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DEVELOPMENT OF ELECTROLESS NICKEL COATING FOR HIGH PERFORMANCE ALUMINUM FUEL PLATES

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CONTENTS

	Page
Abstract	4
Keywords	
Introduction	5
Previous Studies	6
ORNL Analysis and Development	8
Future Development	14
Acknowledgements	15

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ABSTRACT

There is a limit to the applicability of aluminum as a fuel cladding and matrix material in high performance water cooled research reactors. This limit is associated with corrosion, oxide thermal insulation, radiation damage, and loss of strength at high temperatures. One approach to extending the usefulness of aluminum is to deposit a corrosion resistant, electroless nickel coating on the surface of the fuel plates.

An investigation using specimens coated with nickel by a new technique revealed that as-plated samples successfully withstood bend, thermal shock, and autoclave and dynamic corrosion tests without cracking, measurable corrosion or sloughing off. In one additional dynamic corrosion test a tubular specimen was electrically heated so as to provide a high heat flux through the nickel coating; small cracks developed, but there was no sloughing of the nickel. Following these tests an ORR fuel element was partially coated with nickel so as to introduce the effects of radiation. After ten weeks of normal operation, the nickel coating appeared to be in excellent condition.

The tests mentioned above were conducted in deionized water. A few out-of-pile tests were also conducted in pH 5 (HNO_3) water, and the results indicated an excessively high corrosion rate of the nickel.

Keywords

Nickel coating, electroless coating, fuel plates, corrosion protection, aluminum, light water research reactors.

INTRODUCTION

In high performance ATR* and HFIR**-type water-cooled reactors any significant increase in the power density or fuel element life could make aluminum unsatisfactory as a cladding and matrix material. The limiting factors are corrosion attack, the thermal insulation of the aluminum oxide formed, and radiation damage and loss of strength at high temperatures. At the high heat fluxes and water-cladding interface temperatures in this type of reactor, the aluminum oxide is appreciable in terms of temperature drop, and its growth is very sensitive to coolant film temperature and pH.[1] By adjusting the coolant pH to 5.0 with HNO_3, the oxide growth has been reduced to a minimum and acceptable rate for the HFIR. However, for higher performance cores even the minimum rate could be excessive. Furthermore, the oxygen addition required for stabilizing HNO_3 under radiation can be detrimental to stainless steel portions of the system in terms of chloride-induced stress corrosion cracking.[2] Thus, there is a need for the development of a better aluminum alloy and/or a suitable protective coating.

This report is concerned with the development of electroless nickel as a protective coating. Such a coating could provide corrosion protection to the aluminum and could permit the use of high purity, oxygen-free water as a coolant.

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*Advanced Test Reactor, National Reactor Testing Station

**High Flux Isotope Reactor, Oak Ridge National Laboratory

PREVIOUS STUDIES

In 1955, personnel at the Argonne National Laboratory[3] reported the results of out-of-pile and in-pile corrosion studies of a 0.3 mil coating of electroless nickel on 1100 alloy aluminum. Four specimens in a static corrosion test subjected to 315°C deionized water for one week failed by blistering or rupture. One of five samples in an out-of-pile test loop, containing 315°C, deionized water flowing at 18 fps, failed after 1250 hours; the others showed pitting and weight gains. Experiments on the same type of specimens were also conducted by ANL investigators in a water loop at the MTR. Specimens were placed both in and out of the reactor core region within the same loop. Water in the loop was deionized and had a velocity of 25 fps. The water temperature was 260°C for 530 hr, 232°C for 50 hr and 177°C for 150 hr. At the conclusion of the run it was found that the nickel coating had sloughed off of the in-pile specimens but not off of the out-of-pile specimens.

In 1964 Johnson[4] reported on a series of out-of-pile dynamic corrosion studies of electroless nickel on two aluminum alloys. An 0.8 mil coating provided significant protection to 330°C, pH 6.6 water flowing at 25 fps. Samples heat treated at 400°C for 40 hours had the lowest rate of corrosion; however the diffusion bonding heat treatment appeared to promote plate cracking in dynamic exposures.

