DEVELOPMENT OF PROTECTIVE COATINGS FOR CHROMIUM-BASE ALLOYS

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Technical Management
NASA Lewis Research Center
Cleveland, Ohio
R. E. Oldrieve, Project Manager
S. J. Grisaffe, Research Advisor

BATTELLE MEMORIAL INSTITUTE
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

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DEVELOPMENT OF PROTECTIVE COATINGS FOR CHROMIUM-BASE ALLOYS

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ABSTRACT

Chromium alloy sheet was clad with 5 to 10-mil-thick oxidation-resistant nickel-base alloy foils. Specimens also contained 1/2 to 1-mil-thick intermediate layers of platinum, tungsten, and/or W-25Re. Cladding was done by the isostatic hot gas-pressure bonding process. The clad chromium-alloy specimens were cyclic oxidation tested at 2100 F and 2300 F for up to 200 hours to determine the effectiveness of these metal claddings in protecting the chromium alloy Cr-5W from oxidation and contamination. Cladding systems consisting of 5-mil-thick Ni-20Cr-20W modified with 3 to 5 weight percent aluminum and containing a 1/2-mil tungsten diffusion barrier demonstrated potential for long-time service at temperatures as high as 2300 F.

DEVELOPMENT OF PROTECTIVE COATINGS
FOR CHROMIUM-BASE ALLOYS

by

J. J. English, C. A. MacMillan,
D. N. Williams, and E. S. Bartlett

Battelle Memorial Institute
Columbus Laboratories

SUMMARY

Chromium-base alloys are very attractive high-temperature structural materials for advanced gas-turbine vanes and blades. These alloys have good inherent oxidation resistance but will require a protective coating to minimize oxidation and contamination for long-time applications. This research program is investigating the feasibility of using ductile nickel-chromium alloy claddings for protecting chromium alloys at temperatures up to 2300 F for 600 hours.

Eight cladding systems were applied to 1/16-inch-thick Cr-5W-0.07Y (hereinafter designated Cr-5W) sheet by the isostatic hot gas-pressure bonding process. These cladding systems consisted of 5 to 10-mil-thick surface layers of Ni-30Cr or Ni-20Cr-20W usually modified with 3 to 5 weight percent aluminum for added oxidation resistance. Between the nickel-base alloys and the Cr-5W substrate were 1/2 to 1-mil-thick layers of platinum to promote compatibility, and 1/2 to 1-mil layers of unalloyed tungsten or W-25Re to retard interdiffusion. In general, excellent bonds were obtained between the various metal foil layers by gas-pressure bonding at 2150 F for 2 hours at 10,000 psi. Cyclic oxidation resistance of these cladding systems was excellent at 2100 F. Oxidation tests conducted at 2300 F indicated that the aluminum-modified Ni-20Cr-20W cladding had the best potential for long-time protection of the chromium alloy at this higher temperature.

Composition and thickness of the intermediate foil layers of the cladding systems were found to be of primary importance in cyclic oxidation behavior. One-half-mil-thick tungsten was observed to stop gross interdiffusion at 2100 F for a minimum of 200 hours. However, this tungsten layer developed small, localized discontinuities during cyclic oxidation at 2100 F. Substrate hardening occurred at these localized tungsten discontinuities. W-25Re was found to be incompatible with Ni-30Cr; brittle, weak bonds were obtained. The insertion of platinum between the Ni-30Cr and W-25Re appeared to relieve this compatibility problem to some extent. The presence of too thick a platinum compatibility layer in a cladding system rapidly dissolved much of the tungsten thereby reducing its effectiveness as a diffusion barrier.

INTRODUCTION

Chromium-base alloys are promising candidates for gas-turbine vane and blade applications. These alloys have potentially higher temperature capabilities than the current superalloys. Also, they are not subject to catastrophic oxidation as are the more refractory alloys of columbium, molybdenum, tantalum, and tungsten.

Protective coatings will be required for the chromium-base alloys to retain their structural integrity in hot-air environments. These coatings must be able to retard nitridation and excessive oxidation of the alloys. More important, the coatings must maintain their protectiveness in the rigorous environment of the gas-turbine engine.

The objective of this program is to develop a ductile metallic coating system to protect chromium-alloy turbine vanes and blades at temperatures as high as 2300 F. The ductile coating system is to consist of a 5 to 10-mil-thick layer of an oxidation-resistant Ni-Cr-base alloy for primary protection of the prototype chromium-alloy substrate. Between the Ni-Cr surface layer and the chromium substrate is a 1/2 to 1-mil-thick layer of tungsten to retard interdiffusion. Further, a thin platinum layer may be required between Ni-Cr and tungsten to improve the mechanical compatibility of these layers. The various layers of the coating system are to be applied as metal foils to the substrate using the gas-pressure-bonding process.

During the first 6-month work period, studies were directed at (1) defining the cyclic oxidation behavior of 10-mil-thick Ni-Cr-base alloy foils which were chosen as potential cladding materials and (2) determining the gas-pressure-bonding parameters for applying the various metal foils to the chromium-alloy substrate. The results of these earlier studies, which were presented in the First Semiannual Report, are summarized below:

(1) It was recognized at the start of the program that Ni-Cr foil alloys might be limited to temperatures of less than 2400 F in air environments. Modification of the alloys with aluminum was deemed necessary to improve their maximum temperature capabilities. Through the use of a pack-cementation process and an homogenization anneal, aluminum additions of 3 to 5 weight percent were added to the alloys Ni-30Cr and Ni-20Cr-20W. These aluminum-modified alloys had good oxidation resistance at temperatures through 2300 F. Ten-mil-thick foils of these alloys lost only 1/2 mil per side when oxidized 50 2-hour cycles of 2300 F, and they retained their good bend ductility after testing. The oxidation resistance of these alloys at 2400 F was not sufficient to permit their use as thin foil claddings at this temperature.

(2) Gas-pressure-bonding parameters were determined for preparing the composite coating system. Good bonds were achieved in the composites with 10,000-psi isostatic pressure at 2150 F for 2 hours.

EXPERIMENTAL PROGRAM

During the second 6-month work period, foil-clad chromium-alloy specimens have been prepared and cyclic oxidation tested at 2100 F and 2300 F. Some revisions in the original program plan have occurred as the result of these tests. The description of the cladding systems, their behavior during oxidation testing, and the program modifications are discussed in the sections which follow.

Cladding Systems

Eight cladding systems are currently being evaluated in the program. These systems are

System	Substrate-Coating Diffusion Barrier	"Compatibility" Layer	Nickel-Base Alloy Surface-Layer
I	1/2-mil W	None	5-mil Ni-20Cr-20W modified with aluminum
II	1/2-mil W	1/2-mil Pt	5-mil Ni-20Cr-20W modified with aluminum
III	1/2-mil W	1/2-mil Pt	5 and 10-mil Ni-30Cr
IV	1/2-mil W	1/2-mil Pt	5-mil Ni-30Cr modified with aluminum
V	1-mil W-25Re	1/2-mil Pt	5-mil Ni-30Cr modified with aluminum
VI	1-mil W-25Re	None	5-mil Ni-30Cr modified with aluminum
VII	1-mil W	1/2-mil Pt	5-mil Ni-30Cr modified with aluminum
VIII	1/2-mil W	1-mil Pt	5-mil Ni-30Cr modified with aluminum

The diffusion barrier, "compatibility" layer, and nickel-base alloy surface layer are applied to the chromium-alloy substrate in a one-step gas-pressure-bonding operation. After bonding, about 3 to 5 weight percent aluminum is added to the nickel-base alloy by a pack-cementation treatment followed by a diffusion anneal. The function of the platinum compatibility layer in the cladding system is to stop the formation of brittle intermetallic compounds between the diffusion barrier and the nickel-base alloy.

For System III, two different surface-layer thicknesses were used, 5-mil-thick Ni-30Cr for evaluation at 2100 F and 10-mil-thick Ni-30Cr for tests conducted at 2300 F. Two 1/2-mil-thick layers of tungsten and platinum were used in Systems VII and VIII, respectively, to obtain the desired 1-mil layer thickness as appropriate. Table 1 lists the sources of the materials being used in these cladding systems.

It was initially planned to prepare and evaluate Systems I through V. However, the experimental results that will be discussed later indicated additional information was required concerning the behavior of the diffusion barrier during cyclic oxidation. Systems VI, VII, and VIII were included to obtain this information.

TABLE 1. SOURCES OF MATERIALS FOR CLADDING SYSTEMS

Material	Dimensions	Source
Tungsten	1/2 mil thick x 2 inches wide	Henry Cross Metals
W-25Re	1 mil thick x 2 inches wide	Chase Brass and Copper Co.
Platinum	1/2 mil thick x 3-inches minimum width	Baker Platinum Division, Engelhard Industries, Inc.
Tophet 30 (Ni-30Cr)	5 mils thick x 3 inches wide	Wilber B. Driver Company
Ni-20Cr-20W	5 mils thick x 3 inches wide	Battelle Memorial Institute

General Electric Company, Refractory Metals Plant, Cleveland, Ohio, is the supplier of the chromium-alloy substrate under a separate NASA contract. The nominal composition of the alloy in weight percent is Cr-5W-0.07Y. Analyses of two heats of Cr-5W being used in the program and their bend transition temperatures are given in Table 2.

TABLE 2. ANALYSES OF 1/16-INCH-THICK Cr-5W SHEET PREPARED BY GENERAL ELECTRIC

Element	Heat 58-100	Heat 64-100
W	4.86 wt%	4.82 wt%
Y	0.07 wt%	0.11 wt%
S	20 ppm	50 ppm
C	80 ppm	80 ppm
P	<10 ppm	10 ppm
O	80 ppm	50 ppm
N	45 ppm	35 ppm
H	1 ppm	8 ppm
4T Bend Transition Temperature	550 C<T<575 C	225 C<T<250 C

Experimental Procedure

Specimen Design and Preparation

Figure 1 shows the components of a typical cladding system prior to assembly for gas-pressure bonding. First, these components are chemically cleaned in the solutions listed in Table 3, degreased in methyl-ethyl-ketone, and rinsed in acetone and alcohol. The Cr-5W sheet, 1/16 inch thick, with length and width dimensions of 1 x 1 inch, 1 x 2 inches, or 3/4 x 3-1/2 inches, is fitted into a yoke (picture frame) of 1/16-inch-thick Ni-30Cr having side walls 1/8 inch thick. The diffusion barrier and compatibility layer are cut to the length and width dimensions of the Cr-5W substrate and tack-welded to the substrate using a Hughes Micro Circuit Welder. Figure 2 shows this tack welding operation; Table 4 gives the welding parameters. The nickel-base alloy cladding is then laid

