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**CYCLIC FURNACE OXIDATION  
OF CLAD WI-52 SYSTEMS  
AT 1040° AND 1090° C**

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16. Abstract <p>Cyclic furnace oxidation studies were conducted on the cobalt alloy WI-52 clad with Ni-30Cr, Fe-25Cr-4Al, and Ni-20Cr-4Al foils (0.051 to 0.254 mm thick). Tests as long as 400 hours using 1- and 20-hour cycles showed that the Ni-Cr and Fe-Cr-Al claddings were about equally protective at both temperatures. The protective ability of these alloys was influenced by exposure temperature and cladding thickness. At both temperatures, they protected WI-52 about as well as, or better than, a widely used commercial aluminide coating. The Ni-Cr-Al claddings did not protect WI-52 nearly as well. Interdiffusion generally influenced the oxidation behavior of all clad WI-52 systems.</p>		14. Sponsoring Agency Code	
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# CYCLIC FURNACE OXIDATION OF CLAD WI-52 SYSTEMS AT 1040° AND 1090° C

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## SUMMARY

Cyclic furnace testing was used primarily to characterize the protective potential of three claddings on WI-52 and to compare their oxidation resistance to that of a commercial aluminide coating presently used on cobalt materials in gas turbine engines. The claddings were Ni-30Cr, Fe-25Cr-4Al, and Ni-20Cr-4Al. They ranged in thickness from 0.051 to 0.254 millimeter. WI-52 specimens were clad with these alloys on all surfaces by diffusion bonding and were tested at 1040° and 1090° C for as long as 400 hours employing 1- and 20-hour exposure cycles.

The Ni-30Cr and Fe-25Cr-4Al claddings were equally protective on WI-52 at 1040° C, while the Ni-20Cr-4Al claddings were much less protective. At 1090° C, the Ni-30Cr claddings appeared to be slightly more protective than the Fe-25Cr-4Al claddings of equivalent thicknesses. At both temperatures, however, the protective ability of the latter two claddings was equal to, or better than, that of a widely used commercial pack aluminide coating.

Depending on temperature and time, the test results indicated that the oxidation resistance of all three clad systems was influenced to varying degrees by interdiffusion. Cobalt, tungsten, and/or manganese from the WI-52 diffused readily through the claddings and apparently had an effect on spinel formation, at least on the Ni-30Cr and Fe-25Cr-4Al claddings.

## INTRODUCTION

Cobalt superalloys such as WI-52 are used as stator vane materials for aircraft gas turbine engines. While they have strength potential for use to approximately 1050° C, oxidation limits their use in the uncoated condition to about 900° C. To increase allowable use temperatures, and thus engine efficiency, and/or to extend service life, current WI-52 vanes are aluminide coated. In this condition, they can be satisfactorily used to about 980° C but even then they can experience rapid attack when uneven combustion

produces hot spots of about 1090<sup>o</sup> C (ref. 1). For this reason, alternate protection systems with higher-temperature and longer-life potential are being sought.

In a previous study (ref. 2), the feasibility of protecting WI-52 with diffusion-bonded, highly oxidation resistant alloys was explored. These alloys were nickel - 30-weight-percent chromium (Ni-30Cr), nickel - 20-weight-percent chromium - 4-weight-percent aluminum (Ni-20Cr-4Al), and iron - 25-weight-percent chromium - 4-weight-percent aluminum (Fe-25Cr-4Al). Claddings (0.127 mm thick) of all three alloys protected WI-52 in cyclic furnace tests (20 hr per cycle) for 200 hours in air at 1040<sup>o</sup> C. The Ni-30Cr and the Fe-25Cr-4Al also were about equally protective for 200 hours at 1090<sup>o</sup> C, while the Ni-20Cr-4Al, at the thickness studied, was much less protective.

The prime purpose of the present study was to further characterize the protection potential of varying thicknesses of the three claddings on WI-52 in extended cyclic furnace oxidation and to compare their oxidation resistance under the same conditions to that of a widely used commercial aluminide coating on WI-52 (ref. 1). To accomplish this, several thicknesses of each cladding (0.254, 0.127, or in some cases 0.051 mm) were diffusion bonded to WI-52 and oxidized for as long as 400 hours at 1040<sup>o</sup> and 1090<sup>o</sup> C. Cycle frequencies of 1- and 20-hour exposures per cycle were employed. The 1-hour cycles were used to accentuate the tendency toward protective oxide spalling as has been observed to occur in aluminide-coated WI-52 (ref. 1) and to more closely approximate the cyclic operation anticipated in engine service. A second purpose of this study was to select the most protective cladding for advanced testing in a simulated gas turbine environment.

Clad system evaluation and comparisons of cladding and aluminide coating oxidation behavior were primarily based on gravimetric (weight change) and metallographic analyses. Supplemental analyses, including X-ray diffraction, X-ray fluorescence, and electron microprobe as well as limited tensile tests, were also made on the clad systems.

## EXPERIMENTAL PROCEDURES

### Materials and Specimen Preparation

Table I lists typical chemical analyses of cast WI-52 and of the cladding materials used in this study: Tophet 30(Ni-Cr), GE 2541(Fe-Cr-Al), and DH 245(Ni-Cr-Al). The WI-52 was cast to 50.8-millimeter by 25.4-millimeter by 2.5-millimeter coupons. The cladding materials were from a single heat of each alloy and were procured commercially in the forms of foils 0.051 (except Fe-Cr-Al), 0.127, and 0.254 millimeter thick and 2.5-millimeter plate. Clad thickness variation was in the range of  $\pm 5$  percent to  $\pm 20$  percent from the nominal thickness.

Completely clad WI-52 coupons and similarly shaped clad cladding-alloy (cladding foil applied to cladding-alloy plate) specimens were fabricated by gas pressure bonding at 1090<sup>o</sup> C and a helium pressure of 103 meganewtons per square meter (15 000 psi) for 2 hours. Clad cladding-alloy specimens, processed under the same conditions, were used to provide baseline oxidation data in the evaluations of the claddings on WI-52. A more detailed description of test specimen preparation is given in reference 2. As described in reference 1, WI-52 coupons were also coated with a widely used, proprietary, pack aluminide coating. The coating was deposited to a thickness of about 0.056 millimeter. Figure 1 presents the microstructures of the three 0.127-millimeter-thick claddings and the aluminide coating on WI-52 in the as-bonded and as-coated conditions.

### Cyclic Oxidation Testing

Specimens were cyclic oxidation tested at 1040<sup>o</sup> and 1090<sup>o</sup> C for as long as 400 hours in furnaces controlled to  $\pm 5^{\circ}$  C. Some specimens were laid across alumina boats in a horizontal, alumina multitube, silicon carbide, resistance-heated furnace. These were manually withdrawn at 20-hour intervals and allowed to cool to room temperature before being lightly brushed and weighed. During testing, filtered air was passed (0.05 m<sup>3</sup>/hr) through the alumina tubes. Other specimens, individually suspended from platinum wires in a vertical, alumina multitube, wire-wound, resistance- heated furnace were automatically withdrawn at 1-hour intervals and cooled to about 100<sup>o</sup> C before being automatically reinserted. During this testing, natural convection maintained the airflow through the alumina tubes. At various times these specimens were also cooled to room temperature, lightly brushed, and weighed. Generally, a single specimen of each material combination was tested for each oxidizing condition reported herein. Although not determined, it was felt that the oxidizing environments in the horizontal and vertical furnaces were similar; and data from both types of tests are compared in this report.

### Additional Evaluations

Cross-sectional metallographic analysis was made on the as-oxidized specimens at magnifications to X750 by using bright field and polarized light illumination. In order to better understand the oxidation behavior, X-ray diffraction (XRD) and X-ray fluorescence (XRF) analyses were performed on specimens after oxidation. XRD was performed on either in-situ or as-scraped scales and on naturally spalled scales, whereas XRF was performed only on the in-situ scales. Summaries of XRD and XRF analyses are presented in appendix A.

Also, to increase understanding of the degradation process, electron microprobe (EMP) analyses were made on selected 0.127-millimeter-thick-clad WI-52 and cladding-alloy specimens before and/or after oxidation. Three EMP techniques were used. The most widely used technique consisted of taking X-ray raster scan micrographs (at X500) for selected elements on the cladding-substrate cross sections. The second technique consisted of taking uncorrected concentration line scans across the specimens, generally for the major elements only. The third technique, employed on only one specimen, involved a partial spectral scan and a point analysis within an area of interest. Summaries of the EMP raster and concentration line scans are given in appendix B.

Some tensile tests were made on the most oxidation resistant systems (Ni-Cr and Fe-Cr-Al clad WI-52). A completely clad WI-52 specimen of each system was cyclic oxidation tested for 400 hours at 1090<sup>o</sup> C before being machined into two tensile specimens of the design shown in figure 2. The tensile specimens were tested at a crosshead speed of 1.27 millimeters per minute at 1090<sup>o</sup> C in argon.

## RESULTS AND DISCUSSION

The Ni-Cr and the Fe-Cr-Al claddings on WI-52 were found to be very protective in cyclic furnace oxidation for as long as 400 hours at 1090<sup>o</sup> C when applied in thicknesses of 0.127 millimeter or more. Only the thickest (0.254 mm) Ni-Cr-Al cladding, however, offered 200-hour protection at 1090<sup>o</sup> C in this study. The details of the test results and their implications are presented in the following sections for the systems in the order of their decreasing oxidation resistance.

### Ni-Cr Clad WI-52

Figure 3 shows the effects of cladding thickness and cycle frequency on the oxidation weight change behavior of WI-52 clad with Ni-Cr. At 1040<sup>o</sup> C, even the thinnest cladding offered greatly improved oxidation resistance when compared to unprotected WI-52. At this temperature, cycle frequency and cladding thickness differences appeared to exert only a minor influence on weight change. After about 300 hours of 1-hour cyclic testing, the 0.051-millimeter-thick cladding began to slowly lose weight as a consequence of some spalling of the surface oxides - Cr<sub>2</sub>O<sub>3</sub>, NiCr<sub>2</sub>O<sub>4</sub>, NiO, and SiO<sub>2</sub> (appendix A).

At 1090<sup>o</sup> C, the oxidation resistance was directly related to cladding thickness and cycle frequency. Here, the 0.051-millimeter-thick clad was not very protective; and, in the more severe 1-hour cyclic tests, the 0.127-millimeter-thick cladding began to spall after 280 hours. Even at 400 hours, the latter did not, however, show a net weight

loss. The 0.254-millimeter-thick cladding showed only gradual weight gains, reflecting continued good protection. The Ni-Cr clad Ni-Cr (not shown in fig. 3) performed very nearly the same as WI-52 clad with 0.254-millimeter-thick Ni-Cr.

