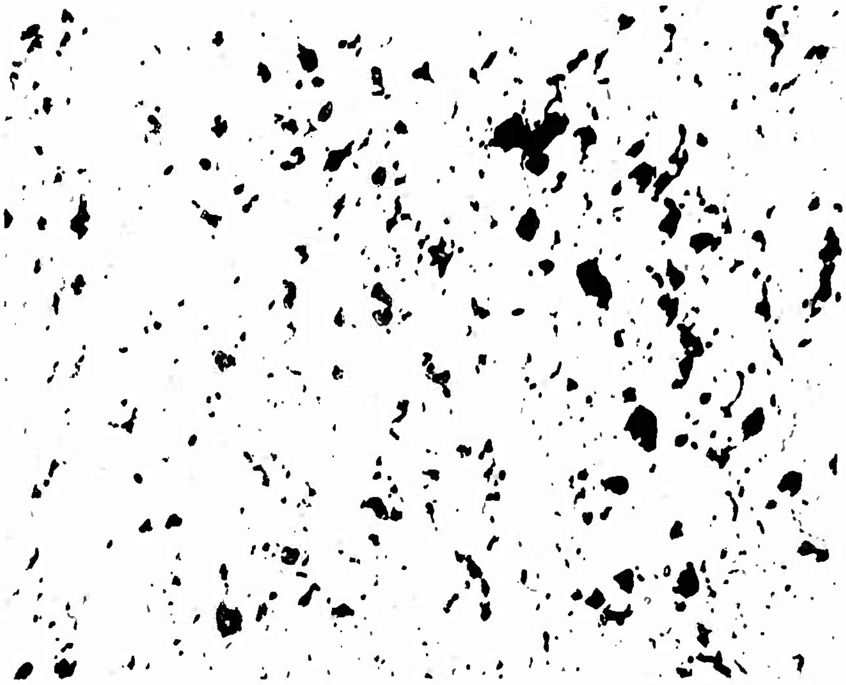


Figure 20. 75 w/o Hastelloy X-ZrO_2 material after exposure for 100 hrs at 2200°F in an inert environment. The same characteristics found in the 10 hour exposed material are seen here. No changes in distribution or character of the material from the 10 hour exposure are apparent.



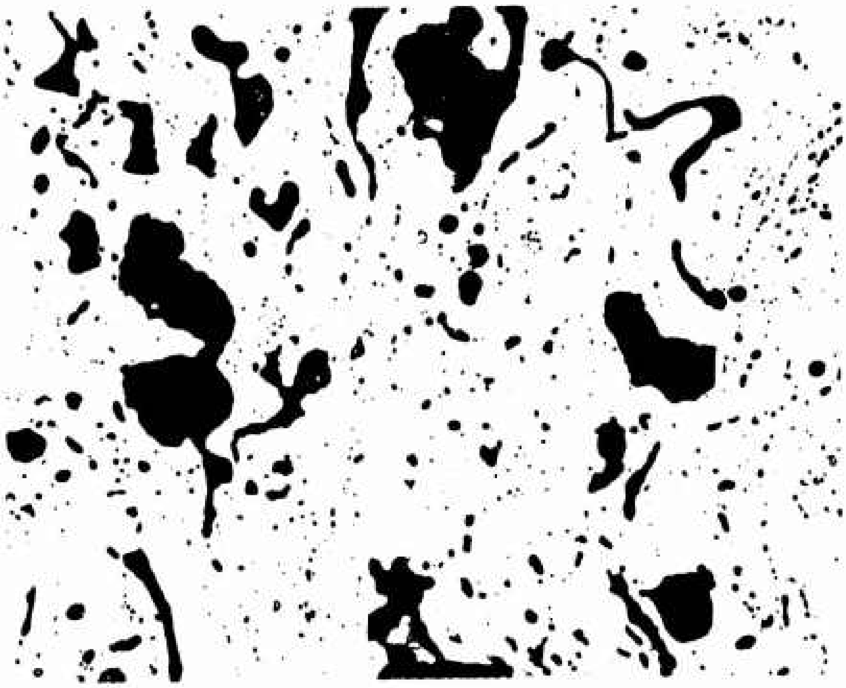
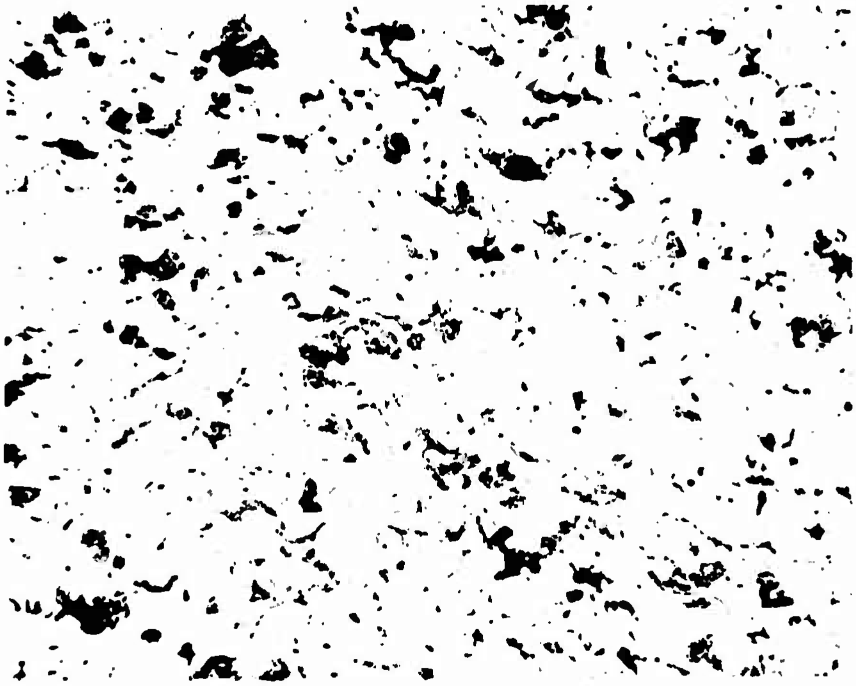
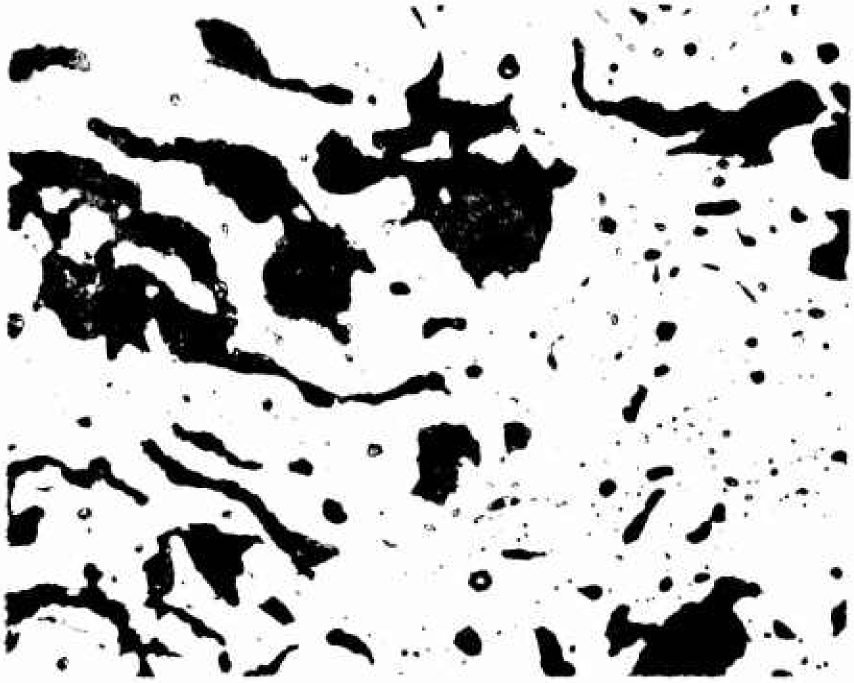


Figure 21. 75 w/o Hastelloy X-ZrO_2 material after exposure for 10 hrs at 2200°F in an inert environment followed by exposure to a dynamic oxidizing environment for 7 hours at 2125°F.



100X



500X

Figure 22. 75 w/o Hastelloy X-ZrO_2 material after exposure for 10 hrs at 2200°F in an inert environment followed by exposure to a dynamic oxidizing environment for 16 hours at 2125°F.

2.4.3 Microstructure Discussion (Cont' d)

temperature sensitive, i.e., radial thermal gradient during the oxidation exposures, and/or atmosphere sensitive, i.e., air or inert gas environment.

Specimens of the 50 w/o and 75 w/o Hastelloy X material which had been exposed for 10 hours at 2200°F in an inert environment were simultaneously exposed in still air or slowly flowing argon at 1800, 2000, and 2100°F for 7 hours. Samples were placed in the same alumina boats during the exposure. A record of the microstructures after the exposures, shown in Table VII, indicate that the precipitate occurred only in the 50 w/o Hastelloy X material and then only when exposed to the air environment. Figures 23 and 24 show the microstructure found in both materials after exposure for 7 hours at 2100°F in air or argon environments. The precipitate-atmosphere relationship is clearly shown in these figures. The precipitates in the 2000°F and 1800°F exposed materials were similar except that the precipitated phase was slightly smaller. In order to determine the thermal stability of this precipitate phase a sample having the precipitate present was exposed for 2 hours at 2200°F in a flowing argon environment. Examination of the microstructure after this exposure showed that the phase had re-solutioned. Since the solution temperature of the precipitate has been established to be as low as 2200°F, the absence of this phase near the surface of the dynamic oxidation samples (see Figures 16 and 17) could have been the result of this zone being above the precipitation range of the phase. Surface temperature measurements as high as 2150°F were measured during the oxidation exposures. This fact coupled with the possible existence of a radial thermal gradient in the higher zirconia material would help explain the precipitate gradient observed in the sample. In addition to the thermal gradient an O_2-N_2 potential gradient from the surface of the sample to the core of the material would explain the absence of the precipitate near the center of the bar since this precipitate reaction has been slower to be O_2-N_2 sensitive.

The absence of the precipitate phase in the 75 w/o material is probably due to two factors. First the lower ZrO_2 content would result in a higher thermal conductivity and therefore a lower radial thermal gradient in the samples. The lower ZrO_2 content results in lower porosity (less O_2-N_2 diffusion paths from the surface) thus limiting the O_2-N_2 below that required for the phase to precipitate.