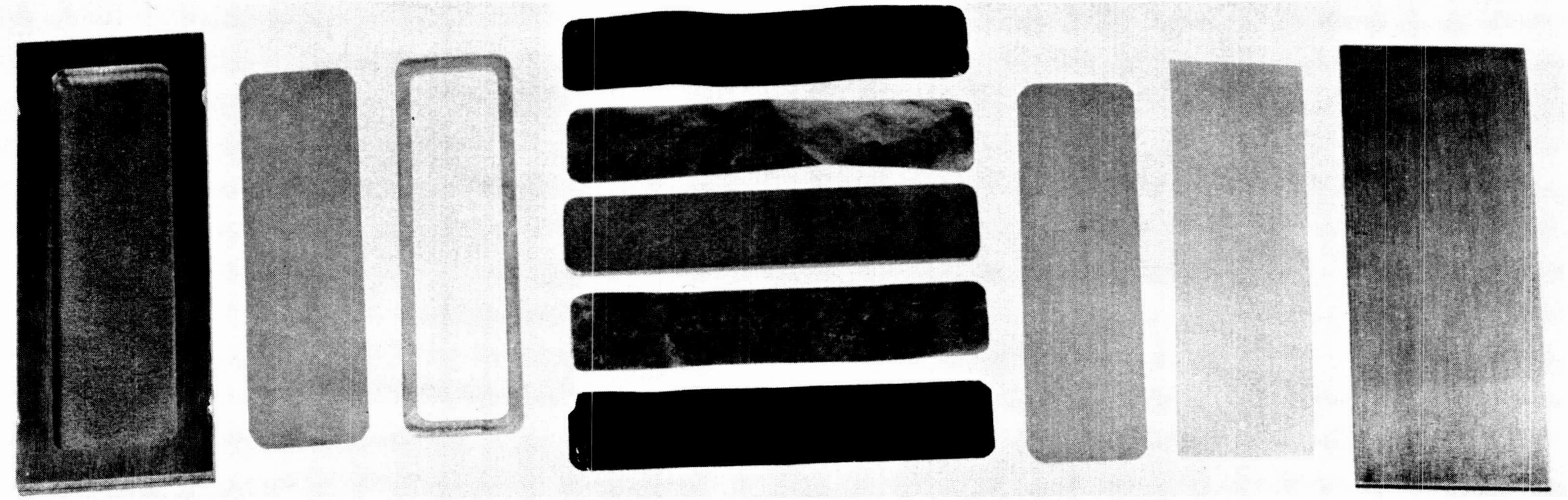

FIGURE 1. COMPONENTS FOR PREPARING 1/16 x 3/4 x 3-1/2-INCH CLADDING SPECIMEN

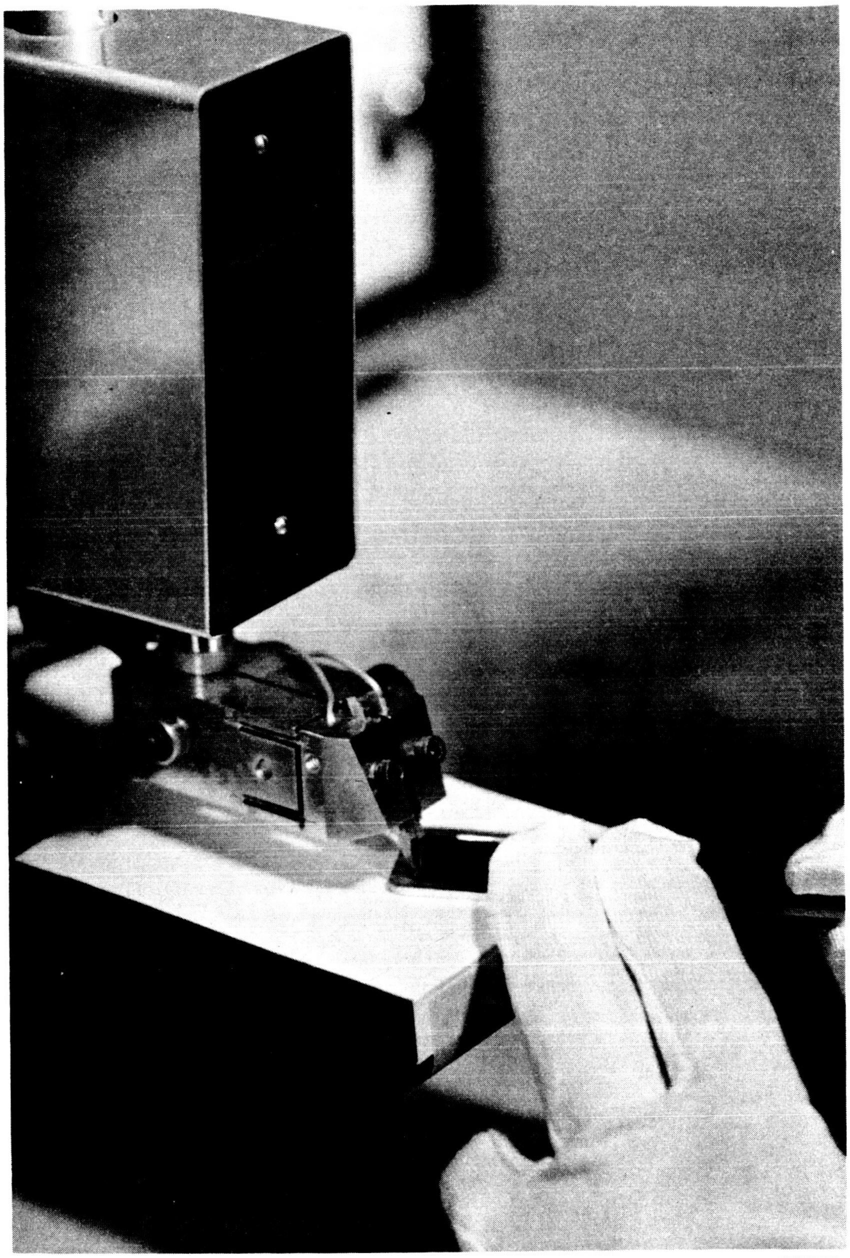

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FIGURE 2. TACK WELDING 1/2-MIL FOILS IN POSITION DURING ASSEMBLY FOR GAS-PRESSURE BONDING

over these layers, overlapping the Ni-30Cr yoke. These components are placed inside a mild-steel yoke and cover assembly. A layer of 3-mil-thick molybdenum foil is present between the steel and nickel-base cladding to prevent iron contamination of the cladding. The assembly is then clamped between thick copper cooling blocks and weld sealed under vacuum.

TABLE 3. ETCHING SOLUTIONS AND CONDITIONS FOR CLEANING THE COMPONENTS OF THE CLADDING SYSTEMS

Component	Etchant	Etching Conditions
W foil	$45HF-20HNO_3-35H_2O$	Ambient
W-25Re foil	$45HF-20HNO_3-35H_2O$	Ambient
Cr-5W substrate	$1/3HF-1/3HNO_3-1/3H_2O$	Boiling
Ni-30Cr yokes and foil	$1/3HF-1/3HNO_3-1/3H_2O$	Boiling
Ni-20Cr-20W foil	$1/3HF-1/3HNO_3-1/3H_2O$	Boiling

TABLE 4. PARAMETERS FOR SPOT WELDING FOILS TO SUBSTRATE

Parameter	W, W-25Re Foil	Pt Foil
Electrode	Mo	Cu
Gap	0.010 in.	0.010 in.
Voltage	1.6V	1V
Duration	15 μsec	10 μsec
Force	6 lb	1/2 lb

After welding, the assembly is leak tested and gas-pressure bonded at 2150 F, 10,000-psi isostatic pressure for 2 hours. The steel and molybdenum are then leached from the nickel-base cladding and Ni-30Cr picture frame in a nitric acid bath. After the steel is leached from the clad Cr-5W, the edges of the Ni-30Cr picture frame are radiused in preparation for the aluminum modification step of the process.

About 5 weight percent aluminum is added to the nickel-base cladding of appropriate systems using a pack-cementation process. Aluminizing the clad Cr-5W at 1750 F for 12 hours in a mixture of 1 weight percent aluminum, 1 weight percent NaCl, 98 weight percent Al_2O_3 powder applies the required amount of aluminum, about 5 mg/cm^2 for 5-mil-thick nickel-base alloy foils. The aluminized specimens are then homogenized in an argon atmosphere at 2100 F for 4 hours, heated directly to 2200 F, and held for an additional 16 hours. This treatment diffuses the aluminum into the nickel-base cladding and dissolves any brittle intermetallic compounds formed on the cladding surface during the pack-cementation operation. Some subsurface porosity is produced in the nickel-base cladding as a result of the diffusion treatment.

Evaluation Procedures

The protective capabilities of the eight cladding systems are being evaluated in cyclic oxidation tests conducted in triplicate at 2100 F and 2300 F. The tests are performed in an ambient air atmosphere for a maximum time of 200 hours. The specimens are cycled (air cooled) to room temperature every 2 hours during the first 100 hours and every 20 hours for the second 100 hours of testing. All specimens used in these oxidation tests have been prepared from Cr-5W Heat 58-100. Specimen sizes are 1/16 x 1 x 1 inch and 1/16 x 3/4 x 3-1/2 inches.

Cr-5W specimens, 1/16 x 3/4 x 3-1/2 inches, clad with Systems I through VI are being subjected to bend tests after they receive 100 hours of cyclic oxidation at 2100 F. The 4T bend transition temperature is being determined for these oxidized specimens according to the Materials Advisory Board Specifications, MAB Report 192-M. Uncoated Cr-5W sheet is also being bend tested after oxidation for short times at 2100 F. The BTT for the coated and uncoated materials will be compared to establish the effectiveness of the six cladding systems in protecting the substrate from contamination. Cr-5W Heat 64-100, the low BTT substrate, is being used for the bend tests.

Controlled defect testing is being conducted to study the extent of damage that occurs at a coating discontinuity. Cladding Systems I, IV, and V are being used for this test. The defects are 30-mil-wide slots cut to depths of 5, 7, and 10 mils into the cladding, exposing the inter-layers of the cladding system and the substrate to the atmosphere. Such factors as (1) maximum depth of contamination and (2) the extent of oxide undercutting of the nonoxidation-resistant diffusion barrier are to be determined by metallographic analysis.

Upon completion of the above series of tests, two of the more promising systems will be subjected to further oxidation testing at 2100 F and 2300 F for up to 600 hours using 20-hour cycles. The size of the oxidation test specimens will be 1/16 x 1 x 2 inches. Bend transition temperature will also be determined for the two systems after long-time oxidation. Sequential high-temperature, low-temperature, high-temperature oxidation tests will be conducted to evaluate the stability of the two systems in varying temperature conditions such as might be encountered in an operating gas-turbine engine. Cr-5W Heat 64-100 will be used in the advanced testing.

The nickel-base alloy coating system which performs best in the advanced tests will be applied to wedge-shaped Cr-5W specimens for simulated gas-turbine rig tests conducted by NASA.

EXPERIMENTAL RESULTS

Preparation of Cladding Systems

Machining of the 1/16-inch-thick Cr-5W sheet to the required dimensions to fit the Ni-30Cr picture frames presented some difficulties. Initial attempts to edge grind the Cr-5W resulted in the formation of cracks. The majority of the specimens containing these cracks were suitable for oxidation testing. However, such cracks made the machined material unsatisfactory for bend testing.

A brief machinability study and literature search was conducted which resulted in a procedure for obtaining crack-free Cr-5W sheet after edge grinding. The specimens were rough cut to size using a soft cut-off wheel. The Cr-5W was edge ground in packs of about 15 specimens using mild-steel shims between each specimen. Only 0.0002 inch of material was removed per pass with a silicon carbide type of grinding wheel and water coolant. Specimens prepared in this manner were found to be free of any cracks, as indicated by dye penetrant and microscopic inspection techniques.

Gas-Pressure Bonding

Gas-pressure bonding of all specimens required for the preliminary evaluation of the cladding systems was completed during this report period. These specimens included:

(1) Six specimens each of Cladding Systems I through VIII for the 2100 F and 2300 F cyclic oxidation tests - Cr-5W substrate dimensions: 1/16 x 1 x 1 inch and 1/16 x 3/4 x 3-1/2 inches of Heat 58-100.

(2) Two specimens each of Systems I, IV, and V for the defect test - Cr-5W substrate dimensions: 1/16 x 1 x 1 inch and 1/16 x 3/4 x 3-1/2 inches of Heat 58-100.

(3) Six specimens each of Systems I through VI for bend tests - Cr-5W substrate dimensions: 1/16 x 3/4 x 3-1/2 inches of Heat 64-100.

Initially, some difficulty was encountered in assembling the specimens without misaligning the various metal foil layers. The tack welding technique described in the procedure section was devised to eliminate shifting of the foil interlayers.

Preparation of some of the components that will be required for the more advanced tests of two systems is in progress. Steel yokes and cover-plates, and Ni-30Cr yokes for the long-time oxidation tests have been machined. Machining of the 1/16 x 1 x 2-inch and 1/16 x 3/4 x 3-1/2-inches Cr-5W specimens for these tests is nearing completion. In addition, fabrication and assembly procedures for gas-pressure cladding the more complex wedge-shaped test specimens are being developed.

Aluminum Modification

With the exception of the aluminum-free System III, 4 to 6 weight percent aluminum was added to the 5-mil-thick nickel-base claddings Ni-30Cr and Ni-20Cr-20W. (One mg/cm^2 of aluminum deposited is equivalent to about one weight percent for the 5-mil-thick nickel-base alloy foils.) The number of specimens being aluminized and the small size of the graphite retort being used, 2-1/2 x 5 x 8-inches inside dimensions, necessitated processing of specimens in five batches of about 20 specimens each. Aluminizing temperature was 1750 F for all batches. Four batches of specimens were aluminized for 12 hours and a fifth batch for 18 hours to assure a high enough aluminum deposit for good oxidation resistance at 2300 F. Aluminum weight gains for individual specimens are listed in Appendix Table A-1. Data are summarized below:

BATCH ONE – 1750 F for 12 hours

Number of Specimens – 6
Minimum Weight Gain – 5.0 mg/cm^2
Maximum Weight Gain – 5.2 mg/cm^2
Average Weight Gain – 5.1 mg/cm^2

BATCH TWO – 1750 F for 12 hours

Number of Specimens – 28
Minimum Weight Gain – 3.1 mg/cm^2
Maximum Weight Gain – 4.6 mg/cm^2
Average Weight Gain – 4.0 mg/cm^2

BATCH THREE – 1750 F for 18 hours

Number of Specimens – 27
Minimum Weight Gain – 4.8 mg/cm^2
Maximum Weight Gain – 7.1 mg/cm^2
Average Weight Gain – 5.8 mg/cm^2

BATCH FOUR – 1750 F for 12 hours

Number of Specimens – 15
Minimum Weight Gain – 4.2 mg/cm^2
Maximum Weight Gain – 5.2 mg/cm^2
Average Weight Gain – 4.7 mg/cm^2

BATCH FIVE – 1750 F for 12 hours

Number of Specimens – 15
Minimum Weight Gain – 4.0 mg/cm^2
Maximum Weight Gain – 4.3 mg/cm^2
Average Weight Gain – 4.2 mg/cm^2

The increase in cladding thickness resulting from the aluminizing treatment was about 0.5 to 0.8 mil per side. A few of the specimens had a black surface along the edges and corners of the Ni-30Cr picture frame after aluminizing instead of the usual light gray color. These were regions of low aluminum content (1) where the specimens had inadvertently contacted the graphite retort or (2) where the specimens had not been completely covered by the pack mixture. Such surface irregularities were the result of settling of the pack mixture during the thermal treatment and were readily eliminated in later runs by tamping the mixture during the packing operation.

Homogenization of the specimens was also conducted in five batches. Some slight oxidation (about 0.1 mg/cm^2 weight gain) occurred during the air cool step of the treatment which slightly discolored the specimens. (The weights of the specimens after the homogenization treatment were used as the starting weights for the oxidation tests.) No blistering or cracking of the claddings occurred as the result of the homogenization anneal.

Metallography of the As-Prepared Specimens

Specimens from each of the cladding systems were metallographically prepared and examined in the following conditions: (1) as gas-pressure bonded, (2) as aluminized, and

(3) as homogenized. The specimens were examined in the as-polished condition and after etching. An etchant of 50 parts lactic acid, 15 parts nitric acid and 2 parts hydrofluoric acid was used to accentuate the aluminide coating structure. Tungsten was etched with the Murakami's solution. An electrolytic, 5 wt% chromic acid solution (4 volts dc) was the etchant for the nickel-base claddings and also for the Cr-5W substrate. These various etchants usually had an adverse effect on one of the components of the cladding system and required the specimens to be repolished between each application.

Gas-pressure bonding at 2150 F and 10,000 psi for 2 hours produced good bonds in all systems with one exception. System VII, the system with a 1-mil tungsten diffusion barrier composed of two 1/2-mil-foil layers, showed only partial bonding between the two tungsten layers. (One-mil-thick tungsten was not available at the time and the 1/2-mil layers were used only for expediency.) The bond junction between the Ni-30Cr picture frame and Cr-5W was usually continuous in these specimens. On occasion, there were voids where the fit between the picture frame and substrate was too loose. These voids were bridged by the 5-mil-thick Ni-30Cr or Ni-20Cr-20W claddings. Partial solution of the tungsten diffusion barrier by the platinum compatibility layer occurred in Systems II, III, IV, and VIII, reducing the thickness of the tungsten to about 0.3 mil. The tungsten barrier in the platinum-free System I was 0.5 mil. Platinum also dissolved some of the original 1-mil W-25Re layer in System V, decreasing the thickness to about 0.6 mil. (The W-25Re in the platinum-free System VI was 0.9 mil.)

