DIFFUSION KINETICS STUDIES

IN THE

Al-Ni-U SYSTEM

By

R. A. HARLOW
OTTO GAMBA

ATOMICS INTERNATIONAL

A DIVISION OF NORTH AMERICAN AVIATION, INC.
P.O. BOX 309   CANOGA PARK, CALIFORNIA

DISCLAIMER

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

DISTRIBUTION

This report has been distributed according to the category "Metals, Ceramics, and Materials" as given in "Standard Distribution Lists for Unclassified Scientific and Technical Reports," TID-4500 (21st Ed.) June 1, 1963. A total of 625 copies was printed.

ACKNOWLEDGMENT

CONTENTS

TABLES

FIGURES

FIGURES

ABSTRACT

A diffusion couple technique was developed and standardized for the purpose of obtaining meaningful data regarding the diffusion kinetics of the Al-Ni-U system. The technique entailed hot pressing under a dynamic vacuum and subsequent isothermal soaking treatments within evacuated quartz tubes for periods of 10 to 7000 hr at temperatures of 650, 750, 850, and 950°F.

In addition, the nickel barrier bond between Type 1100 aluminum cladding and cast U - 3.5% Mo fuel alloy was metallographically examined on four fuel cylinders fabricated according to Piqua procedure. One cylinder was inspected in the "as fabricated" conditions, and the three others after 1000, 2000, and 4000 hr of isothermal soaking in Santowax OMP at 750°F in an autoclave under 100 psig of nitrogen.

The following conclusions were obtained:

1) The penetration of aluminum into nickel followed a parabolic relationship with time. The penetration coefficient was graphically determined as a function of temperature.

2) The nickel penetration data generated by the diffusion couple technique were slightly higher than those derived from the cylinder bond study. The maximum discrepancy was 20%. This disagreement was attributed to the geometry of the tubular specimens and to the interface displacements which occurred during the annealing process due to differential thermal expansion between fuel and cladding, both at the OD and ID.

3) A low-aluminum phase AlNi or $AlNi_3$ nucleated at the Al_3Ni/Al_3Ni_2 interface when the supply of additional free Al into the system was restricted due to void formation or separation between intermetallics and Al. The growth of the low-aluminum phase progressed at the expense of the Al_3Ni until all this phase was consumed, then consumption of the Al_3Ni_2 phase began.

4) The interdiffusion rate of uranium and nickel also followed the parabolic relationship with time. The diffusion coefficient as a function of temperature was plotted.

I. INTRODUCTION

For several years, uranium base metallic fuels clad with aluminum have been of primary interest for use in organic cooled reactors. The metallic fuels, such as U - 3.5 wt % Mo or U - 10 wt % Mo, offer such advantages as high uranium density, fabricability, and structural strength. Aluminum has proven very satisfactory as a cladding material, primarily because of its high resistance to organic corrosion, and its relatively low neutron absorption cross section. Because of the high reaction rates between uranium and aluminum at the reactor operating temperatures (above 600°F)[1] which would ultimately result in the loss of the fuel protection by the original cladding, a satisfactory diffusion barrier was required. Based on limited data, nickel was chosen as one of the more promising barrier materials, because of its relatively low reaction rates with aluminum and uranium and the simplicity of its application.

The primary purpose of this work was to determine quantitatively the reaction rates between Al/Ni and Ni/U. In addition to providing designers with data regarding the consumption rates of nickel, a somewhat more basic investigation was included, to assist in understanding the development and behavior of the Al/Ni and Ni/U intermetallic phases.

Two lines of effort were applied to the problem. One approach involved a series of diffusion couples which were systematically heat treated and examined. The other approach entailed a group of cylindrical Al-clad U-metal fuel elements, fabricated to include a Ni diffusion barrier of constant thickness. The fuel elements were isothermally heated and metallographically evaluated, to determine the rate of nickel consumption and the general diffusion characteristics.

II. EXPERIMENTAL PROCEDURE

A. DIFFUSION COUPLE TECHNIQUE

In order to obtain diffusion data on the Al-Ni-U system, the primary approach was to develop and standardize a technique for diffusion couple preparation. It was necessary to assure that the results would not be affected by contamination from the surrounding atmosphere during the soaking treatments. The technique developed to satisfy this requirement entailed hot pressing the components under a dynamic vacuum to effect a metallurgical bond, and then heat treating the diffusion couple within an evacuated quartz tube.

The first step in fabricating the "standard diffusion couples" involved careful preparation of the metal surfaces. Numerous methods of obtaining "clean" surfaces prior to bonding were attempted which included abrading, pickling, and electropolishing. The following procedures yielded the best contamination-free bonds:

1) Aluminum — Abraded with No. 600 grit paper, scrubbed with hot detergent and water solution, rinsed with hot water, rinsed with alcohol, dried in air blast, and stored under vacuum prior to use.