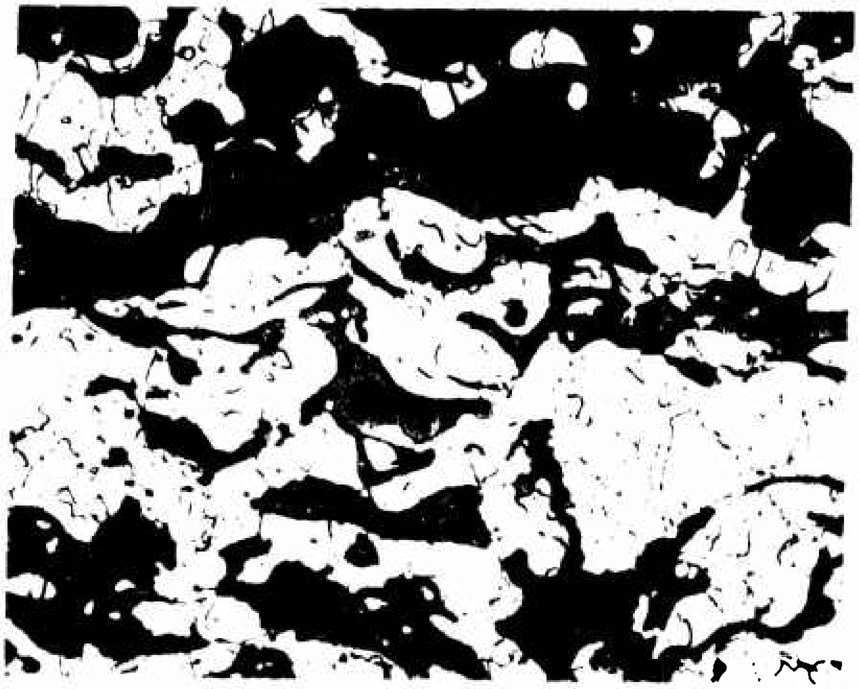
Table VII

Record of Microstructures of 50 and 75 w/o Hastelloy X-ZrO_2 Material After 7 Hours Exposure

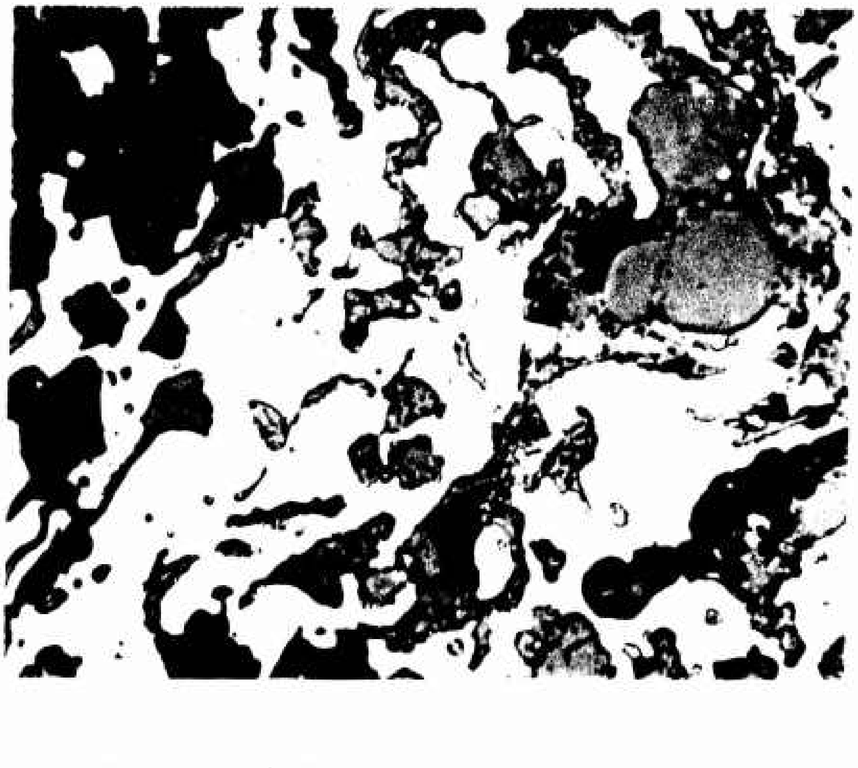
Material	Temperature °F	Environment	
		Air	Argon
50 w/o	2100	PPT*	None
75	2100	None**	None
50	2000	PPT	None
75	2000	None	None
50	1800	PPT	None
75	1800	None	None

* Precipitate phase noted in Hastelloy X

** No precipitate phase noted in Hastelloy X

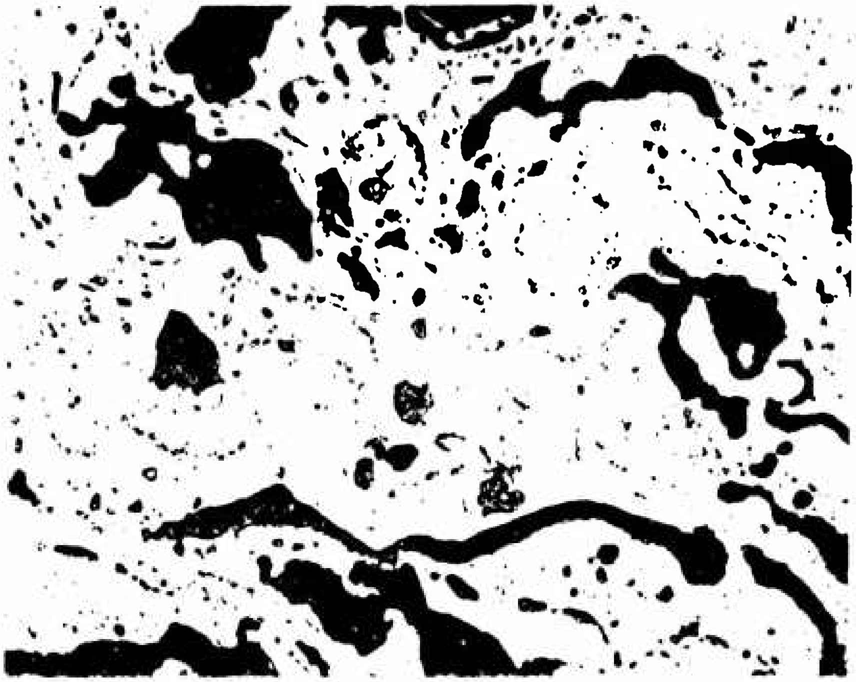


Air
Exposure



Argon
Exposure

Figure 23. 50 w/o Hastelloy X-ZrO_2 material after exposure for 10 hours at 2200°F in an inert environment followed by exposure for 7 hrs at 2100°F in air or argon environments.
(Magn: 500X) Etchant: HCl - H_2O_2



Air
Exposure

Argon
Exposure

Figure 24. 75 w/o Hastelloy X-ZrO_2 after exposure for 10 hours at 2200°F in an inert environment followed by exposure for 7 hours at 2100°F in an air or argon environment. (Magn: 500X) Etchant: HCl - H_2O_2

2.5 Electron Microbeam X-ray Analysis

Electron beam microanalyses were conducted on samples to establish chemical element distributions in order to (1) identify the laminar phase found in the as sprayed 75 w/o Hastelloy X material, (2) characterize the changes in the ZrO_2 phase in both the 75 w/o and the 50 w/o Hastelloy X material after the 2200°F inert environment exposures and (3) characterize the precipitate phase found in the 50 w/o Hastelloy X material after exposure to the dynamic oxidation environment.

Figure 25 shows the microstructure of the 75 w/o Hastelloy X material in the as-sprayed condition. The chemical element distribution profile of this sample is shown in Figures 26 and 27. Examination of these figures show an increase in the chromium and silicon content of the laminar phase (thin wisp). This phase is probably the normal Hastelloy X oxide formed when the material was arc plasma sprayed. The constant calcium content across the ZrO_2 phase indicates a uniform distribution of the CaO in this stabilized ZrO_2 material.

Figure 28 shows the microstructure of the 75 w/o Hastelloy X material after exposure in an inert environment at 2200°F for 100 hours. The two phase nature of the ZrO_2 phase is very evident in this photomicrograph. Figures 29 and 30 show the electron microbeam element distribution profiles of this material. Calcium, chromium and silicon as seen to be coincidently segregated in the ZrO_2 phase in contrast to the uniform distribution of calcium and absence of chromium and silicon in the as-sprayed material. The only available source of chromium and silicon is the Hastelloy X material.

Figure 31 shows the microstructure of the 50 w/o Hastelloy X material after exposure in an inert environment for 10 hours at 2200°F. A small amount of a second phase material can be seen in the ZrO_2 material. The same appearance was noted in samples exposed for 100 and 1000 hours. Figures 32 and 33 show the electron microbeam element distribution profiles of the sample shown in Figure 31. Examination of these profiles discloses the segregation of calcium and silicon in the ZrO_2 phase, much the same as was found in the 75 w/o Hastelloy X material. However, there was no chromium found in this ZrO_2 phase in contrast to the chromium segregation found in the ZrO_2 phase of the 75 w/o Hastelloy X material. No explanation can be made for this variation in the chromium segregation in the ZrO_2 phase of the 50 and 75 w/o Hastelloy X materials.

