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EXPLORATORY INVESTIGATION OF YTTRIUM, LANTHANUM, AND HAFNIUM COATINGS FOR NITRIDATION PROTECTION OF CHROMIUM ALLOYS

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16. Abstract

Chromium alloys were coated with yttrium, lanthanum, and hafnium, either singly or in combination, by pack cementation. Based on ductile-brittle transition temperature, a complex Cr + Y + La coating offered the most potential for protecting chromium alloys from nitrogen embrittlement. For example, the transition temperature for a chromium - 0.17-wt %-yttrium substrate coated with this complex Cr + Y + La coating was 450 K (350° F) after isothermal exposure in air at 1420 K (2100° F) for 200 hours, compared to a transition temperature of 840 K (1050° F) for the similarly exposed uncoated substrate. Simple yttrium coatings are more attractive as coatings for chromium alloys than simple lanthanum and halfnium coatings.

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SUMMARY

An investigation was conducted to determine the effectiveness of simple yttrium (Y), lanthanum (La), and hafnium (Hf) coatings as well as more complex coatings containing chromium (Cr), yttrium, and/or lanthanum in preventing nitridation embrittlement of chromium alloys during high-temperature air exposure. Pack cementation was used as the primary method of coating application. Air-exposure tests consisted of heating in static air at 1420 K (2100° F) for 200 hours. The primary means of evaluation was the determination of the ductile-brittle bend transition temperature for specimens after high-temperature air exposure.

Results showed that a simple yttrium coating offered more potential for protecting Cr - 0.17-weight-percent yttrium (Cr-0.17Y) from nitrogen embrittlement than either the simple La or Hf coatings. The ductile-brittle transition temperature (DBTT) of yttrium-coated specimens was 465 K (375° F) after 100 hours air exposure at 1420 K (2100° F), compared to a transition temperature of 365 K (200° F) for the recrystallized starting material. The DBTT of similarly tested specimens with lanthanum and hafnium coatings was from 70 to 150 K (125° to 200° F) above that for the yttrium coating.

Results from cyclic air-exposure tests and impact tests on a Cr-7Mo-2Ta-0.1C-0.2 (Y + La) substrate indicated that yttrium coatings were also protective on this type of highly alloyed substrate.

A complex Cr-Y-La coating offered the most resistance to nitridation embrittlement of any coating investigated in the current program. For example, when protected with the complex coating the impact transition temperature of the highly alloyed substrate Cr-7Mo-2Ta-0.1C-0.2(Y + La) only increased by 111 K (200° F) after 200 hours in air at 1420 K (2100° F).

X-ray diffraction results indicated formation of such surface oxides as Cr_2O_3, $LaCrO_3$, and Y_2O_3 after high-temperature air exposure of the coated specimens. Electron microprobe results revealed yttrium associated with oxygen in coating and oxide layers. Very little if any yttrium or oxygen diffused into alloy substrates during high-temperature air exposure. Electron microprobe results revealed chromium nitride in uncoated and exposed specimens. Nitrogen was not detected in Y-coated and exposed specimens.

INTRODUCTION

Chromium alloys, because of their relatively low densities and high melting points, offer potential for use in advanced air-breathing engines as stator vanes or turbine blades where high operating temperatures are required. Although there has been a renewed interest in Cr over the past several years, the high ductile-brittle transition temperatures (DBTT) of high-strength Cr alloys and their susceptibility to nitrogen embrittlement upon exposure to air at elevated temperatures present severe limitations to their use in advanced air-breathing engines.

Results from a previous coating study (ref. 1) of aluminide, boride, and silicide coatings indicate than an iron-modified silicide coating offers the most potential as a protective coating against nitrogen embrittlement of Cr-base alloys. However, the growth of an unprotective sub-silicide layer after extended exposure was observed, which may limit the use of this coating. Thus, more protective coatings are still being sought.

The use of yttrium as a scavenger of oxygen during induction melting of Cr (ref. 2) and as an alloy addition to improve the oxidation and nitridation resistance of Cr is well documented (refs. 3 and 4). The improved nitridation resistance of Cr upon alloying with very small amounts of Y is postulated to result from an improvement in the adherence of the protective Cr_2O_3 scale normally formed on Cr during high-temperature air exposure (ref. 3). The Cr_2O_3 oxide layer is believed to act as a barrier to nitrogen and thus prevent diffusion of nitrogen into the chromium substrate, causing embrittlement. Previous studies under NASA contract have also explored yttrium or complex yttrium coatings on Cr-base alloys. Attempts to coat Cr with Y by a metalliding process were unsuccessful due to oxygen contamination in the metalliding cell and because of the low solubility of Y in Cr (ref. 5). The best coating system identified in a second study (ref. 6) was made by first chromiding in a lithium fluoride - chromium fluoride (LiF - CrF_3) metalliding bath, followed by plasma spraying of a Cr - 10-volume-percent Y_2O_3 powder mixture, and then preoxidation in pure oxygen. Coating effectiveness was attributed to Li reducing the parabolic oxidation rate and to Y_2O_3 which also reduced the oxidation rate and promoted scale adherence. This coating was effective under isothermal exposure conditions, but suffered from excessive blistering of the coating-oxide layer under cyclic exposure conditions where relatively high cooling rates were experienced. The ductile-brittle transition temperature also increased substantially under these conditions.

The purpose of the present program was to explore the effectiveness of pack-cementation-deposited Y for nitridation protection of Cr-base alloys subjected to air exposure at 1420 K (2100° F).

Lanthanum; hafnium; and several complex Cr + Y, Cr + La, Y + La, and Cr + Y + La coatings were also explored. Lanthanum was chosen because it forms an oxide similar to yttrium, and hafnium was chosen because it is also a strong oxide former. Coatings were applied by pack cementation on bend specimens cut from Cr-0.17Y, Cr-5W-0.18Y, and Cr-7Mo-2Ta-0.1C-0.2(Y + La) alloy sheet; all compositions in weight percent. In all cases, DBTT after high-temperature air exposure was the primary criterion of coating effectiveness and was supplemented by metallography and electron microprobe evaluation.

EXPERIMENTAL PROCEDURE

Substrate Materials

Three chromium-base alloys were used as substrates for this study. Cr-0.17Y was prepared by arc melting 80-gram (0.18-lb)[1] buttons, drop casting into a square-cross-section water-cooled copper mold, and subsequently fabricated to approximately 0.89-millimeter (0.035-in.) thick sheet by rolling. Melting and fabrication procedures have been described previously (ref. 7).

A Cr-5W-0.18Y alloy was obtained as approximately 0.63-millimeter (0.025-in.) thick sheet. This alloy was prepared by induction melting as a 45.4-kilogram (100-lb) ingot followed by extrusion and rolling to sheet. Details of melting and fabrication prodecures can be found elsewhere (ref. 8).

Two lots of Cr-7Mo-2Ta-0.1C-0.2 (Y + La) alloy were obtained for this study. Alloy sheet approximately 1.65 millimeters (0.065 in.) thick was used for bend test specimens. The alloy was prepared by induction melting as a 45.4-kilogram (100-lb) ingot followed by extrusion to sheet bar and rolling to sheet. Alloy plate approximately 9.53 millimeters (0.375 in.) thick was cut directly from an extruded sheet bar from a second lot of material and used for impact specimens. Melting and fabricating conditions have been described previously (ref. 9).

Chemical analysis of the substrate alloys are listed in table I.

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[1] The customary English System of units was used for the principal measurements and calculations. However, SI units will appear as the primary system in the report with the customary units in parentheses.

TABLE I. - CHEMICAL ANALYSIS AND GRAIN SIZE OF CHROMIUM ALLOY SUBSTRATES

Alloy nominal composition, wt %	W	Mo	Ta	Y	La	C	O	N	H	S	P	As-recrystallized grain size, cm
	Content, wt %						Content, ppm					
Cr-0.17Y	----	----	----	0.17	----	0.006	51	6	5	--	--	6.7×10^{-3}
Cr-5W-0.18Y	5.02	----	----	.18	----	.012	95	24	12	20	20	2.4
Cr-7Mo-2Ta-0.1C-0.2(Y + La) sheet - bend specimens	----	7.12	2.14	.18	0.12	.096	30	37	31	<10	<20	3.3
Cr-7Mo-2Ta-0.1C-0.2(Y + La) plate - impact specimens	---	6.87	2.16	.10	.11	.090	46	45	13	<10	<20	3.6

Specimen Preparation

Bend specimens measuring 8 millimeters (0.3 in.) by 23 millimeters (0.9 in.) were cut from the Cr-0.17Y and Cr-5W-0.18Y alloy sheet, with the long dimension of the specimen parallel to the rolling direction. Bend specimens 13 millimeters (0.5 in.) by 38 millimeters (1.5 in.) were cut in a similar manner from the Cr-7Mo-2Ta-0.1C-0.2 (Y + La) sheet. Cylindrical impact specimens, as shown in figure 1, were machined from the plate material of this alloy with the longitudinal axis parallel to the extruding direction. After cleaning in hydrochloric acid to remove any possible surface contamination resulting from fabrication, bend specimens from Cr-0.17Y and Cr-5W-0.18Y alloys were recrystallized by annealing at 1420 K (2100° F) for 1 hour in high-purity argon. The Cr-7Mo-2Ta-0.1C-0.2(Y + La) alloy for bend and impact specimens was recrystallized by a 1-hour anneal at 1590 K (2400° F). The average grain size for each as-annealed alloy substrate is listed in table I.

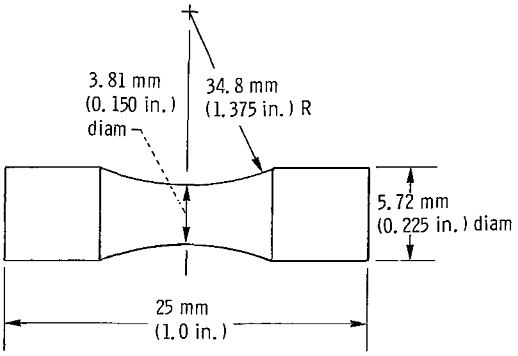


Figure 1. - Cylindrical impact specimen design.

Coating Procedure

Pack cementation was used as the primary coating process to apply the Y, La, and Hf coatings. The details of this coating procedure have been previously described (ref. 1). Initial coating packs included approximately 25-volume-percent coating element, potassium chloride (KCl) carrier (4 wt %), and 75-volume-percent aluminum oxide (Al_2O_3) as a filler. After heating specimens in the pack for 4 hours at 1255 K (1800° F) in an argon atmosphere, it was found that Al was deposited on the specimens. Apparently, the strong oxide formers Y, La, and Hf had reduced Al_2O_3, resulting in deposition of Al on the test specimens. Because of this, all subsequent packs consisted only of the coating element and the carrier (KCl). In addition, it was necessary to reduce the coating temperature to 1090 K (1500° F) to prevent sintering of the pack. Coating times ranged from 4 to 16 hours. Since Y and La have extremely low solubilities in Cr (ref. 10), the amount of coating that could be applied was limited. In order to increase the amount of Y or La in the coating, a porous layer of Cr was deposited on the surface of the alloy specimens by electroplating. The porous layer increased the surface area, thus allowing more Y and La to be deposited on the surface. Electroplating was conducted at room temperature for 1 hour in a solution of 250 grams of CrO_3 per liter of water. A potential of 5 volts was applied between the specimen and a lead anode, which resulted in a current density of approximately 0.5 ampere per square centimeter. A 0.05-millimeter (0.002-in.) layer of Cr was deposited on the specimens. To ensure adherence of the electroplated Cr layer, specimens were annealed for 1 hour at 1255 K (1800° F) in vacuum. Then Y and La were subsequently applied consecutively by pack cementation. A total of seven coating systems were explored. These included simple coatings of Y, La, and Hf and complex coatings including Cr + Y, Cr + La, Y + La, and Cr + Y + La.

Air-Exposure Tests

Air-exposure tests were conducted at 1420 K (2100° F) for times of 100 hours for screening purposes and 200 hours under isothermal and cyclic conditions for final evaluation. Tests were conducted in a horizontal alumina tube furnace using alumina supports for the specimens. During the first 20 hours of cyclic testing, specimens were heated at 1420 K (2100° F) in approximately $1\frac{1}{2}$ minutes and cooled to room temperature in about 4 minutes every 2 hours. Thereafter, specimens were thermal cycled after every 20 hours of exposure for the remainder of the test. No observable reaction occurred between coated specimens and the alumina supports.

Evaluation

The primary evaluation of coating effectiveness was by determination of the bend DBTT after high-temperature air exposure. Bend tests were conducted on three specimens from each coating series at a crosshead speed of 25 millimeters (1.0 in.) per minute over a bend radius approximately four times the as-coated specimen thickness (4T). The bend DBTT is defined as the lowest temperature at which a specimen could be bent 100°, the limiting angle of the bend fixture. Because of the limited number of specimens, the DBTT could be determined only within 15 to 30 K (25° to 50° F).

Micro Izod impact tests were conducted on cylindrical specimens machined from plate of a Cr-7Mo-2Ta-0.1C-0.2(Y + La) alloy. The impact transition temperature is defined as the lowest temperature at which a specimen could absorb the maximum energy of the impact tester. Specimens were heated by torch, and specimen temperature was determined by means of a Chromel-Alumel thermocouple mechanically attached to the specimen. No visible reaction occurred between the thermocouple and the impact specimens.