2) Nickel — Pickled with a solution of 500 ml H_3PO_4, 200 ml HNO_3, and 250 ml acetic acid at 55 to 80°C for 2 to 6 minutes, rinsed with water, rinsed with alcohol, dried with air blast, and stored under vacuum prior to use.

3) Uranium — Electropolished with 8 parts H_3PO_4, 5 parts glycerine, 5 parts ethyl alcohol until surface was visually free of all traces of oxide, rinsed with water, rinsed with alcohol, dried in air blast, and used immediately.

4) All Spacer and Encapsulating Materials — Scrubbed with a hot detergent and water solution, rinsed with water, rinsed with alcohol, dried in air blast, and stored in vacuum prior to use.

The bonding was achieved by hot pressing the Al-Ni-U sandwiches encapsulated in stainless steel cans under dynamic vacuum, as shown in Figure 1.

PRESSURE

HYDRAULIC PRESS PLATEN

GLASS WOOL INSULATION

RAM

Ni

U

Al

SPLIT FURNACE

RAM

EVACUATED SS CAN

SS SPACER

Zr FOIL

HEATING COIL

HYDRAULIC PRESS PLATEN

PRESSURE
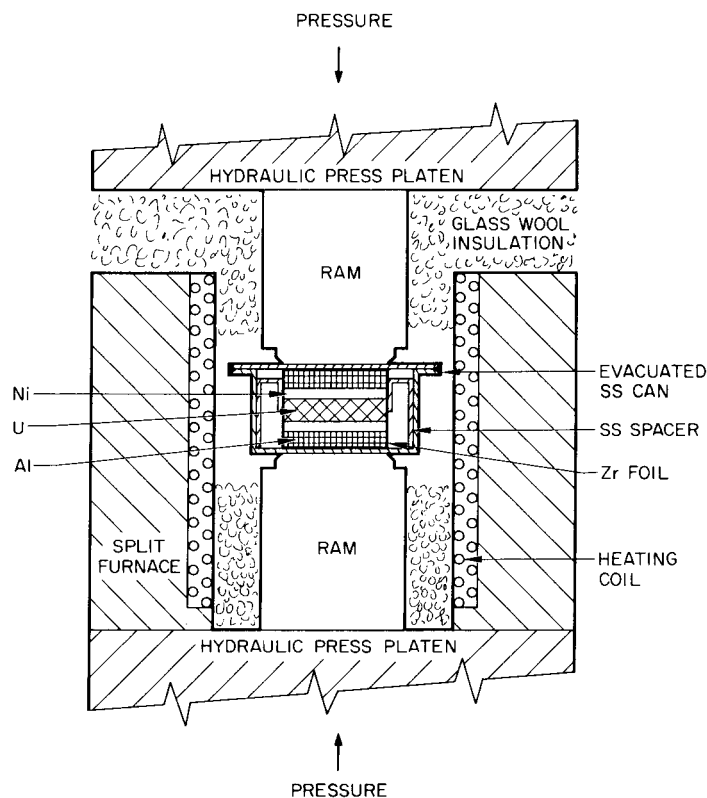
Figure 1. Cross Section of Diffusion Couple
Bonding Apparatus

The sandwiches were wrapped in zirconium foil to getter contaminants during
the hot pressing operation. To minimize contamination of the specimen during
seal welding the end of the can prior to bonding, the entire assembly was cooled
by: (1) submerging the can (except the end being welded) in a water bath, (2) using
copper chill blocks, and (3) purging the interior of the can with argon via the
evacuation tube. This process proved to be very successful. The can was evac-
uated to 4×10^{-6} mm Hg for a minimum of 4 hr prior to pressing, and main-
tained at 1×10^{-4} mm Hg during bonding.

The hot pressing conditions used to achieve good Al-Ni bonds were 7000 psi
and 1050°F for 2-1/2 hr. The conditions necessary to achieve satisfactory Ni/U
bonds were 7000 psi and 1175°F for 2-1/2 hr. Because the higher temperature
for Ni/U bonding greatly accelerated the Al-Ni diffusion, separate couples of
Al-Ni were prepared at 1050°F to supplement the data acquired from the Al-Ni-U
couples.

The bonded diffusion couples, which were 1 in. square, were sectioned into four pieces. One piece was retained as a control sample, and the other three were wrapped in zirconium foil (to getter contaminants) and sealed separately in evacuated quartz tubes for isothermal soaking treatments. The samples were subjected to temperatures of 650, 750, 850, and 950°F for periods from 10 to 7000 hr. In most cases, duplicate samples were run.

Upon completion of the thermal exposure, the diffusion zone and free nickel thickness measurements were taken by using a microscope with a filar eyepiece. Readings were taken at five random locations on each sample and averaged.