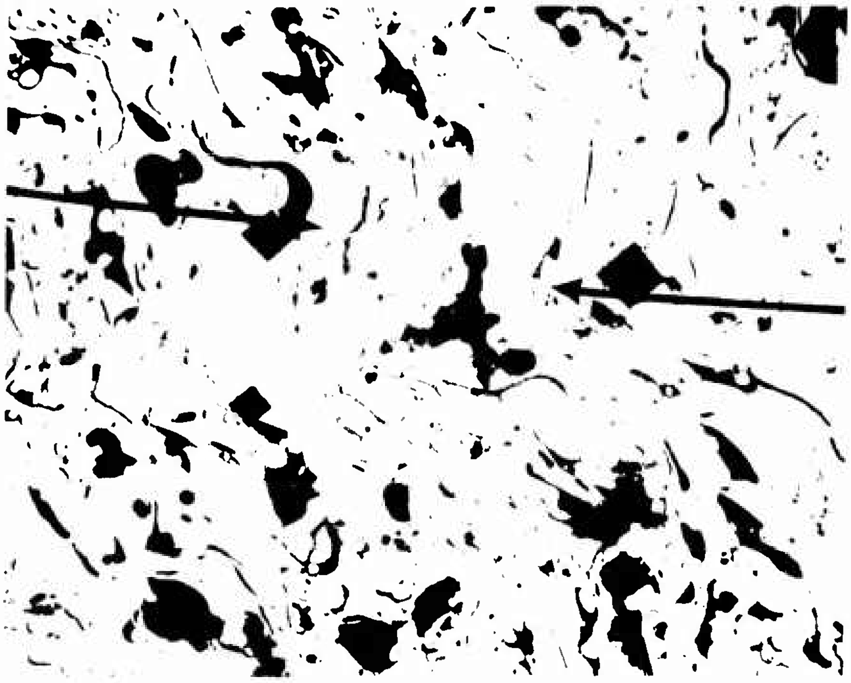


Figure 25. 75 w/o Hastelloy X-ZrO_2 - As-sprayed condition. Arrows denote line of chemical element distribution determination. (Magn: 500X)

Detroit Diesel Allison
Division of General Motors Corporation
Indianapolis, Indiana 46206

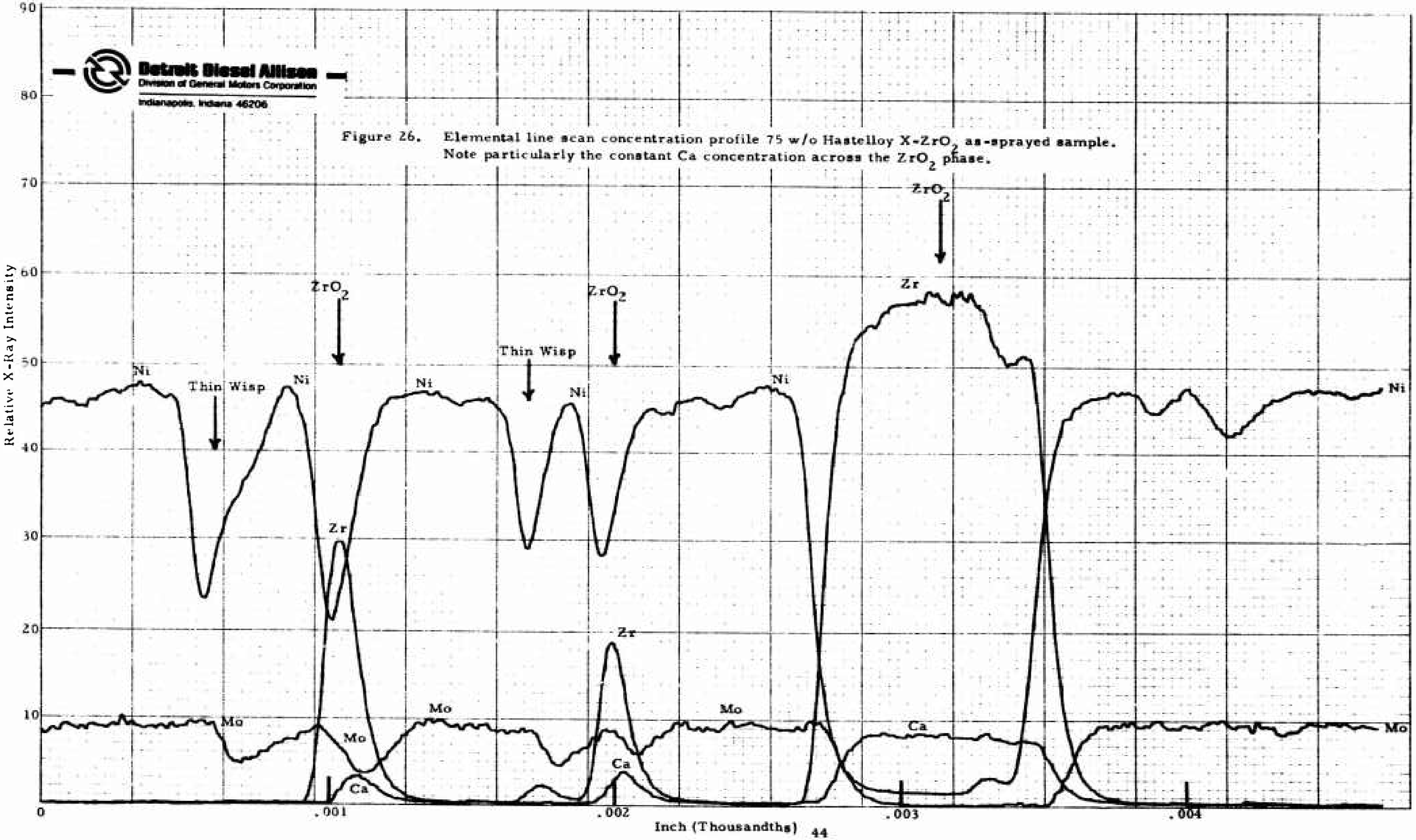


Figure 26. Elemental line scan concentration profile 75 w/o Hastelloy X-ZrO_2 as-sprayed sample. Note particularly the constant Ca concentration across the ZrO_2 phase.

Detroit Diesel Allison
Division of General Motors Corporation
Indianapolis, Indiana 46206

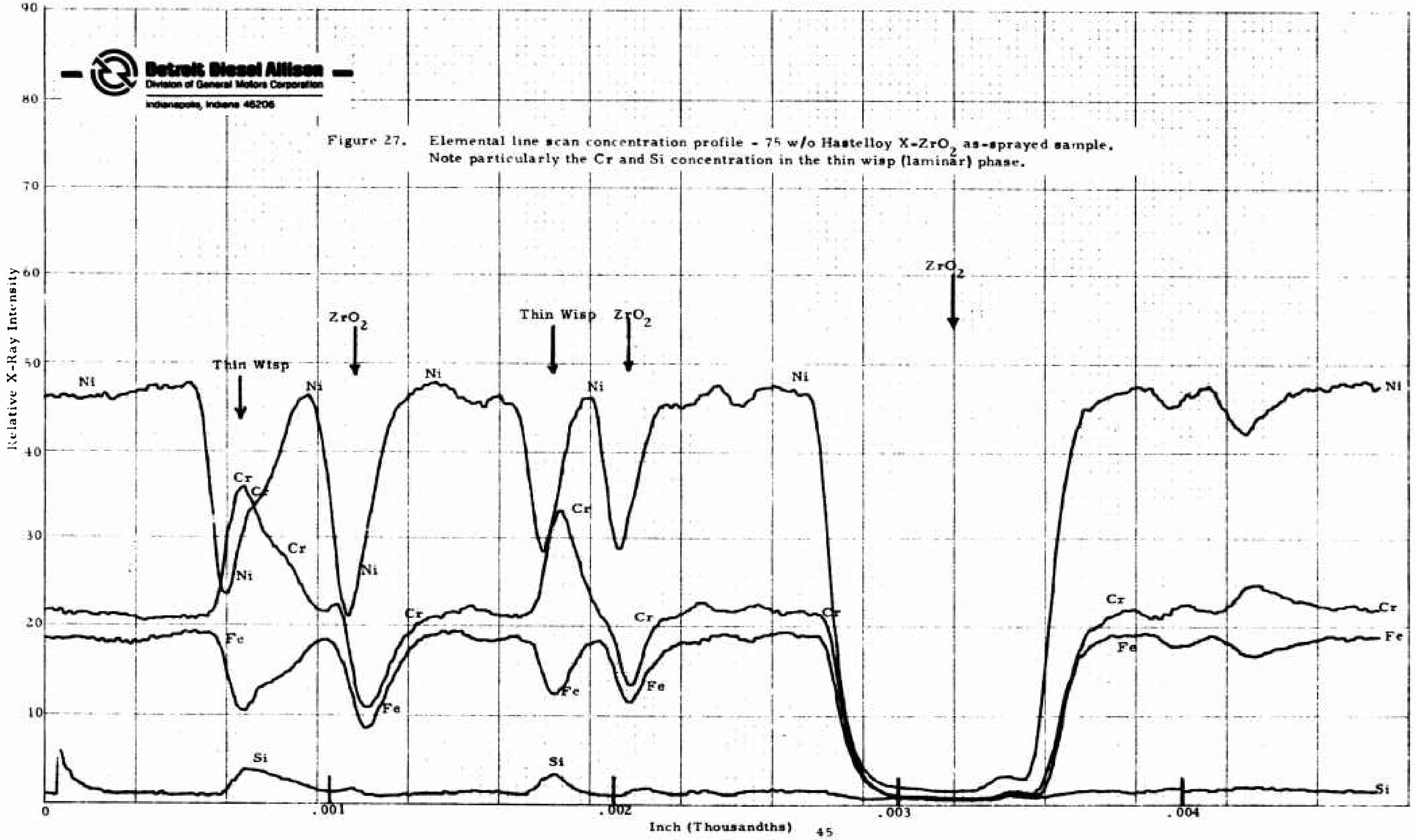


Figure 27. Elemental line scan concentration profile - 75 w/o Hastelloy X-ZrO_2 as-sprayed sample. Note particularly the Cr and Si concentration in the thin wisp (laminar) phase.

Figure 28. 75 w/o Hastelloy X-ZrO_2 material after 100 hours at 2200°F in an inert environment. Arrows denote line where element concentration profiles were determined. Note the second phase in the ZrO_2 particles. (Magn: 500X)

Detroit Diesel Allison
Division of General Motors Corporation
Indianapolis, Indiana 46206