Representative photomicrographs of cladding/WI-52 cross sections show the influence of exposure conditions and are presented in figure 4 (1040<sup>o</sup> C) and figure 5 (1090<sup>o</sup> C). In each figure, the photomicrographs are arranged in order of increasing Ni-Cr cladding thickness from left to right and in order of increasing exposure time from top to bottom. Several of these photomicrographs show evidence of pullout and slight differences in etching attack. However, they generally show that, in the 1040<sup>o</sup> to 1090<sup>o</sup> C temperature range, temperature has a strong influence on cladding degradation (compare fig. 4(a) with 5(a) or fig. 4(b) with 5(b)). Increasing cladding thickness appears beneficial at both temperatures (compare fig. 4(a) with 4(b) or fig. 5(a) with 5(b) and 5(c)). Cycle frequency effects in these furnace tests appear negligible even at 1090<sup>o</sup> C (compare fig. 5(e) with 5(f)). This is somewhat in contrast to the spalling observed between 300 and 400 hours on the 1-hour-cycled specimen, as shown in figure 3(b). Except for the thinnest cladding, exposure time between 200 and 400 hours at 1090<sup>o</sup> C also exerts only a minor influence on the cross-sectional microstructures shown in figure 5.

X-ray fluorescence and electron microprobe data (appendixes A and B) suggest that within 200 hours at both temperatures generally cobalt, tungsten, columbium, and perhaps manganese rapidly diffused from the WI-52 into the Ni-Cr cladding. Nickel also appears to diffuse inward from the cladding. These changes in the cladding composition apparently affected the composition of the oxide scale and, thus the oxidation behavior, to some degree. Primary oxides formed were, as noted, Cr<sub>2</sub>O<sub>3</sub>, NiCr<sub>2</sub>O<sub>4</sub>, and probably SiO<sub>2</sub> (appendix A). However, once NiO was observed in the scale or in the spalled oxide, failure (i. e., rapid weight loss) was imminent.

In summary, the weight change data combined with metallographic data indicate that, as might be expected, temperature (within the range studied) is the overriding factor in determining the oxidation behavior of Ni-Cr clad WI-52. Electron microprobe analyses (appendix B) confirm that temperature exerted a very large influence on the interdiffusion of substrate and cladding elements. Such interdiffusion is believed to be the major reason why only the thicker claddings (0.127 and 0.254 mm) offer over 400 hours of protection at 1090<sup>o</sup> C. This is because the thicker claddings suffer less dilution due to substrate element interdiffusion near the oxide-cladding surface than do thinner claddings. Thus, the thicker claddings perform similarly to Ni-Cr clad Ni-Cr (ref. 2).

## Fe-Cr-Al Clad WI-52

In comparison to Ni-Cr clads, the Fe-Cr-Al clads on WI-52 were equally protective at 1040° C and only slightly less protective at 1090° C.

The effects of temperature, cycle frequency, and cladding thickness (here, only 0.127- and 0.254-mm claddings were tested) on the weight change of Fe-Cr-Al clad WI-52, Fe-Cr-Al clad Fe-Cr-Al, and bare WI-52 are depicted in figure 6 for as much as 400 hours of oxidation. The data presented are for tests at 1040° C (fig. 6(a)) and at 1090° C (fig. 6(b)). For the clad thicknesses examined at 1040° C, cladding thickness and even the more severe 1-hour cycling had little effect on the good oxidation protection afforded WI-52. Both thickness claddings showed light spalling of the oxide scales which contained alpha alumina ( $\alpha\text{Al}_2\text{O}_3$ ),  $(\text{Cr}, \text{Fe})_2\text{O}_3$ , and a spinel (appendix A). At 1090° C, cycle frequency had a definite effect on the weight change behavior of the 0.127-millimeter-thick cladding after about 340 hours of testing. The weight losses observed were due to moderate spalling of the same oxides observed at 1040° C. The 1-hour cycles did not markedly affect the 0.254-millimeter-thick cladding even after 400 hours although some light spalling did occur. The 20-hour-cycled 0.127- and 0.254-millimeter-clad WI-52 performed similarly to Fe-Cr-Al clad Fe-Cr-Al tested in 20-hour exposures, but the latter showed no visual evidence of spalling.

Figure 7 contains cross-sectional photomicrographs of 0.127-millimeter-clad WI-52 specimens after testing to show the effects of temperature, time, and cycle frequency. The 1090° C oxidation resulted in more oxide penetration and internal oxidation (compare fig. 7(a) with 7(c)), while increased exposure time (compare fig. 7(c) with 7(d)) and cycle frequency (compare fig. 7(d) with 7(e)) had only moderate degrading effects, as anticipated from the weight change data in figure 6. The thicker claddings (not shown) showed even less attack. However, for claddings of both thicknesses tested at 1090° C using 1-hour cycles, large local multioxide penetrations were observed (see the left side of fig. 7(e)). These penetrations, as shown in figure 8, almost extended to the WI-52 substrate in the 0.127-millimeter-clad specimens. Under polarized light illumination, the penetrations are a mixture of charcoal grey and brown oxides (probable spinels), while the protective scale consists mainly of white (alpha alumina) and red-green oxides ( $(\text{Cr}, \text{Fe})_2\text{O}_3$ ). Based on XRD lattice parameter measurements (table II), these spinels are probably chromites.

X-ray fluorescence and electron microprobe data (appendixes A and B) suggest that within 200 hours at both temperatures generally cobalt diffused rapidly, and perhaps tungsten and manganese also diffused, from the WI-52 into the Fe-Cr-Al claddings. Iron appeared to diffuse into the WI-52 from the cladding. The scales on the Fe-Cr-Al claddings were primarily alpha alumina and  $(\text{Cr}, \text{Fe})_2\text{O}_3$  with considerable spinel, probably  $\text{CoCr}_2\text{O}_4$ , developing within 200 hours or less at both temperatures. Spalling of the pro-

protective alumina film and a significant increase in spinel formation is believed to be related to extensive interdiffusion and to correspond with the losses in oxidation resistance described above.

The evidence presented here indicates that in the 1040<sup>o</sup> to 1090<sup>o</sup> C range, the lifetime of Fe-Cr-Al claddings on WI-52 is also greatly influenced by exposure temperature and moderately influenced by cladding thickness and cycle frequency. At 1040<sup>o</sup> C, both the 0.127- and 0.254-millimeter-thick claddings offered more than 400 hours of protection; at 1090<sup>o</sup> C, claddings at least 0.254 millimeter thick are probably required for the same degree of protection.

## Ni-Cr-Al Clad WI-52

Of the three systems studied, the Ni-Cr-Al clad WI-52 system showed the least oxidation resistance at the two test temperatures. The furnace oxidation weight change data, for 20-hour exposure cycles only, are presented in figure 9 for the 1040<sup>o</sup> C (fig. 9(a)) and the 1090<sup>o</sup> C (fig. 9(b)) tests. The post-test photomicrographs are presented in figure 10.

Taken together, the weight change and metallographic data show that at 1040<sup>o</sup> C, Ni-Cr-Al claddings must be 0.127 millimeter thick or thicker to protect WI-52 since the 0.051-millimeter-thick cladding was almost completely oxidized within 200 hours. The weight gain behavior for the latter cladding thickness reflects merely an almost complete retention of the heavy oxide scale, and not good oxidation resistance. At 1090<sup>o</sup> C, the 0.127-millimeter-thick cladding showed surface and internal oxidation and was rapidly attacked; the 0.254-millimeter-thick cladding showed a weight change turnaround after 100 hours, reflecting spalling of the heavy oxide scale. Due to its poor performance, no 1-hour cyclic tests were conducted on this system.

The weight change and metallographic results combined with the electron microprobe analyses (appendix B) suggest that rapid interdiffusion occurs between Ni-Cr-Al and WI-52. This interdiffusion results primarily in a decrease in aluminum concentration in the cladding, which is probably the reason for its poor oxidation resistance. Without a suitable diffusion barrier to prevent aluminum loss and substrate element dilution, cladding thicknesses in excess of 0.254 millimeter appear necessary for more than 200 hours of protection, at least at 1090<sup>o</sup> C.

## Tensile Test Results

Tensile data were obtained on the two most oxidation resistant clad WI-52 systems

(Ni-Cr clad WI-52 and Fe-Cr-Al clad WI-52) to determine the effects of oxidation and interdiffusion on mechanical properties. Duplicate tensile specimens of each system, both as clad and as oxidized for 400 1-hour cycles at 1090<sup>0</sup> C, were machined as shown in figure 2. For purposes of comparison, two unprotected (bare) WI-52 specimens were given a duplex thermal treatment in argon to simulate the bonding and oxidation exposure cycle temperatures and times. These were then also machined into four tensile specimens. The average tensile data for these specimens tested at 1090<sup>0</sup> C are given in figure 11. The strengths given in this figure for the clad specimens are based on the approximate cross-sectional areas of the WI-52 substrates before bonding, and thus they include the interdiffusion zones. In either the as-clad or the as-oxidized condition, the tensile strengths of the Fe-Cr-Al clad WI-52 were 8 to 27 percent higher than those of Ni-Cr clad WI-52. Also, the strengths of Fe-Cr-Al clad WI-52 decreased about 6 percent during 400 hours of oxidation, as compared to about 18 percent for Ni-Cr clad WI-52.

Some of the losses in strength, as well as in elongation, during oxidation could be attributed to interdiffusion. The tensile properties to both oxidized systems were lower than those of thermally treated, bare WI-52; however, the 1090<sup>0</sup> C tensile strengths of WI-52 were retained to a greater extent with the Fe-Cr-Al cladding. Therefore, these comparisons suggest that, based on high-temperature-strength considerations, the Fe-Cr-Al claddings are a better choice than the Ni-Cr claddings.

## Comparison of Ni-Cr and Fe-Cr-Al Clad Systems with Aluminide-Coated WI-52

The 1090<sup>0</sup> C weight change data obtained from reference 1 for a widely used, proprietary, pack-cementation, aluminide coating (about 0.056 mm thick) on WI-52 are compared in figure 12 with those obtained in this study for WI-52 clad with 0.051- and 0.127-millimeter-thick Ni-Cr and 0.127-millimeter-thick Fe-Cr-Al. Data for considerably thicker aluminide coatings are not available because such coatings are not produced commercially since they do not have optimum properties; that is, resistance to impact and to thermal-stress-induced spalling.