Further studies by Johnson[5] showed that electroless nickel coated and heat treated samples were compatible with deionized water and pH 10 NH_4OH, but not with pH 10 LiOH in semistatic and dynamic (25 fps) tests at 330°C.

In 1966, as a part of the ATR design studies, the feasibility of applying an electroless nickel coating to

aluminum clad fuel elements to reduce the oxide build-up was investigated.[6] Corrosion tests were performed in a conventional out-of-pile pressurized water loop and in the G-12 pressurized loop in the ETR. In most cases, the base metal was aluminum alloy 6061. The electroless nickel coating was 0.8 mil thick and had a phosphorus content of 8 to 10 weight percent (typical of most electroless nickel coatings). Comparative corrosion tests were performed on uncoated base metal, as-plated, and plated and heat treated samples. The heat treatment consisted of heating the plated specimen for periods of time from 1-1/2 to 75 hours in the temperature range 410°C to 485°C to produce various degrees of diffusion bonding between the coating and the base metal.

One set of specimens was tested for 800 hours in a dynamic corrosion loop operated at 190°C with a pH of 5.0 to 5.3 and a water velocity of 45 fps. The uncoated and the as-plated specimens underwent severe corrosion. The specimens which had been heated to 410°C for 12 hours, a heat treatment that produced very little diffusion, had excellent corrosion resistance. Specimens heat treated at higher temperatures to produce distinct layers of aluminum-nickel intermetallic compounds had only moderate corrosion resistance.

All of the electroless nickel coated specimens tested in the ETR G-12 loop were heat treated, some at 410°C and some at 450°C. These specimens contained enough fuel to produce heat fluxes of 1.0 to 2.4 x 10^6 Btu/hr.ft^2. The water temperature was 218°C, the velocity was 46 fps, and the pH was 5.0 to 5.3 In all cases the coating sloughed off at the beginning of the cycle over a large portion of the fueled region.

Another "ATR" result of possible interest was observed during the cooling down portion of the heat treatment cycle; several of the specimens experienced sloughing of the nickel coat. This leaves some doubt regarding the integrity of the bond of those specimens that later failed in the in-pile loop. Unfortunately, the ATR nickel program was terminated before conclusive results were obtained.

ORNL ANALYSIS AND DEVELOPMENT

During 1968 personnel at the Oak Ridge Gaseous Diffusion Plant developed a new surface preparation and plating technique[7] that helped to revive interest in electroless nickel coatings for aluminum fuel plates. At about this same time the authors were reviewing the previously reported results and had concluded that heat flux appeared, on the basis of the test results, to be a significant factor in nickel sloughing. However, a simple analysis of the differential expansion associated with the heat flux indicated that heat flux values of general interest should not cause significant differential expansion relative to the isothermal heating differential expansion. This is illustrated below for the following material properties and typical high performance reactor conditions:

	Al.	Ni. Coating
Linear coefficient of thermal expansion ($°F^{-1}$)	13×10^{-6}	8×10^{-6}
Thermal conductivity, (Btu/hr·ft°F)	100	3

Isothermal temperature increase = 330°F
Heat flux = 2×10^{6} Btu/hr·ft^{2}
Nickel coating thickness = 0.5×10^{-3} in.
Fuel plate thickness = 40×10^{-3} in.

Using the above numbers the isothermal differential expansion between the nickel coating and fuel plate was calculated to be 2×10^{-3} in/in. The heat flux across the nickel coating produces an average differential expansion of about 2×10^{-4} in/in.

There is some question regarding the thermal conductivity and expansion coefficient data for the nickel coating, but the indications are that the differential expansion induced by the heat flux is small compared to the isothermal differential expansion.

There is also the possibility that nuclear radiation could have an effect on the nickel coating adherence; however, in the ETR G-12 loop test the nickel sloughed off almost immediately and thus without exposure of the specimen to much radiation.

Another factor of some concern is the chemistry of the water. As indicated above, the "ATR experiments were conducted in pH 5.0 to 5.3 water, while the others were conducted in deionized and pH 10 water. Early in the HFIR project our experience[8] with electroless nickel in pH 5.0 water indicated very poor nickel-coating corrosion resistance compared to that obtained in deionized water.