Figure 3 shows a representative microstructure of an aluminized nickel-base cladding. The outermost coating layer is typically 1.0 to 1.5-mils-thick and is probably based on a compound of 50 to 60 atomic percent aluminum. Below this layer is a 0.5-mil-thick multiphase region. The quality of the bond junctions after aluminizing was the

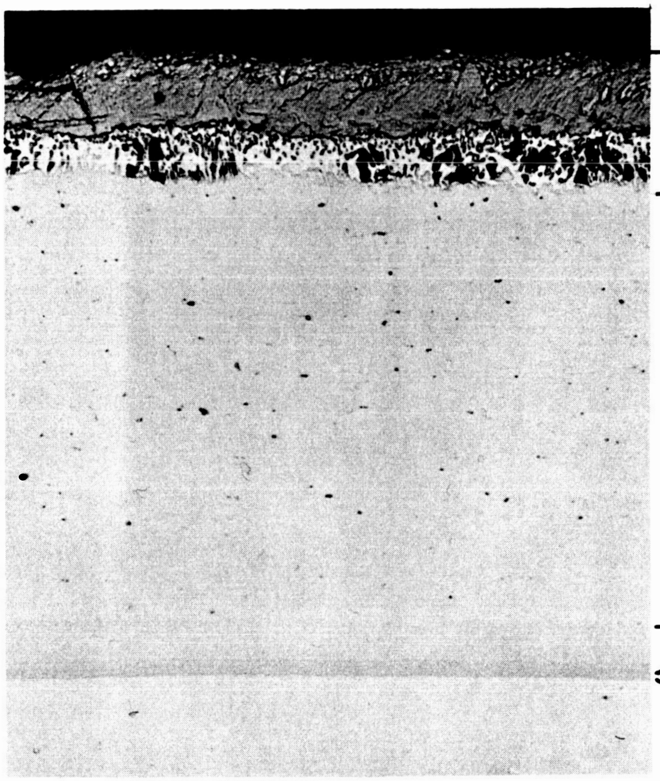


FIGURE 3. ALUMINIZED STRUCTURE OF CLADDING SYSTEM IV

Specimen etched in the lactic/nitric/hydrofluoric acid solution.

same as the gas-pressure-bonded condition. The thickness of the W-25Re layer decreased slightly in System VI during aluminizing. System VIII, the system with a 1-mil-thick platinum layer, also showed a slight decrease in the thickness of the diffusion barrier; tungsten was 0.2 mil thick. Otherwise, no appreciable dimension changes were observed.

Homogenizing the specimens at 2100 F for 4 hours and 2200 F for 16 hours completely dissolved the aluminide coating layer deposited on the 5-mil-thick nickel-base alloy claddings. Figure 4 shows the homogenized aluminum-modified Ni-30Cr layer of Cladding System IV. The extent of porosity in the claddings after homogenizing varied from area to area. The porosity was usually located 1.0 to 1.5 mils below the surface and very seldom extended to the surface. A small quantity of second phase was usually present in the aluminum-modified Ni-20Cr-20W claddings of Systems I and II. This phase is thought to be the result of a decrease in the tungsten solubility limit as aluminum is added to Ni-20Cr-20W. No appreciable decrease in the thickness of the tungsten diffusion barrier was observed during homogenization in the systems which contained the 1/2-mil-thick platinum layer. The platinum layer was no longer discernible in these systems and a two-phase region was present in its place. Total cladding thickness of these specimens after homogenization varied between 7 and 8 mils, depending on the system.

Extensive solution of the 1/2-mil tungsten barrier occurred in the system which contained the 1-mil platinum layer, System VIII, during the homogenizing treatment. The tungsten thickness varied from zero to a maximum of 0.2 mil. Figure 5 shows a region of the system where nearly all of the tungsten is in solution.

A serious compatibility problem was found to exist between W-25Re and aluminum-modified Ni-30Cr after homogenizing. Fracture of the bond between the two materials had occurred, Figure 6. This separation could have been caused by the air cool after the treatment or during metallographic sectioning. Either way, it indicated very poor bond strength. The presence of a platinum layer between the W-25Re and aluminum-modified Ni-30Cr, System V, appeared to eliminate the compatibility problem. A good bond was maintained in System V.

The homogenization treatment improved the bonding between the two 1/2-mil layers of tungsten in System VII. The location of the junction was still marked by some porosity, however. One region of the particular cross section which was examined did contain cracks extending along the junction and perpendicular to the junction through the cladding and into part of the substrate. The total cladding thickness for System VII was 8 mils; the tungsten was 0.7 mil thick.

Table 5 lists the microhardness values of cladding System IV after each of the three stages of preparation. These measurements show that the solution of aluminum into the Ni-30Cr increases the hardness of the nickel-base alloy by about 100 KHN. The hardness of the platinum-rich region was found to decrease about 300 KHN as the result of the homogenization treatment. No contamination of the substrate was indicated by these measurements.

Complete solution of the aluminide coating was not always obtained at the edges of the Ni-30Cr picture frame. In some regions, about 1 mil of intermetallic compound was observed. Porosity was present between the compound and inner Ni-30Cr picture frame at these regions.

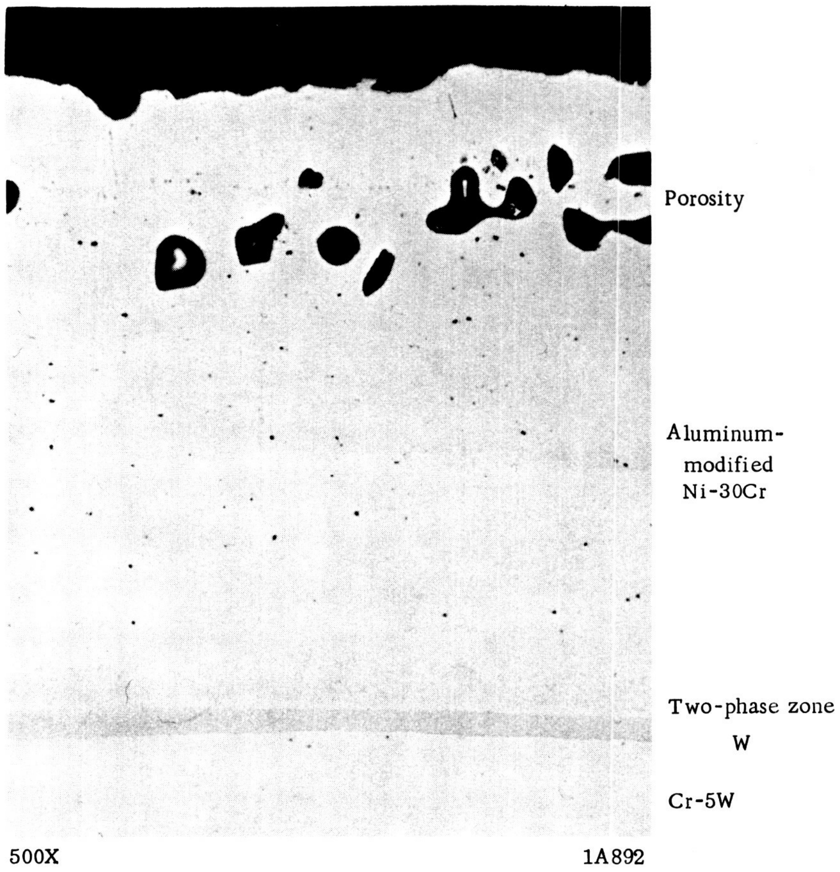


FIGURE 4. HOMOGENIZED STRUCTURE OF CLADDING SYSTEM IV

Specimen etched in the lactic/nitric/hydrofluoric acid solution.

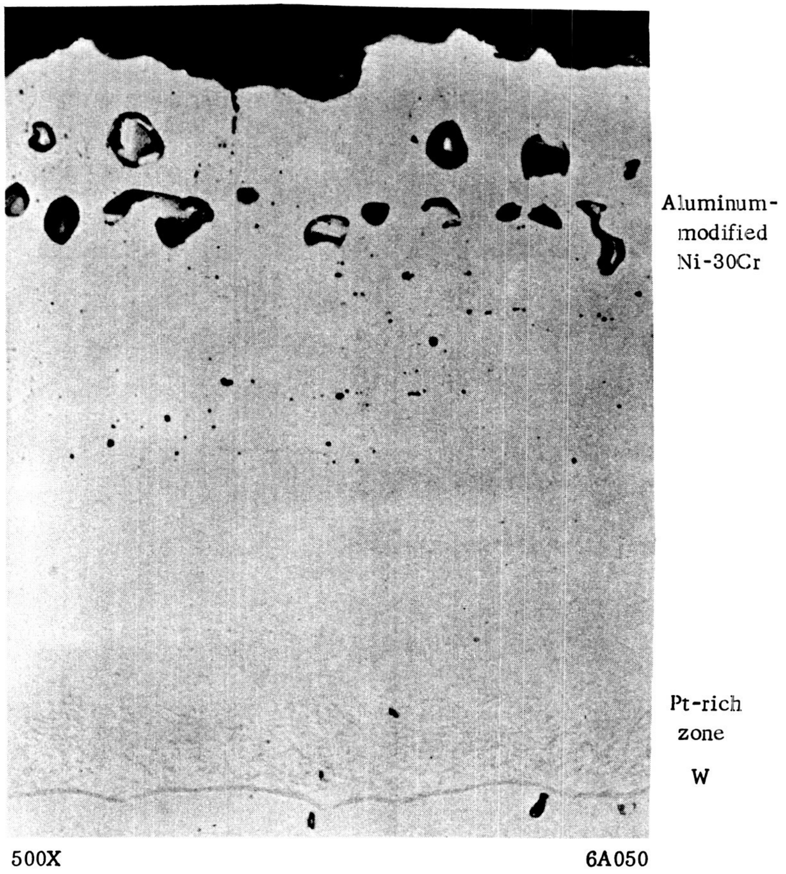


FIGURE 5. HOMOGENIZED STRUCTURE OF CLADDING SYSTEM VIII

Specimen is in the as-polished condition.

TABLE 5. KNOOP HARDNESS VALUES FOR CLADDING SYSTEM IV, Cr-5W:1/2-MIL W: 1/2-MIL Pt:Ni-30Cr + Al

100-Gram Load

Distance from Tungsten Layer, mils	Gas-Pressure-Bonded Condition		Aluminized Condition[a]		Homogenized Condition[b]	
	KHN	Comments	KHN	Comments	KHN	Comments
			Cladding Hardness			
			400	In aluminide coating	Porosity in cladding	
5-1/2	180	1 mil from surface	200	1 mil from coating	280	2-1/2 mils from surface
4	170		220		270	
3			220		280	
2	280		240			
1-1/2	330		290		270	
1/2	630	Pt-rich zone	680	Pt-rich zone	320	Two-phase region
0	370	In tungsten	300	In tungsten	380	In tungsten
			Cr-5W Hardness			
1	200		220		220	
2	200		230		210	
3	230		230		210	
4	220		240		220	
5	240		220		230	
10	210		220		230	
15	220		230		260	
20	230		240		240	
25	230		220		230	
30	230		220		220	

(a) See Figure 3 for cladding microstructure.

(b) See Figure 4 for cladding microstructure.

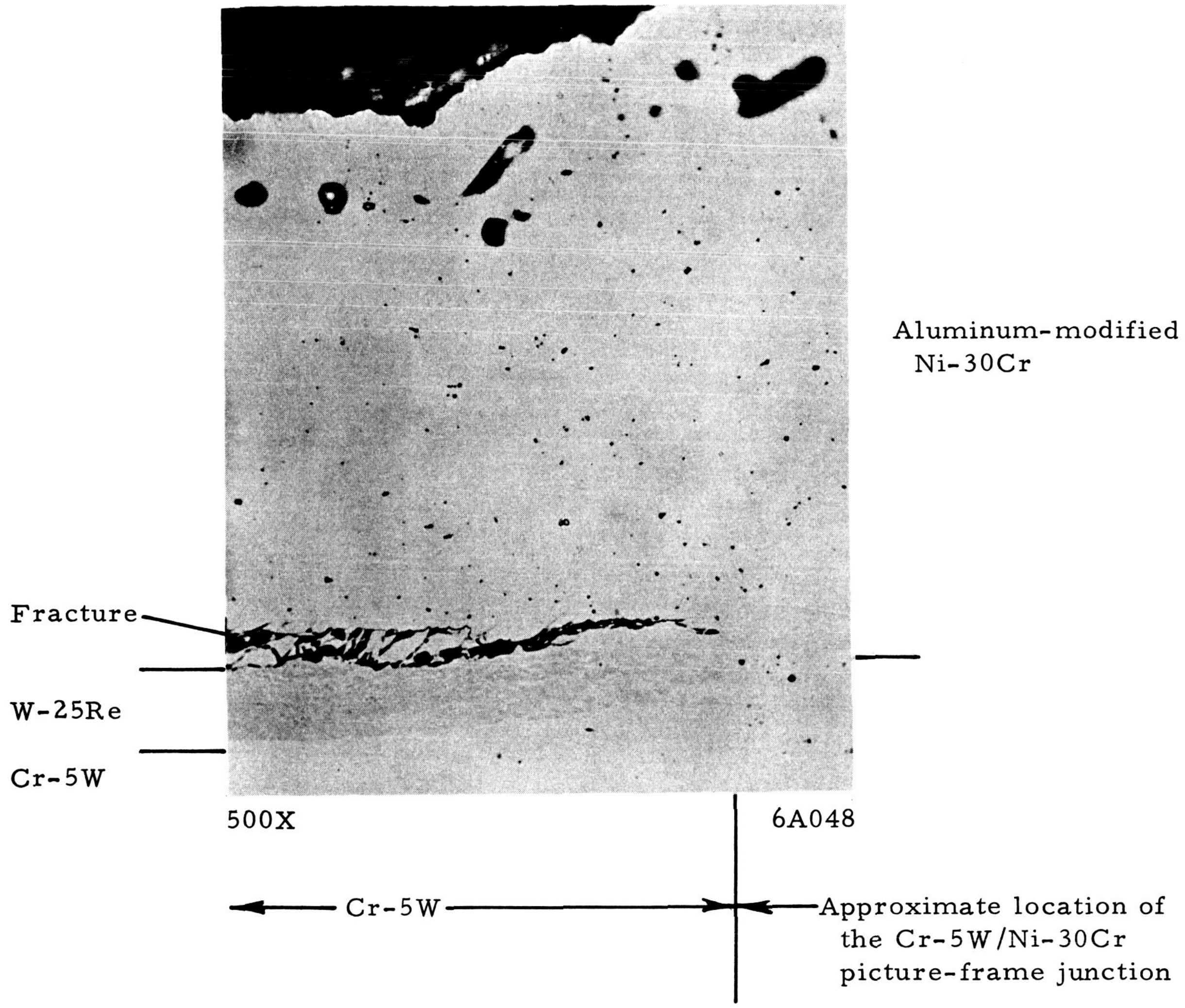


FIGURE 6. HOMOGENIZED STRUCTURE OF CLADDING SYSTEM VI

Specimen is in the as-polished condition.