B. Al-Ni-U BOND STUDY ON CYLINDRICAL FUEL ELEMENTS

1. Experiment

To perform this study, four fuel cylinders were available. The cylinders were representative of those units used in the Piqua fuel elements, and were fabricated according to the procedure developed at Atomics International.[10] The cylinders consisted of a cast U - 3.5% Mo cylinder, electroplated with nickel and clad with Type 1100 Al at the OD and ID. The cladding was welded to aluminum end plugs at the top and bottom of the cylinder.

One cylinder was retained as a control, and used for the bond evaluation in the as-fabricated condition. The remaining three cylinders were subjected to an isothermal treatment in an autoclave containing agitated Santowax OMP at 750°F under 100 psig of nitrogen. After the three specimens underwent the first exposure of 1000 hr, one cylinder was removed and evaluated. The second cylinder was removed after an additional exposure of 1000 hr, and the remaining cylinder was removed after an additional exposure of 2000 hr (4000 hr total). The immersion and removal of the cylinders was performed at 350°F; the pressurizing and depressurizing of the autoclave was done at 600°F.

All of the cylinders were visually and dimensionally inspected prior to loading and after each exposure.

2. Equipment

The soaking was performed in an electrically heated 5-gal stainless steel autoclave. To hold three cylinders and avoid any vibration, a special fixture

was fabricated and firmly attached to the head of the autoclave. Each cylinder was positioned on stepped rings which simulated the actual "seat" in the Piqua fuel elements. A three-point centering piece kept the top of each cylinder in position without impeding its longitudinal expansion (see Figures 2a and 2b). A propeller, located at the bottom of the holder, stirred the organic (200 rpm). Four thermocouples (Chromel-Alumel couple in a stainless steel sheath) were positioned in a wall of the autoclave at the middle level of the Santowax OMP. These thermocouples were connected to a temperature recorder, a temperature controller, a potentiometer, and an overheating circuit breaker. The autoclave was provided with a Bourdon type pressure gauge, a rupture disc, a bleed valve, and a pressure-controlled nitrogen access.

3. Metallography

Standard metallographic techniques were used in this study. Complete transverse sections of the cylinders, and specimens showing longitudinal views, were prepared metallographically and evaluated. Cold mounts (epoxy resins) and hot pressed mounts were used, and some complete rings were prepared and inspected without mounting.

Tests were performed to determine whether the cutting of the specimens altered the original bond conditions. Three different techniques were compared: (a) a metallurgical cutoff wheel (Buehler) with carborundum (Crystalon) medium grit size wheel, (b) the cutoff machine with rotating specimen and diamond wheel (Cresta), and (c) a metal erosion core-boring machine (Elox electric discharge process). After grinding, the metallurgical specimens were finished on a Syntron vibratory polisher. Final inspection indicated similar bond conditions for all the specimens, ruling out the cutting techniques as a factor affecting the observations. The cutoff wheel was frequently used to section complete rings; the Elox metal erosion machine proved to be more versatile for obtaining individual 1-in. diameter OD-to-ID specimens.