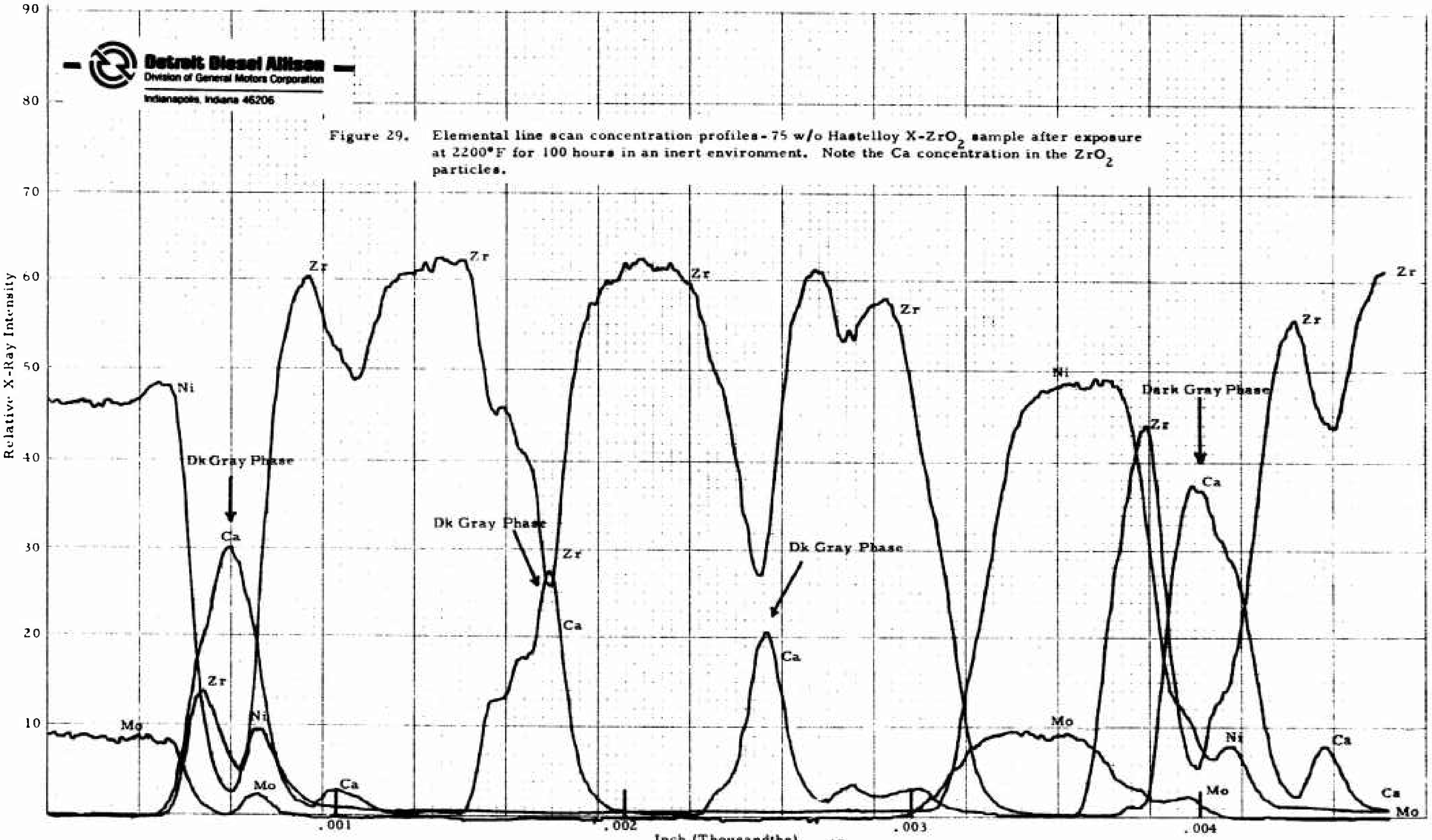


Figure 29. Elemental line scan concentration profiles - 75 w/o Hastelloy X-ZrO_2 sample after exposure at 2200°F for 100 hours in an inert environment. Note the Ca concentration in the ZrO_2 particles.

Detroit Diesel Allison
Division of General Motors Corporation
Indianapolis, Indiana 46206

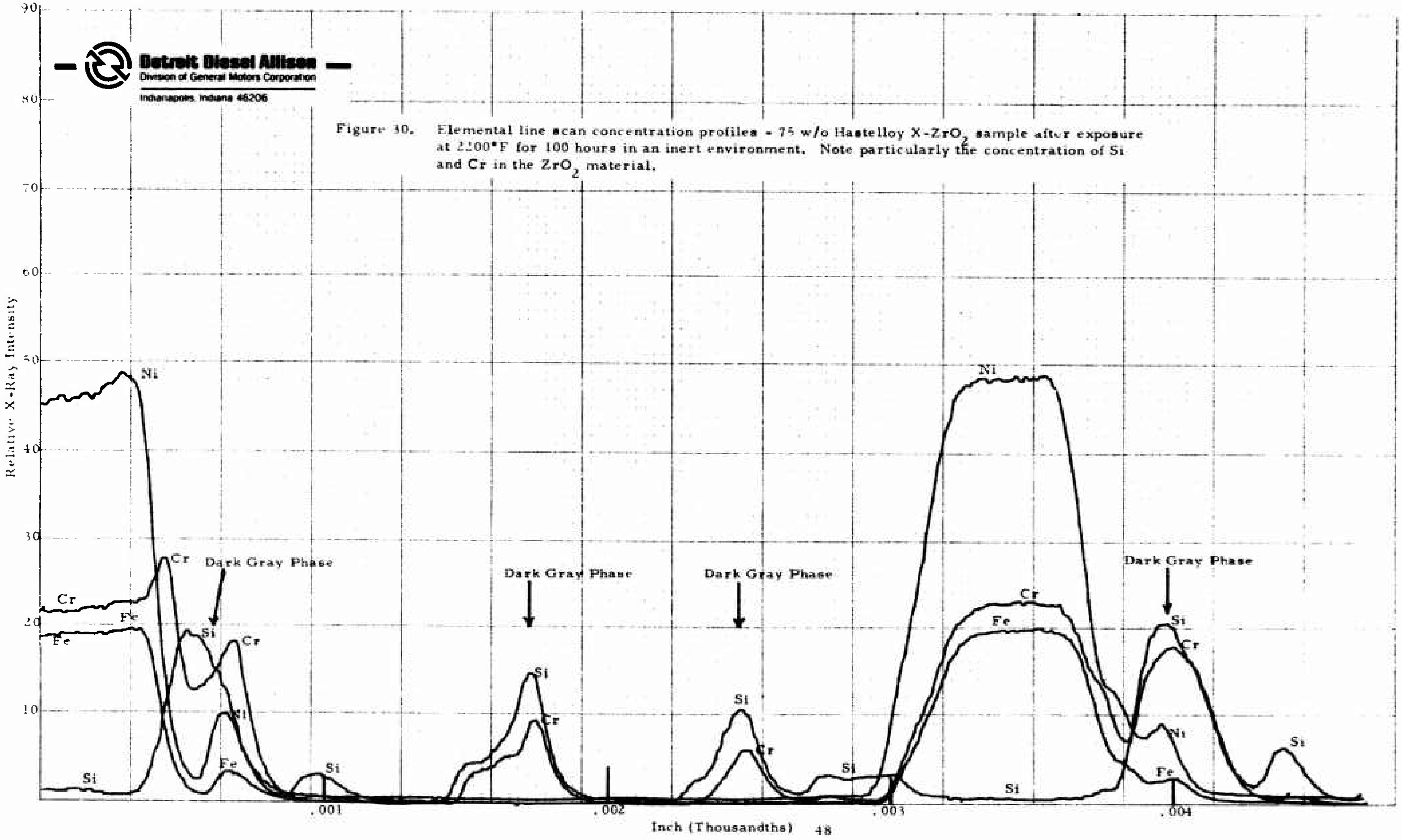


Figure 30. Elemental line scan concentration profiles - 75 w/o Hastelloy X-ZrO_2 sample after exposure at 2200°F for 100 hours in an inert environment. Note particularly the concentration of Si and Cr in the ZrO_2 material.

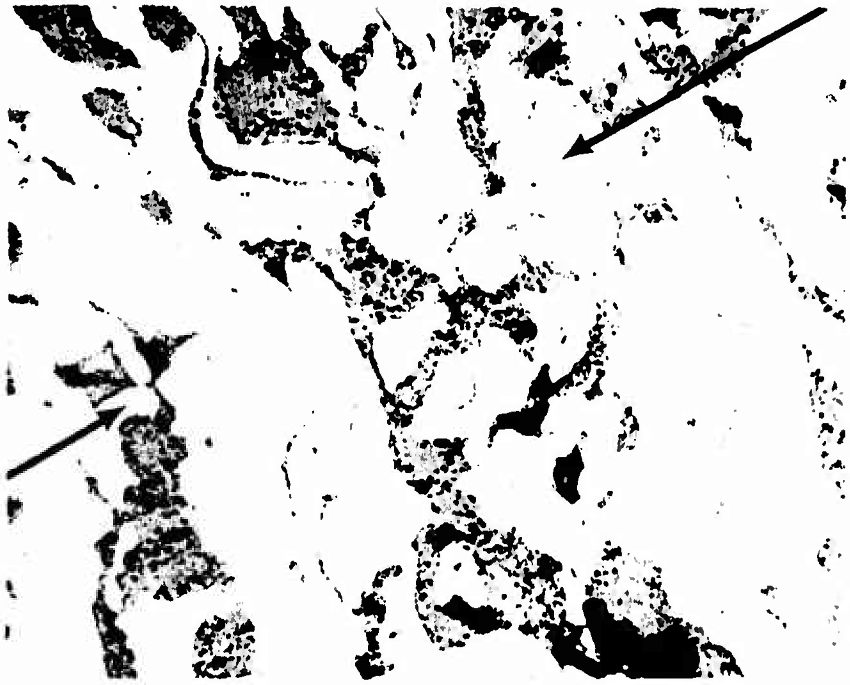


Figure 31. 50 w/o Hastelloy X-ZrO_2 material after 10 hours at 2200°F in an inert environment. Arrows denote line where element concentration profiles were determined. (Magn: 500X)