Cyclic Oxidation Tests

Oxidation tests of the eight cladding systems at 2100 F and 2300 F were completed during this report period. Metallographic examination of some of the specimens has been completed but a large amount of this work is yet to be performed.

2100 F Cyclic Oxidation

Table 6 summarizes the results of the cyclic oxidation tests conducted at 2100 F. Detailed weight-change data are given in the Appendix Table B-1. The conditions of the specimens after oxidation are shown in Figure 7. The dark edges and corners present on some of the specimens were obtained during aluminizing and probably are regions of carbon contamination from the retort or regions of low aluminum content.

TABLE 6. SUMMARY OF 2100 F CYCLIC OXIDATION TESTS

Specimen[(a)]	Weight Change After Indicated Time and Cycle, mg/cm^2 100 Hours, 50 Cycles	Weight Change After Indicated Time and Cycle, mg/cm^2 200 Hours, 55 Cycles	Comments
I-1	1.5[(b)]	--	Cladding in excellent condition; defects at 90° corner of Cr-5W (see Figure 7)
I-4[(c)]	0.6	0.6	Cladding in excellent condition; no defects at radiused corners of Cr-5W
I-5[(c)]	0.7	0.7	Cladding in excellent condition; defect at one radiused inside corner
II-1	2.0[(b)]	--	Same as I-1
II-2	0.7	0.7	Ditto
II-3	0.8	0.9	"
II-9[(d)]	1.2	1.9	"
II-10[(d)]	2.6[(b)]	--	"
III-1	1.2	1.0	Spalling of black oxide; defects at 90° corners of Cr-5W
III-2	0.9[(b)]	--	Ditto
III-3	0.7	0.2	"
IV-1	2.4	--	Same as I-1
IV-2	2.2	2.8	Ditto
IV-3	1.9	2.5	"
V-3	1.1	1.3	Same as I-1
V-4	1.2[(b)]	--	Ditto
V-5	1.3	1.6	"
VI-1	1.0	1.3	1/4-inch-diameter blister in cladding near defected corner of Cr-5W
VI-2	1.1[(b)]	--	Numerous small blisters in cladding; defects at one 90° corner of Cr-5W
VI-4	2.3 at 40 hrs[(e)]		Small cracks visible in cladding after 20 hours, 10 cycles
VII-1	1.4	1.7	Two 1/16-inch-diameter blisters observed in cladding after 90 hours; slightly defected Cr-5W corners

TABLE 6. (Continued)

Specimen(a)	Weight Change After Indicated Time and Cycle, mg/cm^2		Comments
	100 Hours, 50 Cycles	200 Hours, 55 Cycles	
VII-3	1.2 at 50 hrs(e)	--	1/2-inch-diameter blister in cladding
VII-4	2.2 at 90 hrs(e)	--	1/16-inch-diameter blisters observed in cladding after 50 hours
VIII-1	2.2(b)	--	Darker oxide color than other Al-modified Ni-30Cr claddings; defects at corners of Cr-5W
VIII-2	2.5	3.0	Same as VIII-1
VIII-3	1.8	2.1	Ditto

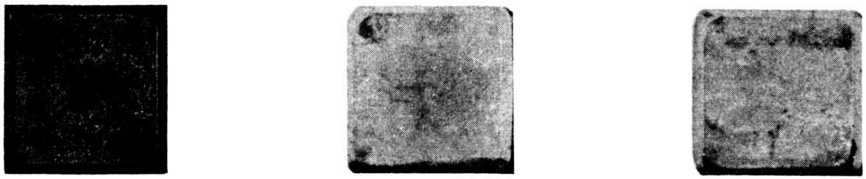
(a) Roman numeral refers to cladding system; Arabic numeral refers to specimen number in the system.

(b) Test discontinued after 100 hours.

(c) 1/2-mil-thick tungsten was between the Ni-30Cr picture frame and edges of the Cr-5W. This modification of the specimen design appeared to minimize fractures at the picture-frame bond junction.

(d) Specimens are modifications of cladding System II; the W and Pt layers are each 1 mil thick instead of 1/2 mil thick.

(e) Test discontinued at indicated time.



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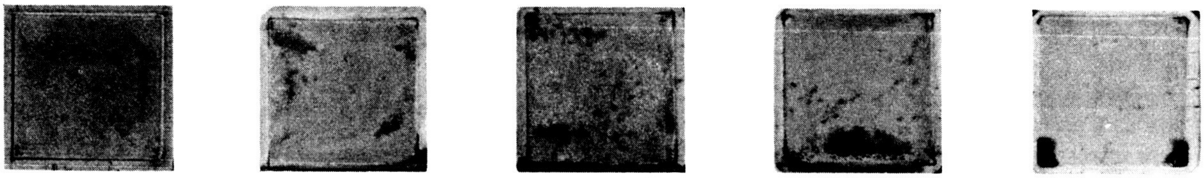
Specimen I-1, 100 Hr Specimen I-4, 200 Hr(a) Specimen I-5, 200 Hr(a)



2A725 6A418 6A418 6A418 5A893

Specimen II-1, 100 Hr Specimen II-2, 200 Hr Specimen II-3, 200 Hr Specimen II-9, 200 Hr(a) Specimen II-10, 100 Hr(a)

2A723 2A723 2A724 2A724

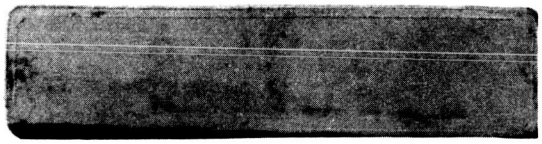
Specimen III-1, 200 Hr Specimen III-2, 100 Hr Specimen IV-1, 100 Hr Specimen IV-2, 200 Hr

2A723 2A724

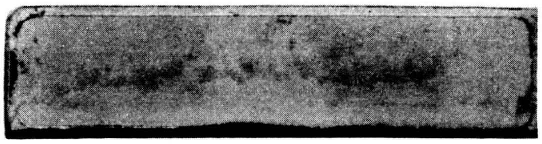
Specimen III-3, 200 Hr Specimen IV-3, 200 Hr

FIGURE 7. SPECIMENS OF CLADDING SYSTEMS I THROUGH VIII AFTER CYCLIC OXIDATION AT 2100 F

Magnification – 1X
(a) See footnotes Table 6.


6A418

Specimen V-3, 200 Hr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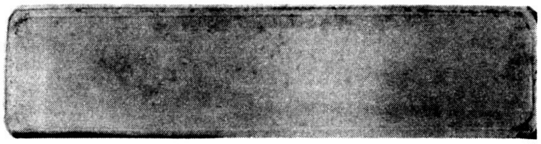
Specimen V-4, 100 Hr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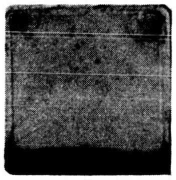
Specimen V-5, 200 Hr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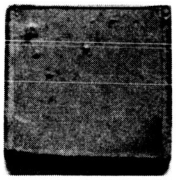
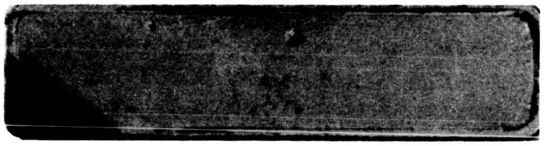
Specimen VI-1, 200 Hr


5A893

Specimen VI-2, 100 Hr


5A892

Specimen VI-4, 40 Hr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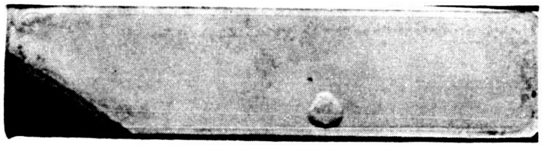
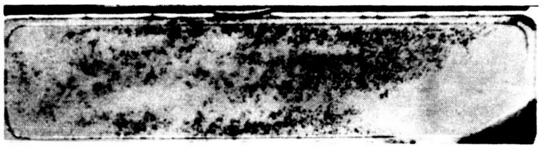
Specimen VII-1, 200 Hr


5A892

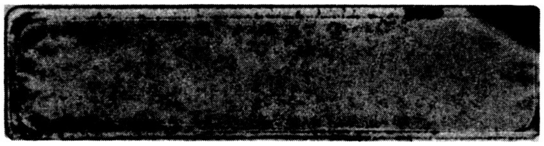
Specimen VII-3, 50 Hr


5A892

Specimen VII-4, 90 Hr


5A892

Specimen VIII-1, 100 Hr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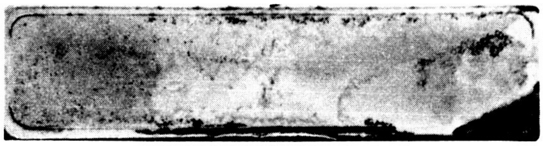
Specimen VIII-2, 200 Hr


6A418

Specimen VIII-3, 200 Hr

FIGURE 7. (Continued)

Aluminum-modified Ni-30Cr and Ni-20Cr-20W claddings demonstrated excellent oxidation resistance at 2100 F, as indicated by the nominal weight gains of 1 to 3 mg/cm^2 after 200-hours' exposure, and the tenacious oxide scale shown in Figure 8. The aluminum-free System III also performed satisfactorily. This later system formed a black, partially adherent oxide as compared to the light gray adherent oxide of the aluminum-modified systems.

The performance of the cladding systems at 2100 F appeared to be a function of the as-homogenized structure of the diffusion barriers rather than being related to the inherent oxidation resistance of the nickel-base claddings. Cladding System VI, the platinum-free system with the W-25Re diffusion barrier, developed numerous blisters during testing. This demonstrates further the poor compatibility between W-25Re and aluminum-containing Ni-30Cr. System VII, the system in which poor bonds were obtained between the two 1/2-mil tungsten layers, also blistered in these tests. The patches of dark oxide visible on the specimens of System VIII, Figure 7, suggest that the original light gray oxide of the aluminum-modified system has been contaminated. This oxide contamination might be related to the solution of the tungsten by the 1-mil-thick platinum layer originally contained in System VIII. Otherwise the performance of the claddings was very similar to the behavior of the 10-mil-thick nickel-base alloy foils tested earlier in the program.

Inherent weaknesses were present in the picture frame specimen construction which caused some cladding cracks to occur. These cracks initiated at the inside corners of the Ni-30Cr picture frame and progressed to a lesser extent along the picture frame/Cr-5W junction. Oxide discoloration is visible at these junctions in most specimens in Figure 7. Such cladding cracks were not classified as valid systemic failures since these regions did not contain a diffusion barrier or compatibility layer. Attempts to alleviate this deficiency were made by inserting 1/2-mil tungsten foil between the picture frame and 1/16-inch edge of the Cr-5W and by using radiused inside corners. Specimens I-4 and I-5 were prepared in this manner and showed some improvement. No cladding cracks formed in Specimen I-4 through 200 hours while one of the radiused corners of I-5 showed some cracking after 25 2-hour cycles.

2300 F Cyclic Oxidation

Table 7 summarizes the results of the cyclic oxidation tests conducted at 2300 F. Detailed weight-change data are given in the Appendix Table B-2. Figure 9 shows the conditions of the specimens after completion of the tests.

Composition of the nickel-base surface layer was a more important factor in the performance of the cladding systems at 2300 F than at 2100 F. Cladding Systems I and II, which had the aluminum-modified Ni-20Cr-20W surface layer, were superior to the aluminum-modified Ni-30Cr claddings of Systems IV through VIII. Systems I and II retained their adherent light-gray aluminum-modified oxide for about 140 hours after which some oxide spalling occurred. The aluminum-modified Ni-30Cr claddings began to develop a dark, crusty, partially adherent oxide product after only 30 hours' exposure, with the exception of Specimen VII-2. This particular specimen retained its light gray oxide through 200 hours at 2300 F. Specimen VII-2 had a 1-mil tungsten diffusion barrier which might account for its improved performance. System III, the aluminum-free 10-mil-thick Ni-30Cr-clad system, spalled continuously during oxidation but did appear to protect the Cr-5W for the 200 hours. This system probably benefited from the added strength of the 10-mil-thick (instead of the nominal 5-mil-thick clad) cladding, especially at the picture frame/Cr-5W junction.