4. Measurements

The outside diameters of the cylinders were measured before and after the soaking treatments with a micrometer (two readings at right angle on three elevations). The inside diameters were measured with a trimicrometer at three elevations. Go-gauges (1.5 in. long) were machined for each cylinder OD and ID, with the tightest fitting to detect misalignment and blistering. No measurements of elastic deformation of the cylinders during annealing were contemplated for this study.
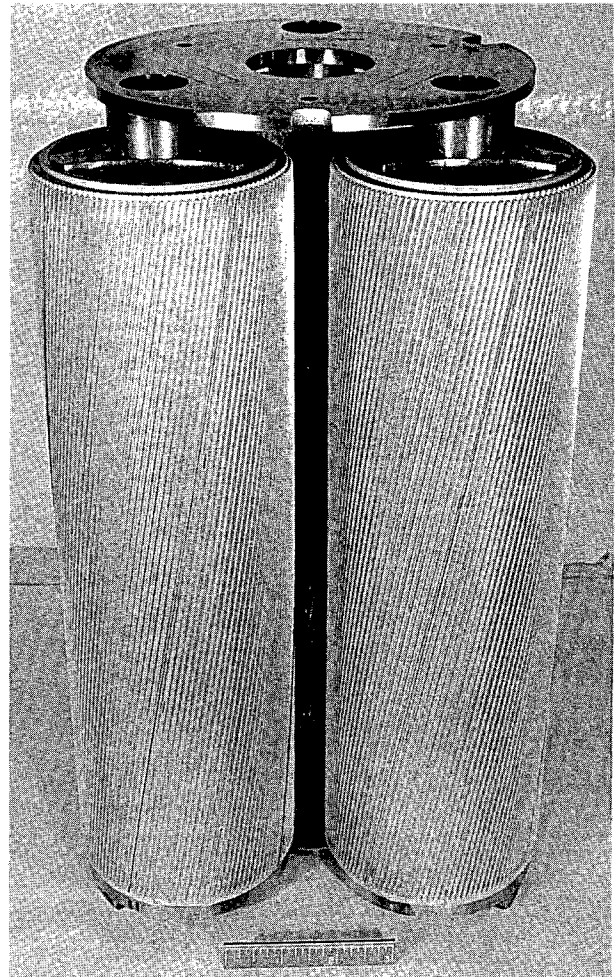
Qualitative observations of the bond quality in the as-fabricated conditions were performed by means of the crack-propagation test described in another report (NAA-SR-8128).
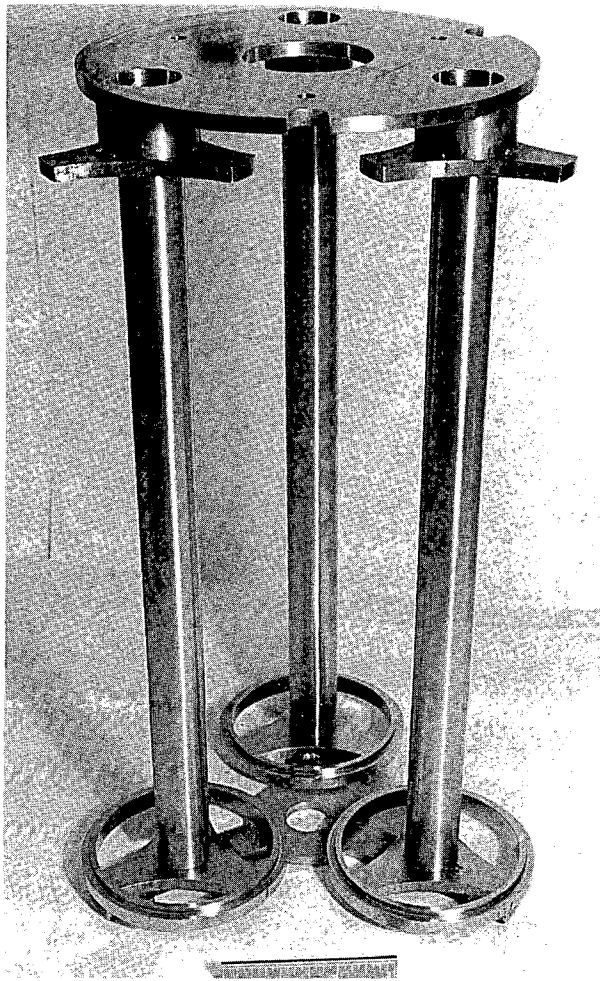
a. Holder

7597—5102A

b. Elements in Holder

7597—5102C

Figure 2. Cylindrical Fuel Element Soaking

III. DISCUSSION OF RESULTS

A. DIFFUSION COUPLE RESULTS

As mentioned, the primary purpose of this study was to supply reactor designers with consumption rates of free nickel at various temperatures, in order to properly predict the thickness required for a given in-reactor exposure time. In addition, information regarding the behavior of the Al-Ni and Ni-U intermetallics under these conditions was desired.

The as-bonded diffusion couples revealed two distinct Al-Ni intermetallic phases, which were identified previously by others as Al_3Ni and Al_3Ni_2[2,3] (see phase diagram, Figure 3).[4] A typical example is shown in Figure 4a. Figure 4b shows a representative Al-Ni diffusion zone after prolonged exposure to isothermal soaking treatments. A slight porosity was found in nearly all specimens that were heated for periods of time between 1000 and 7000 hr.

Two major Ni-U intermetallics were apparent on the as-bonded couples, as shown in Figure 5. In addition, traces of several other intermetallics were evident. The two major phases were previously identified as UNi_5 and U_6Ni.[3] Upon heating, smaller phases, which nucleated between the two original, became more easily resolved. By comparing with References 3 and 9, and the Ni-U phase diagram (Figure 6),[5] the phases were tentatively identified as shown in Figure 7. The area designated as "X + Y" is believed to be a two-phase region, presently unidentified. Much additional work, using x-ray diffraction analysis, is required to substantiate these identifications.