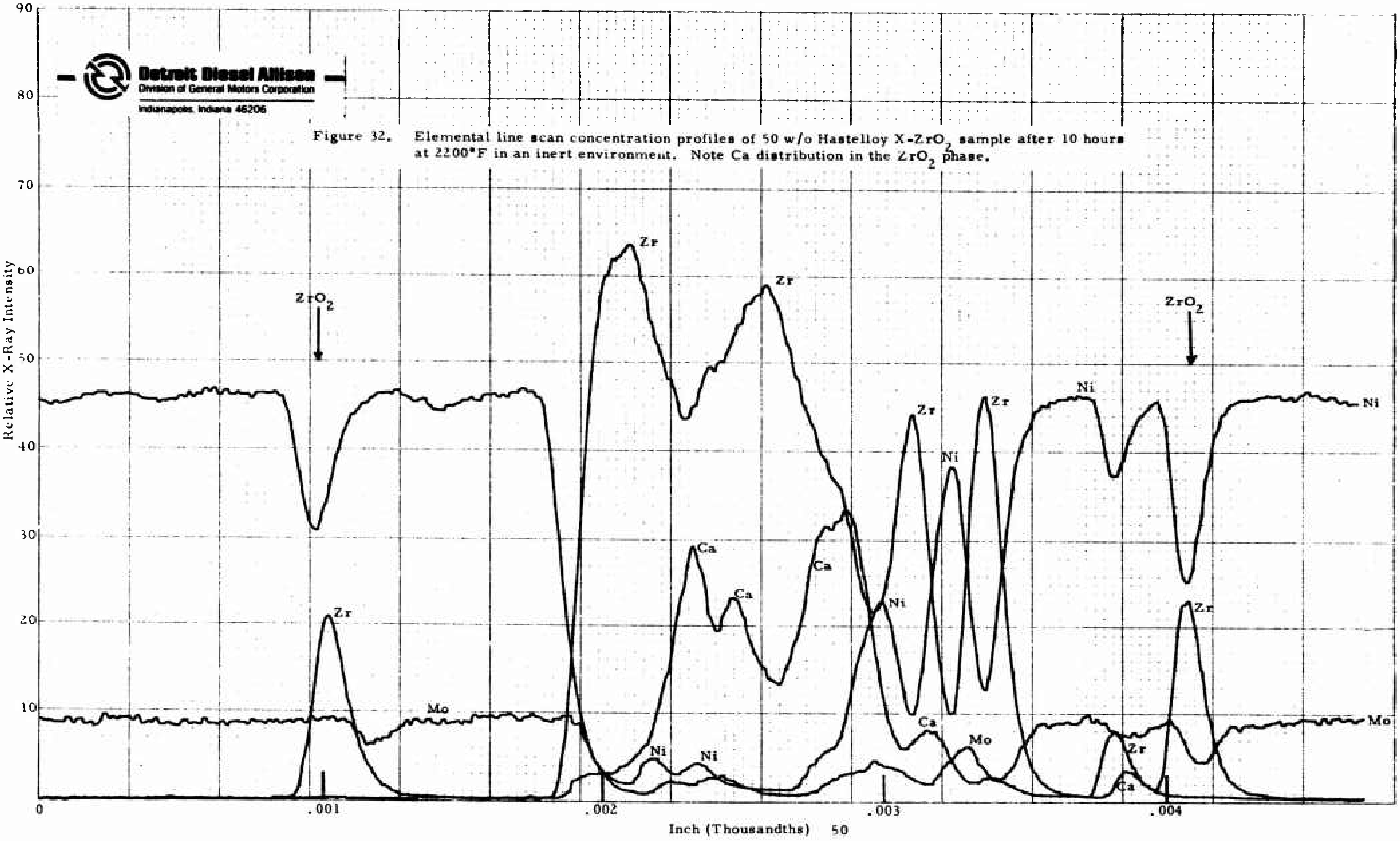


Figure 32. Elemental line scan concentration profiles of 50 w/o Hastelloy X-ZrO_2 sample after 10 hours at 2200°F in an inert environment. Note Ca distribution in the ZrO_2 phase.

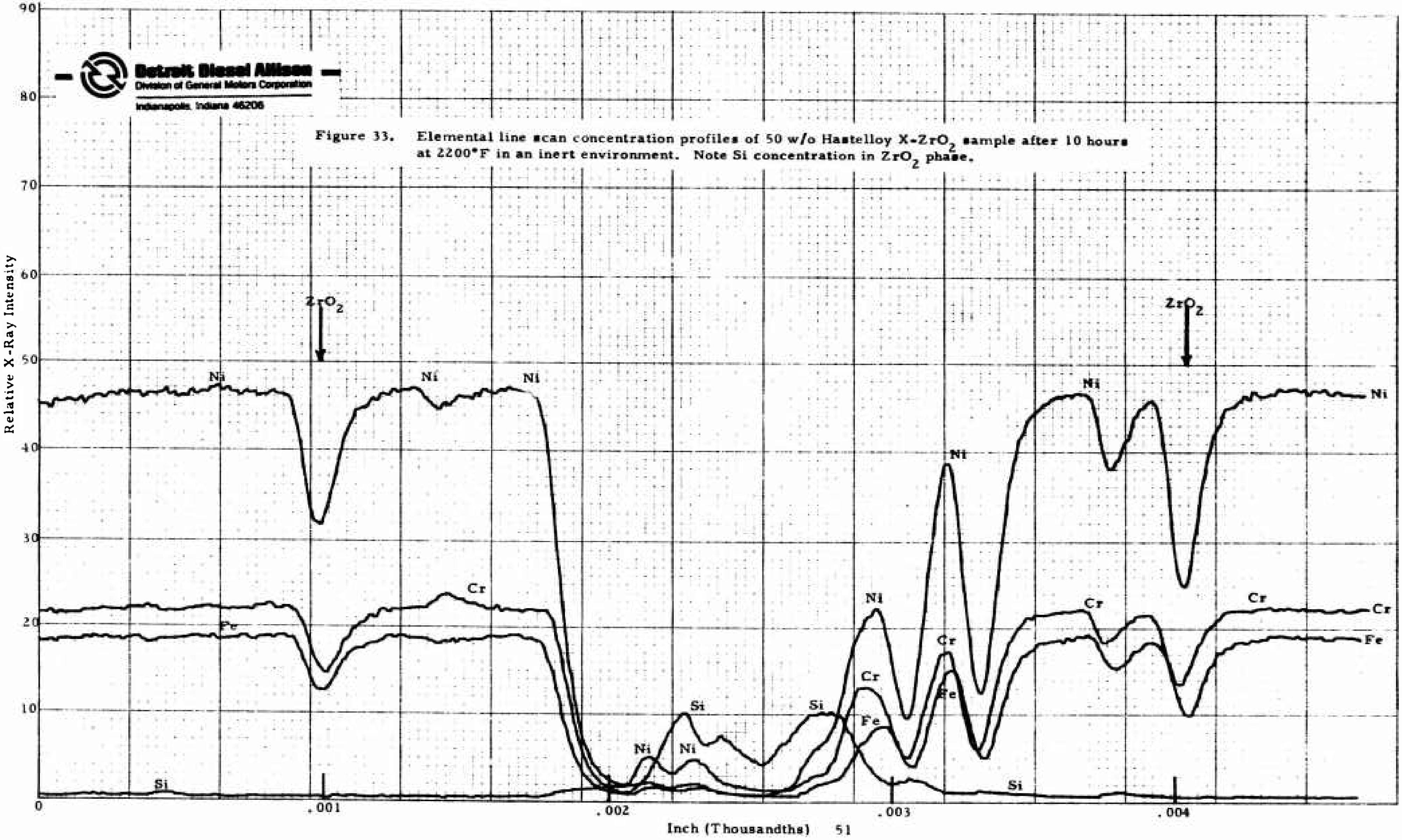


Figure 33. Elemental line scan concentration profiles of 50 w/o Hastelloy X-ZrO_2 sample after 10 hours at 2200°F in an inert environment. Note Si concentration in ZrO_2 phase.

2.5 Electron Microbeam X-ray Analysis (Cont'd)

Figures 34 and 35 show the precipitated phase found in the 50 w/o Hastelloy X material which had been exposed to a dynamic oxidizing environment for 7 hours at 2125°F. Two discrete particles were selected for electron microbeam X-ray analysis. Table VIII shows the results of these analyses. These results show that the precipitated particles were rich in chromium and molybdenum compared to Hastelloy X matrix material. Limited discussion and metallographic examination of selected specimens by laboratory personnel at Stellite Division, Cabot Corporation, Kokomo, Indiana failed to positively identify the particles. Further consideration of this Hastelloy X-Zirconia system would require positive identification and classification of the mechanism of formation of this phase.

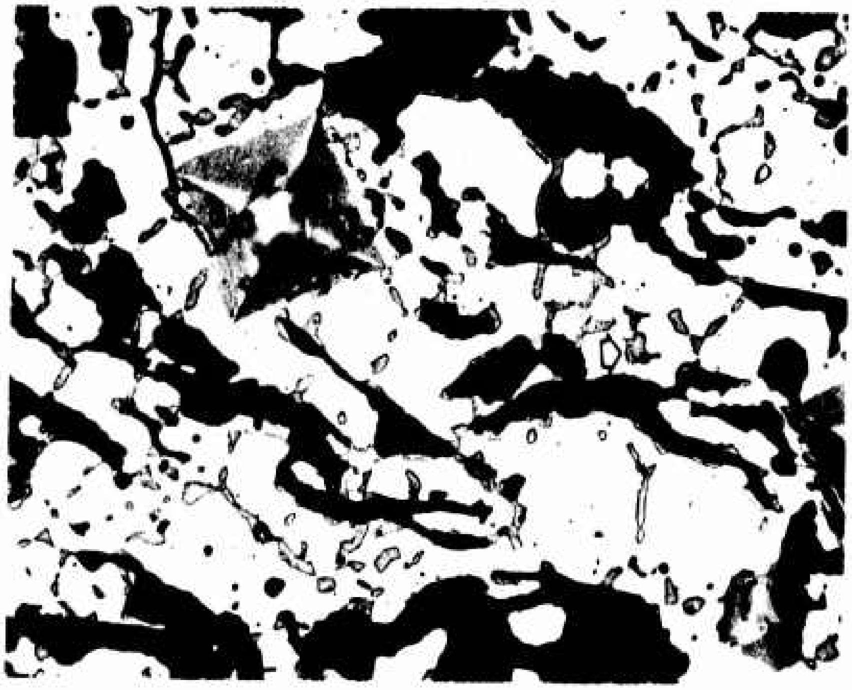
2.6 Fractography - SEM

Fracture surfaces of all failed tensile specimens were examined in the scanning electron microscope in order to characterize the fractures and identify, if possible, the strengthening mechanism of the various materials. Figures 36, 37, 38, and 39 depict the general features found in the 50 w/o Hastelloy X-ZrO_2 materials in the as-sprayed condition as well as after exposure at 2200°F for 10, 100 and 1000 hours.

These fractographs showed the as-sprayed material (Figure 36) failed by separation at particle and interphase boundaries and by fracture through the ZrO_2 phase. No ductile fracture of the Hastelloy X phase could be detected in the as-sprayed condition and fracture of the ZrO_2 material occurred in only a small percentage of that phase. The strength of the as-sprayed material appeared to depend primarily on the mechanical bonding of the particles. After exposure to the 2200°F environment (Figures 37, 38 and 39) the fracture changed so that ductile tensile characteristics were found in some areas of the metal phase. The two phase particulate nature of the ZrO_2 material became quite apparent. Fracture in the two phase ZrO_2 and separation at metal-ceramic boundaries were also observed. No significant change in fracture surface characteristics as a function of exposure time at 2200°F in the inert environment was observed.