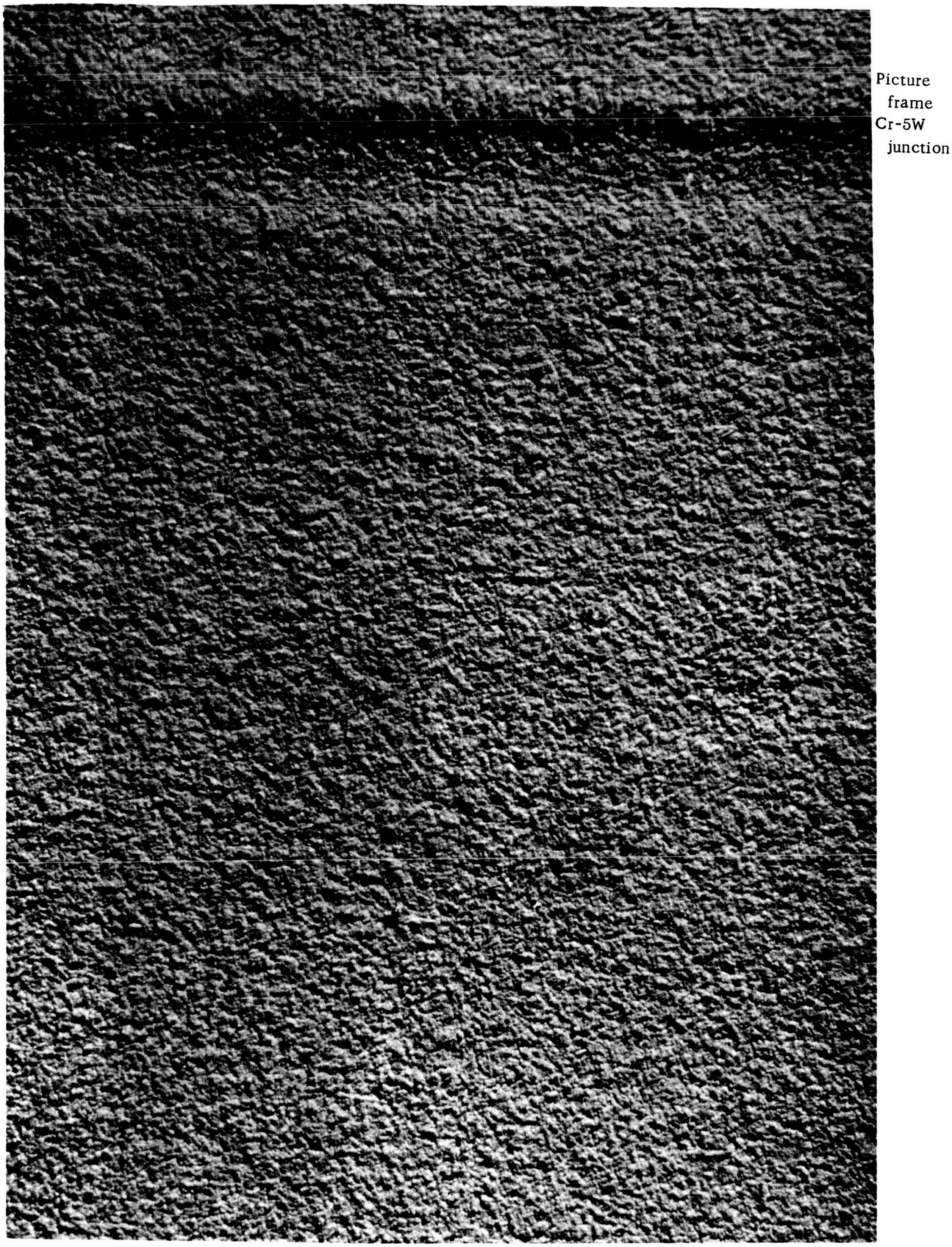


FIGURE 8. SURFACE OF CLADDING SYSTEM IV AFTER 200 HOURS, 55 CYCLES, OF OXIDATION AT 2100 F

TABLE 7. SUMMARY OF 2300 F CYCLIC OXIDATION TESTS

Specimen[(a)]	Weight Change After Indicated Time and Cycle, mg/cm^2 100 Hours, 50 Cycles	Weight Change After Indicated Time and Cycle, mg/cm^2 200 Hours, 55 Cycles	Comments
I-6	1.5	1.0	Cladding in good condition; some oxide spalling; junction between Ni-30Cr picture frame and Cr-5W is fractured and oxidized
I-7	8.9 at 80 hr[(b)]	--	Rupture of cladding near radiused corners of Cr-5W; substrate badly warped
I-8	6.2	7.2	Extensive cladding damage near radiused corners of Cr-5W; spalling of oxide
II-5	3.6	2.5	Cladding in good condition except near picture frame junction; warpage of Cr-5W; oxide spalling
II-6	2.5	0.2	Same as II-5
II-7	6.8[(c)]	--	Gross blistering of cladding near picture frame junction; oxide spalling
III-5	-6.5[(c)]	--	Spalling of black oxide; slight warping of Cr-5W; cladding cracked at radiused corner of Cr-5W
III-6	-6.9	-20.1	Same condition as III-5 except no apparent cladding cracks
III-7	-9.2	-18.0	Same as III-5
IV-5	11.0 at 80 hr[(b)]	--	Gross rupturing of much of the cladding; failure appeared to initiate at corners of Cr-5W; black, crusty oxide
IV-6	16.7 at 80 hr[(b)]	--	Same as IV-5
IV-7	14.3 at 80 hr[(b)]	--	Ditto
V-6	9.0[(c)]	--	Black, crusty oxide covers most of the cladding; much cladding damage at picture-frame junction

TABLE 7. (Continued)

Specimen[a]	Weight Change After Indicated Time and Cycle, mg/cm^2 100 Hours, 50 Cycles	 200 Hours, 55 Cycles	Comments
V-7	8.3	5.0	Same as V-6; much oxide spalling
V-8	3 at 10 hr[b]	--	Cracks formed in cladding
VI-5	0.7 at 2 hr[b]	--	Numerous cladding cracks formed on one side of specimen
VI-6	4.9 at 6 hr[b]	--	Extensive cracking of cladding
VI-7	3.3 at 6 hr[b]	--	Ditto
VII-2	-1.0	0.0	Majority of cladding has an adherent, gray oxide; much cladding damage at picture-frame junction
VII-5	2.3 at 10 hr[b]	--	Cladding cracks observed after one 2-hr cycle; slight warping of substrate
VII-6	10.8[c]	--	Black crusty oxide on cladding; Cr-5W substrate is badly warped; much cladding damage at picture-frame junction
VIII-4	14.6	21 at 140 hr[b]	Much blistering of cladding; cladding covered with a black, crusty oxide
VIII-5	11.9[c]	--	Cladding covered with black, crusty oxide; much warping of the substrate
VIII-6	14.0	15.8	Cladding covered with black, nonadherent, crusty oxide; Cr-5W is badly warped

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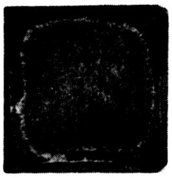
(a) Roman numeral refers to cladding system; Arabic numeral refers to specimen number in the system.

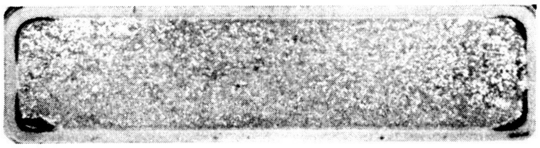
(b) Test discontinued at indicated time.

(c) Test discontinued after 100 hours.



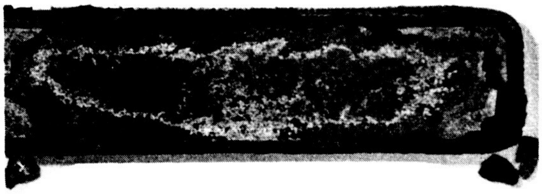
6A419

Specimen I-6, 200 Hr



5A895

Specimen I-7, 100 Hr



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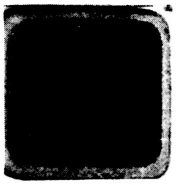
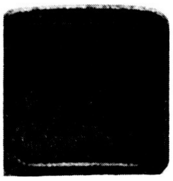
Specimen I-8, 200 Hr



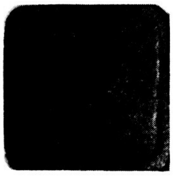
4A774

Specimen III-5, 10 Hr



6A419

Specimen III-6, 200 Hr



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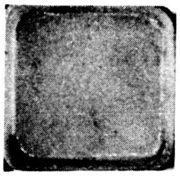
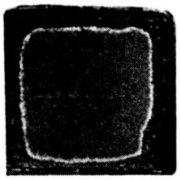
Specimen III-7, 200 Hr



5A895

Specimen II-5, 100 Hr



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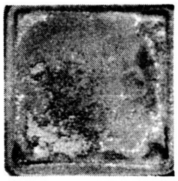
Specimen II-6, 200 Hr



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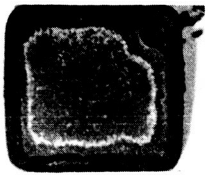
Specimen II-7, 100 Hr



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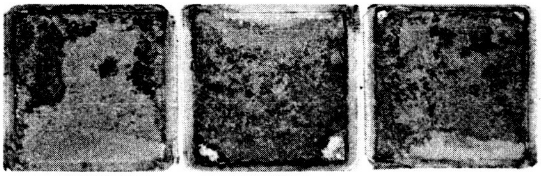
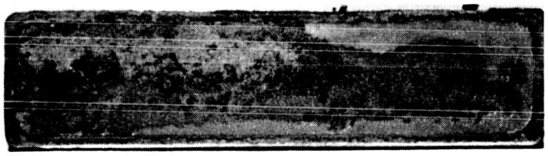
Specimen II-5, 200 Hr



5A895

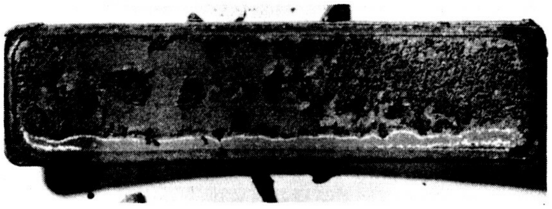
Specimen IV-5, 80 Hr Specimen IV-6, 80 Hr Specimen IV-7, 80 Hr

FIGURE 9. SPECIMENS OF CLADDING SYSTEMS I THROUGH VIII AFTER CYCLIC OXIDATION AT 2300 F



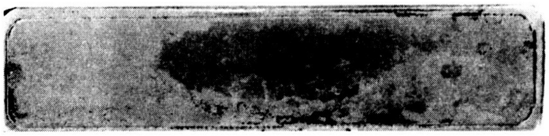
5A894

Specimen V-6, 100 Hr



6A419

Specimen V-7, 200 Hr



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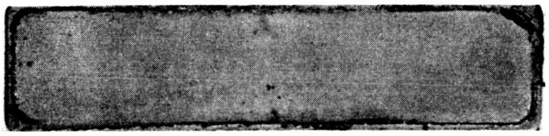
Specimen V-8, 10 Hr

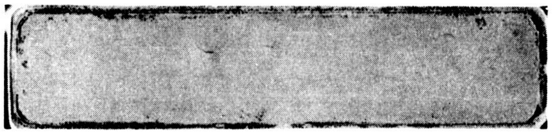


5A894

Specimen VII-2, 100 Hr

6A419

Specimen VII-2, 200 Hr



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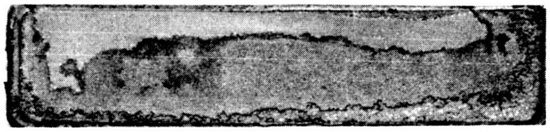
Specimen VII-5, 10 Hr



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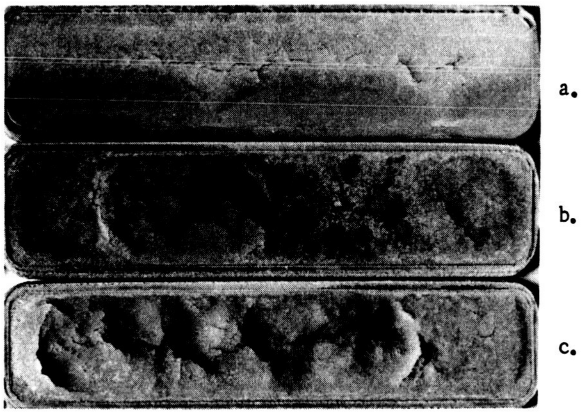
Specimen VII-6, 100 Hr



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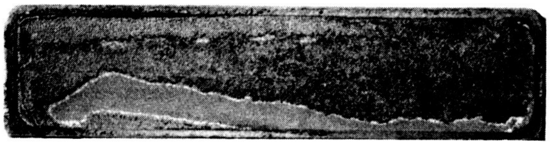
a. Specimen VI-5, 2 Hr

b. Specimen VI-6, 6 Hr

c. Specimen VI-7, 6 Hr

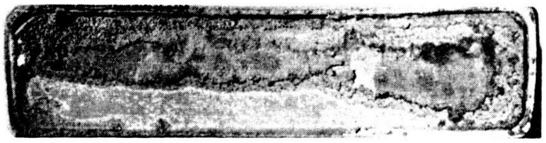


6A419

Specimen VIII-4, 140 Hr

5A894

Specimen VIII-5, 100 Hr



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Specimen VIII-6, 200 Hr

FIGURE 9. (Continued)

With the exception of Specimen III-6, all claddings suffered some damage caused by cracking at the picture frame/Cr-5W junction. Once cracking occurred, additional cladding damage progressed at these regions causing the claddings to blister and peel away from the Cr-5W. The claddings were also subjected to mechanical damage at 2300 F caused by extensive warping of the specimens. The 1/16 x 3/4 x 3-1/2-inch specimens were especially prone to this type of failure. When the warping became too severe, the picture frame and Cr-5W would partially separate at the inside corners rupturing the claddings.

Warping was purposely aggravated in a few of the specimens by always permitting the same side of these specimens to cool more rapidly than the other. The more rapidly cooled side became concave thus producing specimens in which one side of the cladding was in compression while the opposite side was in tension. Metallographic examination of the diffusion barriers in these specimens is expected to give an insight to the performance of these barriers under stress.

Thin layers of coating peeled away from the edges of the aluminized Ni-30Cr picture frames throughout the 2300 F oxidation tests. These layers were regions of high aluminum content where complete solution of the aluminide coating had not occurred during homogenization. When the edge peeling became excessive, the loose material was forcibly removed from the specimens and weighed. The oxidation weight-change measurements were then corrected for the removal of this known amount of material.

Metallography of Oxidized Specimens

Metallographic examination of the oxidized cladding systems was partially completed during this report period. Oxidized specimens from the following systems were examined:

(1) Systems I, II, III, and IV oxidized at 2100 F

(2) Systems V and VI oxidized at 2300 F.

The three nickel-base alloy cladding compositions -- aluminum-modified Ni-30Cr and Ni-20Cr-20W, and unmodified Ni-30Cr -- demonstrated excellent oxidation resistance at 2100 F. Less than 0.5 mil of cladding was consumed by oxidation for as much as 200 hours. Oxide-filled cracks, normal to the specimen surface, extended about 1-1/2 mils into the aluminum-modified Ni-20Cr-20W claddings. The aluminum-modified Ni-30Cr cladding of System IV was generally free of such cracks. A representative System IV structure is shown in Figure 10. The outer 2 mils of these claddings contained pockets of oxide in the voids that were produced during homogenization. Unmodified Ni-30Cr of System III had a very rough and irregular surface after oxidation. This resulted from continuous oxide spalling. The outer 1.5 mils of the Ni-30Cr cladding contained much internal oxide with the inner 3 mils being free of such oxide. With the exception of the cladding fractures which occurred at Ni-30Cr picture frame/Cr-5W junctions, a minimum of 3 mils of dense crack-free nickel-base cladding remained between the cladding surface and cladding/substrate interface in all specimens examined after oxidation at 2100 F.

Frequent, localized discontinuities were found in the tungsten diffusion barriers of the specimens oxidized at 2100 F. A typical tungsten discontinuity observed in System III is shown in Figure 11. The Cr-5W substrate present next to these discontinuities contained either a diffusion zone, as shown in the figure, or what appeared to be a void. Some of the more severely affected regions contained a dark, grain-boundary precipitate in the Cr-5W to a depth of 3 or 4 mils below the tungsten barrier. Grain-boundary diffusion of a continuous, light etching phase was also observed in the substrate near these discontinuities. In regions where the tungsten was continuous, compatibility between the diffusion barrier and the nickel-base claddings appeared to be satisfactory. The thickness of the tungsten in such regions showed no measurable change from the as-prepared condition.