In addition to the mechanical property tests described, specimens of all systems were further evaluated by metallography, microhardness, X-ray diffraction, and electron microprobe analysis.

RESULTS AND DISCUSSION

Screening of Y, La, and Hf Coatings

Ductile-brittle transition temperature. - The effectiveness of the Y, La, and Hf coatings in protecting a Cr-0.17Y alloy substrate was measured primarily by DBTT. Pertinent test data are summarized in table II. Figure 2 shows the transition temperatures for the unexposed substrate and for uncoated and coated specimens after isothermal air exposure for 100 hours at 1420 K (2100° F). It should be noted in figure 2 that yttrium was the most effective of the three simple coatings studied. The DBTT was approximately 465 K (375° F) after 100 hours at 1420 K (2100° F), compared to 365 K (200° F) for the unexposed substrate. In comparison an Fe-modified silicide coating which offered the most potential of several coatings investigated previously (ref. 1) provided similar protection for the same Cr alloy substrate under similar exposure conditions. A DBTT of 450 K (350° F) resulted after exposure of the Fe-Si coated specimens in air at 1420 K (2100° F) for 100 hours. The difference of 15 K (25° F) is probably not meaningful.

The La and Hf coatings also provided moderate protection for the Cr-0.17Y alloy substrate, but resulted in higher DBTT's than the Y coating. As noted previously, pro-

TABLE II. - SUMMARY OF COATING CONDITIONS AND RESULTS OF COATINGS, AIR EXPOSURES AND DUCTILE-BRITTLE TRANSITION TEMPERATURES

Number	Substrate	Coatings[a]			Air-exposure weight gain, mg/cm^2	Ductile-brittle transition temperature	
		Coating	Coating time at 1090 K (1500° F), hr	Weight gain, mg/cm^2		K	°F
Coatings screening, 100 hr at 1420 K (2100° F) air-exposure condition							
95	Cr-0.17Y	None	-------	----	Unexposed	365	200
101		None	-------	----	2.0	700	800
139		Y	8	0.6	1.7	465	375
145		La	4	1.0	.7	535	500
177		Hf	10	.6	5.1	575	575
153		Cr + Y[b]	4	1.9	2.3	420	300
158		Cr + Y[b,c]	4	1.1	2.7	480	400
Advanced coatings testing, 200 hr at 1420 K (2100° F) isothermal and cyclic air-exposure conditions; yttrium coatings on various substrates							
173	Cr-0.17Y	Y	4	0.5	Unexposed	365	200
155		Y	8	.7	2.7	480	400
164		Y	8	.5	[d]1.4	535	500
181		None	-------	----	1.5	840	1050
174	Cr-5W-0.18Y	Y	4	0.5	Unexposed	520	475
184		Y	16	.7	0.1	660	725
185		Y	16	.9	[d].5	670	750
182		None	-------	----	1.5	>1090	>1500
175	Cr-7Mo-2Ta-0.1C-0.2(Y + La)	Y	4	0.4	Unexposed	615	650
170		Y	4	.5	1.5	660	725
171		Y	4	.6	[d]2.6	670	750
183		None	-------	----	6.0	>1140	>1600
Complex coatings							
176	Cr-0.17Y	La	4	0.7	Unexposed	365	200
162		La	4	.8	0.7	560	550
163		Cr + La	4	1.9	3.8	560	550
166		Y + La	Y - 4 La - 4	.6 .9	2.6	505	450
167		Cr + Y + La	Y - 4 La - 4	2.5 .7	.6	450	350
186		Cr + Y + La	Y - 4 La - 4	1.3 2.1	[d]3.3	505	450
Impact specimens							
150	Cr-7Mo-2Ta-0.1C-0.2(Y + La)	None	-------	----	Unexposed	[e]590	600
168		Y	4	6.2	2.0	[e]825	1025
180		Cr + Y + La	Y - 8 La - 4	2.1 2.2	1.2	[e]700	800
154		None	-------	----	8.9	[e]>1035	>1400

[a] Pack consisted of coating element plus 4 wt % KCl.

[b] Substrate electroplated with Cr, 0.05 mm (0.002 in.) thick.

[c] Air-exposure conditions - 200 hr at 1420 K (2100° F).

[d] Cyclic exposure conditions, all others isothermal.

[e] Impact transition temperature; all others bend transition temperatures.

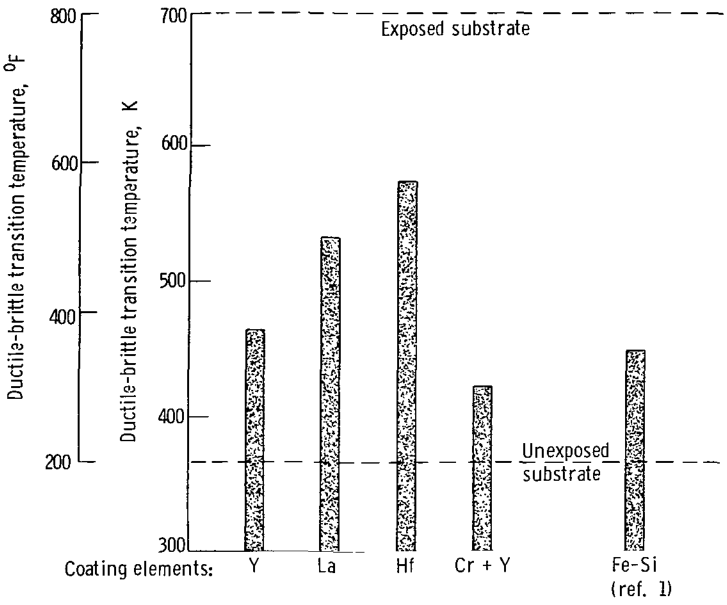
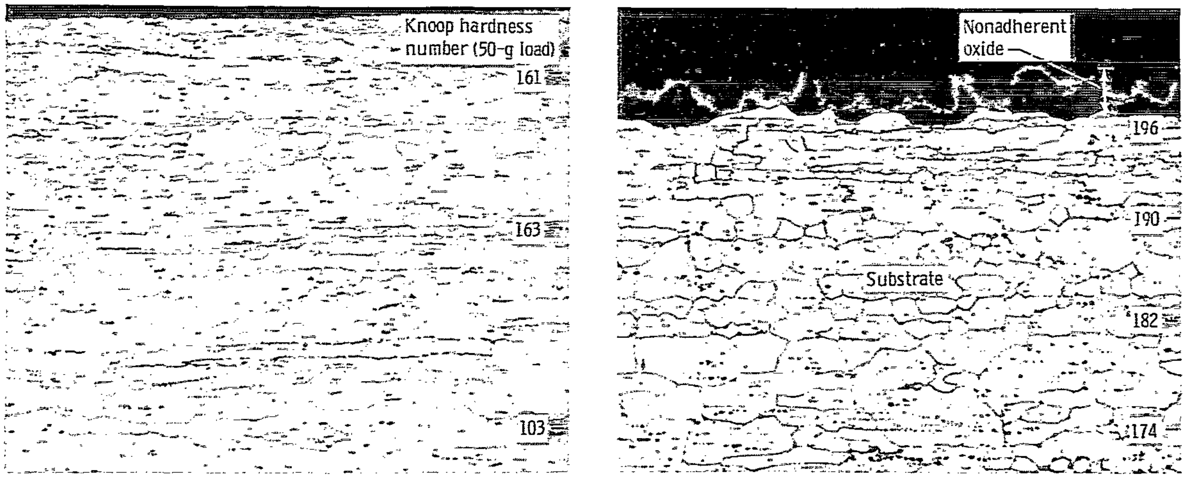


Figure 2. - Ductile-brittle transition temperatures of Cr-0.17Y uncoated; coated with Y, La, Hf, and Cr+Y; and exposed isothermally in air for 100 hours at 1420 K (2100° F).

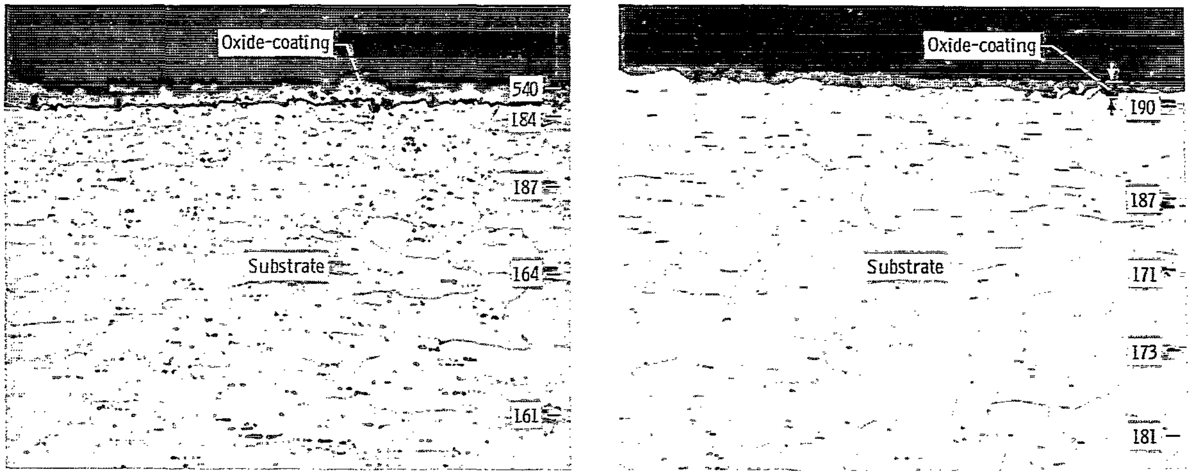
viding increased surface area by electroplating a porous layer of Cr permitted approximately a threefold increase in Y weight gain during coating. This was reflected in the ductility, as noted in figure 2, where a DBTT of 420 K (300° F) resulted for the Cr-plated Y-coated specimens after high-temperature air exposure, or an improvement of 40 K (75° F) in the transition temperature over the simple Y coating. As shown in table II, extending air-exposure times for 200 hours minimized this advantage for the heavier Cr + Y coatings.

Supplementary evaluation. - Photomicrographs of the unexposed Cr-0.17Y substrate and the bare and coated substrate after exposure in air at 1420 K (2100° F) for 100 hours are shown in figure 3. While the microhardness data are presented for information purposes, a correlation between hardness and DBTT could not be determined. The exposed substrate (fig. 3(b)) exhibited a rather nonadherent Cr_2O_3 oxide scale. In contrast, specimens coated with Y or La (figs. 3(c) and (d), respectively) exhibited an adherent thin oxide scale. X-ray diffraction indicated the major portion of the oxide was Cr_2O_3, with some indication of $YCrO_3$ or $LaCrO_3$ present in minor amounts on the coated specimens. Hafnium-coated specimens were characterized by a larger weight gain than the Y- or La-coated specimens (table II). In addition, on the hafnium-coated specimens an increase in grain size occurred during air exposure, as seen when figure 3(e) is compared to the unexposed substrate (fig. 3(a)). Metallography established that light gray precipitates at grain boundaries were Cr_2N and may account for the relatively high DBTT



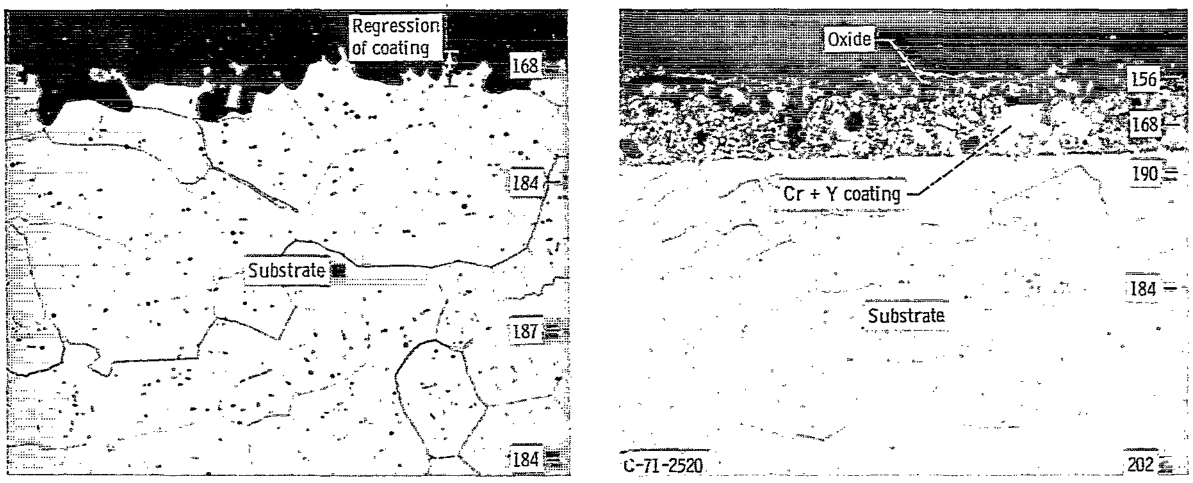
(a) Unexposed substrate.

(b) Exposed substrate.



(c) Y coated; exposed.

(d) La coated; exposed.



(e) Hf coated; exposed.

(f) Cr (plated) + Y coating; exposed.

Figure 3. - Microstructures of unexposed and exposed Cr-0.17Y coated with Y, La, Hf, and Cr + Y. Exposure conditions: 100 hours at 1420 K (2100° F) in air. X250.

of Hf-coated specimens.