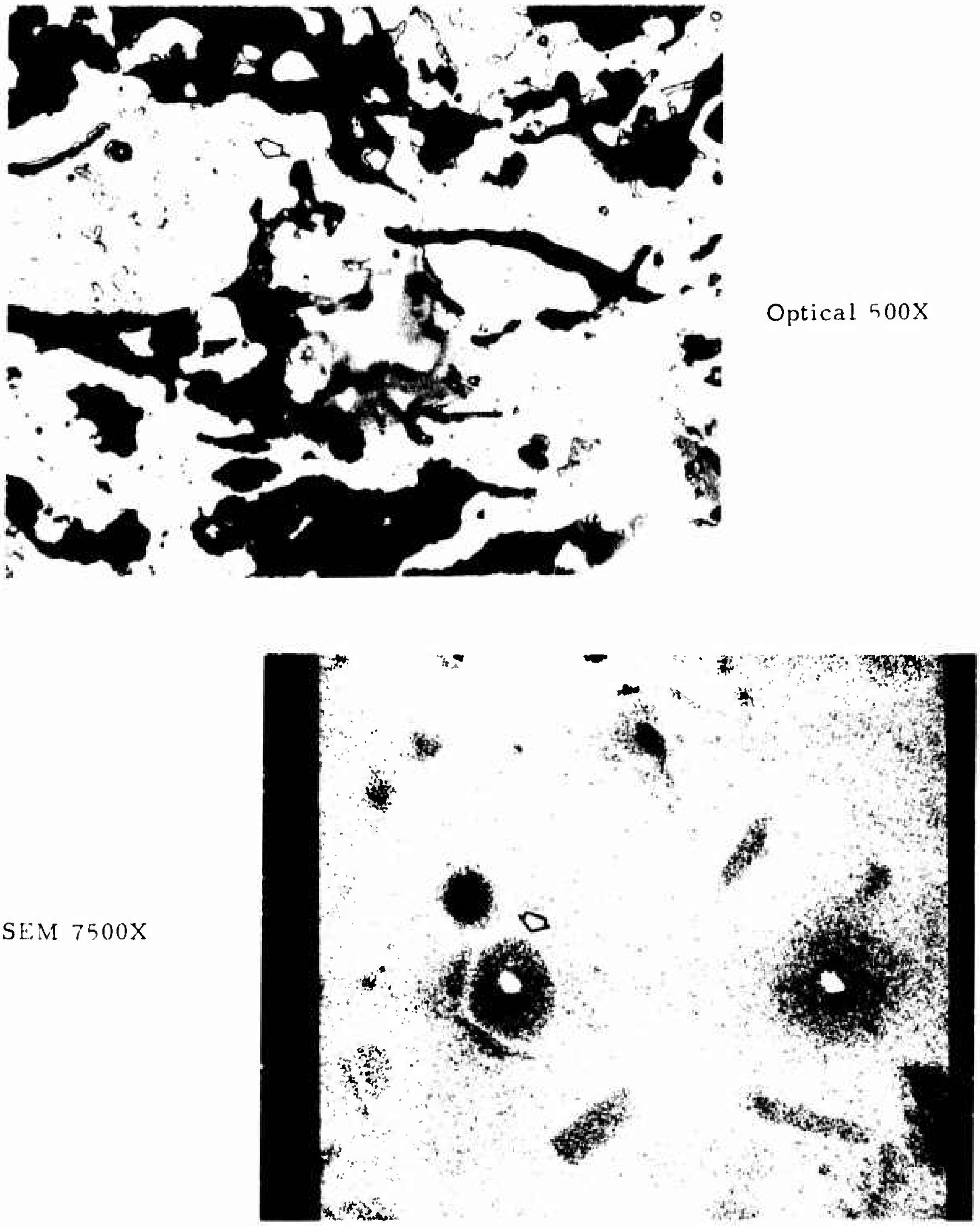
Figures 40, 41, and 42 show the fracture surfaces of the 75 w/o Hastelloy X-ZrO_2 material in the as-sprayed condition and after exposure to an inert environment for 10 and 100 hours, respectively. The as-sprayed specimen typically contained very limited areas of ductile tensile fracture in the Hastelloy X phase. Some brittle fracture characteristics were observed in the ZrO_2

Optical 500X



SEM 7500X

Figure 34. 50 w/o Hastelloy X-ZrO_2 material after exposure for 10 hours at 2200°F in an inert environment followed by exposure for 7 hrs at 2125°F in a dynamic oxidizing environment. Particle Number 1. Arrow denotes particle analyzed.



Optical 500X

SEM 7500X

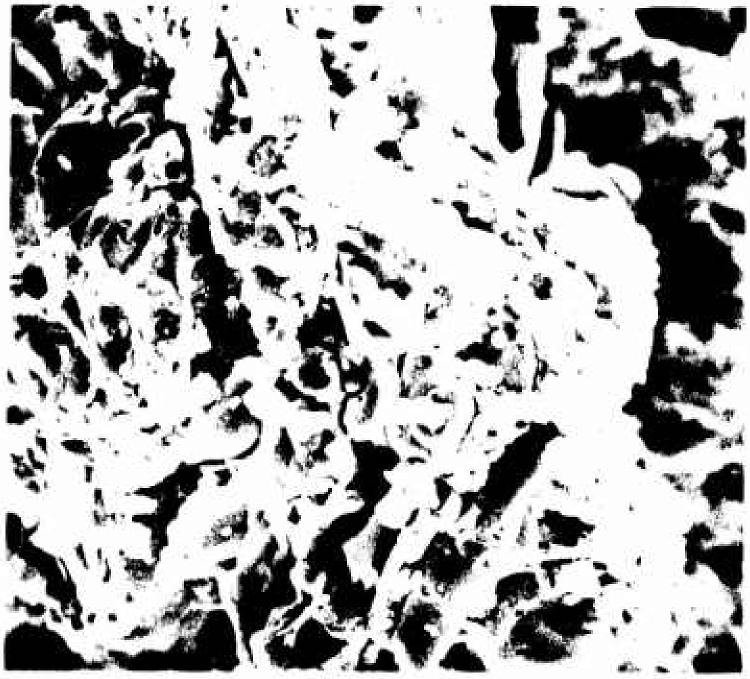
Figure 35. 50 w/o Hastelloy X-ZrO$_2$ after exposure for 10 hours at 2200°F in an inert environment followed by exposure for 7 hours at 2125 in a dynamic oxidizing environment (Particle Number 2) Arrow denotes particle analyzed.

Table VIII

Semiquantative Electron Microbeam X-ray Analysis of Precipitated Particles in 50 w/o Hastelloy X-ZrO_2 Material Exposed to a Dynamic Oxidation Environment for 7 Hours at 2125°F

	% Mo	% Cr	% Fe	% Ni
Particle 1	22	35	11	34
Matrix 1	9	22	28	59
Particle 2	18	22	18	44
Matrix 2	8	18	26	49
Hastelloy X Tubing (nominal analysis)	9	22	18	49

1000X



3000X

Figure 36. Fracture surface of 50 w/o Hastelloy X-ZrO_2 (Group A) tensile specimen in the as-sprayed condition. These are two significant features in this fractograph, the interparticle or interphase separation and the fracture through the ZrO_2 phase. The absence of any ductile tensile fracture of the Hastelloy X phase is also noted.

3000X

10,000X

Figure 37. Fracture surface of 50 w/o Hastelloy X-ZrO_2 (Group A) tensile specimen which had been exposed for 10 hours at 2200°F in an inert environment before testing. This fractograph shows both the ductile tensile fracture of the Hastelloy X phase and the particulate nature of the ZrO_2 phase. Interparticle or interphase separation, tensile fracture of the Hastelloy X phase and fracture across the ZrO_2 phase were all found in this material.

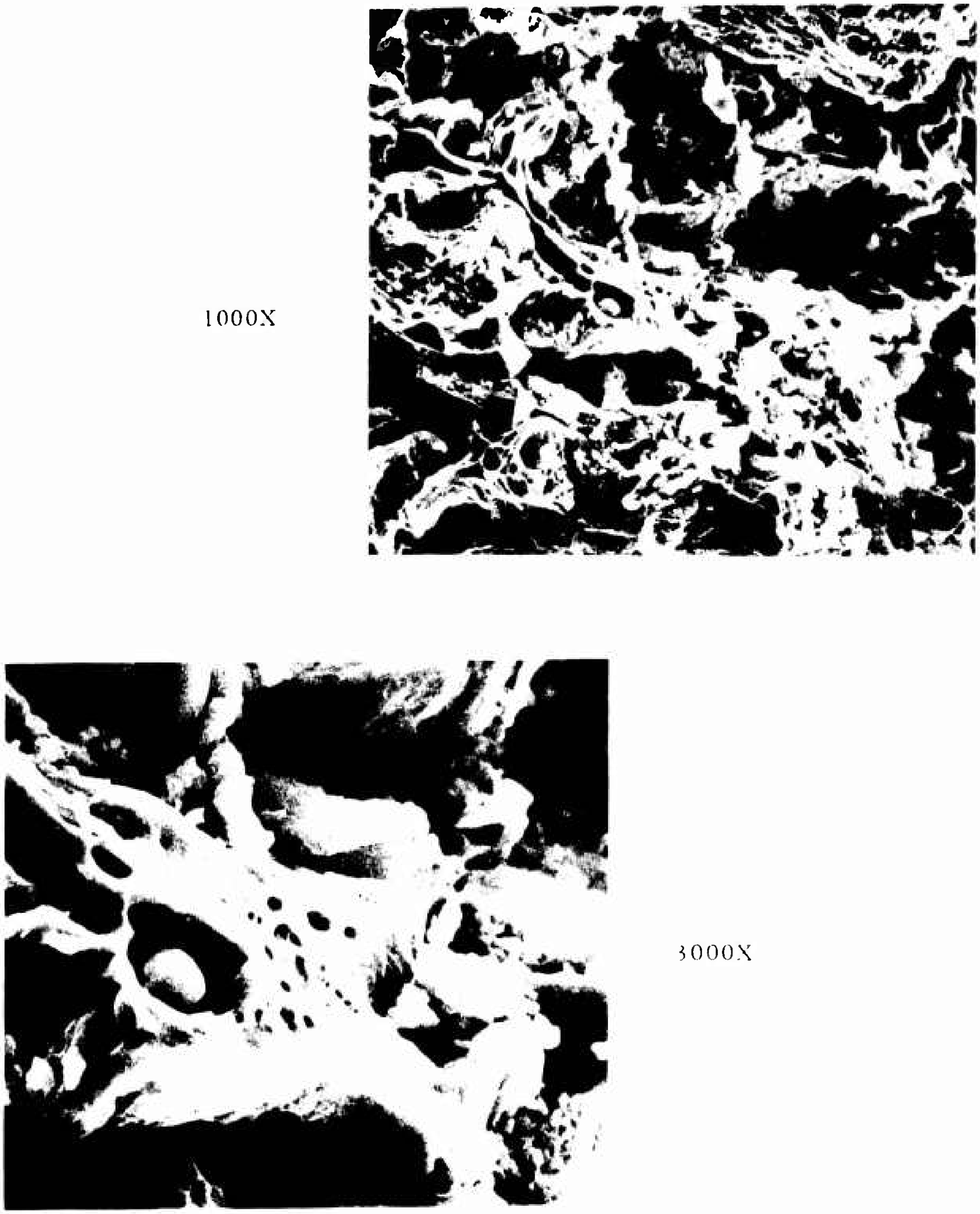
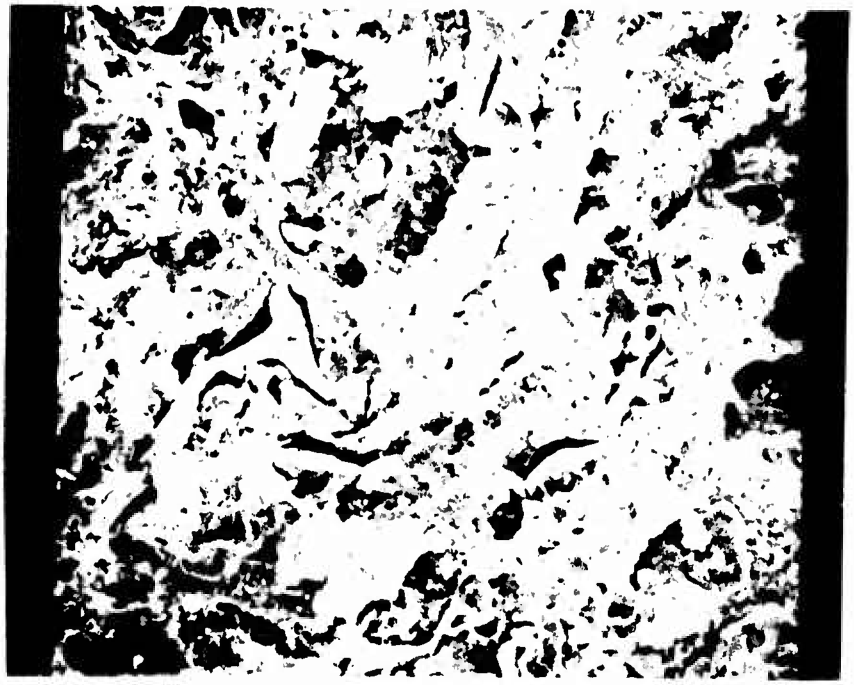