Figure 12 shows that for the same thickness and cycle frequency, the Ni-Cr cladding performs the same as, or slightly better than, the aluminide coating. While a direct comparison is not possible, since thicker aluminide coatings are not available and the 0.051-millimeter-thick Ni-Cr was not tested at 1090<sup>0</sup> C using 1-hour cycles, the figure shows that the sensitivity of the coating to more rapid cycling is greater than that of the thicker claddings. Also, while the 0.127-millimeter-thick claddings are only twice as thick as the aluminide coating, in 1-hour cyclic tests they perform at least eight times better.

Figure 13 shows that, after ten 20-hour cycles at 1090<sup>o</sup> C, the aluminide coating is completely consumed while the Ni-Cr cladding still has some useful remaining life. The 1-hour-cycled coating (ref. 1) was similarly consumed after only 50 hours or less of testing. Figures 5(f) and 7(e), however, show that the 0.127-millimeter-thick claddings of both Ni-Cr and Fe-Cr-Al are still intact after 400 1-hour cycles at 1090<sup>o</sup> C.

Thus, the results of furnace oxidation tests on Ni-Cr and Fe-Cr-Al claddings on WI-52 indicate that they are more protective than a widely used, commercial, pack aluminide coating. Advanced evaluation of both these systems in more realistic simulated engine environments therefore appears warranted.

## SUMMARY OF RESULTS

A study was conducted to characterize the cyclic furnace oxidation resistance of Ni-30Cr, Fe-25Cr-4Al, and Ni-20Cr-4Al claddings (0.051 to 0.254 mm thick) on WI-52 for times to 400 hours using 1- and 20-hour exposure cycles at both 1040<sup>o</sup> and 1090<sup>o</sup> C as well as to compare the better systems to a commercial aluminide coating. A second purpose of the study was to select the most promising cladding for advanced evaluation in simulated turbine engine environments. The results of this study are summarized as follows:

1. The Ni-Cr and Fe-Cr-Al claddings of 0.127 millimeter and thicker offer more than 400 hours of furnace oxidation protection for WI-52 at 1040<sup>o</sup> C. For 400-hour protection at 1090<sup>o</sup> C, Ni-Cr claddings of the same thickness are satisfactory, while 0.254-millimeter-thick or thicker Fe-Cr-Al claddings are required. Ni-Cr-Al claddings must be thicker than those studied to provide similar protection.

2. When compared to the furnace oxidation resistance of a commercial aluminide coating on WI-52, Ni-Cr and Fe-Cr-Al claddings were sufficiently better as to warrant advanced testing in a simulated turbine environment. Some of the apparent superiority of the clads is probably attributable to their greater thickness.

3. Within 200 hours at both temperatures, cobalt diffused rapidly from the WI-52 through the three claddings; tungsten and manganese also diffused through the Ni-Cr and Fe-Cr-Al claddings. Interdiffusion of these and other cladding and substrate elements appeared to affect the oxide scale composition and apparently had at least an indirect effect on spinel formation. Thus interdiffusion influenced oxidation resistance.

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National Aeronautics and Space Administration,  
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## APPENDIX A

### X-RAY DIFFRACTION (XRD) AND FLUORESCENCE (XRF) ANALYSES

Table II summarizes the XRD and XRF analyses on retained oxide scales and spalls for Ni-Cr, Fe-Cr-Al, and Ni-Cr-Al clad WI-52.

In the Ni-Cr clad WI-52 system,  $\text{Cr}_2\text{O}_3$  was the major oxide in the scale. The  $\text{NiCr}_2\text{O}_4$  spinel was also present in considerable quantities after  $1040^\circ\text{C}$  exposure and to a lesser extent after  $1090^\circ\text{C}$  exposure. (Spinel on the oxidized Ni-Cr clad Ni-Cr specimens were observed only by metallographic examination under polarized light.) No crystalline  $\text{SiO}_2$  was detected by XRD, but XRF indicated the presence of silicon in large quantities so that amorphous silica is probably present. NiO was detected in the spall and/or on the scales of specimens immediately prior to rapid weight loss and provided an indication of cladding degradation. In addition to silicon, XRF data showed that increased amounts of tungsten, cobalt, manganese, and columbium were detected at the surfaces of the oxidized Ni-Cr clad WI-52. Since these four elements are primarily substrate elements, this indicates that they must have diffused through the cladding from WI-52. This is in agreement with the electron microprobe data (appendix B).

XRD and XRF data on Fe-Cr-Al clad WI-52 in table II generally showed the surface oxides to be  $\alpha\text{Al}_2\text{O}_3$  and  $(\text{Cr, Fe})_2\text{O}_3$ , similar to the scales formed on Fe-Cr-Al clad Fe-Cr-Al. Spinels, probably  $\text{CoCr}_2\text{O}_4$ , were also detected by XRD on or in the spalls from the 400-hour-tested clad WI-52 specimens. The increase in these spinels was accompanied by a decrease in alumina and was observed with both increasing exposure time and cycle frequency. (Spinels were neither detected by XRD nor observed metallographically under polarized illumination on any of the oxidized Fe-Cr-Al clad Fe-Cr-Al specimens.) XRF data indicated that cobalt and tungsten diffused into the claddings at both temperatures; at  $1090^\circ\text{C}$ , manganese also was observed to be concentrated near the cladding surface. As in the case of the Ni-Cr clad WI-52, interdiffusion may have influenced the oxides formed in the scale and thus indirectly affected cladding oxidation resistance.

In the Ni-Cr-Al clad WI-52 system, spinels and NiO were the major scale constituents, which is consistent with those detected on the oxidized Ni-Cr-Al clad Ni-Cr-Al specimens. Initially, the major spinel was probably  $\text{NiAl}_2\text{O}_4$ ; but after longer exposure times at both temperatures,  $\text{NiCr}_2\text{O}_4$  was more dominant. Minor amounts of  $\text{Cr}_2\text{O}_3$  were detected only on the clad WI-52 specimens. XRF detected silicon, aluminum, cobalt, and columbium in significant amounts. Compared to the Ni-Cr-Al clad Ni-Cr-Al, cobalt and columbium are elements which must have diffused from the WI-52 to dilute the Ni-Cr-Al cladding. The XRF data and the electron microprobe results (appendix B) indicated that amorphous  $\text{SiO}_2$  was also present on all the oxidized Ni-Cr-Al clad specimens.

## APPENDIX B

### ELECTRON MICROPROBE ANALYSES (EMP)

EMP analyses of raster micrographs and line concentration scans for selected clad cladding-alloy specimens and for 0.127-millimeter-thick claddings on WI-52 are summarized in table III. Pertinent data are presented in figures 14 to 16.

At both exposure temperatures, the scales on Ni-Cr clad WI-52 were observed to be rich in chromium, silicon, manganese, and aluminum and also contained some nickel, as shown in figure 14(a). (The scales on the oxidized Ni-Cr clad Ni-Cr were rich only in Cr and Si.) The small amount of aluminum in the cladding (0.3 percent, table I) appears both in the scale and in the internal oxidation products of the Ni-Cr clad WI-52. The manganese in the scale was primarily a result of diffusion from the WI-52. After 400 hours at 1090<sup>o</sup> C, the presence of cobalt and tungsten was also detected near the cladding-oxide interface in the raster and/or line scans. Within the cladding, a chromium-rich, nickel-deficient phase exists which outlines the grain boundaries and also is concentrated at the cladding-substrate interface. This appears to be a chromium carbide.

In figure 14(b), two sets of line scan data are presented for nickel, cobalt, and chromium. One (fig. 14(b-1)) shows the effect of exposure time on the as-bonded material and after 200 and 400 hours of testing at 1090<sup>o</sup> C using 20-hour cycles. The second (fig. 14(b-2)) shows the effect of exposure temperature after ten 20-hour cycles. For the major elements analyzed, this figure illustrates, by the lengths of the bars, the depths of regions whose concentrations are different from that of the cladding or the WI-52. The numbers at the left of each bar represent first approximations of weight percentages for these elements. Since these data are in the form of relative X-ray intensity measurements, they are semiquantitative. The data in this figure indicate that, while the cladding was not completely penetrated by cobalt from the WI-52 after 200 hours at 1040<sup>o</sup> C, it was completely penetrated in the 1090<sup>o</sup> C tests. In the latter test an additional 200 hours of oxidation resulted in only a minor increase in thickness of the diffusion-affected part within the WI-52.

In the case of Fe-Cr-Al clad WI-52, as shown in table III and figures 15(a) and (b), it also appears that cobalt rapidly diffused through the 0.127-millimeter-thick cladding within 200 hours at both temperatures. Interdiffusion in this system, however, was very extensive after bonding. From the raster scans, tungsten and manganese also diffused through the Fe-Cr-Al cladding within 400 hours at 1090<sup>o</sup> C. The oxide scales were rich primarily in chromium and aluminum. The scales formed at 1090<sup>o</sup> C were also rich in manganese. (The scales on the Fe-Cr-Al clad Fe-Cr-Al specimens were rich in iron, chromium, and aluminum after 1040<sup>o</sup> C oxidation, and rich only in aluminum after

1090<sup>o</sup> C oxidation.) In the cladding itself, the light-colored grains observed in figure 7 were determined by point scans to be chromium carbides containing small amounts of iron, tungsten, and cobalt. These carbides formed during bonding along the bond interface, and this interface remained nearly continuous during oxidation. The internal oxides in the cladding were determined to be rich in aluminum (probably aluminum oxide).

The Ni-Cr-Al clad WI-52 and Ni-Cr-Al clad Ni-Cr-Al specimens exhibited scales rich in nickel, chromium, aluminum, silicon, and manganese after oxidation at both temperatures. The 0.127-millimeter-thick cladding, too, was readily penetrated by cobalt even at 1040<sup>o</sup> C, as shown in figure 16. The oxide particles within the claddings and those along the bond interfaces (see fig. 10) were very rich in aluminum, and thus were probably  $\alpha\text{Al}_2\text{O}_3$ .

## REFERENCES

1. Grisaffe, Salvatore, J.; Deadmore, Daniel L.; and Sanders, William A.: Furnace and High-Velocity Oxidation of Aluminide-Coated Cobalt Superalloy WI-52. NASA TN D-5834, 1970.
2. Gedwill, Michael A.: An Evaluation of Three Oxidation-Resistant Alloy Claddings for IN 100 and WI 52 Superalloys. NASA TN D-5483, 1969.

TABLE I. - CHEMICAL ANALYSIS OF WI-52 SUPERALLOY AND  
CLADDING ALLOYS

Element	WI-52	Ni-Cr (Tophet 30)	Fe-Cr-Al (GE 2541)	Ni-Cr-Al (DH 245)
Content, wt %				
Co	61.24	0.001	0.007	0.03
Ni	.55	Balance	.15	Balance
Fe	2.24	.15	Balance	.7
Cr	21.42	29.63	24.82	19.54
Al	<sup>a</sup> <.001	.3	4.12	3.51
Si	.95	1.43	.18	1.22
Ti	-----	-----	-----	-----
Mo	-----	-----	-----	-----
W	11.09	<sup>a</sup> <.05	<sup>a</sup> <.05	<sup>a</sup> <.05
Cb	1.87	-----	-----	-----
Mn	.40	.01	-----	.4
Y	-----	-----	.58	-----
C	.45	.028	.0058	.076

<sup>a</sup>Not detected; less than the limits of detection.