In an effort to rectify some of the apparent inconsistencies in the previous results, the authors initiated a new electroless nickel program. Since it appeared that the newly developed surface preparation and plating techniques would result in a superior nickel coat, only those most recent techniques were used. For the first phase of the program small flat plate specimens of 1100-H14 aluminum (commercially pure aluminum, half hard temper) were electroless nickel coated, some with 0.1 mil and the others with 0.5 mil thicknesses. For each thickness some of the specimens were heat treated at 415°C for 1 hr, some at 500°C for 1 hr, and the remainder were left in the as-plated condition. The purpose of the heat treatments was to provide some

degree of diffusion bonding between the nickel coating and the aluminum. Typical photomicrographs of specimen cross sections are shown in Figures 1, 2, and 3.

To obtain an initial qualitative estimate of coating adherence, as-plated specimens were subjected to a mechanical bend test. Also, one of the as-plated specimens with 0.5 mil nickel coating was subjected to thermally induced differential strains by slowly thermal cycling the specimen between room temperature and 430°C and finally quenching from 430°C with a stream of cool water impinged on one side. The bend tests produced cracks but no sloughing, while the differential expansion test produced no indications of failures. Examination at 10X magnification of the surface while at maximum temperature revealed no cracks.

The first corrosion tests consisted of exposing pairs of each of the above types of specimens to 250°C deionized water in an autoclave for one week. One specimen in each pair was given a mild thermal shock (quench in cool water from 260°C) prior to the autoclave test. The results of the corrosion tests indicated that the 0.1 mil coating was not adequate; that the mild thermal shock was insignificant; and that all but the as-plated specimens were moderately to severely attacked. The corrosion attack on the 415°C heat treated specimens appeared to initiate at "pin holes," with subsequent gross undermining of the nickel coating. Specimens heat treated at 500°C corroded to a dull black finish with scattered spots of aluminum oxide break-through. Photographs of typical as-plated and heat treated specimens with 0.5 mil nickel coatings are shown in Figure 4 for the post-exposure condition. Figures 5, 6, and 7 are 15 X magnifications of the same surfaces. Figure 5 shows the typical surface texture of the as-plated nickel; it was

unchanged as a result of the corrosion test. In Figure 6 the small white areas are aluminum oxide break-through, and the much larger discolored areas are undermined with aluminum oxide. Figure 7 clearly shows the spots of oxide break-through on the specimens heat treated at 500°C.

To further check for the existence of pin holes in the as-plated nickel coating, the specimen that had been thermal cycled between room temperature and 430°C was, after the final quench, placed in a beaker of strong, heated, sodium hydroxide solution. There were no hydrogen bubbles except from a spot on a sharp edge where forceps had broken the coating. At this point the attack was vigorous. As a further check on the sensitivity of pin hole detection by this method, a fine needle was used to puncture the nickel coating. After several minutes in the solution, the bubbles started.

We concluded from this first series of tests that the as-plated nickel coating was far superior to the heat treated specimens, and that it had reasonably good adherence and corrosion resistance in deionized water up to at least 250°C.

The next test was conducted with a small tubular specimen that was electrically heated to produce a high heat flux and that was cooled internally with forced-flow water (see reference 9 for description of apparatus). The internal dimensions of the rectangular tube were 0.5 in. x 0.050 in. x 6.5 in. long. Nickel was applied to the inner surface only and was left in the as-plated condition; the thickness of the nickel was $\sim$ 1.5 mils instead of the desired 0.5 mils. The coolant velocity was 30 fps, and at all times the specific resistivity of the water was $> 10^6$

ohm-cm. During the first 68 hours a heat flux of 1.0×10^6 Btu/hr·ft^2 was maintained, after which it was increased to 1.5×10^6 Btu/hr·ft^2 for the remainder of the test, a period of 459 hours. At the higher heat flux the temperature of the nickel at the nickel-water interface was about 242°C.