Figure 38. Fracture surface of 50 w/o Hastelloy X-ZrO_2 (Group A) tensile specimen which had been exposed for 100 hours at 2200°F in an inert environment. Ductile tensile fracture of the Hastelloy X phase is clearly shown in these fractographs.



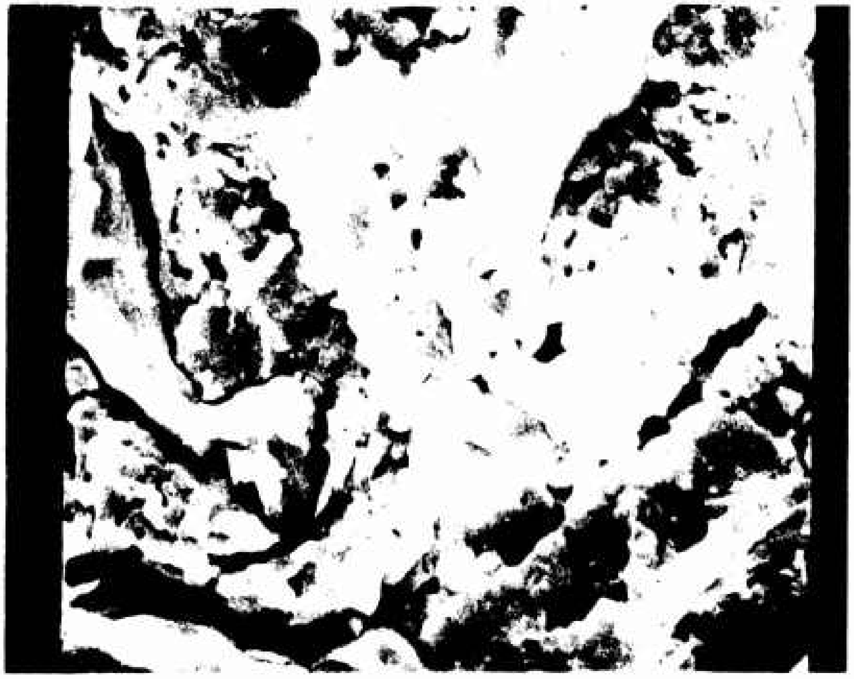


Figure 39. Fracture surface of 50 w/o Hastelloy X-ZrO_2 (Group A) tensile specimen after exposure for 1000 hours at 2200°F, in an inert environment. Interparticle fracture of the ZrO_2 phase was noted, however only slight evidence of ductile tensile fracture was found in the metal phase.

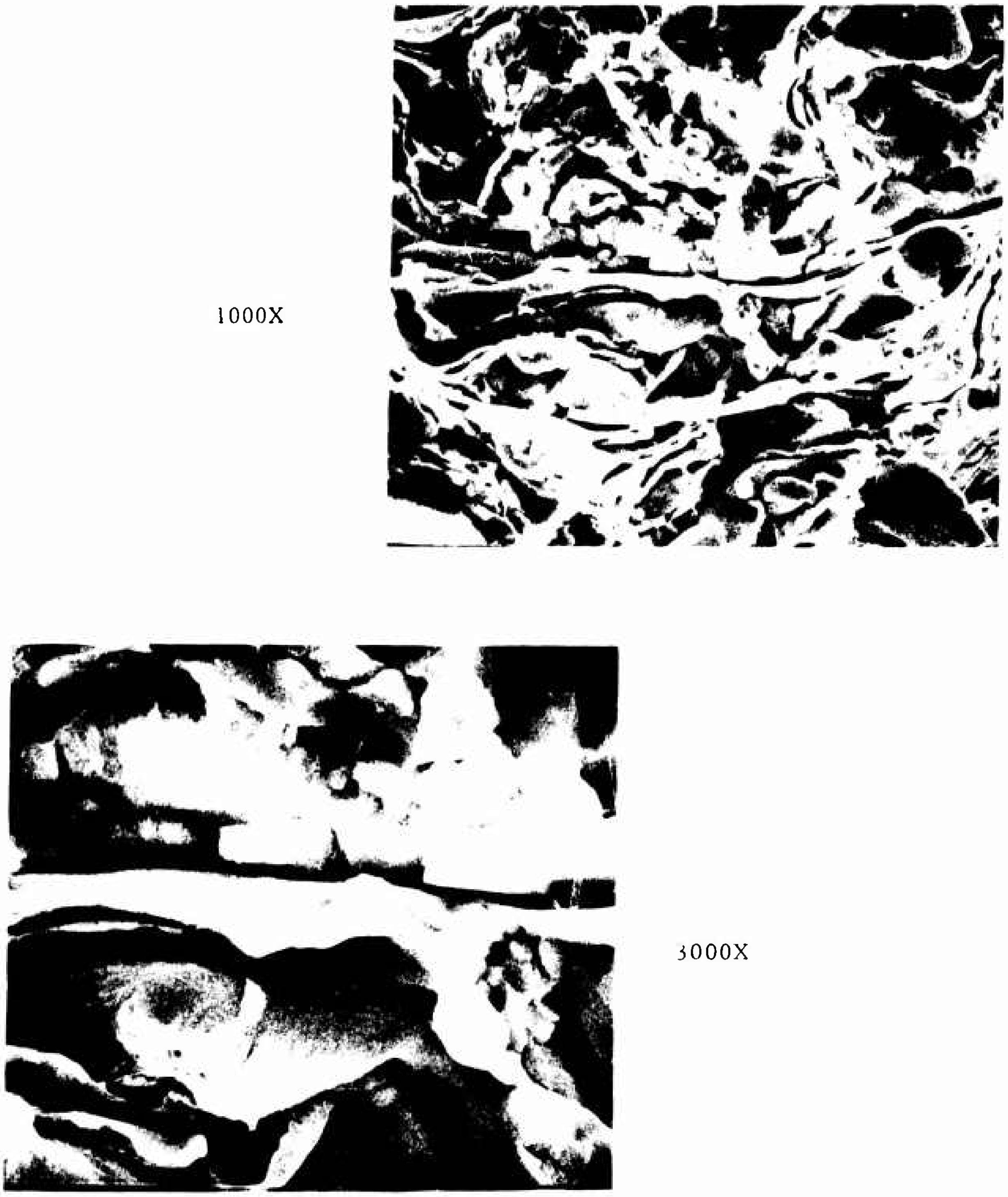


Figure 40. Fracture surface of as-sprayed 75 w/o Hastelloy X-ZrO$_2$ tensile Laminar nature also shown in the optical photomicrographs is seen here. A brittle cleavage fracture is also shown occurring in the ZrO$_2$ platelets.