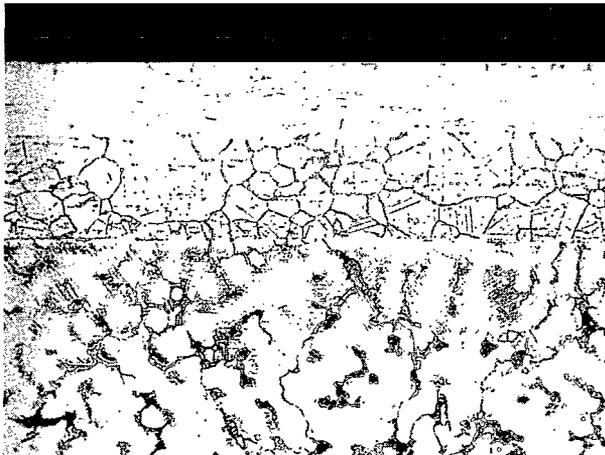
TABLE III. - SUMMARY OF ELECTRON MICROPROBE ANALYSES ON CLAD CLADDING-ALLOY  
AND WI-52 SPECIMENS AFTER CYCLIC OXIDATION

[Original cladding thickness, 0.127 mm.]

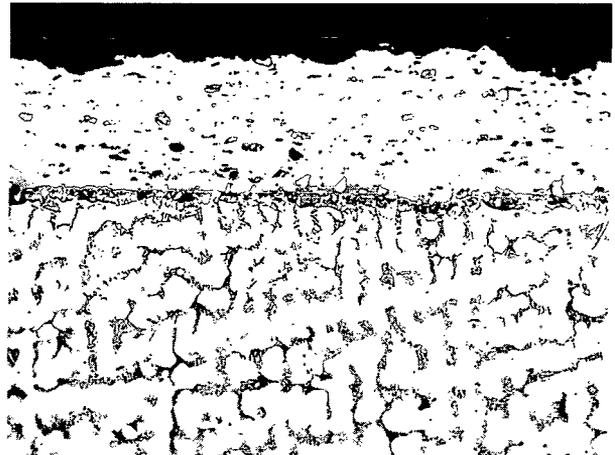
System	Oxidation			X-ray raster micrographs		Line (concentration) scans - elements in oxide scale	
	Total number of cycles	Length of each cycle, hr	Total time, hr	Elements analyzed	Elements definitely present in oxide scales	Yes	No <sup>a</sup>
1040 <sup>o</sup> C oxidation							
Ni-Cr clad Ni-Cr	10	20	200	Ni, Cr, Si, Mn	Cr, Si	(b)	(b)
Ni-Cr clad WI-52	10	20	200	Ni, Cr, Si, Mn, Co, W, Cb, C, Fe, Al	Ni, Cr, Si, Mn, Al	Ni, Cr	Co
Fe-Cr-Al clad Fe-Cr-Al	10	20	200	Fe, Cr, Al, Si, Mn	Fe, Cr, Al	(b)	(b)
Fe-Cr-Al clad WI-52	10	20	200	Fe, Cr, Al, Co, Cb, W, C	Cr, Al	Fe, Cr	Co*
Ni-Cr-Al clad Ni-Cr-Al	10	20	200	Ni, Cr, Al, Si, Mn, Fe	Ni, Cr, Al, Si, Mn, Fe	(b)	(b)
Ni-Cr-Al clad WI-52	10	20	200	Ni, Cr, Al, Si, Mn, Fe, Co, W, Cb	Ni, Cr, Al, Si, Mn	Ni, Cr	Co
1090 <sup>o</sup> C oxidation							
Ni-Cr clad Ni-Cr	10	20	200	Ni, Cr, Si, Mn, Fe	Cr, Si	(b)	(b)
Ni-Cr clad WI-52	3	20	60	Ni, Cr, Si, Mn, Co, W, Cb, C	Cr, Si, Mn	(b)	(b)
Ni-Cr clad WI-52	10	20	200	Ni, Cr, Si, Mn, Co, W, Cb, C, Al	Ni, Cr, Si, Mn, Al	Ni, Cr	Co*
Ni-Cr clad WI-52	20	20	400	Ni, Cr, Si, Mn, Co, W, Cb, C, Al	Ni, Cr, Si, Mn, Al	Ni, Mn	Co*
Fe-Cr-Al clad Fe-Cr-Al	10	20	200	Fe, Cr, Al, Ni, Co	Al	(b)	(b)
Fe-Cr-Al clad WI-52	10	20	200	Fe, Cr, Al, Co, Cb, W, C, Mn	Fe, Cr, Al, Mn	Fe, Cr, Co	----
Fe-Cr-Al clad WI-52	20	20	400	Fe, Cr, Al, Co, Cb, W, C, Mn	Cr, Al, Co, Mn	Fe, Cr, Co	----
Ni-Cr-Al clad Ni-Cr-Al	10	20	200	Ni, Cr, Al, Si, Mn, Fe	Ni, Cr, Al, Si, Mn	(b)	(b)
Ni-Cr-Al clad WI-52	2	20	40	Ni, Cr, Al, Si, Mn, Fe, Co, W, Cb, Mo	Ni, Cr, Al, Si, Mn	(b)	(b)
Ni-Cr-Al clad WI-52	6	20	120	Ni, Cr, Al, Si, Mn, Fe, Co	Ni, Cr, Al, Si, Mn	Ni, Cr, Al, Mn	Co*

<sup>a</sup>Elements with a \* apparently diffused through the complete cladding but are not present in the oxide scales.

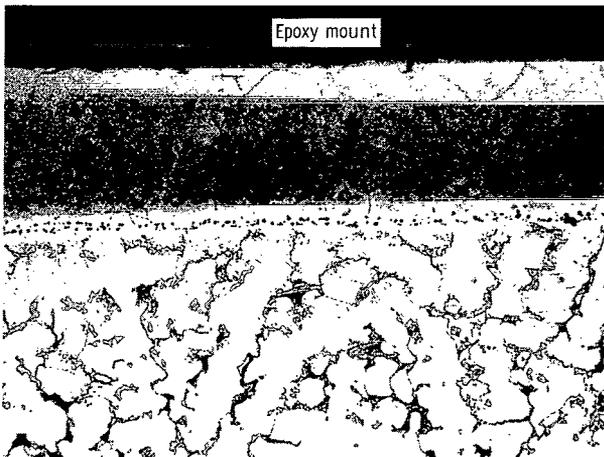
<sup>b</sup>Not detected.



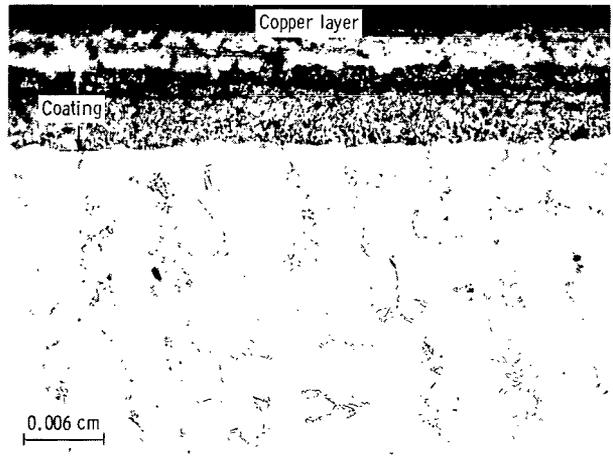
(a) Ni-Cr clad WI-52.



(b) Fe-Cr-Al clad WI-52.



(c) Ni-Cr-Al clad WI-52.



(d) Aluminide-coated WI-52 (from ref. 1).

Figure 1. - Microstructures of as-clad and as-coated WI-52. Nominal cladding and coating thicknesses, 0.127 and 0.056 millimeters, respectively. Etched.

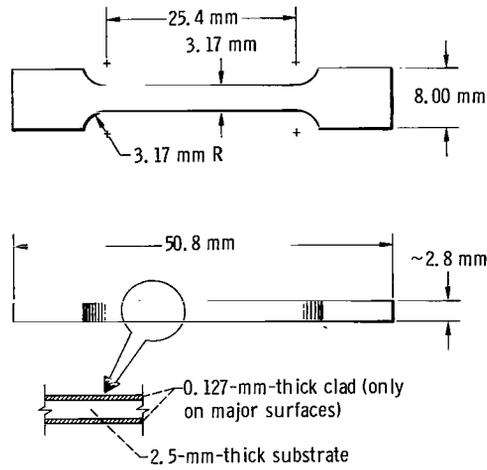


Figure 2. - Tensile specimen design. Scale, 2/1.