At each heat flux the temperatures on the outside of the specimen remained constant, indicating the absence of any significant deposit at the specimen-water interface and thus no sloughing of the nickel. Examination of the specimen inner surface at the conclusion of the test showed no evidence of aluminum oxide corrosion product; the surface had developed only a slight surface discoloration. However, a few very fine cracks in the nickel were apparent, as shown in Figure 8. Since the coating has little ductility it is possible that these cracks resulted from slight deflections of the rectangular tube as the internal pressure made the tube conform to the exact shape of the rigid backup. Sufficient measurements were not taken before the test to determine the magnitude of the strain.

At the bottom of the cracks the aluminum had been attacked to a depth of about 0.5 mil. Part of the crack and the corroded volume were packed with aluminum corrosion products as shown in Figure 9. At no place along any of the cracks was there evidence of the nickel tending to peel from the aluminum surface.

The next phase of our program consisted of exposing several small 6061-T6 specimens with 0.5 mil of as-plated nickel to a range of coolant velocities under isothermal conditions. The test section of the loop was tapered and held several specimens along the length of the tapered channel. Thus each specimen was subjected to a different

coolant velocity, the velocity range being 20 to 120 ft/sec. Two tests were conducted: one with pH 7 water and one with pH 5.0 water. In both cases the water temperature was 205°C.

The pH 7 test was run for two weeks, at the end of which there were no signs of sloughing, and the corrosion of the nickel was very small (1.6 mils/yr at 60 ft/sec). In the maximum velocity region the leading edge of the corresponding specimen showed definite signs of erosion from an eddy created by the slight discontinuity at the junction of two adjacent specimens. The erosion penetrated the nickel and ate into the aluminum. However, even with this discontinuity and exposed nickel-aluminum interface the nickel coating did not tend to slough.

Results from the pH 5.0 test were significantly different insofar as corrosion of the nickel was concerned. This test was stopped at tne end of two days for inspection of the specimens. There was no sloughing, but the nickel corrosion rate associated with specimens exposed to less than 60 ft/sec was about ten times greater than obtained in the pH 7 water (16 mils/yr). Above 60 ft/sec the nickel was very badly pitted, with penetrations into the aluminum substrate. It was tentatively concluded that pH 5.0 water was unacceptable for testing electroless nickel.

Because of the success of the 0.5 mil nickel coating in deionized water under the above varied conditions, our next step was to test a fueled specimen in-pile at reasonably high heat flux, temperature and coolant velocity. Both the HFIR and ETR would provide these conditions, but in both reactors the coolant pH is about 5.0. Therefore, it was decided to irradiate a partially plated ORR fuel element in the ORR, where the pH is about 6.5. The disadvantage

associated with the ORR is a somewhat lower heat flux, temperature and coolant velocity than desired.

Electroless nickel was applied to the outer surfaces of the two outer fuel plates of the particular ORR fuel element. The thickness of the coating was 0.5 mil, and the nickel was left in the as-plated condition. Testing was conducted in about two-week intervals, the element being removed at the end of each interval for under-water inspection with a periscope. The total time of testing was about ten weeks. At no time was there any evidence of cracking or sloughing, even though the coated surfaces were scratched numerous times during extraction and insertion of the element.

FUTURE DEVELOPMENT

Since application of the electroless nickel on aluminum is intended for very high performance cores, there is a need to test the nickel coating under conditions more severe than have been achieved thus far. The out-of-pile facility that electrically heats the specimen has been modified to produce heat fluxes of about 3×10^6 Btu/hr·ft^2 and coolant velocities up to 100 ft/sec. The specimen will be a circular tube, and circumferential and axial strains can be controlled and varied as desired. Experiments using this facility will be conducted during the next several months. From these tests we should be able to determine how much differential strain and how much cycling are required to initiate sloughing of the nickel.

Eventually it will be necessary to subject coated specimens to high performance conditions in-pile. One possibility is to use the ETR G-12 loop with pH 6 to 6.5 water. In this loop it would be possible to achieve a heat flux of at least

2×10^6 Btu/hr·ft^2 and coolant velocities up to 50 ft/sec. To go beyond these conditions in-pile will require special facilities. At the present time there are no definite plans for high performance in-pile experiments.