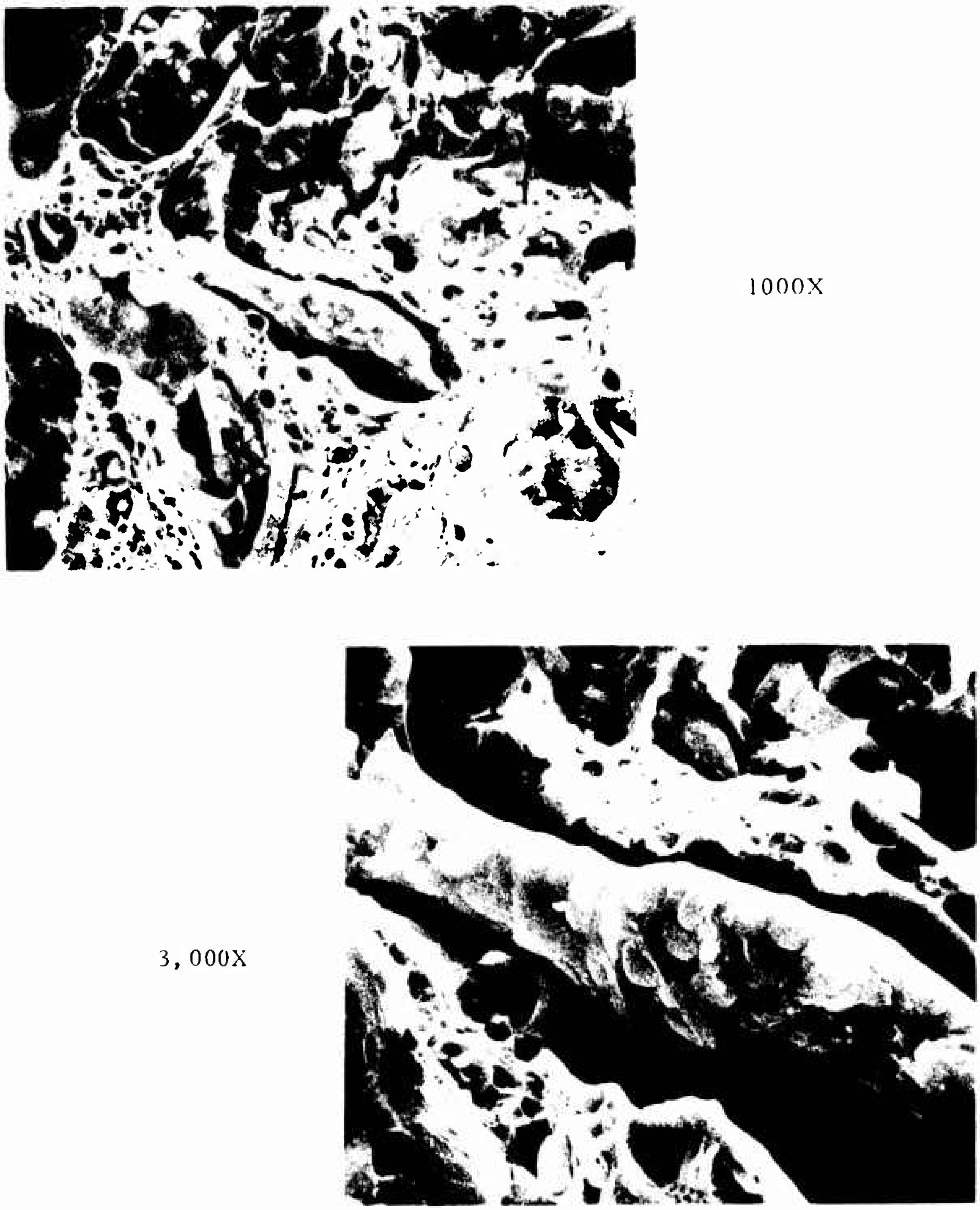
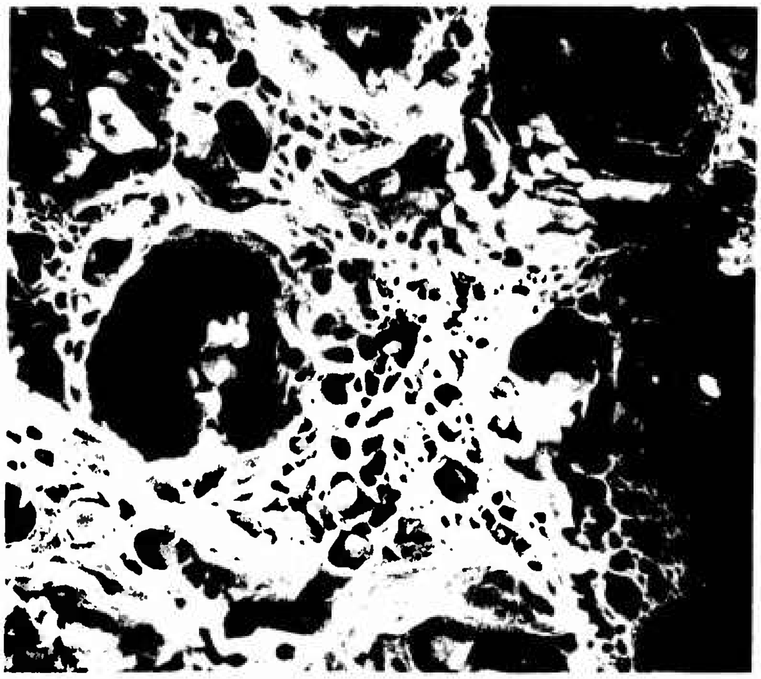
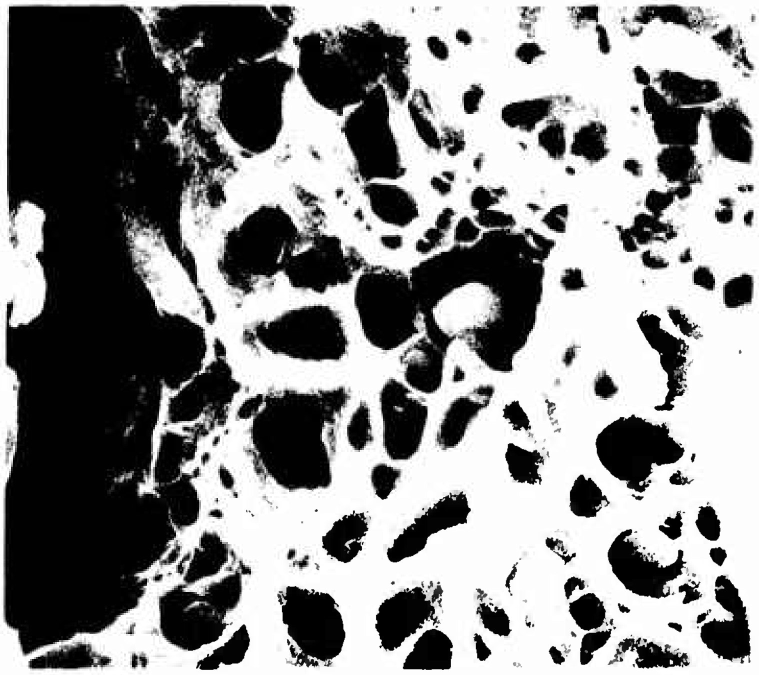


Figure 41. Fracture surface of 75 w/o Hastelloy X-ZrO_2 tensile specimen which had been exposed for 10 hours at 2200°F in an inert environment before testing. The two-phase nature of the ZrO_2 particles is very apparent.

1000X





3,000X

Figure 42. Fracture surface of 75 w/o Hastelloy X-ZrO_2 tensile specimen which had been exposed for 100 hours at 2200°F in an inert environment before testing. Predominate features noted are ductile tensile fracture in the Hastelloy X phase and the two-phase nature of the ZrO_2 component.

2.6 Fractography - SEM (Cont'd)

phase, however, this material seems to owe most of its strength to mechanical bonding between individual particles. After being exposed to the 2200°F inert atmosphere environment for 10 and 100 hours, the fracture surfaces of failed tensile specimens exhibited extensive ductile tensile fracture characteristics in the metal phase while brittle fracture, which was also found in the as-sprayed material, was observed in the ZrO_2 phase, the two phase nature of the ZrO_2, which was observed in the metallographic analysis (Section 2.4) was very obvious in the fractographic analysis. It would appear that the metal phase is the primary source of strength in these specimens.

3.0 SUMMARY AND CONCLUSIONS

A summary of the work performed during this contract is as follows:

- Mechanical mixtures of 50 and 75 w/o Hastelloy X-ZrO_2 powders were arc plasma sprayed onto a Hastelloy X mandrel into configurations suitable for uniaxial tensile and ballistic impact testing. These rough sprayed specimens were subsequently machined to finish dimensions for testing.
- Specimens of each mixture of ZrO_2 and Hastelloy X were exposed to an inert (20 - 30μ argon) environment for 10, 100, and 1000 hours and then tested to determine the effect of such exposures as the tensile and ballistic impact properties when compared to material tested in the as-sprayed condition. Another group of specimens was subjected to a dynamic oxidizing environment for 7 and 16 hours at 2125°F after being exposed to the inert environment for 10 hours at 2200°F. These specimens were then tensile and ballistic impact tested.
- All failed uniaxial tensile specimens were examined metallographically and by scanning electron microscopy to determine microstructural and fractographic characteristics of the materials.
- Electron microbeam X-ray analyses were conducted on selected samples to establish chemical element distributions in various phases found in both the Hastelloy X and ZrO_2 material.

The following conclusions were arrived at after analysis of test results.

- The room temperature tensile properties of the 50 and 75 w/o Hastelloy X-ZrO_2 materials increased from 18 to 32 ksi and 38 to 78 ksi, respectively as a result of exposure to an inert environment at 2200°F. The increase in strength is believed to be due to sintering effects in the Hastelloy X phase which was verified by both metallographic and fractographic analyses.
- Exposure of the 50 w/o Hastelloy X-ZrO_2 material to a dynamic oxidizing environment for times up to 16 hours had little effect on the relatively low room temperature tensile strength.

- Exposure of the 75 w/o Hastelloy X-ZrO_2 material to a dynamic oxidizing environment for times up to 16 hours caused a general decrease in the room temperature tensile strength from 78 ksi down to 57 ksi.

- Room temperature ballistic impact cracking threshold energy of both compositions increased from approximately 1 foot-pound (as-sprayed condition) to the 5-6 foot-pound energy level after exposure to an inert evnironment at 2200°F.

- Elevated temperature (2100°F) ballistic impact cracking threshold energy increased from 2 foot-pounds (as sprayed) to 5 foot-pounds for the 75 w/o Hastelloy X-ZrO_2 material, as a result of the inert environment exposure at 2200°F. However, the 50 w/o material only increased from less than 1 foot-pound (as sprayed) to a maximum of 2 foot-pounds after the 2200°F treatment. This effect was similar to the room temperature tensile property behavior.

- Exposure to the 2125°F dynamic oxidation environment lowered the ballistic impact cracking energy threshold from the 5-6 foot-pound level down to the 2-3 foot-pound level in the 50 w/o Hastelloy X-ZrO_2 material but had no effect on the cracking energy threshold of the 75 w/o Hastelloy X-ZrO_2 material.

- Exposure of the 50 w/o Hastelloy X material to a dynamic oxidizing environment at 2125°F caused the precipitation of a secondary phase in the Hastelloy X material. This phase is thought to be responsible for the decrease in room temperature ballistic impact properties in this material.

- Chemical element segregations of calcium, chromium, and silicon in the ZrO_2 particles were produced by exposure at 2200°F. There was no apparent correlation between these segregations and mechanical properties. No explanation for the mechanism of these segregations is known at this time.

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