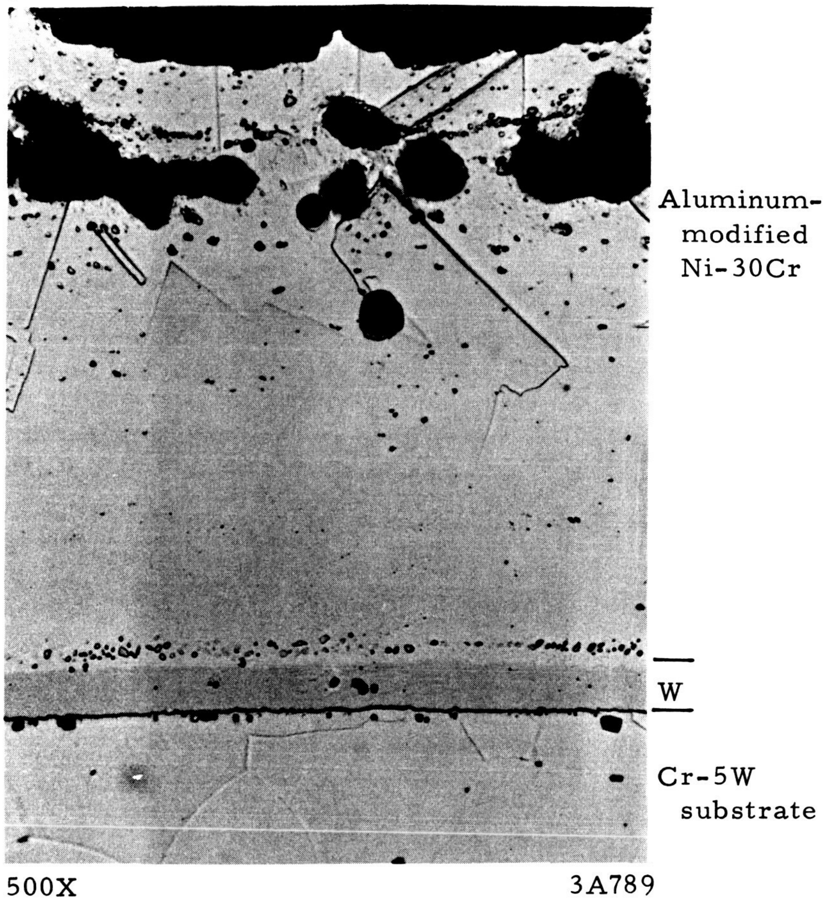
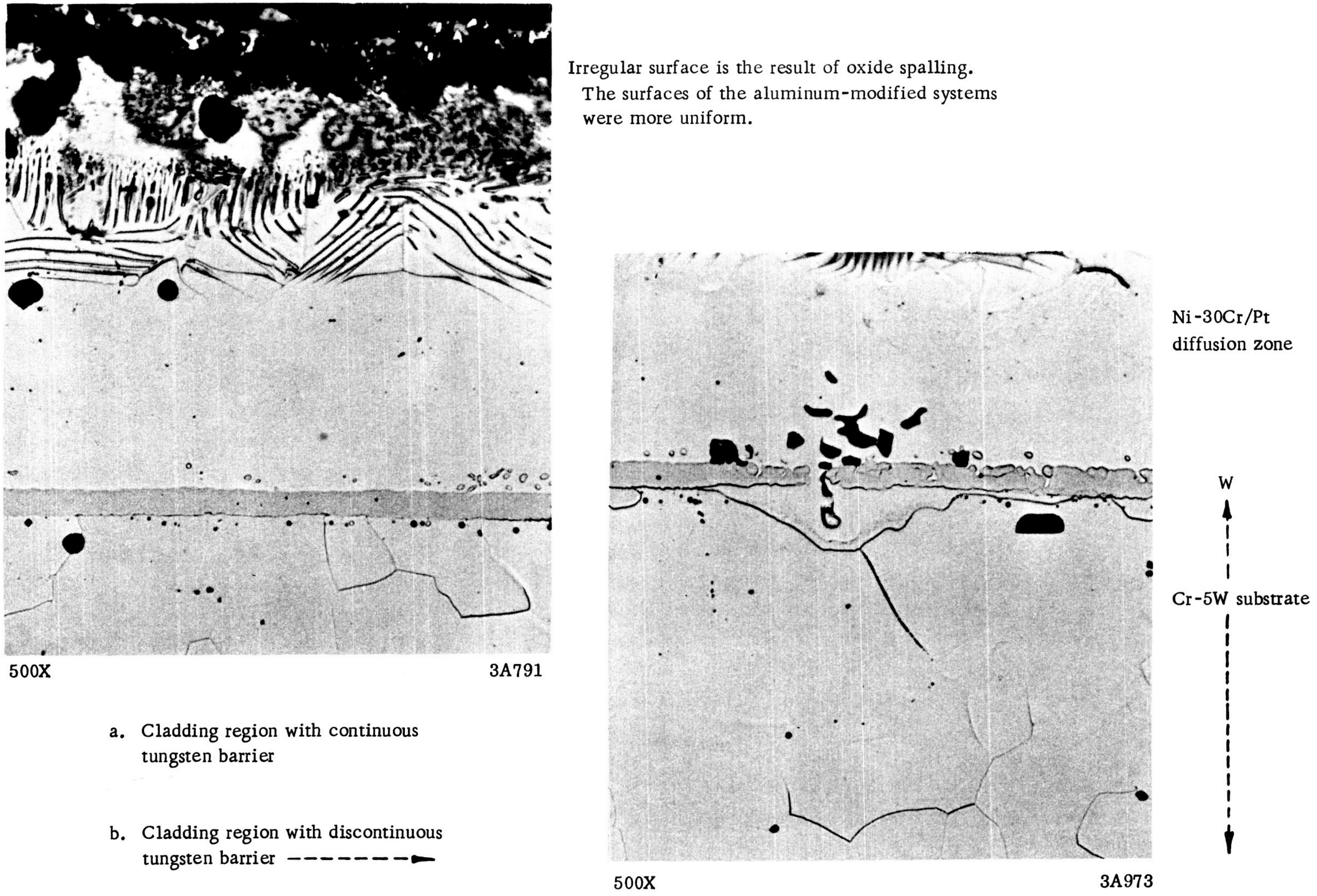


FIGURE 10. APPEARANCE OF CLADDING SYSTEM IV AFTER 200 HOURS OF CYCLIC OXIDATION AT 2100 F

Specimen etched electrolytically in chromic acid and in the lactic/nitric/hydrofluoric acid solutions.

Figure 12 shows the results of Knoop hardness traverses made in System IV in the homogenized condition and after oxidation at 2100 F. The average hardness of the Cr-5W changed very little after oxidation. However, a slight hardness increase was measured in the Cr-5W at a distance 1/2 to 1 mil from the tungsten diffusion barrier. Similar hardness increases of about 30 KHN greater than center hardness were also measured at a depth of about 1 mil below the tungsten in Systems I, II, and III after oxidation at 2100 F. Substrate hardness next to the tungsten discontinuities was very high, 700 to 900 KHN. The hardness of these regions was similar to that measured at the picture frame/Cr-5W junction where no diffusion barrier was located.

Cladding specimens from Systems V and VI which failed within five 2-hour cycles at 2300 F were metallographically examined. Failure of System VI, the platinum-free, W-25Re barrier system, was caused by fracturing of the bond between the W-25Re and the aluminum-modified outer layer. Extensive oxidation of the W-25Re and oxidation and contamination of the Cr-5W had occurred. Cladding System V, the platinum-containing, W-25Re barrier system, apparently failed because of poor diffusional stability of the W-25Re. The barrier was no longer continuous and embrittlement occurred at the



Irregular surface is the result of oxide spalling. The surfaces of the aluminum-modified systems were more uniform.

a. Cladding region with continuous tungsten barrier

b. Cladding region with discontinuous tungsten barrier --------►

FIGURE 11. CLADDING SYSTEM III AFTER 200 HOURS, 55 CYCLES, OF OXIDATION AT 2100 F

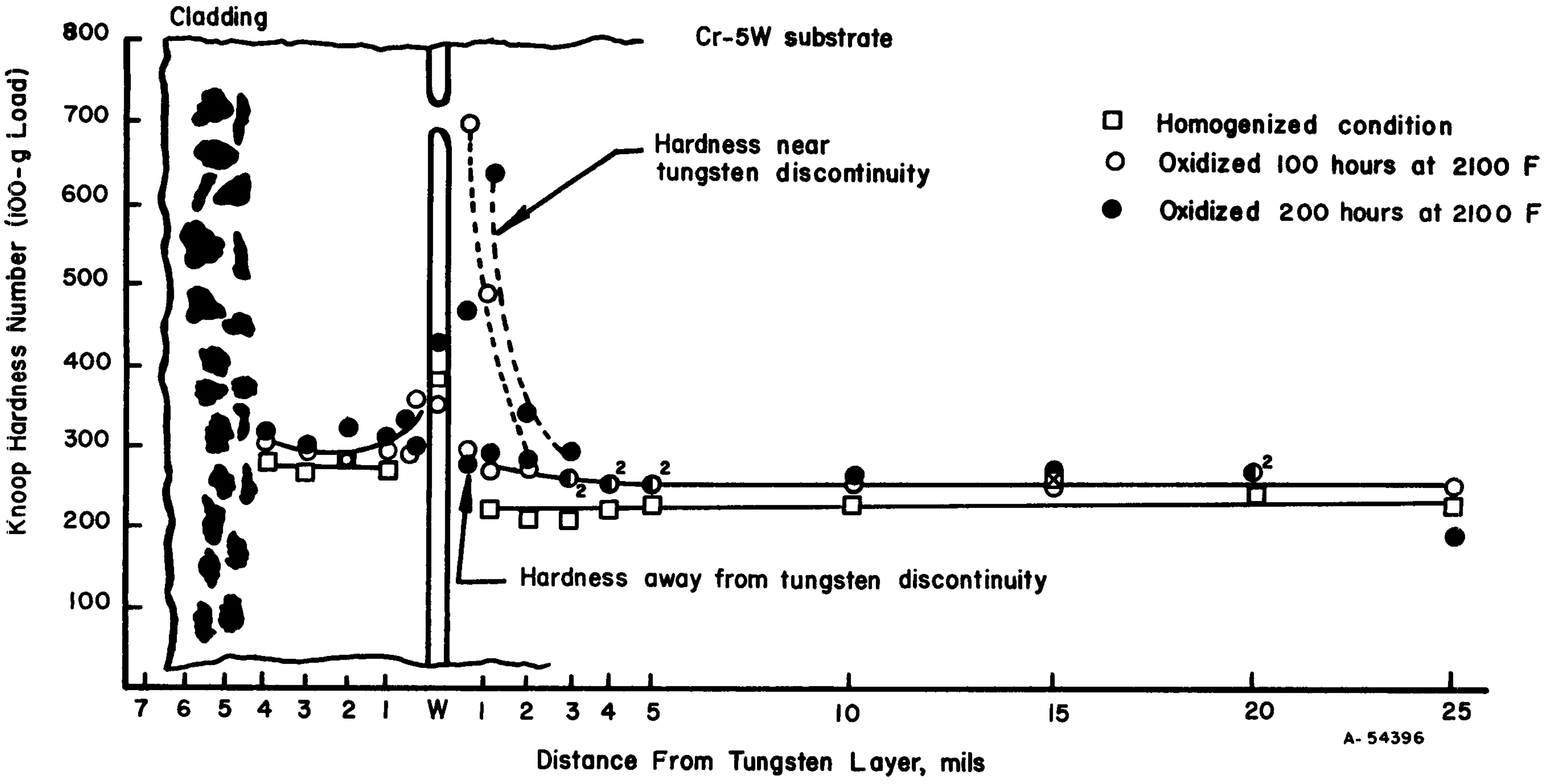


FIGURE 12. HARDNESS OF CLADDING SYSTEM IV BEFORE AND AFTER CYCLIC OXIDATION AT 2100 F

cladding/substrate junction. Figure 13 shows the condition of this cladding after 10 hours at 2300 F.

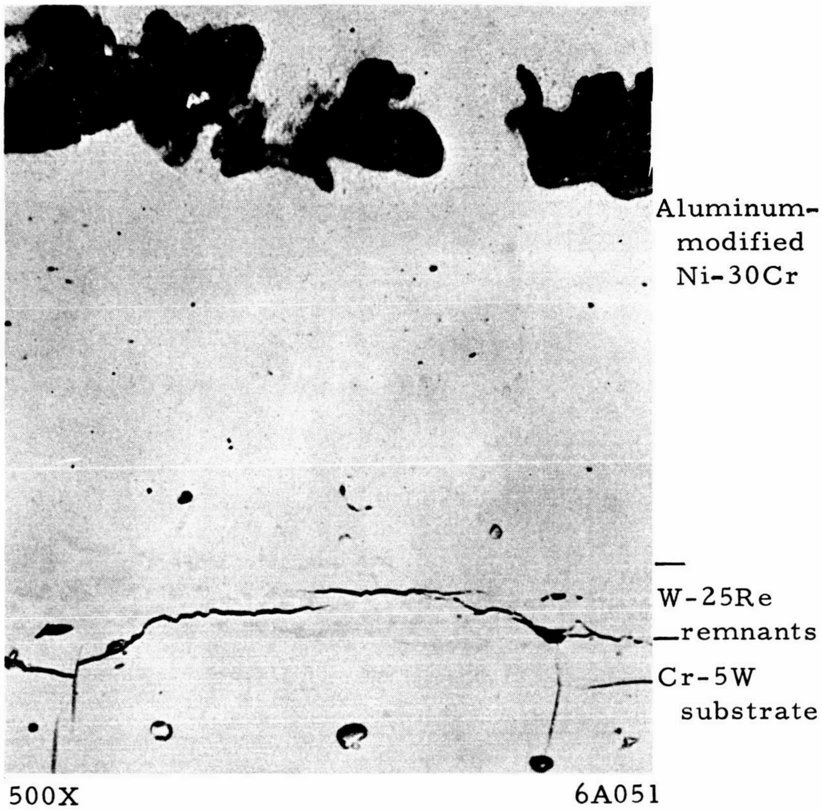


FIGURE 13. SPECIMEN V-8 AFTER 10 HOURS OF CYCLIC OXIDATION AT 2300 F

Specimen is in the as-polished condition.