The combination Cr(plated) + Y coating is depicted in figure 3(f) after high-temperature air exposure. X-ray diffraction indicated the presence of Cr_2O_3, Y_2O_3, and Y in the oxide-coating layer. The coating layer is seen to be porous, with particles assumed to be Y_2O_3 or an Y-rich oxide dispersed throughout the Cr coating layer. The surface oxide layer was again predominately Cr_2O_3, as indicated by X-ray diffraction results.

Figure 4 shows electronmicroprobe scans of Cr, Y, and O through the oxide and coating layers on the Cr-0.17Y substrate coated with Cr + Y. Yttrium is seen to occur in discrete areas, supplementing the metallographic examination where discrete particles within the Cr-plated layer were observed. Although the Y and O peaks do not coincide, it is believed that the scale is a Y-rich Cr oxide. Oxygen concentration is low beneath the coating, further showing the effectiveness of this type of coating.

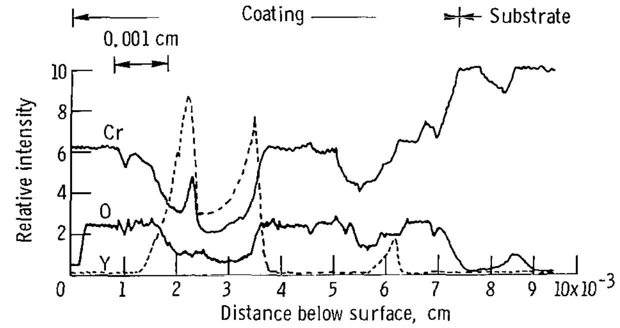


Figure 4. - Microprobe traces of Cr, O, and Y on Cr-0.17Y substrate coated with Cr + Y after air exposure for 100 hours at 1420 K (2100° F).

Based on DBTT results and metallographic and electron microprobe results, it is concluded that of the three simple coatings screened, Y coatings offer the most potential for more extensive investigations.

Y Coatings on Various Cr Alloy Substrates

Two high-strength Cr alloys have been produced in quantity during the past several years under NASA sponsorship. One alloy is a substitutional strengthened alloy, Cr-5W-0.18Y, while the second alloy is a combination substitutional and precipitate strengthened alloy, Cr-7Mo-2Ta-0.1C-0.2(Y + La). Both alloys have relatively high DBTT and are severely embrittled upon high-temperature air exposure, but at least exhibit adequate strength at 1420 K (2100° F) to meet the high-temperature requirements for advanced jet engines.

In order to determine the effectiveness of Y coatings in minimizing nitrogen embrittlement on various Cr substrates, the two high-strength Cr alloys and Cr-0.17Y were used as substrates for more extensive air-exposure conditions, which included 200-hour isothermal and cyclic air exposures at 1420 K (2100° F).

Coating and air exposure conditions, along with resulting weight gains, are summarized in table II.

Ductile-brittle transition temperature. - Figure 5 summarizes bend test results for Y-coated Cr alloy substrates, along with results for uncoated high-temperature-exposed specimens. Extending the air-exposure time to 200 hours increased the DBTT of uncoated Cr-0.17Y to 840 K (1050° F), compared to 700 K (800° F) for 100 hours exposure (fig. 2). Yttrium-coated specimens heated isothermally had a DBTT of 480 K (400° F) after 200 hours at 1420 K (2100° F), compared to a DBTT of 420 K (300° F) for 100 hours exposure. In addition, cyclic heating produced a further increase in DBTT to 535 K (500° F), as noted in figure 5 for the Cr-0.17Y alloy substrate. This represents an increase of 170 K (300° F) from the as-coated starting material and may be due to accelerated oxidation resulting from cracking of the oxide or coating layer. However, spalling of the oxide coating was not observed in this study under cyclic conditions as has been reported for plasma sprayed Cr-Y_2O_3 coatings (ref. 6).

Results of bend tests on Cr-5W-0.8Y substrate are also shown in figure 5. The DBTT of the as-coated substrate was 520 K (475° F) and increased to 660 K (725° F) and

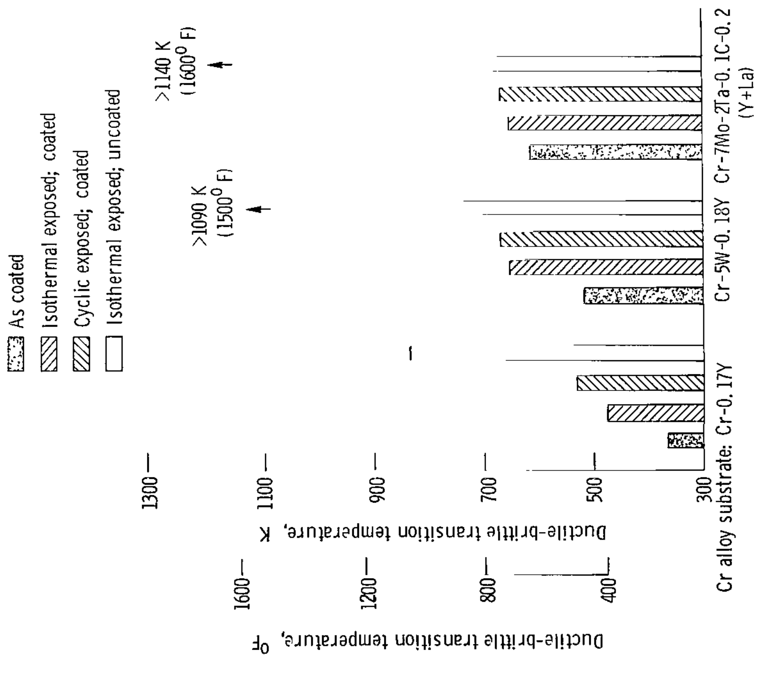


Figure 5. - Ductile-brittle transition temperature of Y-coated Cr alloy substrates as coated and after 200-hour isothermal and cyclic exposures at 1420 K (2100° F).

670 K (750° F) for isothermal and cyclic heating, respectively. In contrast, uncoated specimens exposed isothermally for 200 hours at 1420 K (2100° F) had a DBTT higher than 1090 K (1500° F).

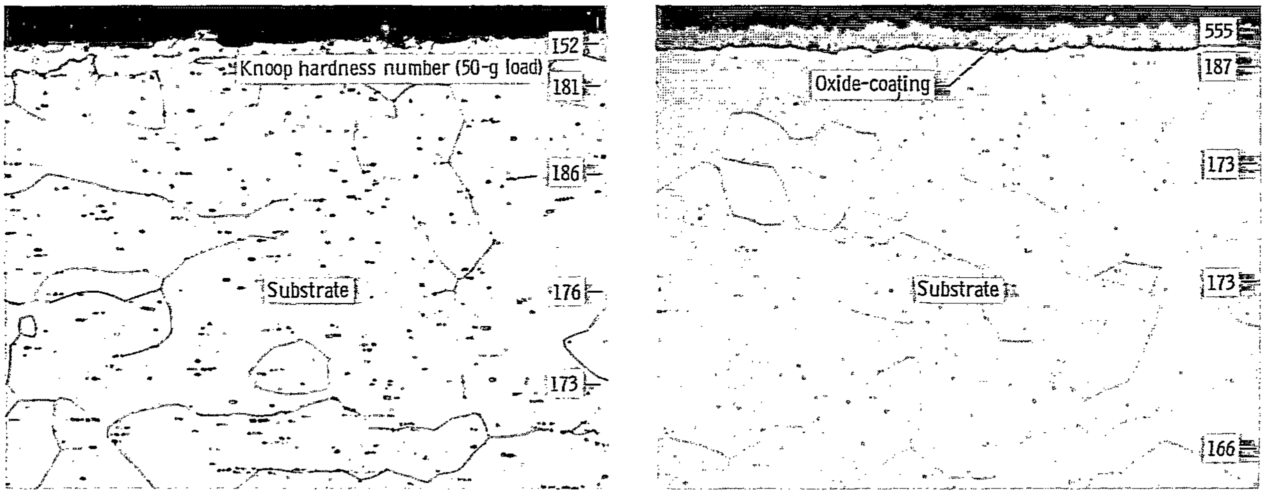
Bend test results for the high-strength Cr-7Mo-2Ta-0.1C-0.2(Y + La) alloy are shown in figure 5. The DBTT of the recrystallized coated substrate was 615 K (650° F). Isothermal and cyclic exposure in air at 1420 K (2100° F) produced increases of 45 K (75° F) and 55 K (100° F), respectively. Uncoated and isothermally exposed specimens had a DBTT in excess of 1145 K (1600° F).

Based on change in DBTT from the as-coated condition, the Y coating is more effective on the high-strength Cr-7Mo-2Ta-0.1C-0.2(Y + La) substrate than on the other two substrates, but the Cr-0.17Y substrate had the lowest DBTT after 200 hours at 1420 K (2100° F) in the coated and exposed condition.

Supplementary evaluation. - Photomicrographs of bend test specimens are shown in figures 6, 7, and 8 for Cr-0.17Y, Cr-5W-0.18Y, and Cr-7Mo-2Ta-0.1C-0.2(Y + La) alloy substrates, respectively. For as-coated specimens, no definitive layer of Y is observed in the photomicrographs. After high-temperature air exposure a thin oxide layer is observed on all three substrates heated isothermally or under cyclic conditions. Nitride precipitates are not observed at grain boundaries or within grains of coated and exposed specimens. However, in the Cr-5W-0.18Y and Cr-7Mo-2Ta-0.1C-0.2(Y + La) alloys, formation of grain boundary oxides in the substrate adjacent to the oxide layer is apparent in the cyclic exposed specimens (figs. 7(c) and 8(c)).

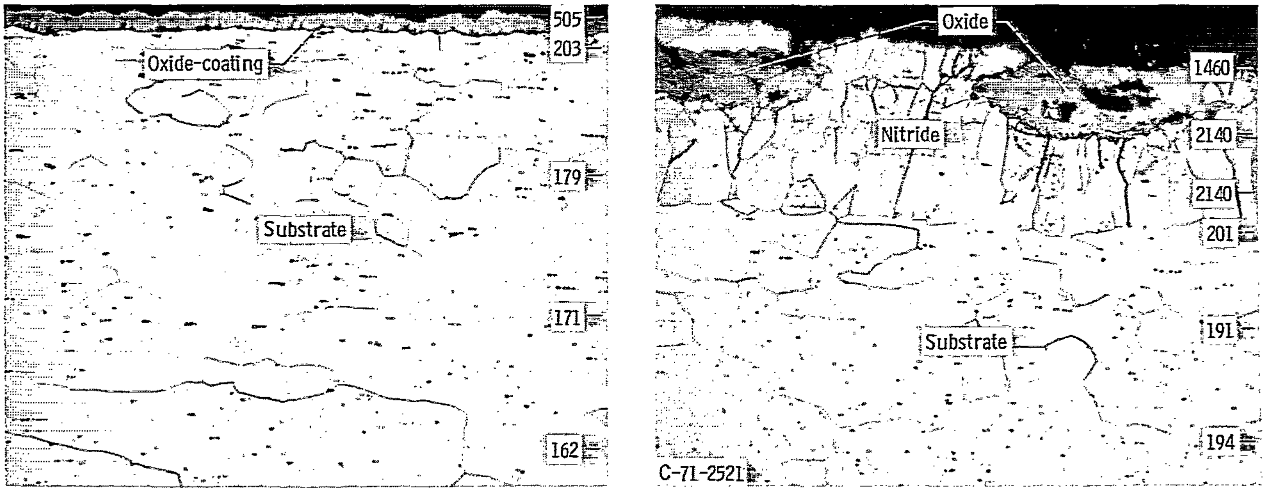
Uncoated specimens exposed to high-temperature air exhibited extensive formation of Cr_2N, as shown in figures 6(d), 7(d), and 8(d). The Cr-0.17Y substrate exhibited massive columnar nitrides both at the surface and beneath a discontinuous oxide layer (fig. 6(d)). In contrast, the more highly alloyed substrates exhibited formation of extensive grain boundary precipitates of Cr_2N, as shown in figures 7(d) and 8(d).

The presence of nitrogen in uncoated and exposed specimens was confirmed by electron microprobe (EMP) step traverses and X-ray images. Figure 9 shows step traverses of Cr and N for the three alloy substrates. Figure 9(a) shows a high-nitrogen-content zone approximately 0.012 centimeter (0.005 in.) thick beneath the surface of the Cr-0.17Y alloy. This corresponds to the columnar structure observed in figure 6(d). In contrast, EMP nitrogen traverses on the more highly alloyed substrates revealed segregated peaks of nitrogen increasing in intensity toward the surface, as shown in figure 9(b) for the Cr-5W-0.18Y alloy and in figure 9(c) for the Cr-7Mo-2Ta-0.1C-0.2(Y + La) substrate. These results correspond to the metallographic observation of grain boundary nitrides, as shown in figures 7(d) and 8(d) for the two more highly alloyed substrates. The low N and Cr zone at the surface in figure 9(c) apparently corresponds to the oxide layer on the surface, as shown in figure 8(d). Based on a standard or CrN, the



(a) As coated.