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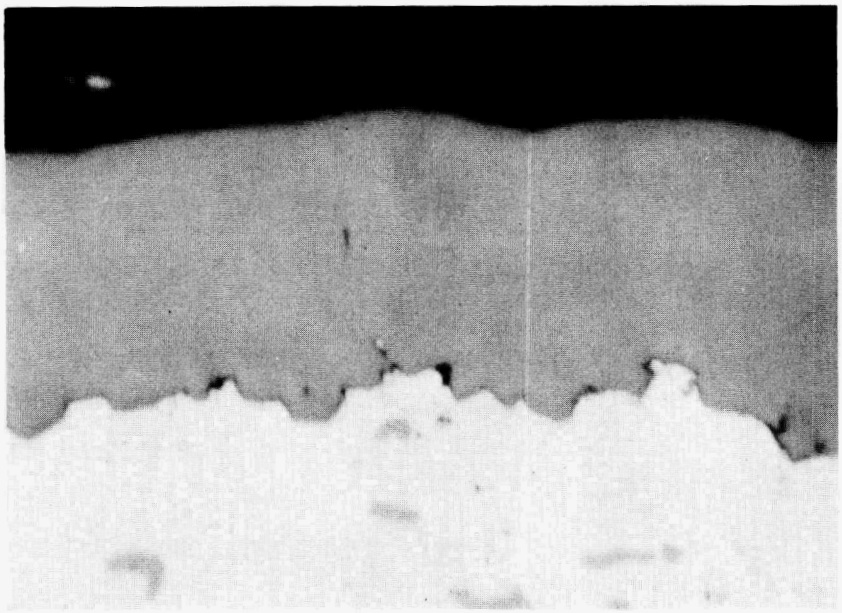
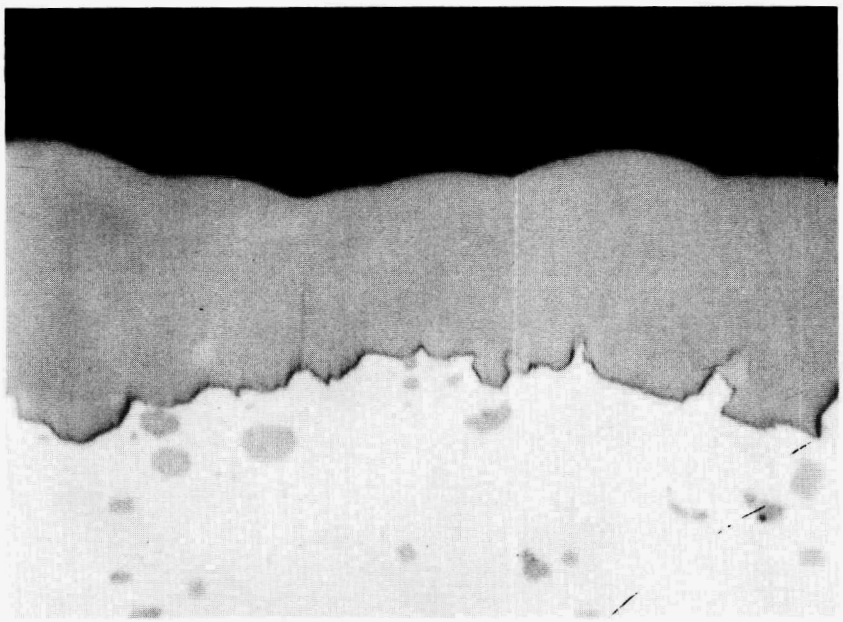


1500X 8939

Figure 1. Electroless Nickel on Aluminum Alloy 1100-H14, As-Plated



1500X 8943

Figure 2. Electroless Nickel on Aluminum Alloy 1100-H14, Diffusion Bonded at 415°C.