Electron Microprobe Analyses

Electron microprobe analyses of an oxidized specimen of Cladding System III was conducted. The particular specimen chosen for the analyses, Specimen III-1, had been oxidized 200 hours at 2100 F. Two regions of the specimen were analyzed:

(1) Traverse analyses for Ni, Cr, W, and Pt along a path perpendicular to the cladding surface and away from any visible discontinuities in the 1/2-mil tungsten

(2) Spot analyses in the Cr-5W substrate near a discontinuity in the tungsten.

Figure 14 shows the results of the traverse analyses. The most significant features of the analyses are as follows:

(1) Platinum is very mobile in the system. The maximum platinum content is 39 wt% and is located where the 1/2-mil foil was initially positioned. About 5 wt% platinum was detected near the surface of the 5-mil-thick cladding.

(2) A small amount of alloying may be occurring between the tungsten barrier and the cladding. At the position where the maximum tungsten content was measured, the analysis was as follows:

94.1 wt% W, 2.3 wt% Pt, 2.9 wt% Ni, and 0.8 wt% Cr.

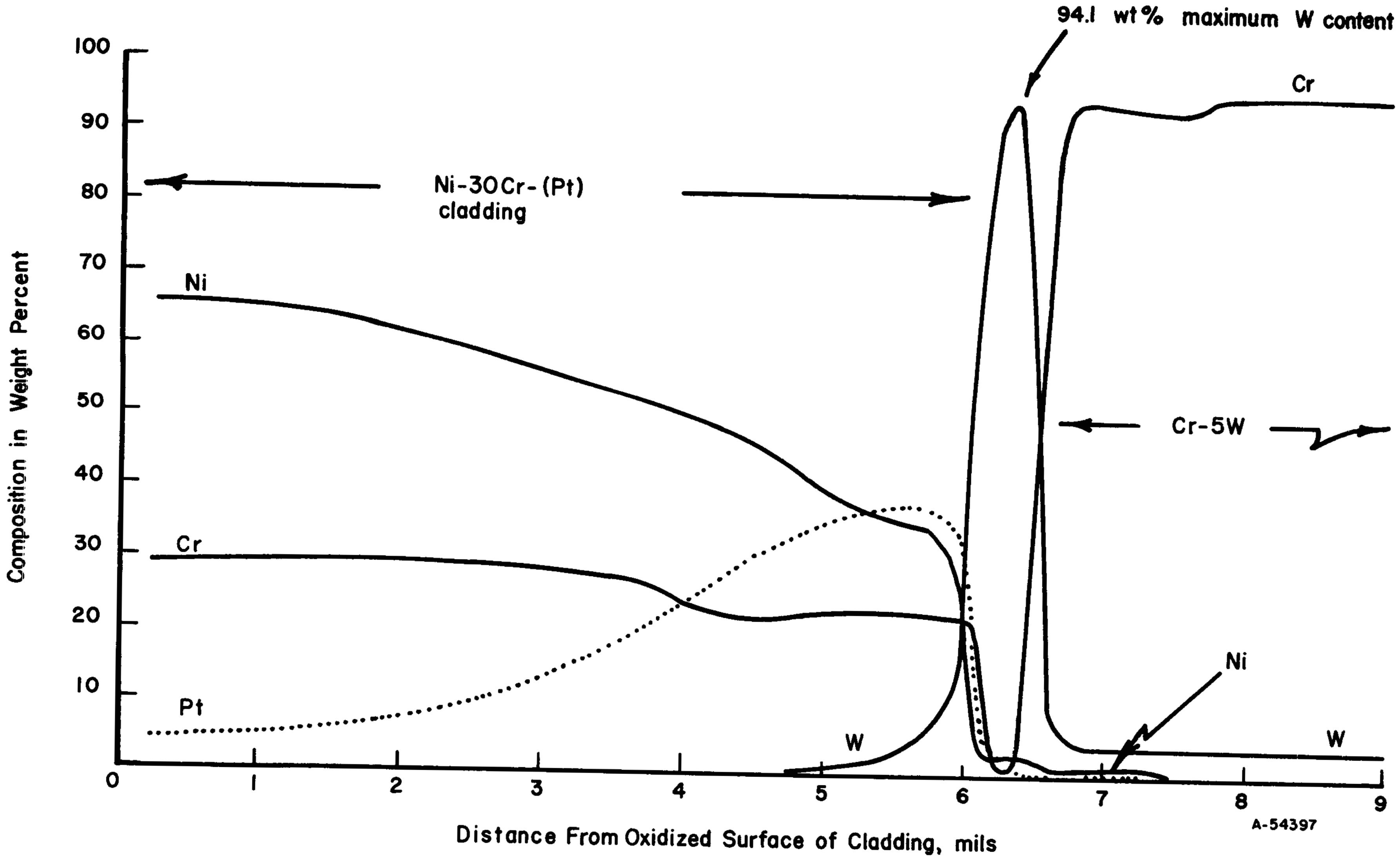


FIGURE 14. ELECTRON MICROPROBE ANALYSES OF CLADDING SPECIMEN III-1 OXIDIZED AT 2100 F FOR 200 HOURS

This analysis suggests that the solubility limit of nickel and platinum in tungsten may have been exceeded.

(3) Nickel and platinum penetration into the Cr-5W substrate was limited to about 1 mil below the tungsten/substrate junction after 200 hours of exposure at 2100 F.

It should be noted that the analyses of the tungsten diffusion barrier and of the substrate could have been affected by neighboring discontinuities in the tungsten barrier. The analyses can also be affected by bond junctions where the electron beam overlaps the junctions.

Figure 15 gives the locations of the spot analyses of the Cr-5W substrate in a region near a tungsten discontinuity. The analyses show that the substrate nearest the discontinuity is rich in tungsten, nickel, and platinum. The affected region is localized, however. At an area 1-1/2 mils from the tungsten-diffusion barrier and 2 mils from the discontinuity the nominal Cr-5W substrate composition is retained.

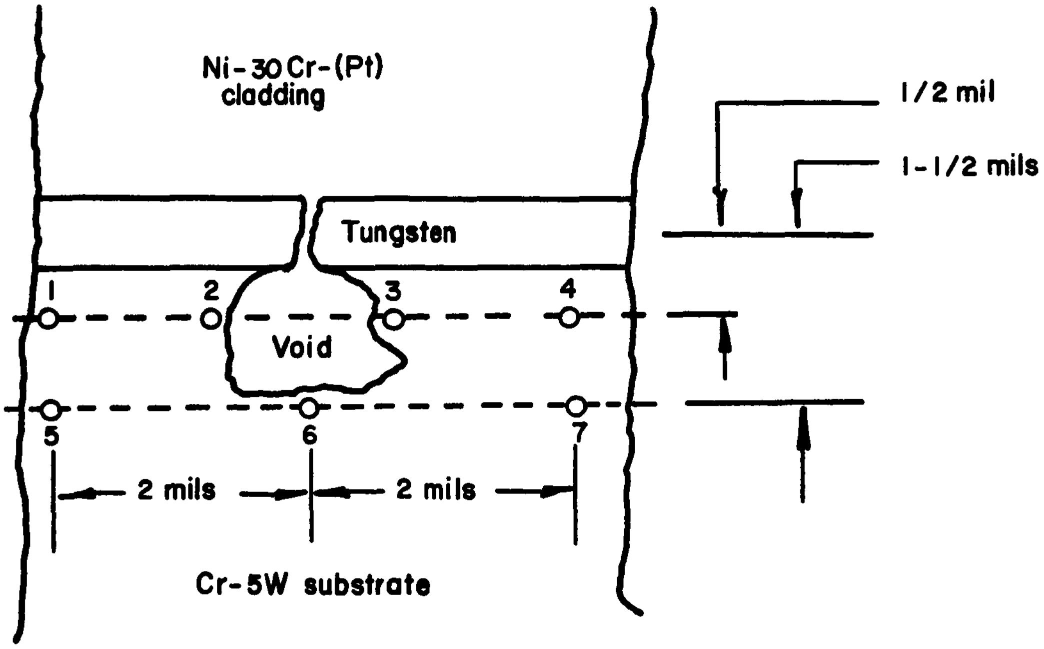
Defect Tests

Two specimens from Cladding Systems I, IV, and V were intentionally defected and oxidized at 2100 F for 10 and 50 hours. The defects were 30-mil-wide slots cut to a depth of 5, 7, and 10 mils into the cladding.

Figure 16 shows the condition of the specimen from System IV after 50 hours of oxidation at 2100 F. The appearances of the specimens from Systems I and V were very similar to that of Figure 16. The two specimens of System V did show slight oxide discoloration of the cladding near the defects. Such discoloration was not observed in Systems I and IV (volatile rhenium oxides in System V specimens are suspected). Slotted regions in these specimens which did not penetrate into the substrate (about 1 to 2 mils of cladding remained) did not change in appearance after 10 to 50 hours at 2100 F. Defects which penetrated into the cladding inflicted very little additional damage to the specimens. A small amount of a yellowish oxide (probably tungsten oxide) was observed within the deeper slots. Very little substrate oxidation occurred in these defects, illustrating a desirable characteristic of chromium alloys.

Anomalous behavior was observed in the specimen from System IV which had been oxidized 10 hours at 2100 F. This specimen suffered the most damage of the six specimens during oxidation. The cladding regions next to the 7 and 10-mil-deep slots in this specimen bulged upward suggesting that much oxidation had occurred along the tungsten barrier. It is suspected that the cladding/substrate bond was fractured by the machining operation and a larger surface area of tungsten was exposed to the atmosphere.

Metallographic examination of the cross sections of these specimens has not been completed at this time. The depth of substrate contamination and the extent of diffusion-barrier oxidation will be determined in this examination.



Position	Composition, wt %			
	Cr	W	Ni	Pt
1 and 4	89.7	8.1	1.3	0.9
2 and 3	76.7	12.4	4.1	6.8
5 and 7	96.6	3.4	-	-
6	89.4	4.5	2.2	3.5

A-54398

FIGURE 15. ANALYSES OF CHROMIUM-ALLOY SUBSTRATE NEAR A DISCONTINUITY IN THE TUNGSTEN DIFFUSION BARRIER

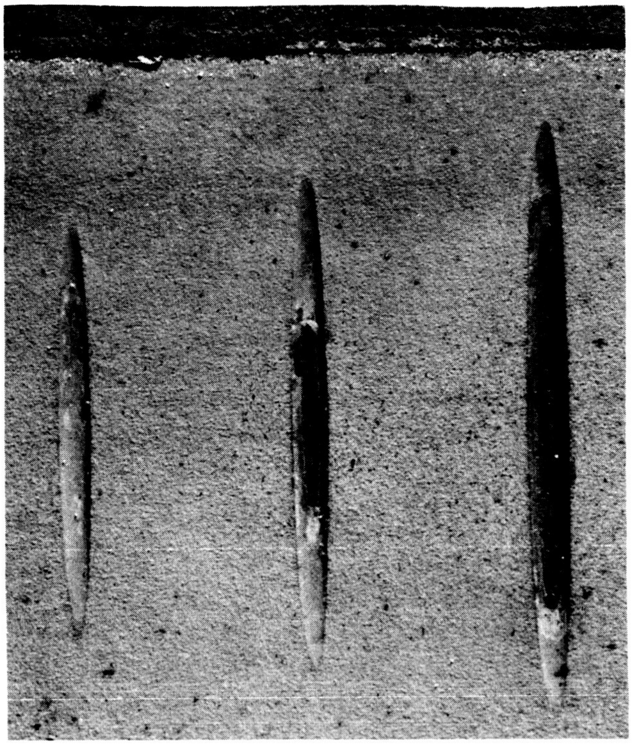


FIGURE 16. TYPICAL APPEARANCE OF AN INTENTIONALLY DEFECTED SPECIMEN AFTER OXIDATION AT 2100 F

5X Specimen IV-II 5A862

50 Hours at 2100 F

Bend Tests

Six 1/16 x 3/4 x 3-1/2-inch specimens of Cladding Systems I through VI have been oxidized 100 hours, 5 cycles, at 2100 F in preparation for bend testing. Table 8 summarizes the weight gains of these specimens after oxidation. All specimen completed the 100-hour exposure in excellent condition. No apparent blistering or cracking of the claddings was observed at the picture frame/Cr-5W junctions. The 1/8-inch-wide x 3-1/2-inch-long sides of the Ni-30Cr picture frames are currently being machined off of these specimens preparatory to bend testing. This machining operation will remove any contaminated region resulting from interdiffusion between the Cr-5W and Ni-30Cr picture frame. (No diffusion barrier is present between the 1/16 x 3-1/2-inch sides of the Cr-5W and the Ni-30Cr.)

TABLE 8. SUMMARY OF THE CONDITION OF THE BEND TEST SPECIMENS AFTER 100 HOURS OF OXIDATION AT 2100 F

	Cumulative Weight Change, mg/cm^2			
System	Minimum	Maximum	Average	Comments
I	0.60	0.81	0.71	Specimens in excellent condition
II	0.81	1.02	0.86	Ditto
III	1.26	1.69	1.51	"
IV	0.48	1.48	0.96	"
V	0.88	1.50	1.23	"
VI	0.95	1.50	1.18	"

DISCUSSION OF RESULTS

Much metallographic work as well as bend testing remains to be conducted prior to choosing the two cladding systems for the more advanced, long-time testing. The information obtained to date, however, favors the aluminum-modified Ni-20Cr-20W alloy as the cladding surface layer. Cladding Systems I and II appeared to be superior to the others in the 2300 F oxidation tests. Furthermore, the earlier oxidation studies with 10-mil-thick metal foils support the choice of the tungsten-containing nickel alloy.

The discontinuities that have been observed in the tungsten diffusion barriers of Systems I through IV are potential areas of weakness. Failure to block cladding/substrate interdiffusion at these discontinuities has resulted in localized substrate regions of high hardness. These discontinuities appear to initiate at the interface between the tungsten and (1) the Ni-20Cr-20W of System I or (2) the platinum-rich regions of Systems II, III, and IV. The nickel-base claddings have a higher coefficient of thermal expansion than the tungsten. So residual stresses produced by the expansion mismatch might be fracturing the tungsten. In addition, the ductility of the tungsten layer is probably being reduced by interdiffusion with the cladding elements, thereby making the tungsten more susceptible to brittle fracture. (Electron probe microanalysis showed the diffusion barrier of an oxidized specimen to contain about 6 wt% of cladding elements.) Grain-boundary diffusion of the cladding elements through the tungsten barrier is another possible source of the discontinuities. Equiaxed tungsten grains, with diameters nearly as large as the thickness of the tungsten, have been observed after oxidation at 2100 F. The boundaries of these relatively large grains could be paths of rapid diffusion and subsequent solution of the tungsten.