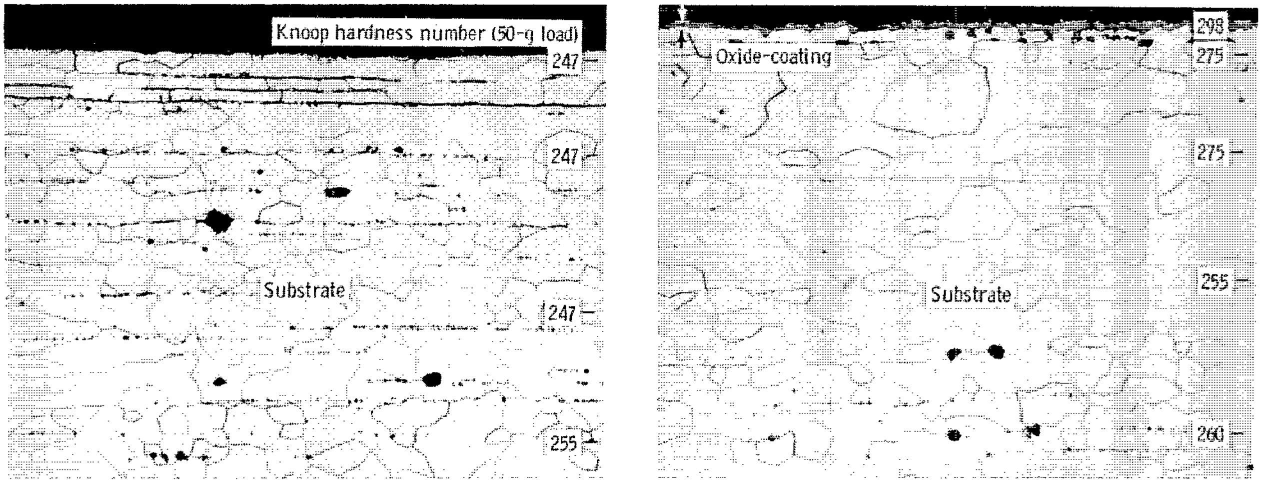
(b) Y coated; isothermal exposure.



(c) Y coated; cyclic exposure.

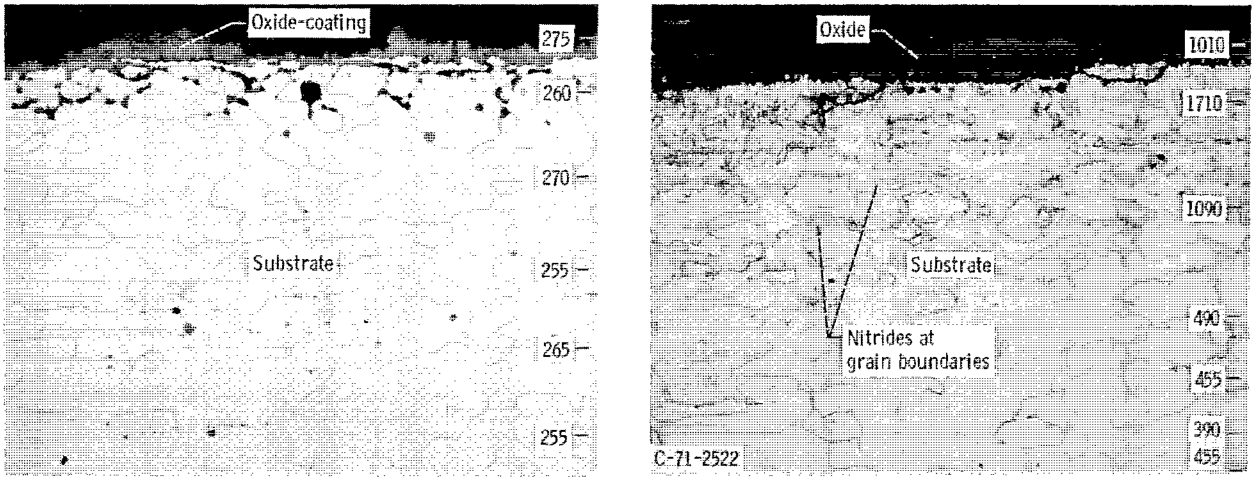
(d) Uncoated; isothermal exposure.

Figure 6. - Microstructures of Cr-0.17Y as coated with Y and after exposure in air at 1420 K (2100° F) for 200 hours under various conditions. X250.



(a) As coated.

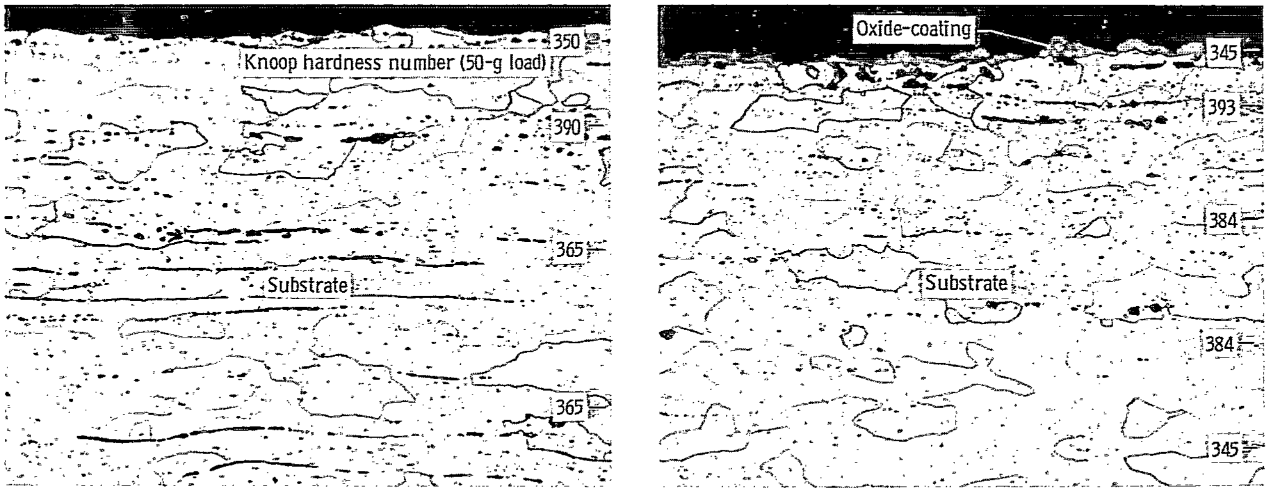
(b) Y coated; isothermal exposure.



(c) Y coated; cyclic exposure.

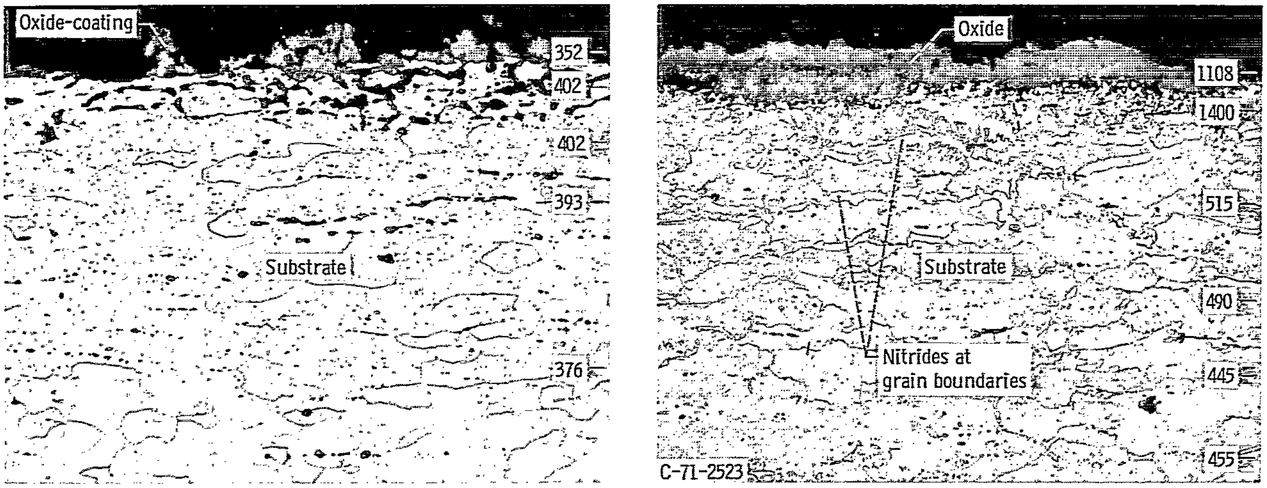
(d) Uncoated; isothermal exposure.

Figure 7. - Microstructures of Cr-5W-0.17Y as coated with Y and after exposure in air at 1420 K (2100° F) for 200 hours under various conditions. X250.



(a) As coated.

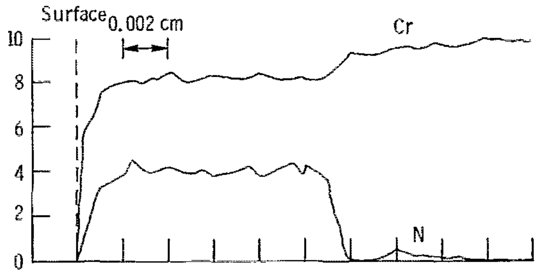
(b) Y coated; isothermal exposure.



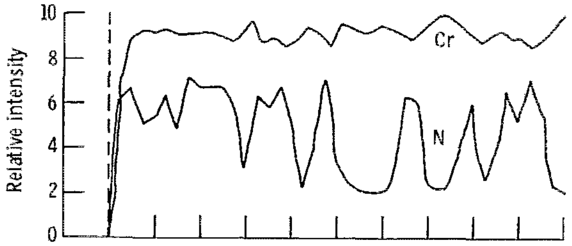
(c) Y coated; cyclic exposure.

(d) Uncoated; isothermal exposure.

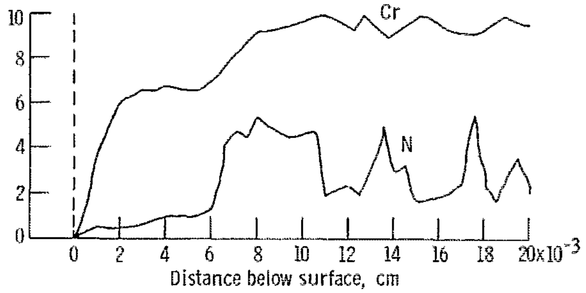
Figure 8. - Microstructures of Cr-7Mo-2Ta-0.1C-0.2(Y + La) as coated with Y and after exposure in air at 1420 K (2100° F) for 200 hours under various conditions. X250.



(a) Cr-0.17Y alloy.



(b) Cr-5W-0.18Y alloy.



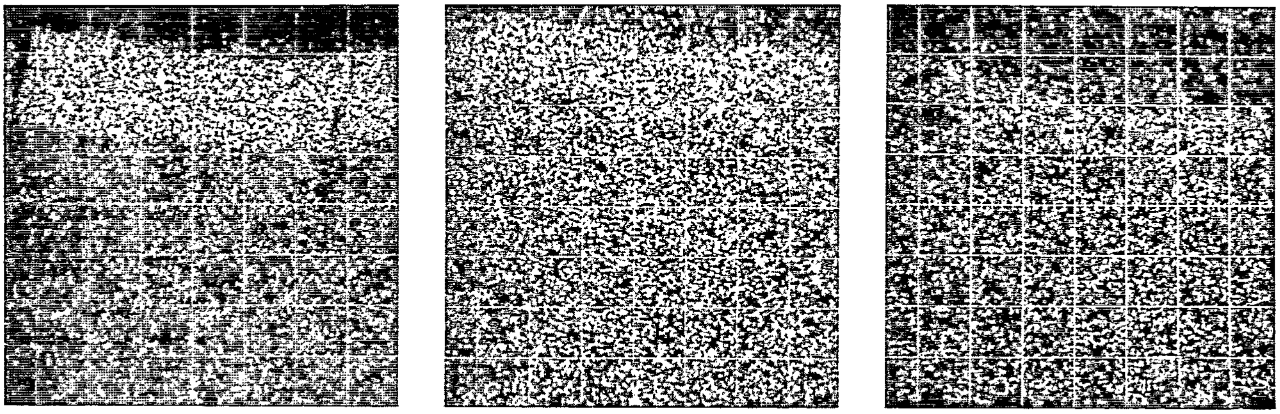
(c) Cr-7Mo-2Ta-0.1C-0.2(Y + La) alloy.

Figure 9. - Electron microprobe traces of Cr and N on various Cr alloy substrates exposed in air for 200 hours at 1420 K (2100° F) in the uncoated condition.

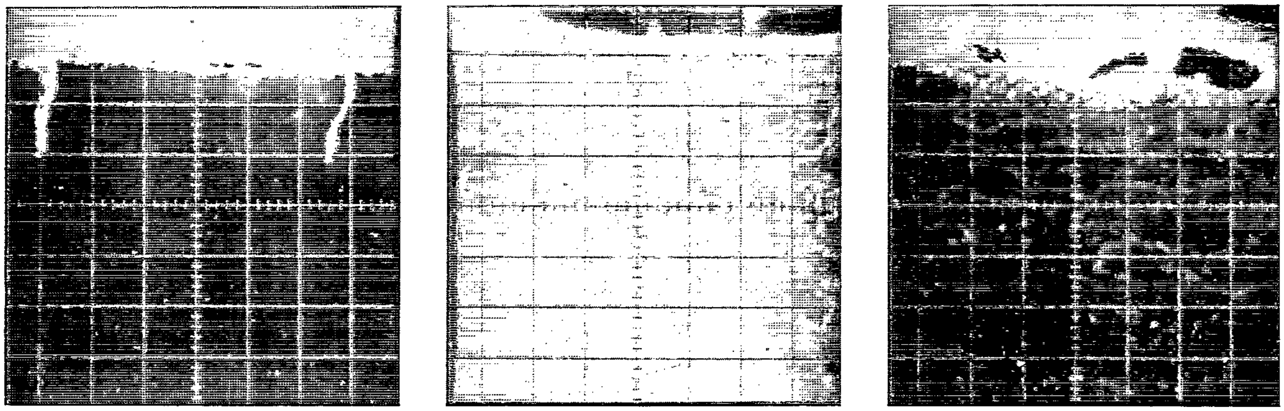
EMP counts for N and Cr at the N peaks in figure 9 compare favorably with the composition of Cr_2N.