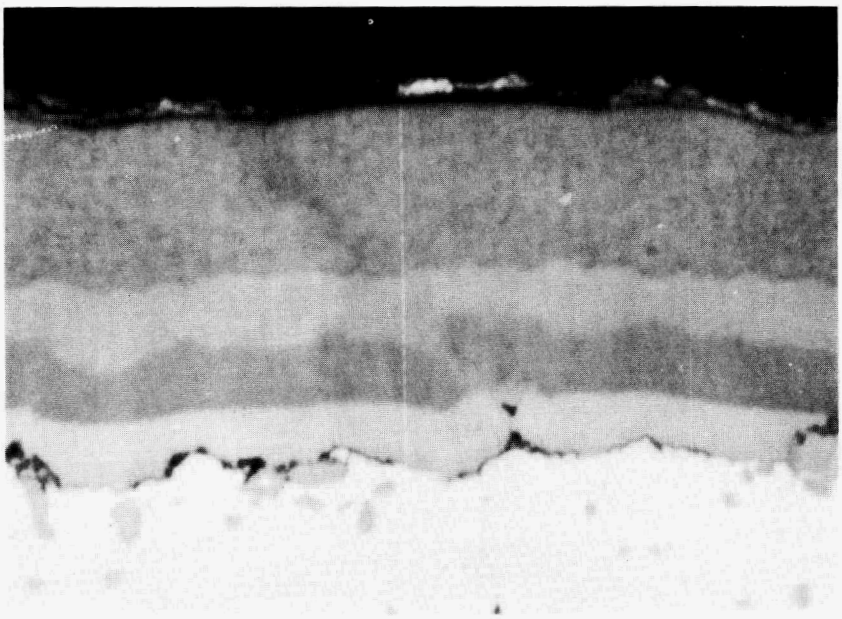


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Figure 3. Electroless Nickel on Aluminum Alloy 1100-H14, Diffusion Bonded at 500°C