To determine the penetration rate of nickel by aluminum, the thicknesses of free nickel were measured metallographically on the Al/Ni couples that had been subjected to diffusion annealing treatments. As shown in Figure 8, the penetration rate obeyed a parabolic equation of the form:

$$K = \frac{x^2}{t} , \qquad \qquad \ldots (1)$$

where

    x = nickel thickness decrease
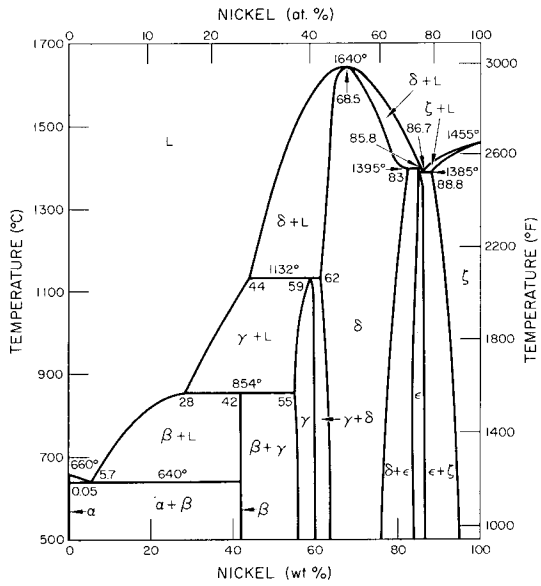
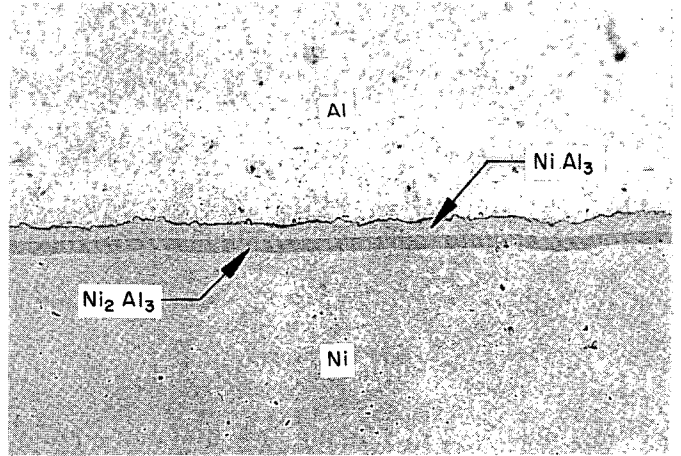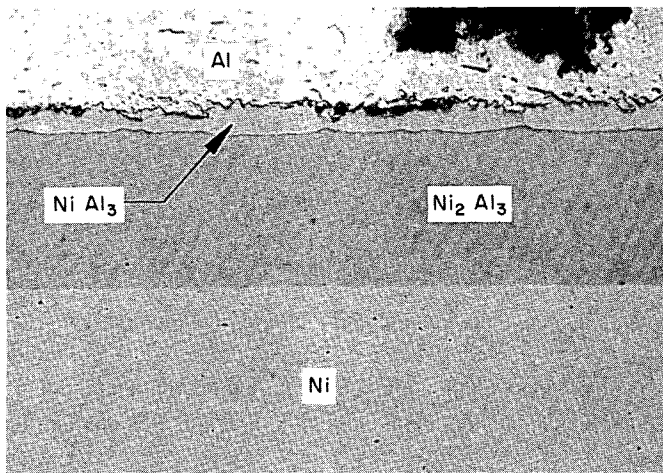   K = diffusion coefficient

    t = time.

Figure 3. Aluminum-Nickel Phase Diagram

a. As Bonded

AS POLISHED 250X
2911-1-1

b. After Isothermal Soaking

AS POLISHED 250X
3724-4-1
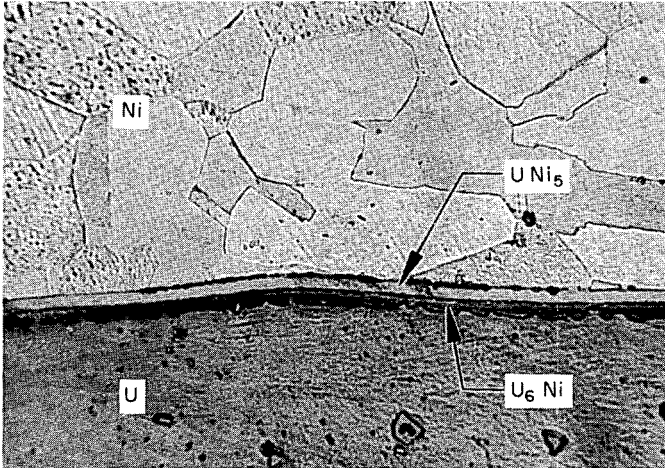
Figure 4. Typical Al-Ni Diffusion Zones