EMP X-ray images are shown in figure 10. The nitride case on the Cr-0.17Y alloy is clearly visible in figure 10(a). Nitrogen in the grain boundaries of the more highly alloyed substrates is shown in figures 10(b) and (c) and explains the segregated nature of nitrogen peaks observed in the step scan traverses in figures 9(b) and (c). The extensive grain boundary nitride formation accounts for the high DBTT observed for the two more highly alloyed substrates after high-temperature air exposures.

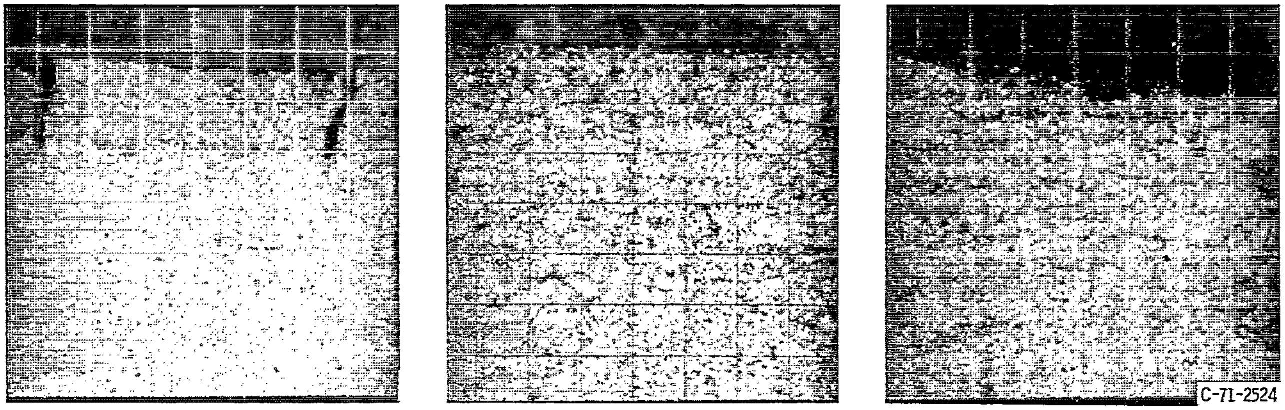
EMP X-ray images revealed the location of coating element, oxygen, and alloying elements for each of the substrates, as illustrated in figures 11 to 13. Nitrogen was not detected in any of the coated specimens by using the electron microprobe, thus confirming the effectiveness of Y coatings. Figure 11 shows the Cr-0.17Y substrate coated



X-rays (nitrogen)



Sample current



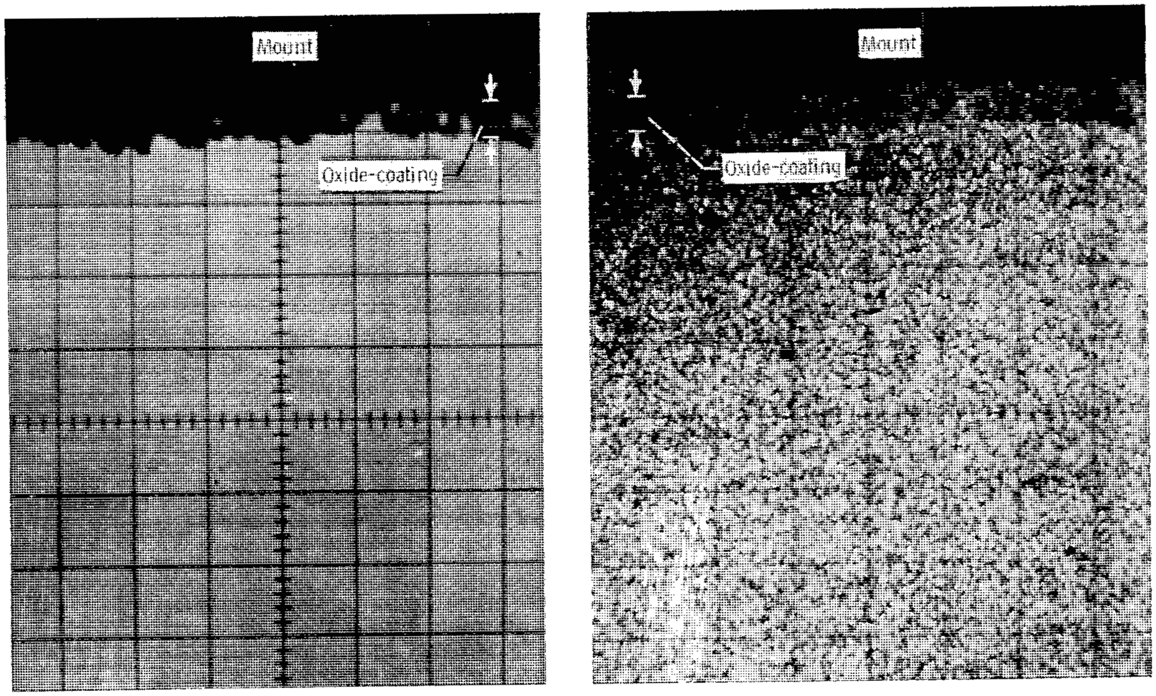
Back scatter electrons

(a) Cr-0.17Y.

(b) Cr-5W-0.18Y.

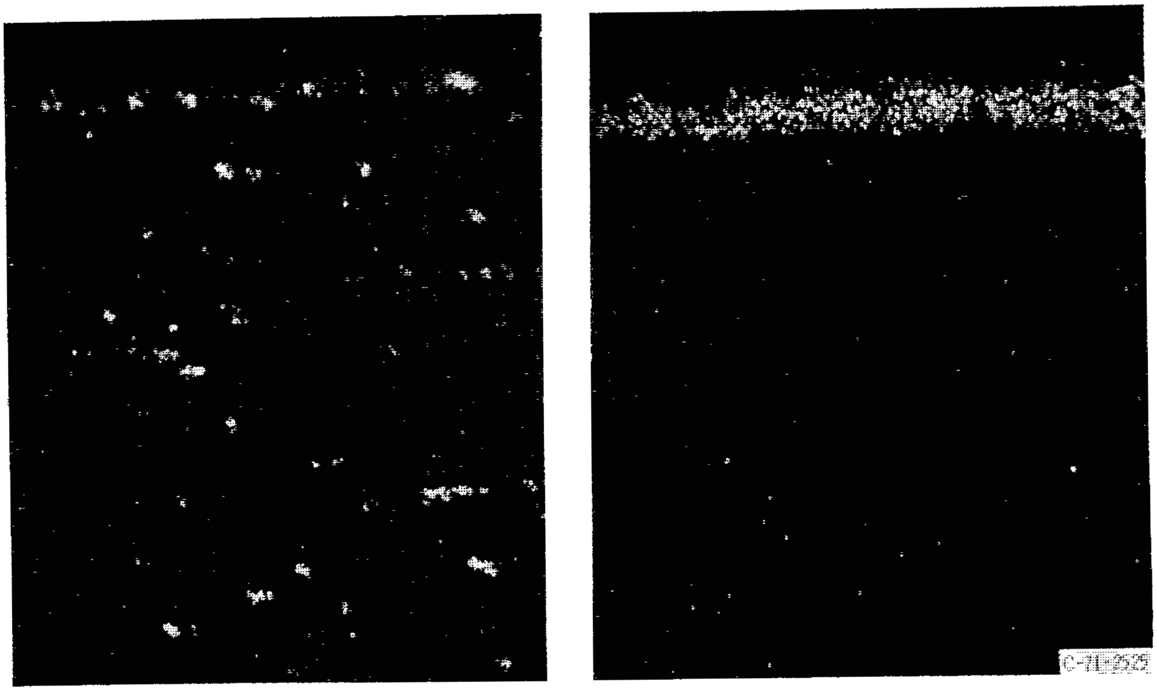
(c) Cr-7Mo-2Ta-0.1C-0.2 (Y + La).

Figure 10. - Electron microprobe images of various Cr alloys exposed in air for 200 hours at 1420 K (2100° F) in the uncoated condition.



(a) Back scatter electrons.

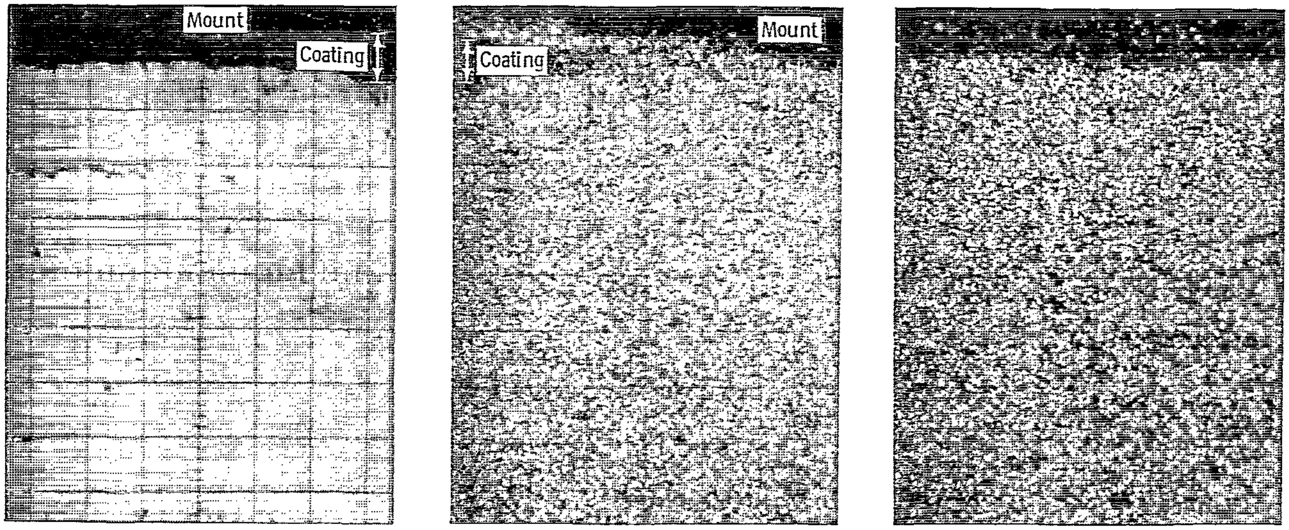
(b) Chromium X-rays.



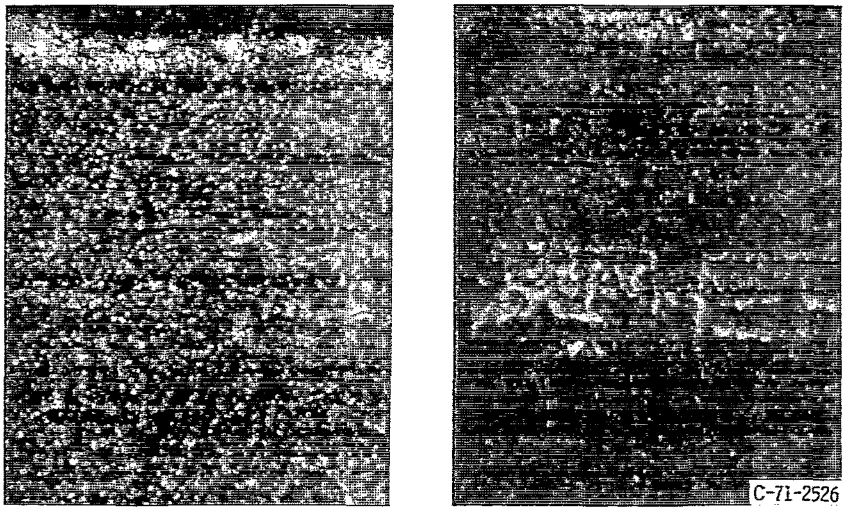
(c) Yttrium X-rays.

(d) Oxygen X-rays.

Figure 11. - Electron microprobe images of Y-coated Cr-0.17Y alloy after cyclic oxidation at 1420 K (2100 F) for 200 hours. X500.