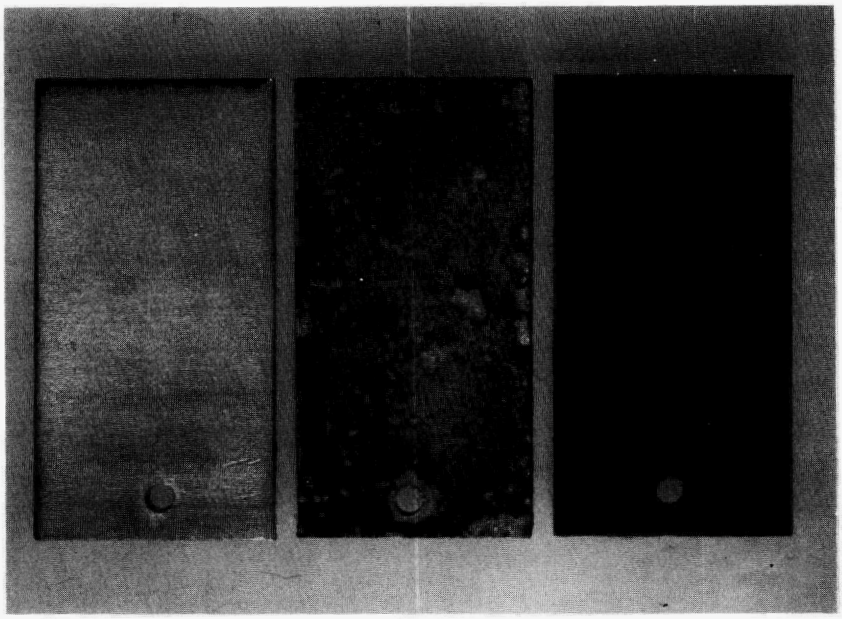

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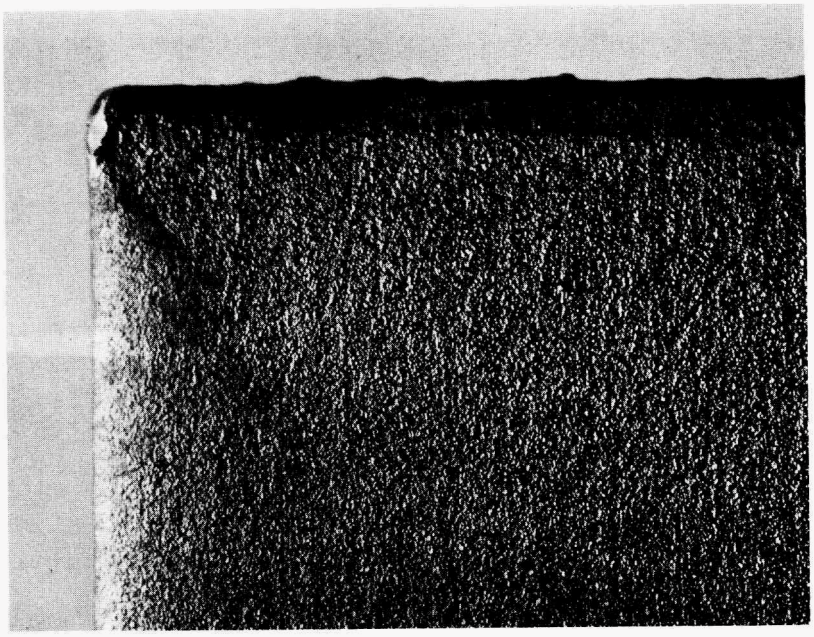
Figure 4. Coupons After 1 Week Exposure to Water at 250°C

Left: As-plated
Center: Diffusion Bonded, 415°C
Right: Diffusion Bonded, 500°C



15X A-3034

Figure 5. As-Plated Electroless Nickel on Aluminum After Hot Water Exposure

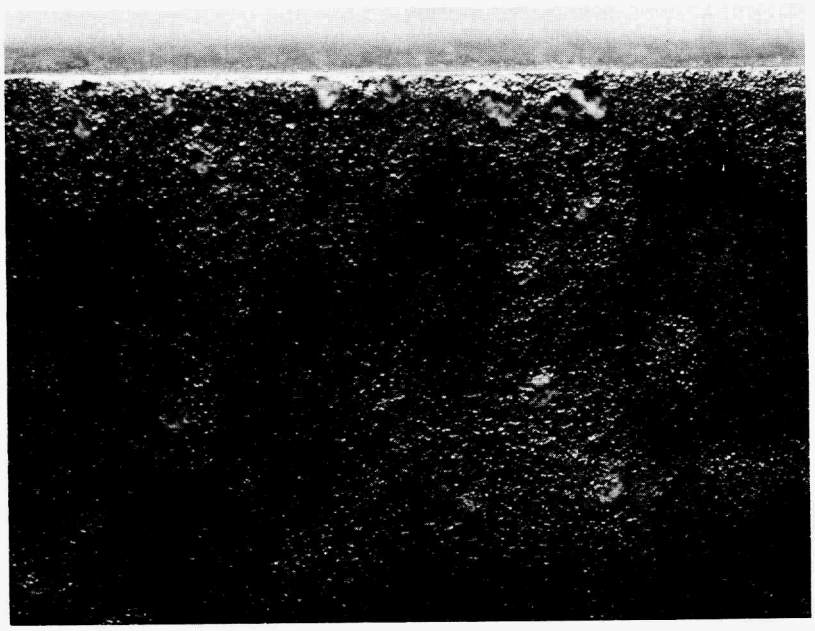


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Figure 6. Diffusion Bonded (415°C) Electroless Nickel on Aluminum After Hot Water Exposure

15X A-3033

Figure 7. Diffusion Bonded (500°C) Electroless Nickel on Aluminun After Hot Water Exposure