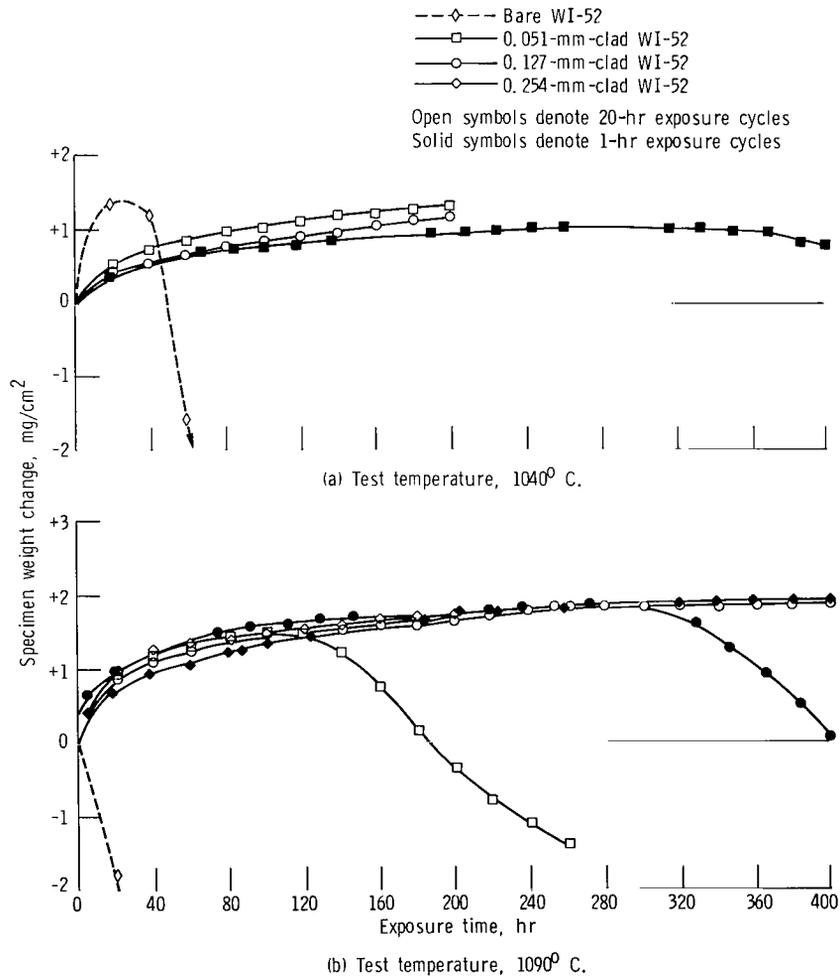
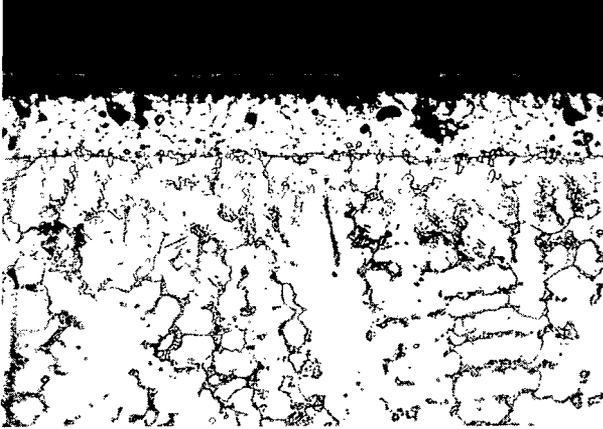
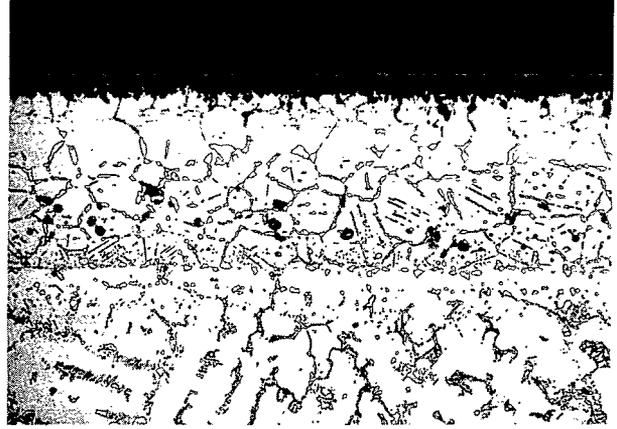


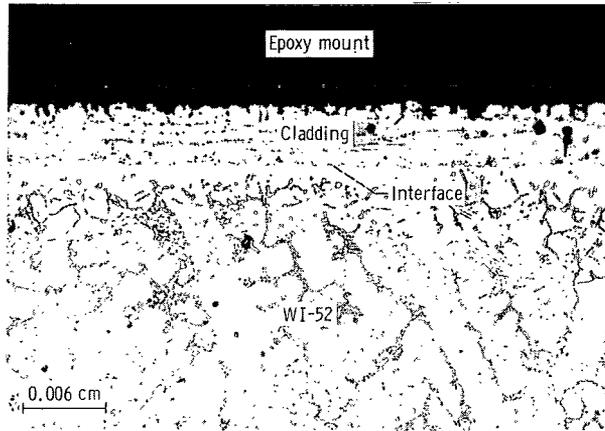
Figure 3. - Effect of cladding thickness, cycle frequency, and temperature on oxidation of Ni-Cr clad WI-52.



(a) After ten 20-hour exposures; original cladding thickness, 0.051 millimeter.

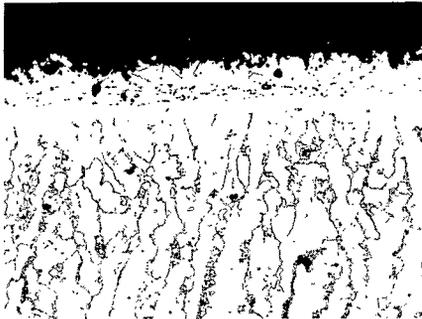


(b) After ten 20-hour exposures; original cladding thickness, 0.127 millimeter.

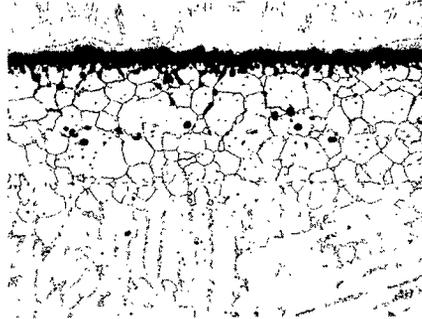


(c) After 400 1-hour exposures; original cladding thickness, 0.051 millimeter.

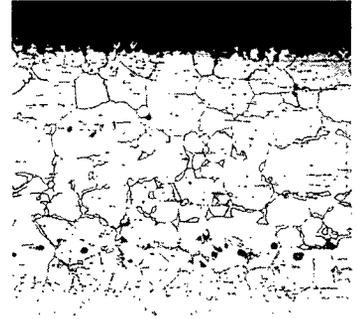
Figure 4. - Effect of 1040° C cyclic furnace oxidation on Ni-Cr clad WI-52. Etched.



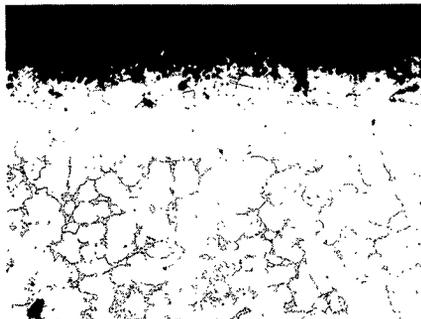
(a) After ten 20-hour exposures; original cladding thickness, 0.051 millimeter.



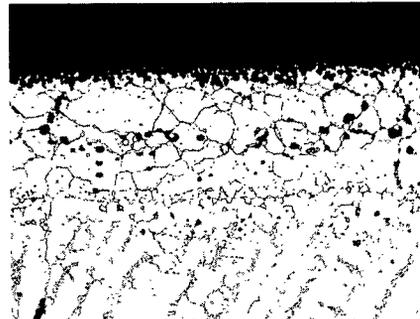
(b) After ten 20-hour exposures; original cladding thickness, 0.127 millimeter.



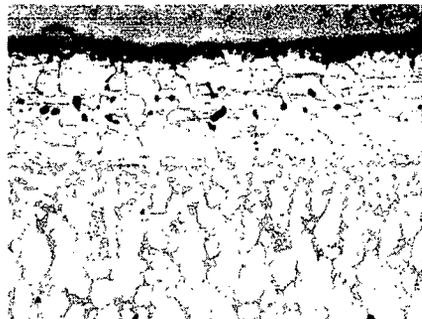
(c) After ten 20-hour exposures; original cladding thickness, 0.254 millimeter.



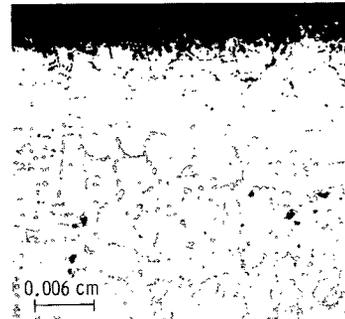
(d) After thirteen 20-hour exposures; original cladding thickness, 0.051 millimeter.



(e) After twenty 20-hour exposures; original cladding thickness, 0.127 millimeter.



(f) After 400 1-hour exposures; original cladding thickness, 0.127 millimeter.



(g) After 400 1-hour exposures; original cladding thickness, 0.254 millimeter.

Figure 5. - Effect of 1090° C cyclic furnace oxidation on Ni-Cr clad WI-52. Etched.

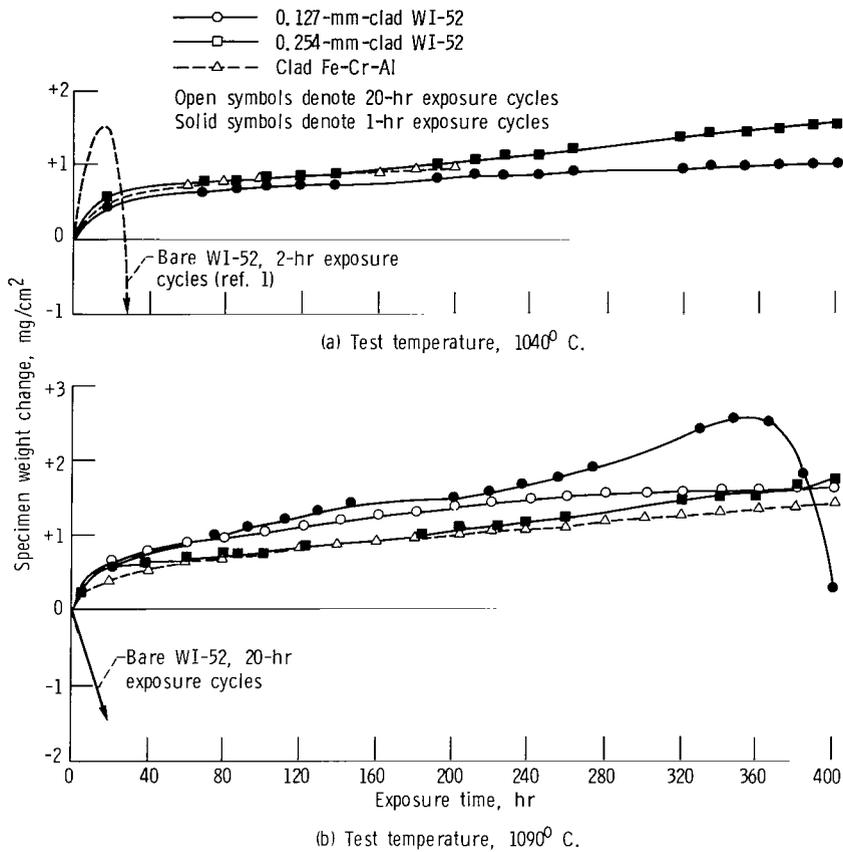
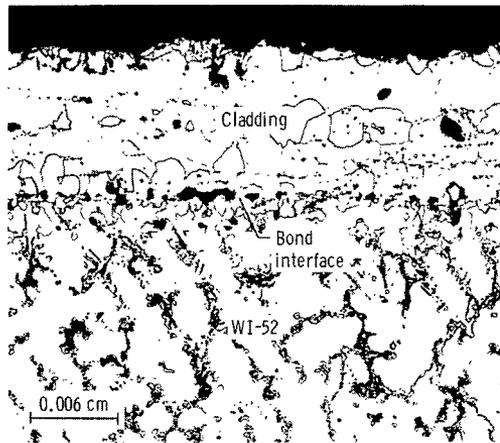
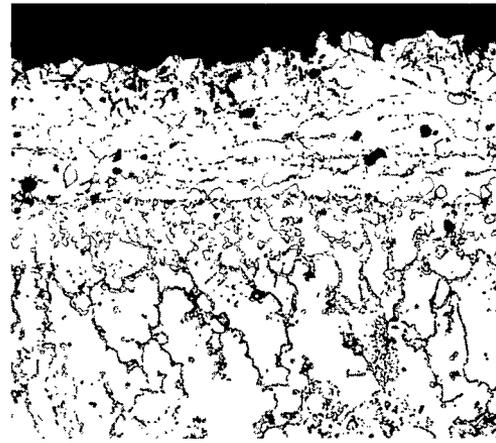