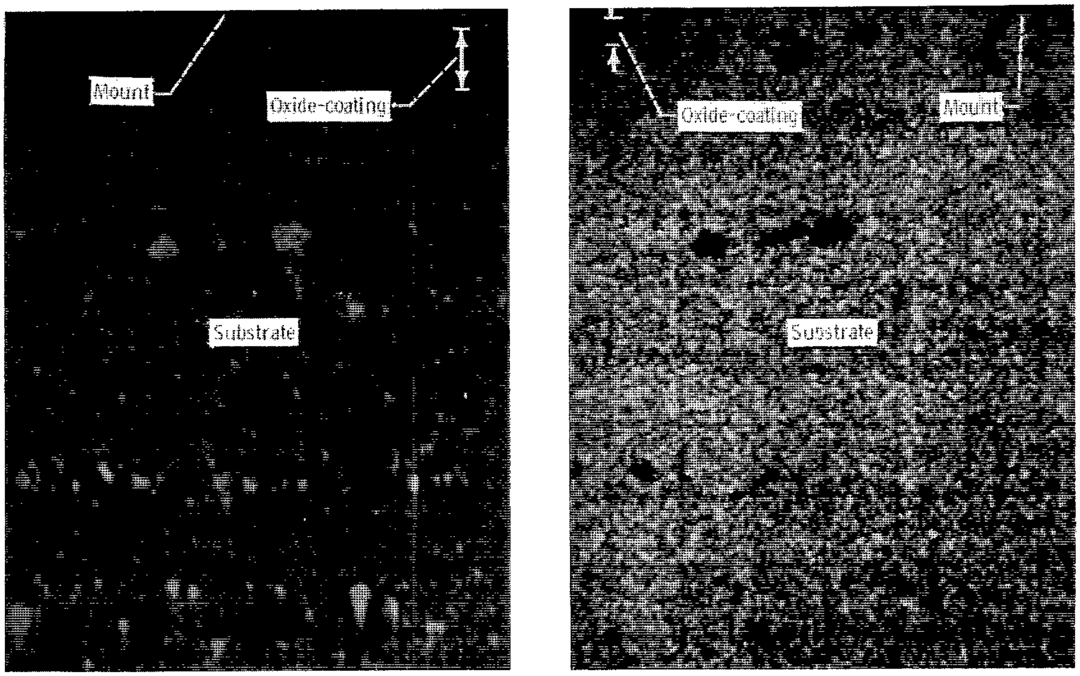
(a) Back scatter electrons. (b) Chromium X-rays. (c) Tungsten X-rays.



(d) Yttrium X-rays. (e) Oxygen X-rays.

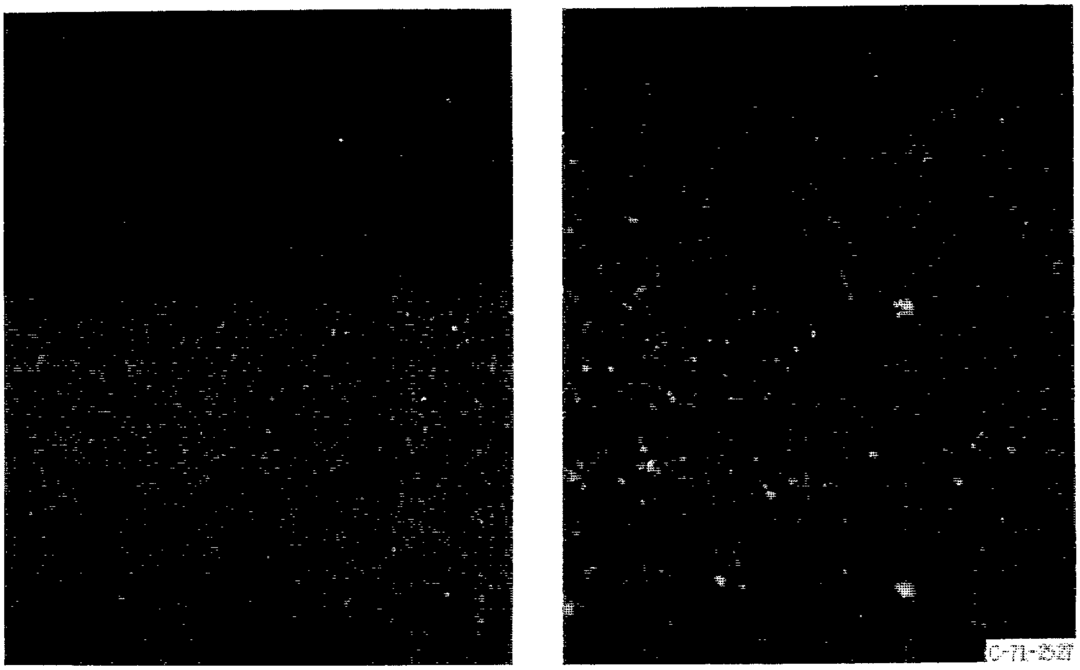
Figure 12. - Electron microprobe images of Y coated Cr-5W-0.18Y alloy in the as-coated condition. X500.

with Y after cyclic exposure. Yttrium is seen to be concentrated near the surface and apparently associated with oxygen. Also, discrete Y-rich particles are observed within the substrate that show no apparent association with oxygen. Figure 12 illustrates EMP images for a Cr-5W-0.18Y specimen in the as-coated (Y coating) condition. X-ray images for oxygen reveal a concentration of oxygen near the surface associated with Y, thus suggesting that Y forms an oxide during coating or upon subsequent exposure to air at room temperature. Figure 13 illustrates EMP images for a Cr-7Mo-2Ta-0.1C-0.2 (Y + La) specimen Y coated and exposed in air for 200 hours at 1420 K (2100° F). Depletion of Mo from the substrate is observed in figure 13(c) to a depth of approximately 0.08 millimeter. Of particular interest are the Y, La, and O images (figs. 13(e), (f), and (g)).



(a) Back scatter electrons.

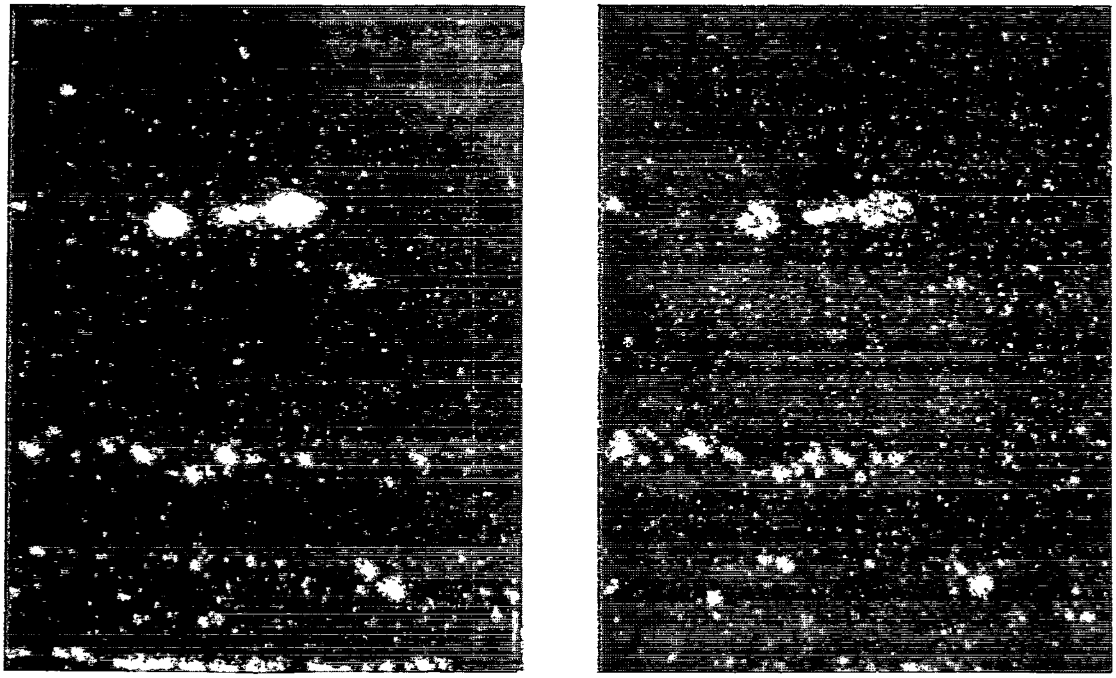
(b) Chromium X-rays.



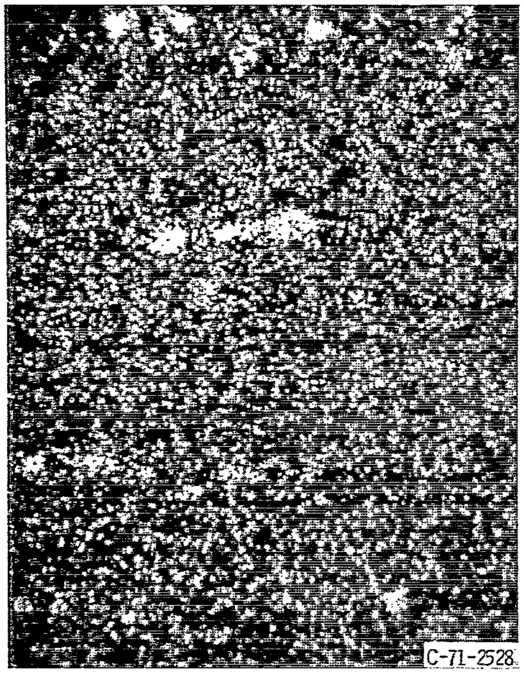
(c) Molybdenum X-rays.

(d) Tantalum X-rays.

Figure 13. - Electron microprobe images of Cr-7Mo-2Ta-0.1C-0.2(Y + La) alloy Y coated and exposed 200 hours isothermally at 1420 K (2100° F). X500.



(e) Yttrium X-rays. (f) Lanthanum X-rays.



(g) Oxygen X-rays.

Figure 13. Concluded.

EMP results show that Y and, to a lesser extent, O are concentrated near the surface. Fluoresence of these particles confirms the presence of Y or modified Cr-Y oxide. In addition, within the substrate, particles are evident in which Y and La are associated with O. These oxides formed during induction melting of the alloy and reflect the scavenging effect of reactive metal additions in Cr.

Complex Coatings

Although a simple La coating was not as protective as Y in the original screening investigation, further studies were conducted on La combined with electroplated Cr and/or with Y.

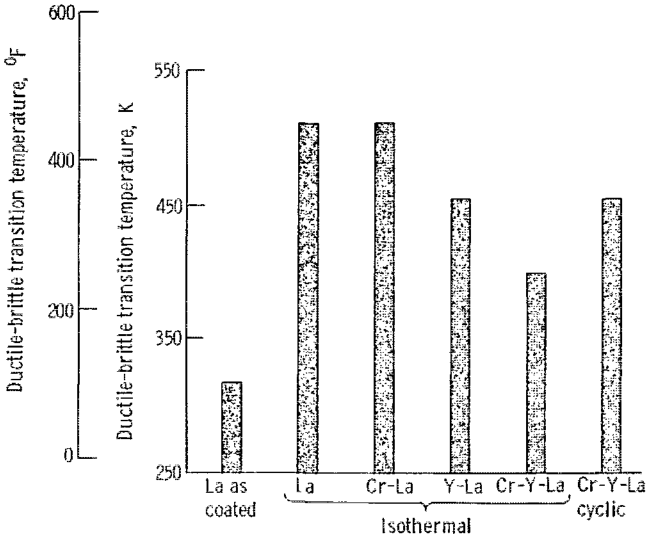
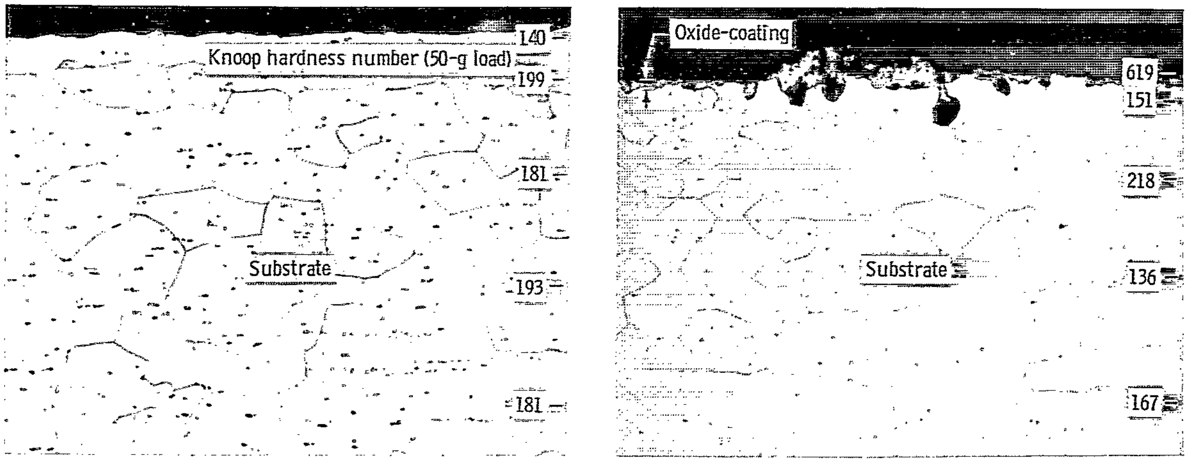


Figure 14. - Ductile-brittle transition temperatures of Cr-0.17Y coated with La and La combined with Y and Cr. As coated and after 200-hour exposure in air at 1420 K (2100° F).