a. As Bonded

ETCHED   500X
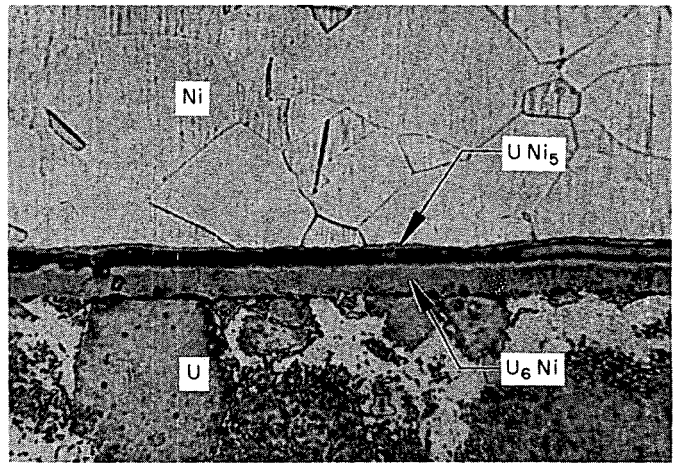   2911-3

b. After Isothermal Soaking

ETCHED   500X
                                              2911-2

Figure 5. Typical Ni-U Diffusion Zones

NICKEL (wt %)

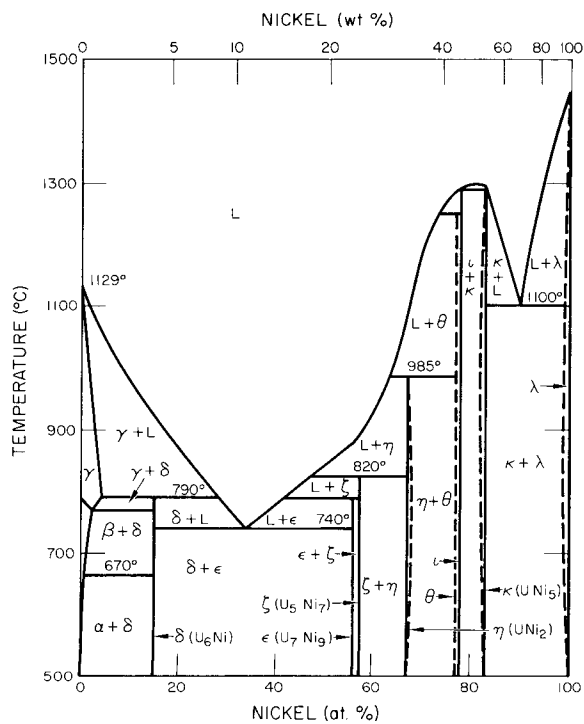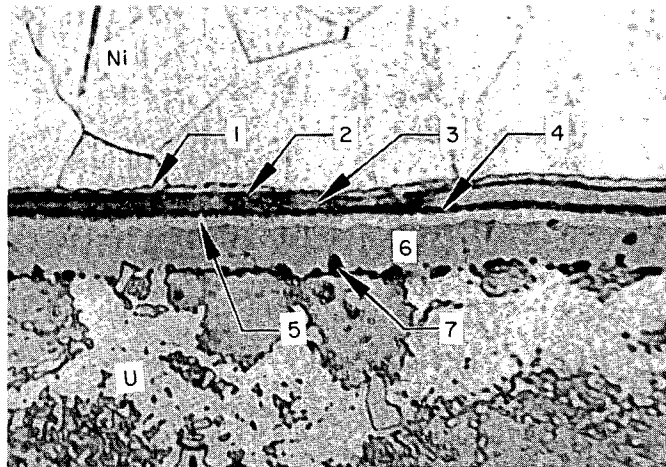Figure 6. Uranium-Nickel Phase Diagram

Figure 7. Ni-U Intermetallic Phases (After 2400 hr at 850°F)