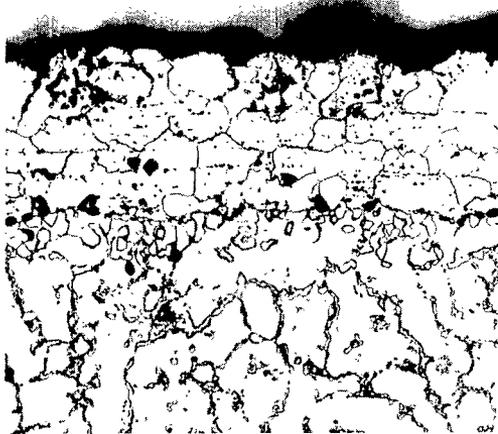
Figure 6. - Effect of cladding thickness, cycle frequency, and temperature on oxidation of Fe-Cr-Al clad WI-52.



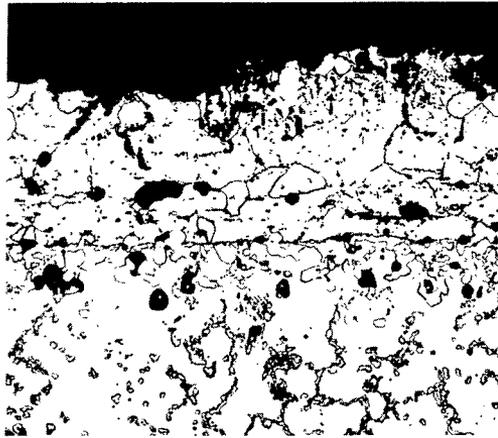
(a) After ten 20-hour exposures at 1040° C.



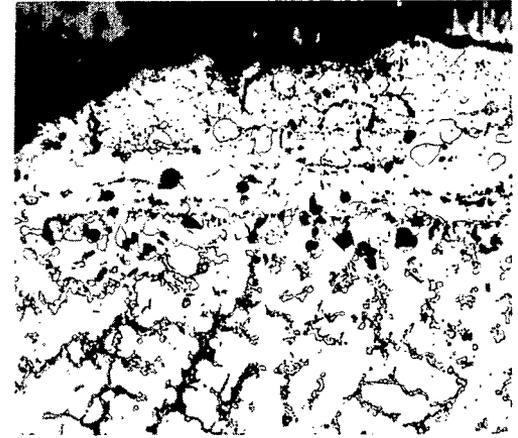
(b) After 400 1-hour exposures at 1040° C.



(c) After ten 20-hour exposures at 1090° C.



(d) After twenty 20-hour exposures at 1090° C.



(e) After 400 1-hour exposures at 1090° C.

Figure 7. - Microstructures of Fe-Cr-Al clad WI-52 after cyclic furnace oxidation at 1040° C and 1090° C. Original cladding thickness, 0.127 millimeter. Etched.

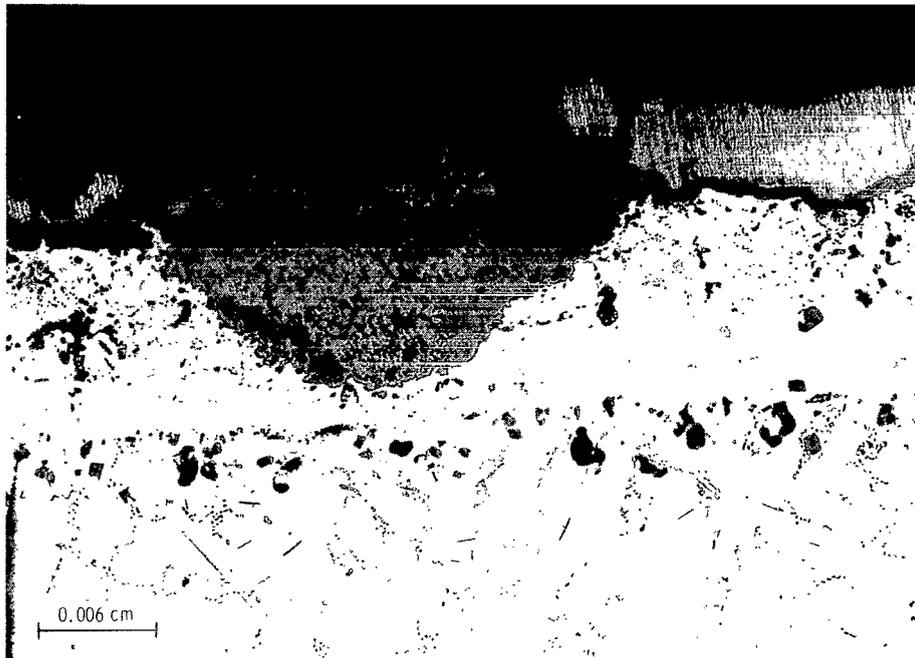


Figure 8. - Photomicrograph showing a deep, localized oxide penetration formed in Fe-Cr-Al clad WI-52 specimen during cyclic oxidation at 1090 °C for 400 1-hour exposures. Original cladding thickness, 0.127 millimeter. Etched.

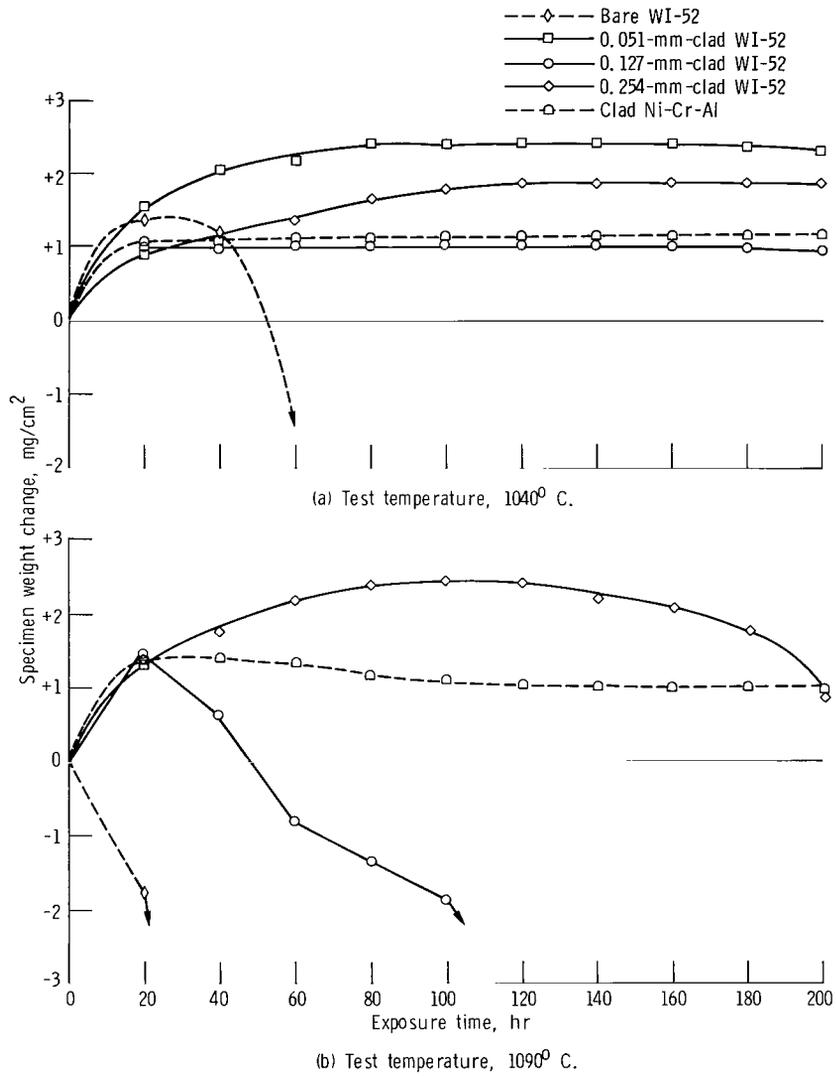
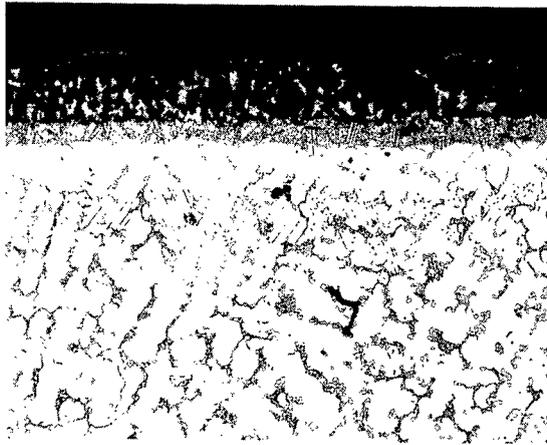
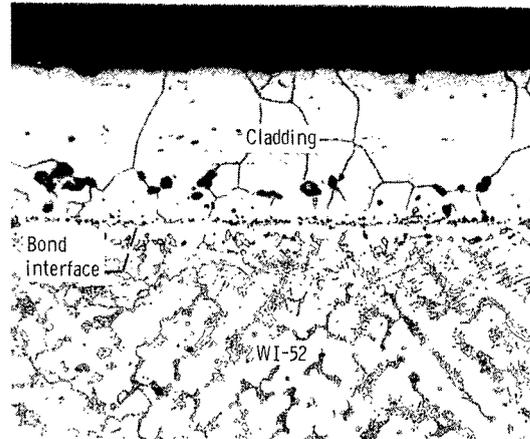


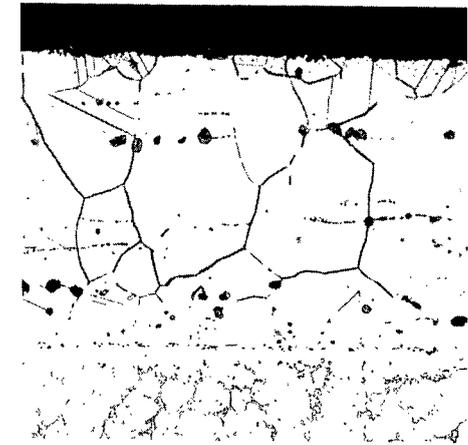
Figure 9. - Effect of cladding thickness and temperature on cyclic furnace oxidation of Ni-Cr-Al clad WI-52. Length of each cycle, 20 hours.