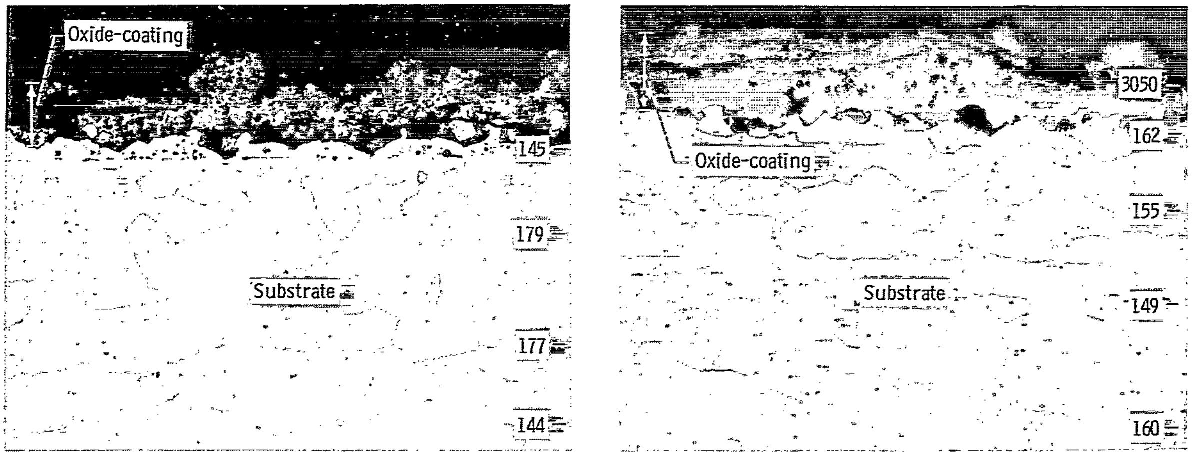
Ductile-brittle transition temperature. - Figure 14 shows bend test results for several complex coatings, along with results for a simple La coating. Beneficial effects were gained by combining Y and La to form a protective coating. Electroplating a layer of Cr onto the surface of the substrate and then coating with Y and La resulted in a DBTT of 450 K (350° F) for isothermally exposed specimens. This is the most protective coating investigated in the present program based on increase in DBTT. Cyclic exposure increased the DBTT to 505 K (450° F), still superior to other coatings tested under similar conditions.

Supplementary evaluation. - Photomicrographs of specimens coated with a simple La coating and with complex coatings are shown in figure 15. All the La-containing



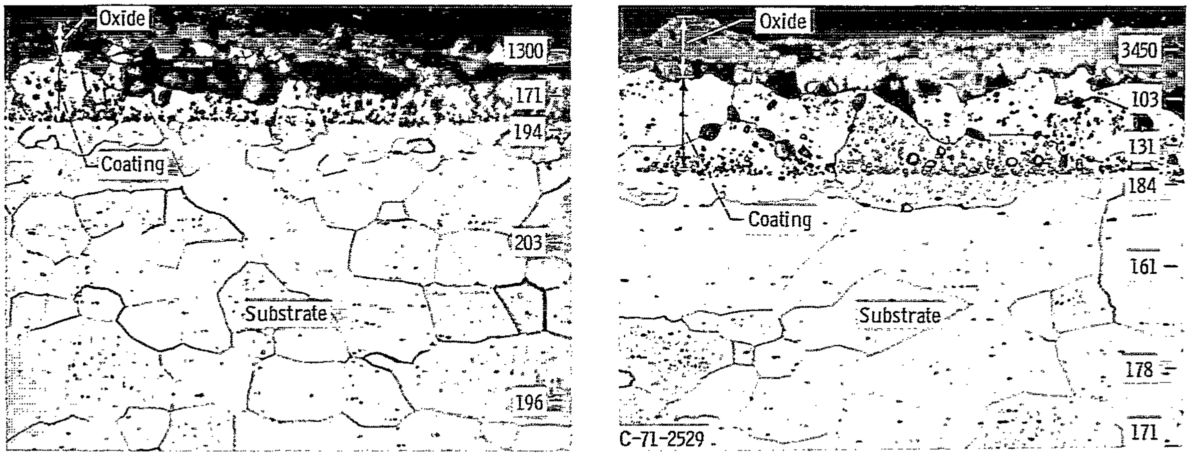
(a) As coated.

(b) La; isothermal exposure.



(c) Cr + La; isothermal exposure.

(d) Y + La; isothermal exposure.



(e) Cr + Y + La; isothermal exposure.

(f) Cr + Y + La; cyclic exposure.

Figure 15. - Microstructures of Cr-0.17Y coated with La and La combined with Y and Cr, exposed in air at 1420 K (2100° F) for 200 hours. X250.

coatings appeared to form heavier oxide scales than those without La observed previously. The effectiveness of the complex Cr + Y + La coatings is illustrated in figures 15(e) and (f). Here, a heavy oxide layer is observed at the surface, under which lies a layer of coating containing a few oxide particles while the adjacent substrate remains free of oxide or nitride precipitates.

As indicated in table II, the weight gains on all coated specimens tested in air at 1420 K (2100° F) in this study were low, normally less than 4 milligrams per square centimeter in 200 hours. Figure 16 illustrates the cyclic weight gains for all three alloys coated with Y and for a Cr + Y + La coating on Cr-0.17Y. Figure 15 showed that the presence of La in the coating resulted in thicker oxide scales. In figure 16 again the Cr + Y + La coating and the Y coating on the La-containing alloy exhibited greater weight gains than Y coatings alone. These weight change and scale thickness data may give some insight into the relative effectiveness of the coatings in resisting substrate contamination.

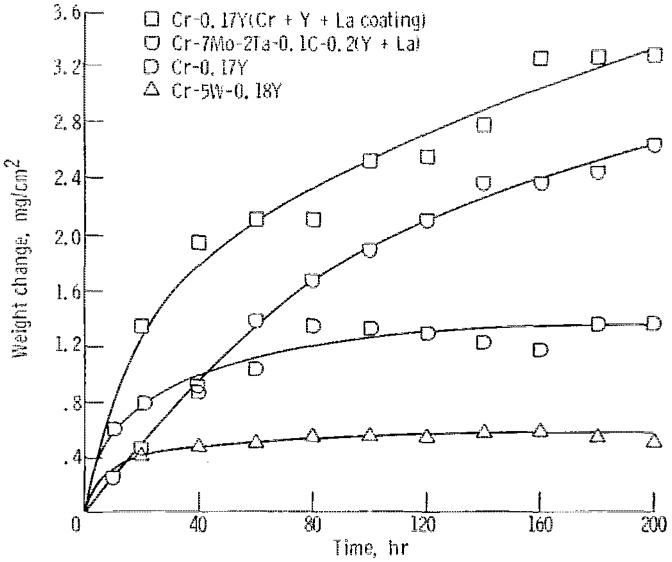


Figure 16. - Weight changes of Y-coated Cr alloy substrates during cyclic air exposure at 1420 K (2100° F).

It is well documented that the oxidation of Cr and its alloys in air at temperatures near 1420 K (2100° F) involves weight gain due to oxide scale (and nitride subscale) formation as well as weight loss due to chromium oxide volatilization (refs. 3, 11, and 12). The presence of La appears to promote heavier oxide scale and/or less total weight loss. Since the Cr + Y + La coating was the most protective system developed in this study, it appears that these thicker scales are more resistant to penetration by nitrogen. While heavier scales could be expected to be more prone to spalling, none of these systems spalled. Thus, La combined with Y appears to form a heavy, spall-resistant scale that minimizes inward diffusion of nitrogen and may also influence chromium oxide volatilization.

Impact Tests

Susceptibility to failure of Cr alloy components in jet engines from foreign object impact is of major concern. Therefore, a limited number of impact tests were conducted on the more highly alloyed Cr specimens to determine the effectiveness of Y and Cr + Y + La coatings tested at high rates of loading.

Impact transition temperature. - Figure 17 shows results of impact tests conducted on specimens of a Cr-7Mo-2Ta-0.1C-0.2(Y + La) substrate. It should be noted that the impact transition temperature is about 590 K (600° F) for the recrystallized uncoated substrate. This is 15 K (25° F) lower than the DBTT in bending. This reversal of the usual relation of increase in DBTT with increase in strain rate is apparently the result

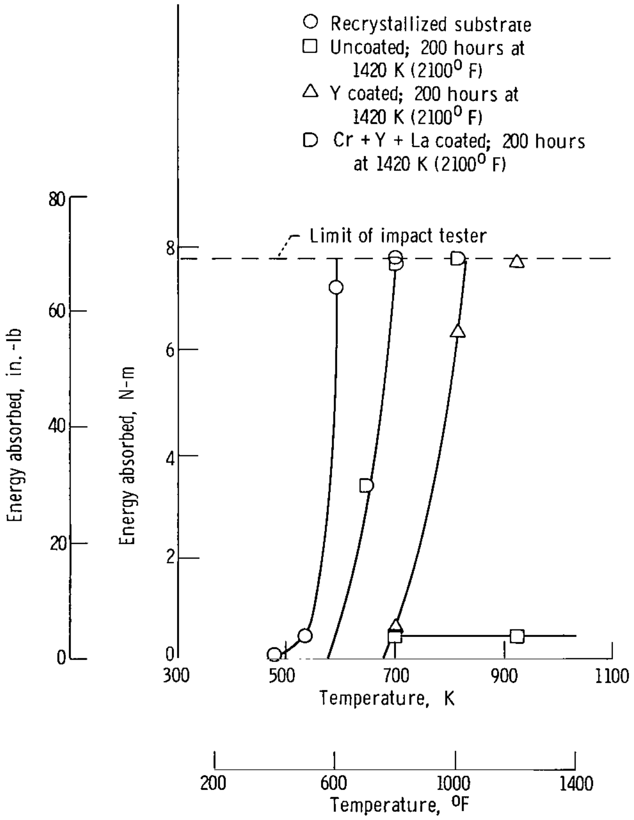
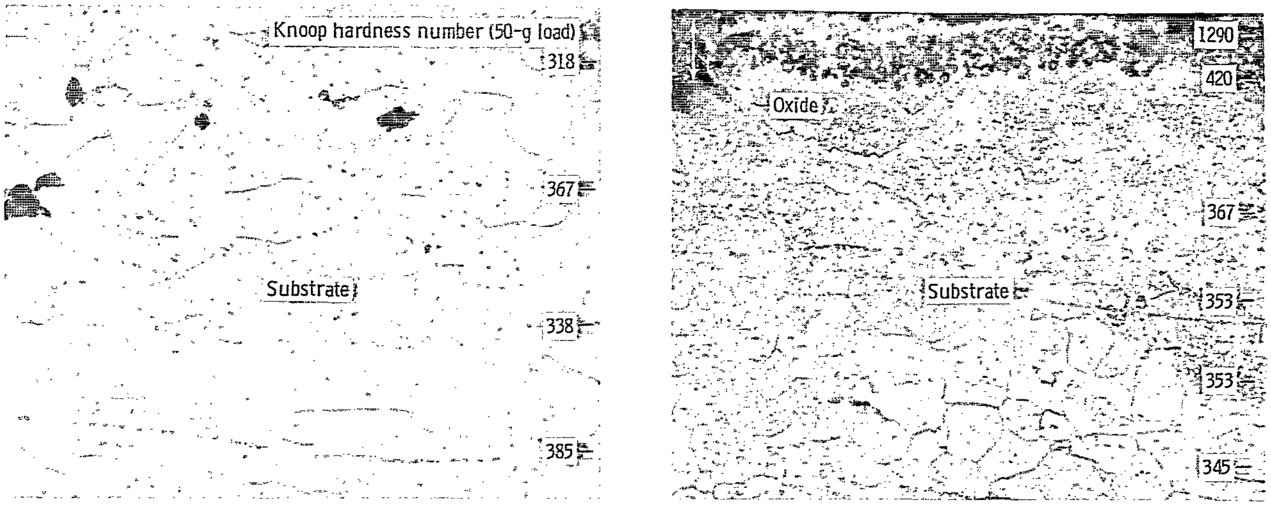


Figure 17. - Impact toughness of Cr-7Mo-2Ta-0.1C-0.2(Y + La) recrystallized, exposed, and isothermally coated and exposed.

of fabrication differences between the two lots of materials, extruding and rolling for bend specimens as compared with extruding only for impact specimens.

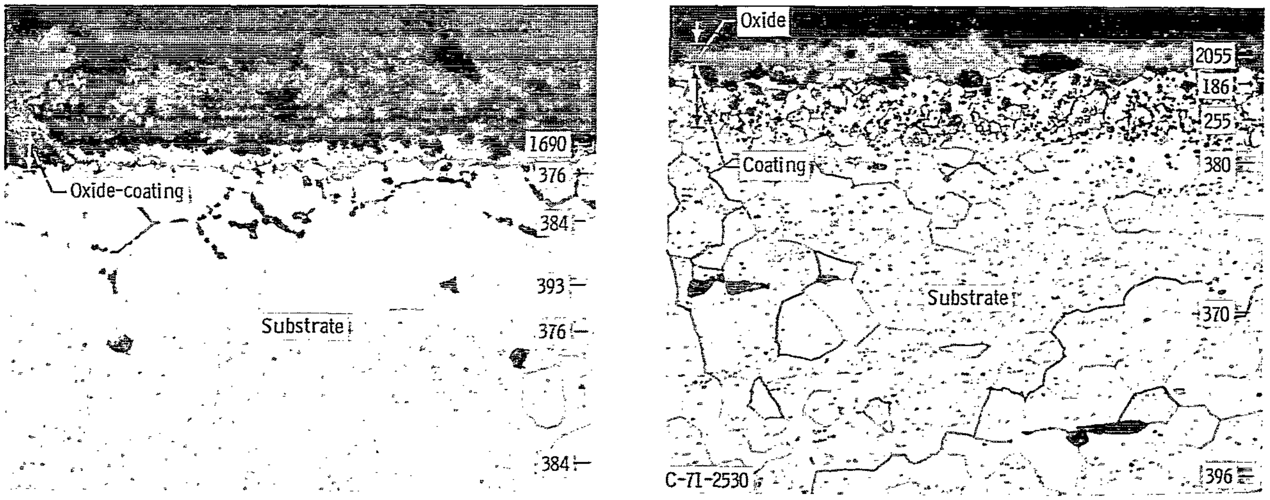
Exposure of the uncoated substrate for 200 hours at 1420 K (2100° F) resulted in an impact transition temperature in excess of 1035 K (1400° F). Both coatings, Y and Cr + Y + La, were effective in protecting the substrate from embrittlement. The complex Cr + Y + La coating was superior to the simple Y coating under high rates of loading.