ETCHED

1000X
2911-5

TENTATIVE IDENTIFICATION

1: UNi_5 5: U_7Ni_9

2: X + Y   6: U_6Ni

3: UNi_2 7: UNKNOWN

4: U_5Ni_7 (PROBABLY UO_2)
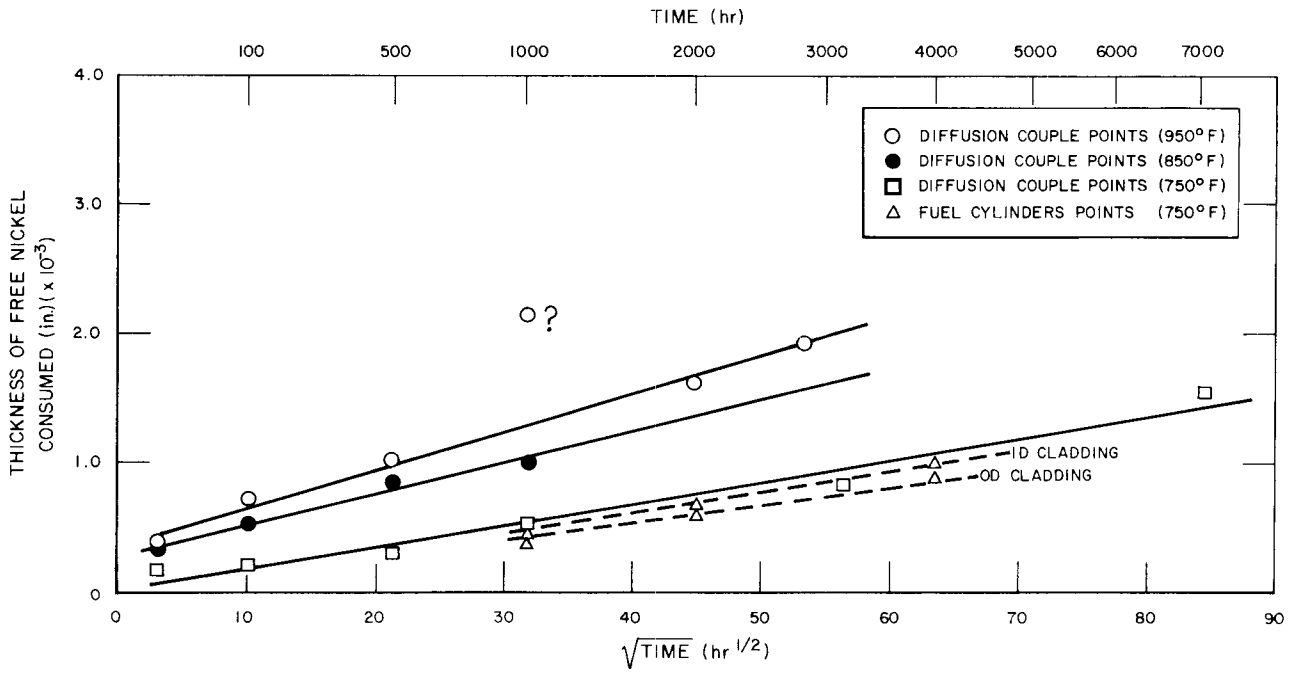
Figure 8. Penetration Rates of Aluminum into Nickel
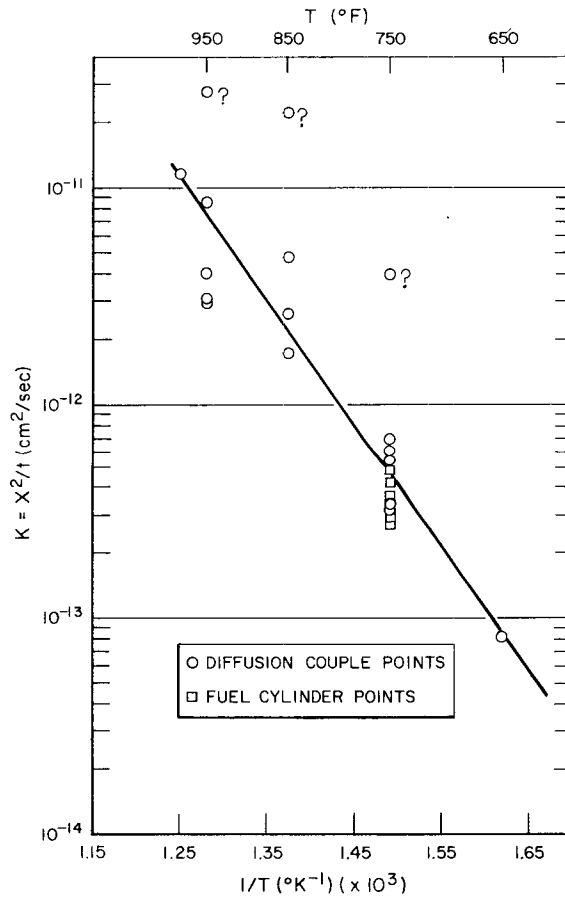
Figure 9. Penetration Coefficient
<u>vs</u> 1/T for Al-Ni Diffusion