Cladding Systems VI, VII, and VIII were added to the program to obtain needed information concerning the behavior of the intermediate cladding layers in cyclic exposure. The compatibility problem encountered with W-25Re has already eliminated System VI, and possibly System V, as solutions to the tungsten-discontinuity problem. Using a platinum layer thicker than the tungsten layer, System VIII, will probably aggravate the tungsten-barrier deficiency, as too much platinum apparently dissolves the tungsten. Evaluation of the effectiveness of increasing the tungsten-barrier thickness to eliminate discontinuities, System VII, may be handicapped by the quality of the 1/2-mil-W/1/2-mil-W bonds. However, one specimen from this system, Specimen VII-2, did complete 200 hours of oxidation at 2300 F in very good condition. Metallographic results of this specimen in particular are expected to aid in the solution of this discontinuity problem.

Specimen design has presented some difficulties in evaluating the cladding systems. In order to obtain a good evaluation of the long-time protectiveness of the metallic cladding systems, premature fractures at the picture-frame junctions should be reduced. A tungsten layer will be placed between the Cr-5W and picture frame to minimize this weakness in the specimen design.

FUTURE WORK

Metallographic examination of the oxidized cladding systems and bend testing of Systems I through VI will be performed during July, 1966. Selection of the two cladding systems will be made and specimens will be gas-pressure bonded. Long-time oxidation testing of the two cladding systems is expected to be initiated by about the first of September.

* * * *

Data upon which this report is based are contained in Battelle Memorial Institute Laboratory Record Books Nos. 22578, 22996, 23085, and 23458.

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APPENDIX A

DETAILED ALUMINIZING RESULTS

TABLE A-1. ALUMINUM WEIGHT GAINS OF THE INDIVIDUAL CLADDING SPECIMENS

Pack Mixture = 1 wt % Al, 1 wt % NaCl, 98 wt % Al_2O_3.

Specimen(a)	Aluminizing Time at 1750 F, hours	Aluminum Weight Gain, mg/cm^2	Specimen(a)	Aluminizing Time at 1750 F, hours	Aluminum Weight Gain, mg/cm^2	Specimen(a)	Aluminizing Time at 1750 F, hours	Aluminum Weight Gain, mg/cm^2
I-1	12	5.1	IV-1	12	5.1	V-14	12	4.1
I-2	12	3.2	IV-2	12	5.0	V-15	12	4.1
I-3	12	3.3	IV-3	12	5.0			
I-4	12	3.4	IV-4	12	5.0			
I-5	12	3.4	IV-5	18	6.7	VI-1	12	3.8
I-6	18	5.2	IV-6	18	6.9	VI-2	12	3.8
I-7	18	6.6	IV-7	18	7.1	VI-3	12	4.1
I-8	18	5.9	IV-8	18	5.2	VI-4	18	5.5
I-9	18	Metallography	IV-9	12	4.3	VI-5	18	5.2
I-10	12	4.5	IV-10	12	4.0	VI-6	18	5.8
I-11	12	4.4	IV-11	12	4.4	VI-7	18	5.2
I-12	12	4.2	IV-12	18	Metallography	VI-8	12	5.0
I-13	12	4.1	IV-13	12	4.5	VI-9	12	4.8
I-14	12	4.1	IV-14	12	4.8	VI-10	12	5.2
I-15	12	4.2	IV-15	12	4.6	VI-11	12	4.1
			IV-16	12	4.3	VI-12	12	4.2
			IV-17	12	4.1	VI-13	12	4.3
II-1	12	5.2	IV-18	12	4.0			
II-2	12	3.1						
II-3	12	3.2				VII-1	12	4.4
II-4	12	3.2	V-1	12	3.6	VII-2	12	4.5
II-5	18	4.9	V-2	12	4.2	VII-3	12	4.4
II-6	18	4.9	V-3	12	4.2	VII-4	12	4.5
II-7	18	4.8	V-4	12	3.9	VII-5	18	5.6
II-8	12	4.2	V-5	12	4.3	VII-6	18	5.8
II-9	18	4.9	V-6	18	5.6	VII-7	18	Metallography
II-10	18	6.7	V-7	18	5.4			
II-11	12	4.4	V-8	18	6.1	VIII-1	12	4.5
II-12	12	4.5	V-9	12	Metallography	VIII-2	12	4.6
II-13	12	4.7	V-10	12	4.8	VIII-3	12	4.4
II-14	12	4.2	V-11	12	4.9	VIII-4	18	6.1
II-15	12	4.2	V-12	12	5.0	VIII-5	18	6.3
II-16	12	4.2	V-13	12	4.2	VIII-6	18	6.7
						VIII-7	12	Metallography

(a) Roman numeral refers to cladding system; Arabic numeral refers to specimen number in the system.

APPENDIX B

DETAILED CYCLIC-OXIDATION-TEST RESULTS

TABLE B-1. DETAILED WEIGHT CHANGES OF

			Cumulative Weight Change After					
	Specimen	Cycle	1	3	5	10	15	20
Specimen(a)	Size(b)	Time, hours	2	6	10	20	30	40
I-1	A		0.1	0.3	0.5	0.8	0.9	0.9
I-4	A		0.2	0.2	0.2	0.3	0.4	0.5
I-5	A		0.2	0.3	0.3	0.3	0.4	0.5
II-1	A		0.3	0.6	0.9	1.1	1.2	1.3
II-2	A		0.2	0.3	0.4	0.4	0.5	0.6
II-3	A		0.2	0.3	0.3	0.4	0.5	0.6
II-9	A		0.3	0.4	0.5	0.7	0.9	1.1
II-10	A		0.1	0.6	0.9	1.3	1.8	2.0
III-1	A		0.4	0.7	0.9	1.2	1.2	1.2
III-2	A		0.4	0.8	0.9	1.2	1.1	1.2
III-3	A		0.4	0.8	0.9	1.1	1.0	1.0
IV-1	A		0.1	0.6	0.9	1.2	1.4	1.6
IV-2	A		-0.1	0.3	0.6	1.0	1.3	1.5
IV-3	A		-0.1	0.3	0.6	0.9	1.1	1.2
V-3	B		0.0	0.3	0.4	0.5	0.7	0.8
V-4	B		0.1	0.3	0.4	0.6	0.7	0.9
V-5	B		0.0	0.2	0.3	0.6	0.8	0.9
VI-1	A		0.1	0.2	0.3	0.4	0.6	0.7
VI-2	A		0.1	0.2	0.3	0.5	0.6	0.7
VI-4	B		0.4	0.8	0.9	1.6	2.0	2.3
VII-1	B		0.1	0.3	0.5	0.7	0.8	1.0
VII-3	B		0.0	0.4	0.5	0.7	0.9	1.1
VII-4	B		0.0	0.3	0.5	0.8	0.9	1.1
VIII-1	B		0.0	0.5	0.7	1.1	1.4	1.7
VIII-2	B		0.0	0.5	0.7	1.2	1.6	1.8
VIII-3	B		0.0	0.4	0.6	0.9	1.2	1.4

(a) Roman numeral refers to cladding system; Arabic numeral refers to specimen number in the system.

(b) A = 1/16 x 1 x 1-inch Cr-5W.
B = 1/16 x 3/4 x 3-1/2-inch Cr-5W.

2100 F CYCLIC OXIDATION TESTS

Indicated Cycle and Time, mg/cm^2										
25	30	35	40	45	50	51	52	53	54	55
50	60	70	80	90	100	120	140	160	180	200
1.0	1.2	1.3	1.4	1.4	1.5	--	--	--	--	--
0.5	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
0.5	0.6	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7
1.4	1.5	1.6	1.8	1.8	2.0	--	--	--	--	--
0.6	0.6	0.7	0.7	0.7	0.7	0.6	0.7	0.7	0.7	0.7
0.7	0.7	0.8	0.8	0.8	0.8	0.8	0.9	0.9	0.9	0.9
1.2	1.3	1.3	1.4	1.5	1.6	1.6	1.7	1.8	1.9	1.9
2.2	2.3	2.4	2.5	2.5	2.6	--	--	--	--	--
1.4	1.4	1.3	1.3	1.2	1.2	1.2	1.2	1.1	1.1	1.0
1.2	1.2	1.1	1.0	1.0	0.9	--	--	--	--	--
1.1	1.1	0.9	0.8	0.8	0.7	0.7	0.6	0.4	0.4	0.2
1.8	1.9	2.0	2.2	2.3	2.4	--	--	--	--	--
1.6	1.7	1.9	2.0	2.1	2.2	2.4	2.5	2.7	2.8	2.8
1.4	1.5	1.6	1.7	1.8	1.9	2.1	2.2	2.3	2.4	2.5
0.8	0.9	1.0	1.0	1.0	1.1	1.2	1.2	1.3	1.3	1.3
0.9	1.0	1.1	1.1	1.2	1.2	--	--	--	--	--
1.0	1.1	1.2	1.2	1.2	1.3	1.4	1.5	1.5	1.6	1.6
0.7	0.8	0.9	0.9	0.9	1.0	1.1	1.2	1.2	1.3	1.3
0.8	0.9	0.9	1.0	1.0	1.1	--	--	--	--	--
--	--	--	--	--	--	--	--	--	--	--
1.1	1.1	1.2	1.3	1.3	1.4	1.5	1.5	1.6	1.7	1.7
1.2	--	--	--	--	--	--	--	--	--	--
1.1	1.2	1.3	1.3	2.2	--	--	--	--	--	--
1.8	1.9	2.0	2.1	2.1	2.2	--	--	--	--	--
2.0	2.1	2.2	2.3	2.4	2.5	2.6	2.8	2.8	2.9	3.0
1.5	1.6	1.6	1.7	1.8	1.8	1.9	2.0	2.0	2.1	2.1

TABLE B-2. DETAILED WEIGHT CHANGES OF

		Cumulative Weight Change After						
	Specimen	Cycle	1	3	5	10	15	20
Specimen[(a)]	Size[(b)]	Time, hours	2	6	10	20	30	40
I-6	A		0.2	0.3	0.4	0.7	0.8	1.0
I-7	B		0.2	0.4	0.6	0.8	0.8	1.2
I-8	B		0.2	0.7	0.9	1.2	1.4	1.5
II-5	A		0.3	0.4	0.5	0.6	0.7	0.7
II-6	A		0.3	0.4	0.5	0.6	0.7	1.0
II-7	A		0.4	0.7	0.9	1.1	1.2	1.3
III-5	A		1.1	1.4	1.2	0.7	0.5	0.2
III-6	A		1.1	1.3	1.2	0.8	0.6	0.3
III-7	A		1.4	1.5	1.3	0.8	0.5	0.3
IV-5	A		0.2	1.5	2.4	4.1	4.6	5.2
IV-6	A		0.3	1.2	2.0	3.3	4.0	4.5
IV-7	A		0.6	1.8	2.7	4.3	5.0	5.5
V-6	B		0.6	1.3	2.1	3.6	4.0	4.3
V-7	B		0.3	1.2	2.0	3.1	3.5	3.6
V-8	B		0.5	1.9	3.0	--	--	--
VI-5	B		0.7	--	--	--	--	--
VI-6	B		0.2	4.9	--	--	--	--
VI-7	B		0.2	3.3	--	--	--	--
VII-2	B		0.3	1.0	1.2	1.1	0.8	0.7
VII-5	B		0.2	1.3	2.3	--	--	--
VII-6	B		0.7	1.5	2.4	3.8	4.3	4.8
VIII-4	B		0.2	1.5	2.4	5.1	6.0	6.8
VIII-5	B		0.3	1.7	2.7	4.6	5.3	6.0
VIII-6	B		0.9	2.0	2.9	4.7	5.5	6.2

(a) Roman numeral refers to cladding system; Arabic numeral refers to specimen number in the system.

(b) A = 1/16 x 1 x 1-inch Cr-5W.
B = 1/16 x 3/4 x 3-1/2-inch Cr-5W.

B-4 and B-5

2300 F CYCLIC OXIDATION TESTS

Indicated Cycle and Time, mg/cm^2										
25	30	35	40	45	50	51	52	53	54	55
50	60	70	80	90	100	120	140	160	180	200
1.1	1.2	1.8	1.6	1.5	1.5	1.1	1.0	0.6	0.8	1.0
3.4	5.4	7.3	8.9	--	--	--	--	--	--	--
1.9	2.2	3.2	4.0	5.0	6.2	7.8	8.9	9.2	9.6	7.2
0.8	1.1	2.2	3.1	3.7	3.6	4.1	4.5	4.8	4.8	2.5
1.5	1.9	2.2	2.4	2.6	2.5	2.4	2.4	2.2	1.1	0.2
1.5	1.6	2.7	4.5	6.1	6.8	--	--	--	--	--
-0.4	-1.2	-2.1	-3.3	-4.6	-6.5	--	--	--	--	--
-0.2	-1.0	-1.8	-3.0	-4.7	-6.9	-9.4	-12.6	-15.8	-18.6	-20.1
-0.2	-1.1	-2.2	-4.0	-6.1	-9.2	-12.7	-15.3	-16.3	-17.5	-18.0
6.3	7.6	9.2	11.0	--	--	--	--	--	--	--
5.9	8.2	11.8	16.7	--	--	--	--	--	--	--
6.3	8.1	10.1	14.3	--	--	--	--	--	--	--
5.1	6.2	7.5	8.0	8.6	9.0	--	--	--	--	--
4.4	5.1	6.1	6.6	7.4	8.3	9.4	10.4	11.2	8.4	5.0
--	--	--	--	--	--	--	--	--	--	--
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--	--	--	--	--	--	--	--	--	--	--
--	--	--	--	--	--	--	--	--	--	--
0.6	0.1	0.0	-0.7	-1.0	-1.0	-0.6	-0.6	-0.7	-0.8	0.0
--	--	--	--	--	--	--	--	--	--	--
5.4	6.5	7.7	9.5	10.2	10.8	--	--	--	--	--
8.5	10.1	11.6	11.6	13.1	14.6	17.1	21.0	--	--	--
7.5	8.7	9.8	10.8	11.4	11.9	--	--	--	--	--
7.6	9.0	10.7	11.6	12.9	14.0	15.5	16.6	17.3	17.7	15.8