Supplementary evaluation. - Photomicrographs of impact specimens are shown in figure 18. The uncoated specimen exposed to high-temperature air was characterized by heavy nitride precipitation within the grains and at grain boundaries. Specimens



(a) Recrystallized.

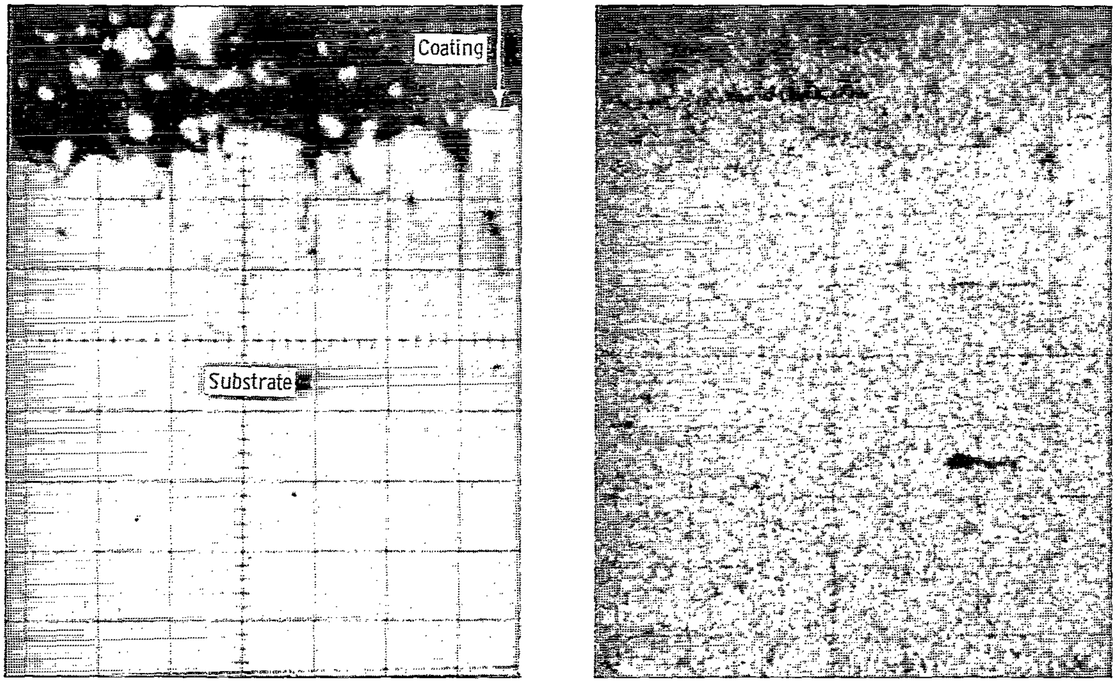
(b) Uncoated; exposed.



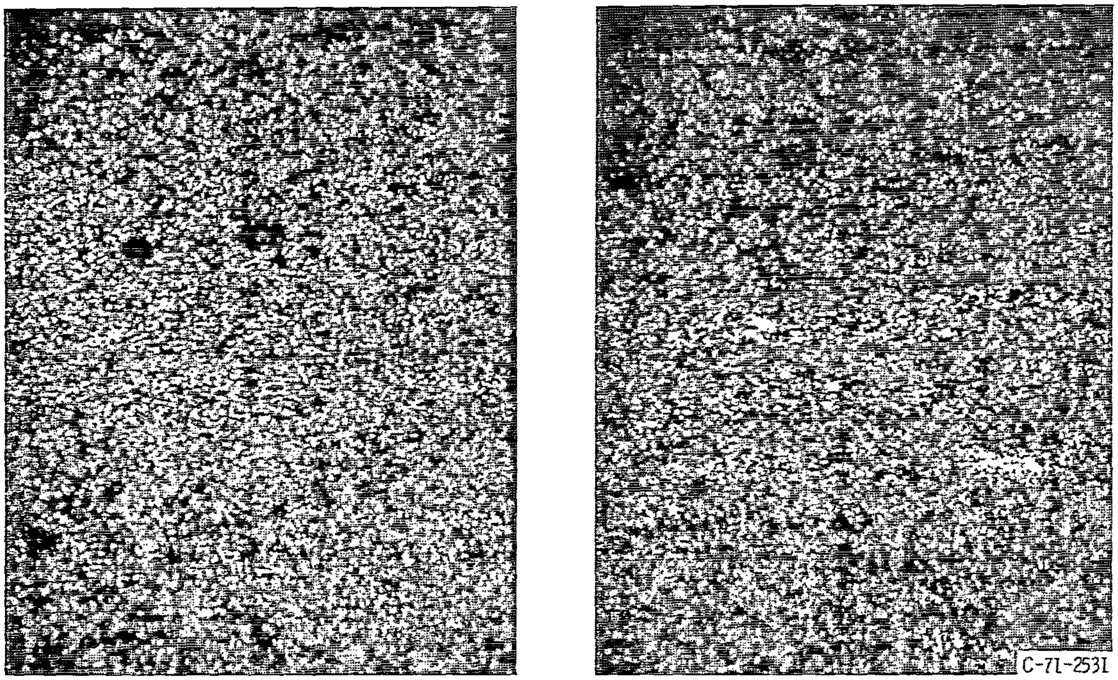
(c) Y coated; exposed.

(d) Cr + Y + La coated; exposed.

Figure 18. - Microstructures of Cr-7Mo-2Ta-0.1C-0.2 (Y + La) recrystallized and after exposure in air at 1420 K (2100° F); uncoated and coated with Y and Cr + Y + La. X250.

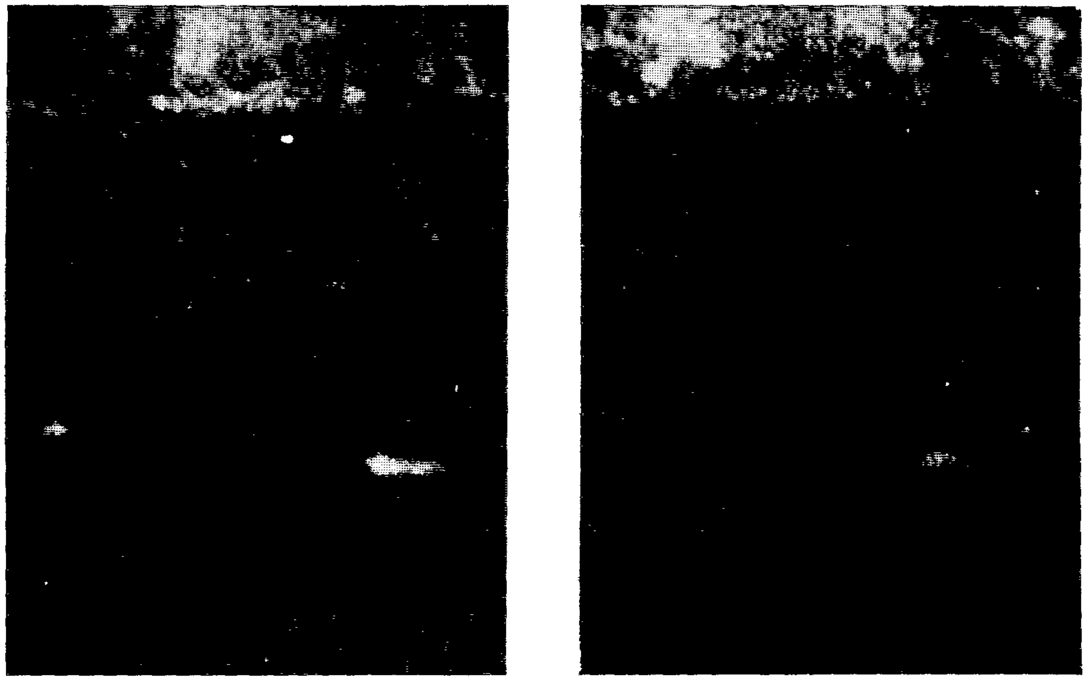


(a) Back scatter electrons. (b) Chromium X-rays.



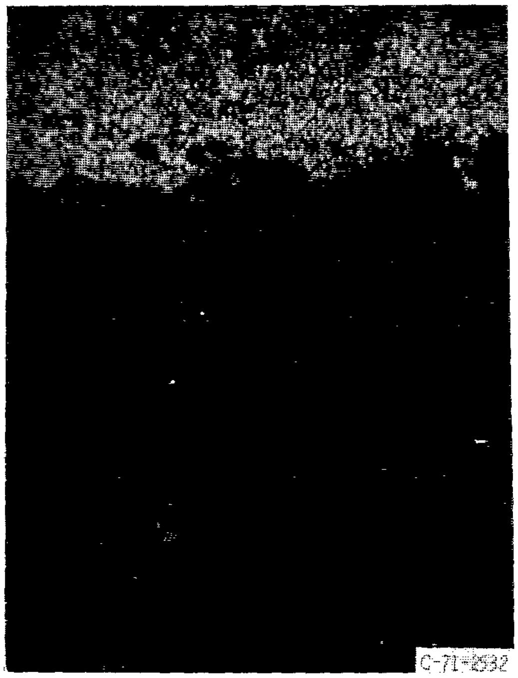
(c) Molybdenum X-rays. (d) Tantalum X-rays.

Figure 19. - Electron microprobe images of an impact specimen coated with Cr + Y + La and exposed 200 hours at 1420 K (2100 F). X500.



(e) Yttrium X-rays.

(f) Lanthanum X-rays.



(g) Oxygen X-rays.

Figure 19. - Concluded.

coated with Y exhibited grain boundary oxides in the substrate beneath the oxide scale. EMP results (not shown) revealed depletion of Mo from the substrate. No degradation of the substrate was observed for specimens coated with Cr + Y + La after high-temperature air exposure. The oxide scale formed was heavier here than in the case of the Y coating alone. EMP images of an exposed specimen having a complex Cr + Y + La coating are shown in figure 19. Both Y and La are noted to be distributed throughout the Cr-plated coating layer and appear to be associated with O. No evidence of inward diffusion of Y, La, or O is apparent in the EMP images.

SUMMARY OF RESULTS

A study was made of the effectiveness of Y, La, Hf, Cr + Y, Cr + La, Y + La, and Cr + Y + La coatings on Cr-0.17Y, Cr-5W-0.18Y, and Cr-7Mo-2Ta-0.1C-0.2(Y + La) alloy substrates. Results based primarily on the ductile-brittle transition temperature (DBTT) after exposure in air at 1420 K (2100° F) showed that Y coatings afford good nitridation resistance for Cr alloys studied in this program for times up to 200 hours under isothermal and cyclic heating conditions. After cyclic heating for 200 hours at 1420 K (2100° F) of Y-coated Cr-7Mo-2Ta-0.1C-0.2(Y + La), an increase in DBTT of only 56 K (100° F) occurred, compared to an increase of over 530 K (950° F) for the uncoated substrate exposed in a similar manner. Simple La and Hf coatings provided moderate protection for Cr alloys, but were not as effective as Y coatings.

Coating with successive layers of Y and La over an electrodeposited and annealed layer of Cr provided the optimum coating studied in this investigation. This more complex coating formed somewhat thicker and yet still very adherent scales. The presence of La in the coating or in the substrate seems to enhance the oxide growth and protectiveness. Both Y and Cr + Y + La coatings offer the advantages of not seriously degrading the substrate DBTT after at least 200 hours at 1420 K (2100° F).

Impact results also showed the Cr + Y + La and Y coatings to be protective on Cr alloy substrates subjected to high loading rates after 200 hours exposure at 1420 K (2100° F).

CONCLUDING REMARKS

The effectiveness of Y coatings appears to be due to the high affinity for O by Y. Coatings of Y, La, or Y + La on Cr form oxide scales that remain adherent under rapid heating and cooling. The oxide, in turn, prevents penetration of N into the Cr alloy substrates, as shown by the EMP results. Due to the low solubility of Y in Cr and the absence of an intermetallic compound in the Cr-Y system, diffusion of Y into Cr is essentially nil and embrittlement or other degrading of the substrate does not result from coating-substrate reaction. Increasing the amount of Y in the coating by first electroplating a porous layer of Cr on the substrate allows formation of a thicker protective oxide layer. This thicker oxide layer is more protective than the thin oxide scales which form on a simple Y coating and derives its protectiveness from minimizing inward diffusion of nitrogen which increases substrate DBTT and loss of Cr by volitilization of oxides.

The Y and Cr + Y + La coatings appear to offer at least 200 hours of protection for Cr-base alloys for applications at temperatures near 1420 K (2100° F). Unfortunately, the high DBTT of current high-strength Cr alloys such as those used in this investigation preclude their being given serious consideration for structural designs such as the gas turbine engine in which cyclic operation over a range of temperatures from below room temperature to near 1420 K (2100° F) is required.

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National Aeronautics and Space Administration,
Cleveland, Ohio, July 9, 1971,
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