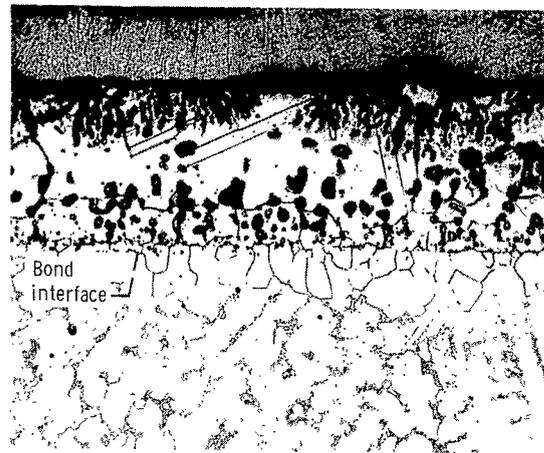
(a) After ten 20-hour exposures at 1040° C; original cladding thickness, 0.051 millimeter.



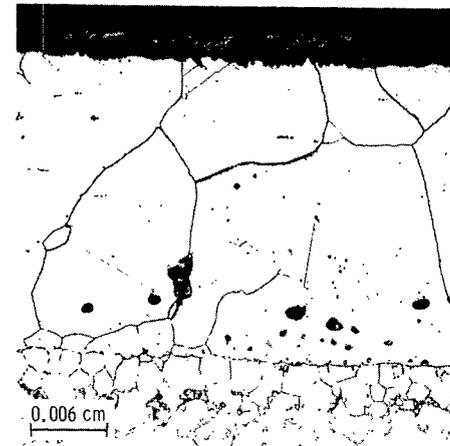
(b) After ten 20-hour exposures at 1040° C; original cladding thickness, 0.127 millimeter.



(c) After ten 20-hour exposures at 1040° C; original cladding thickness, 0.254 millimeter.



(d) After six 20-hour exposures at 1090° C; original cladding thickness, 0.127 millimeter.



(e) After ten 20-hour exposures at 1090° C; original cladding thickness, 0.254 millimeter.

Figure 10. - Microstructures of Ni-Cr-Al clad WI-52 after cyclic furnace oxidation at 1040° C and 1090° C. Etched.

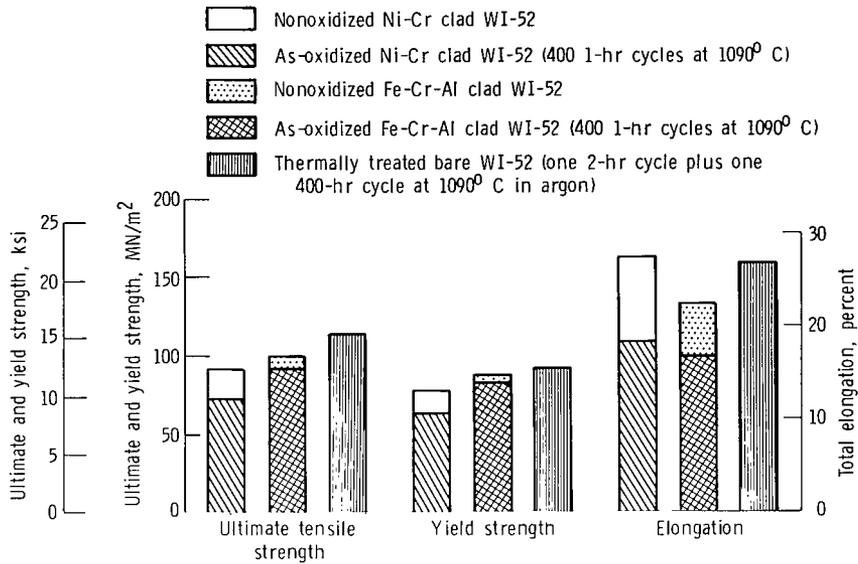


Figure 11. - Comparison of tensile properties of clad WI-52 at 1090<sup>o</sup> C before and after oxidation.

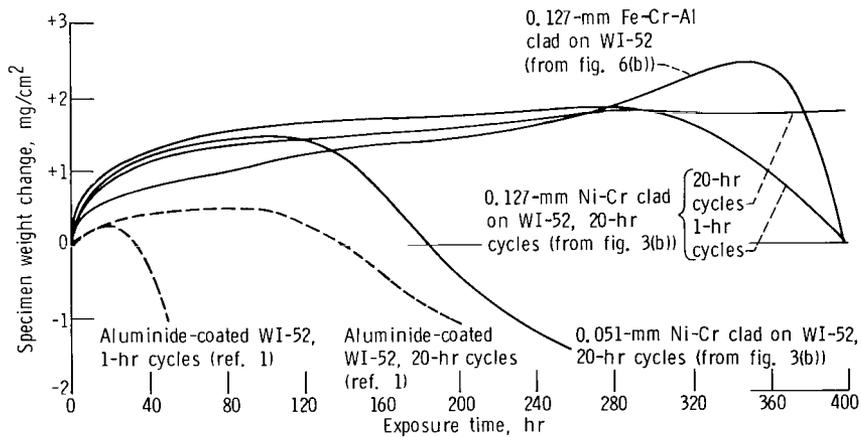
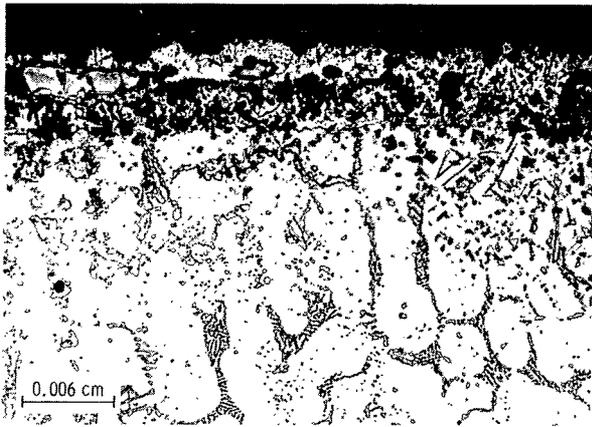
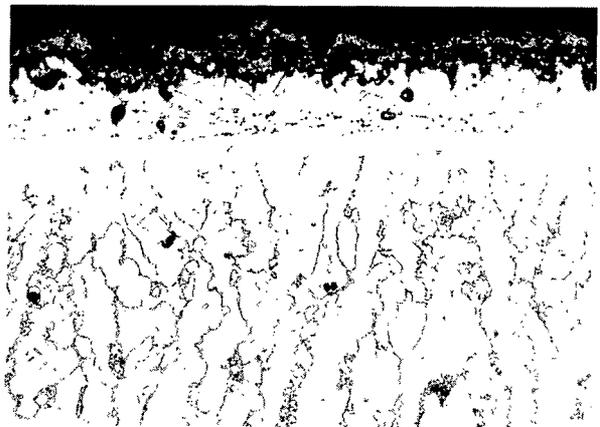


Figure 12. - Comparison of cyclic furnace oxidation effect on weight change at 1090<sup>o</sup> C of aluminide-coated WI-52 and Ni-Cr clad and Fe-Cr-Al clad WI-52.



(a) Aluminide-coated WI-52; original coating thickness, ~0.056 millimeter. (From ref. 1.)



(b) Ni-Cr clad WI-52; original cladding thickness, 0.051 millimeter.

Figure 13. - Microstructures of aluminide-coated and Ni-Cr clad WI-52 after cyclic furnace oxidation at 1090° C for 200 hours in 20-hour cycles. Etched.