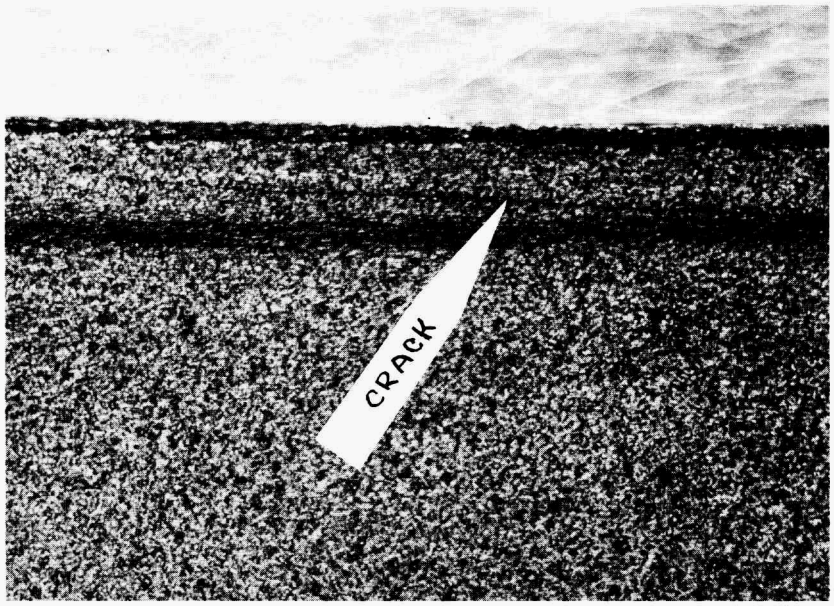

Figure 8. Electrically heated tubular specimen showing crack in nickel coating on inside surface

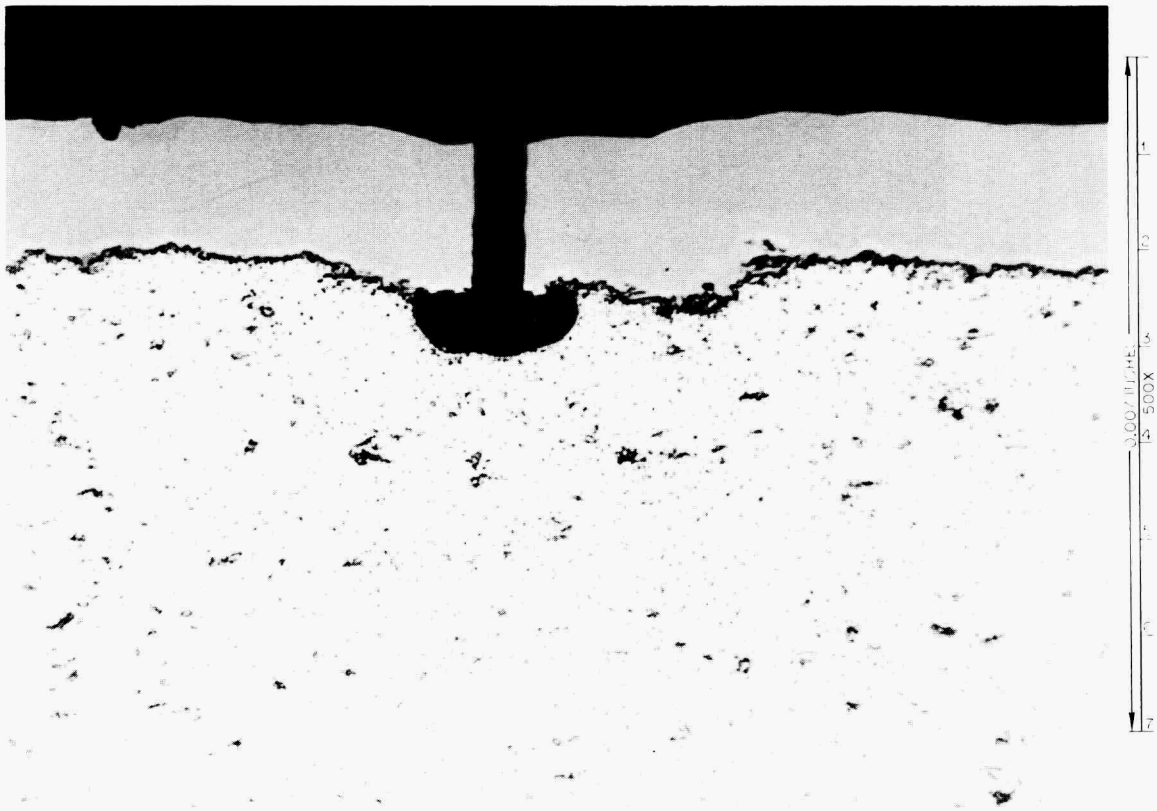

Figure 9. Cross section of crack shown in Fig. 8.

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