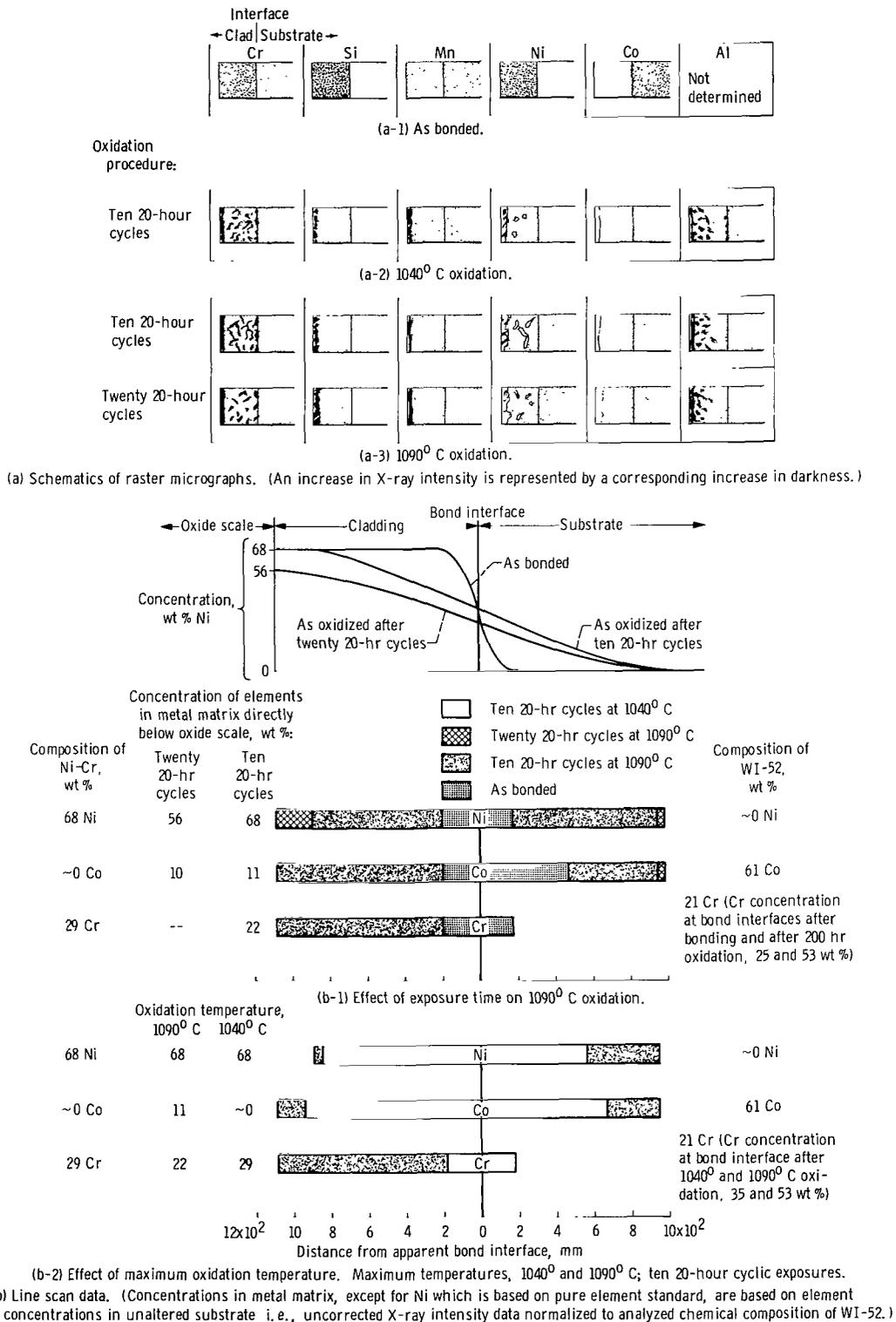
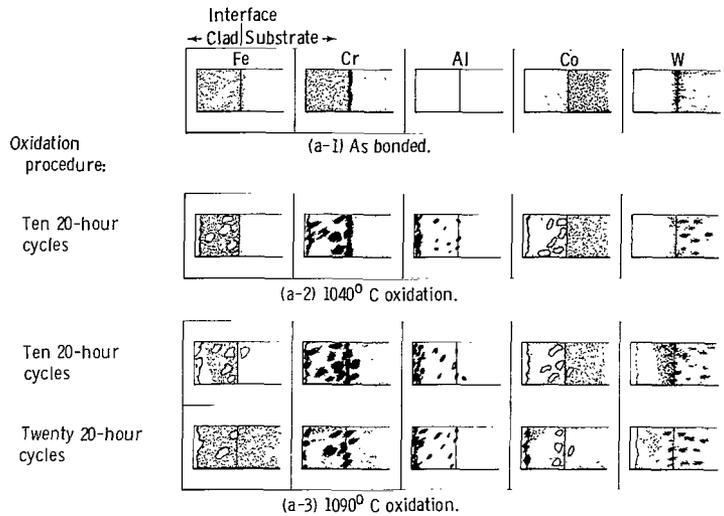
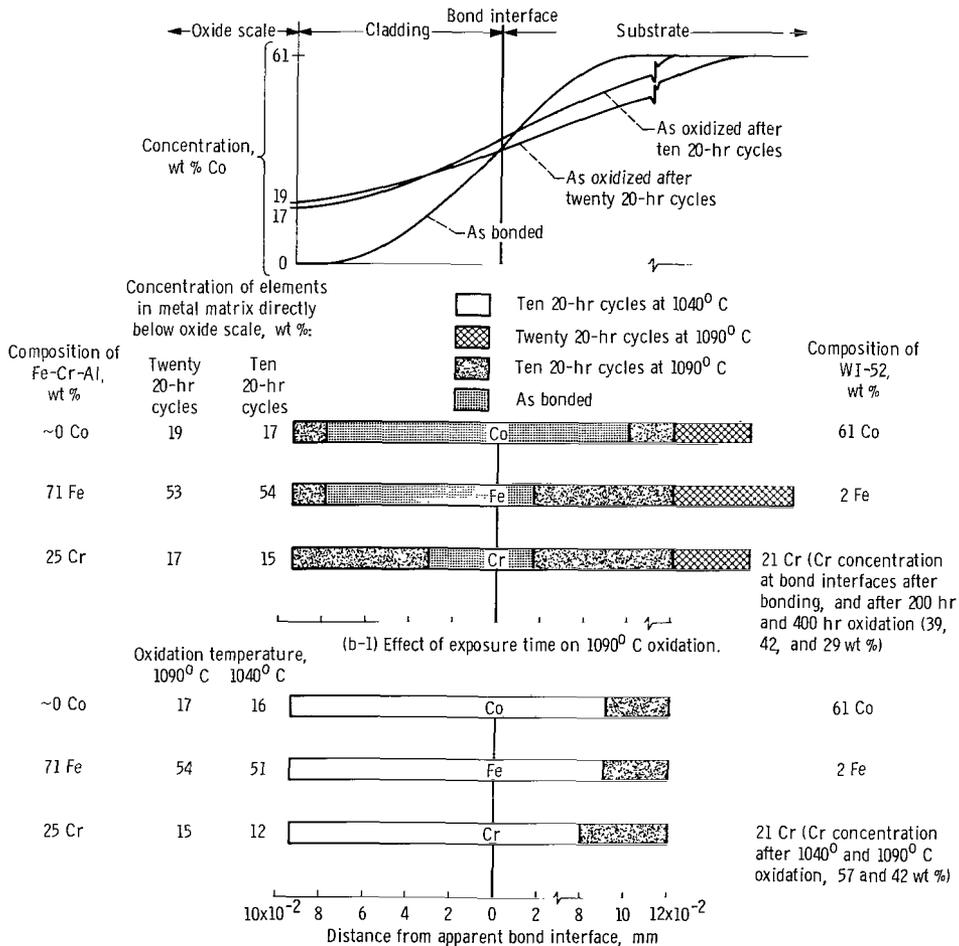


Figure 14. - Schematics of electron microprobe raster micrographs and extent of inter-diffusion of major elements of Ni-Cr clad WI-52 after bonding and oxidation.

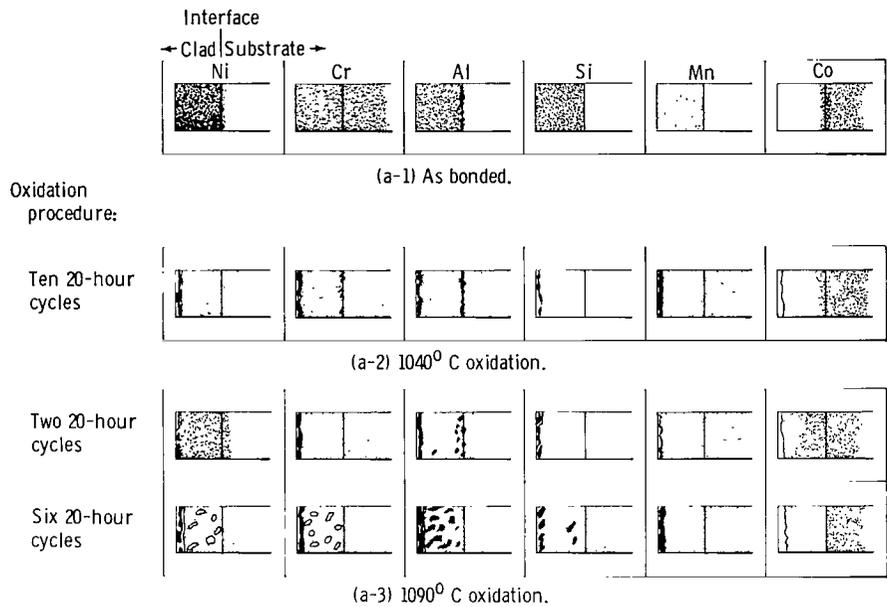


(a) Schematics of raster micrographs. (An increase in X-ray intensity is represented by a corresponding increase in darkness.)

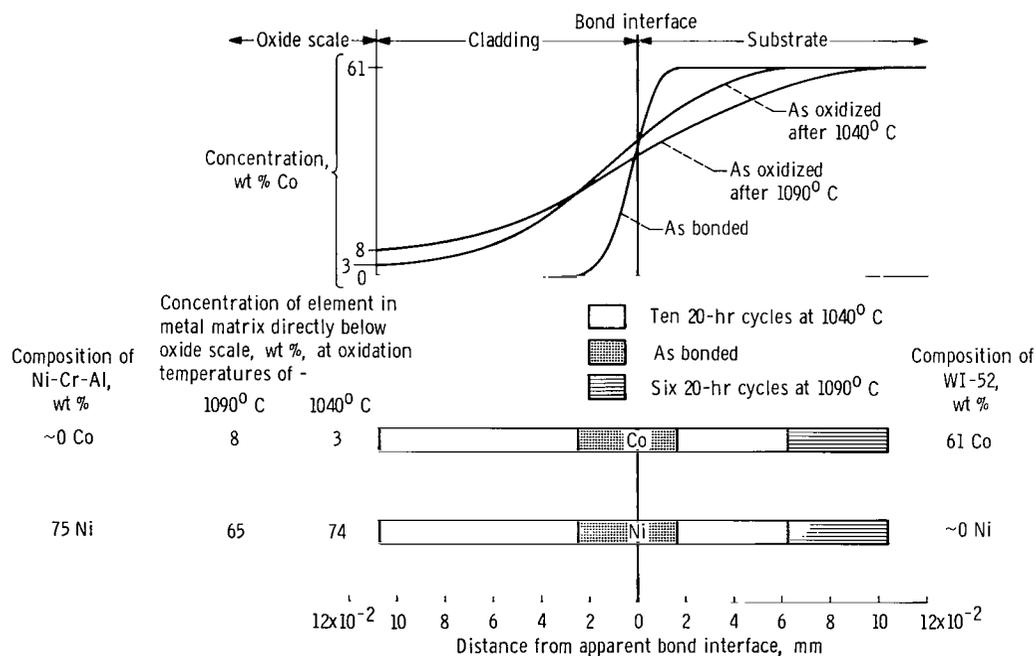


(b-2) Effect of maximum oxidation temperature. Maximum temperatures, 1040° and 1090° C; ten 20-hour cyclic exposures.  
(b) Line scan data. (Concentrations in metal matrix, except for Fe which is based on pure element standard, are based on element concentrations in unaltered substrate, i.e., uncorrected X-ray intensity data normalized to analyzed chemical composition of WI-52.)

Figure 15. - Schematics of electron microprobe raster micrographs and extent of inter-diffusion of major elements of Fe-Cr-Al clad WI-52 after bonding and oxidation.)



(a) Schematics of raster micrographs. (An increase in X-ray intensity is represented by a corresponding increase in darkness.)



(b) Line scan data. (Concentrations in metal matrix, except for Ni which is based on pure element standard, are based on element concentrations in unaltered substrate, i.e., uncorrected X-ray intensity data normalized to analyzed chemical composition of WI-52.)

Figure 16. - Schematics of electron microprobe raster micrographs and extent of inter-diffusion of major elements of Ni-Cr-Al clad WI-52 after bonding and oxidation.

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