NAA-SR-8387

17

PHOTOGRAPHED AT 250X
REDUCED TO 160X

Figure 10.   Al-Ni Interface, Showing Development of Low-Al Phase

ETCHED   500X
                                                         2911-6

Figure 11.   Al/Al-Ni Interface, Showing
Development of Low-Al Phase

To verify the linearity of the relationship between the logarithm of the diffusion coefficient (K) and the reciprocal temperature (T), according to the equation $K = K_o \exp(-Q/RT)$, the data were plotted as shown in Figure 9. The results were in fair agreement with a straight line function. As noted in Figure 9, the 10-hr points (indic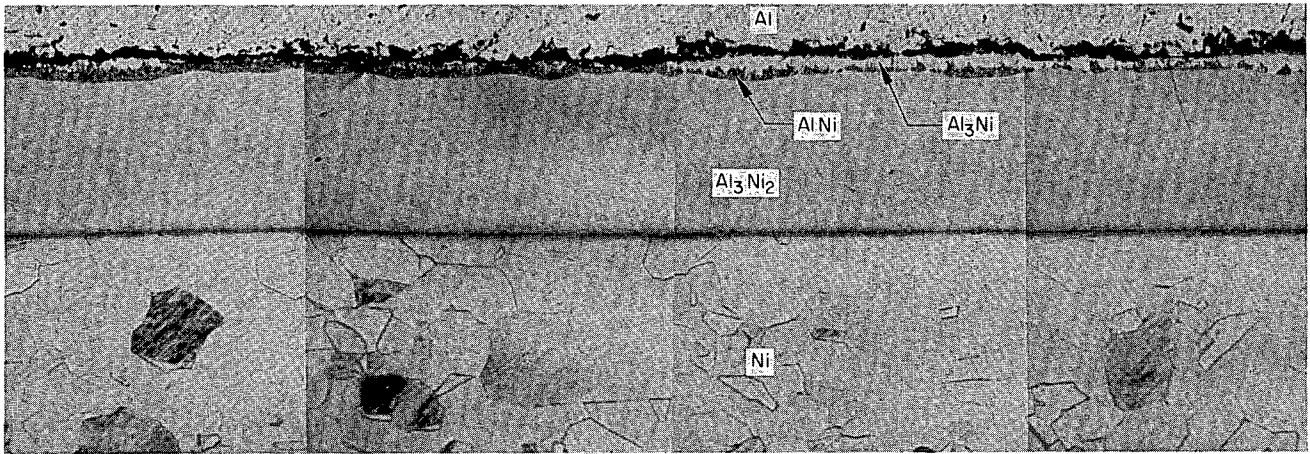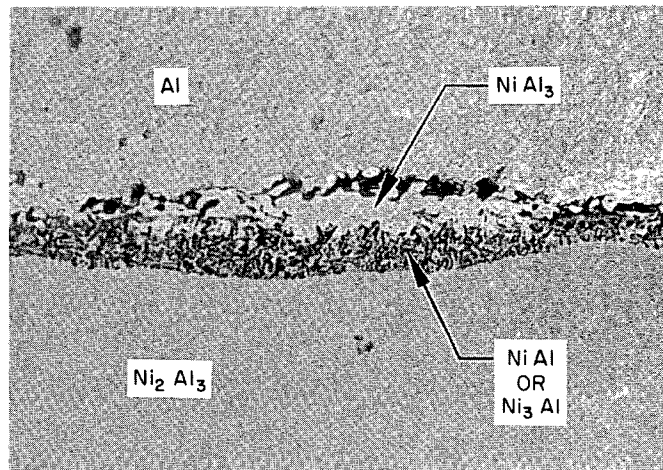ated by "?") consistently fell well above the other longer time data between 100 and 700 hr. The 10-hr points, which essentially fell within a straight line, are somewhat questionable, but may reflect higher initial diffusion rates resulting from: (1) a higher initial concentration gradient, or (2) an initially increased number of nucleation sights for phase formation left by residual stresses from the hot pressing operation (the 7000 psi was maintained upon cooling to 600°F).

It appears that more work is necessary to determine relative growth rates of the Al_3Ni and Al_3Ni_2 intermetallic phases. The data showed inconclusive results, but a few general observations were made. Although a general parabolic relationship with time was apparent, the results were somewhat scattered. The as-bonded couples showed two phases of approximately equal thickness, but subsequent heating showed that the Al_3Ni_2 phase generally grew much more rapidly. In some cases, a decrease in the Al_3Ni was noticed after an increase previously had been observed at shorter soaking times. These data will be reported in detail, at a later date, when their validity is established.

The presence of low-aluminum intermetallics ($AlNi$ or $AlNi_3$) among the Al-Ni diffusion phases was mentioned in recent literature.[6,7] This formation was observed in several diffusion couples that had undergone prolonged isothermal soaking treatments. The phase, as shown in Figures 10 and 11, began to nucleate in areas between the Al_3Ni_2 and Al_3Ni at locations where apparently the supply of aluminum atoms was limited by extensive Kirkendall void formation or mechanical separation resulting from differential thermal expansion. The phase continued to grow, at the expense of the Al_3Ni phase, until the Al_3Ni was finally consumed. This phenomenon was observed similarly on the fuel cylinders which are discussed later.

The interdiffusion of nickel and uranium was determined by measuring the total thickness of the Ni/U diffusion zone. Figure 12 shows the parabolic relationship between total diffusion zone thickness and time. The diffusion coefficients revealed essentially a linear relationship with reciprocal temperature, as shown in Figure 13.
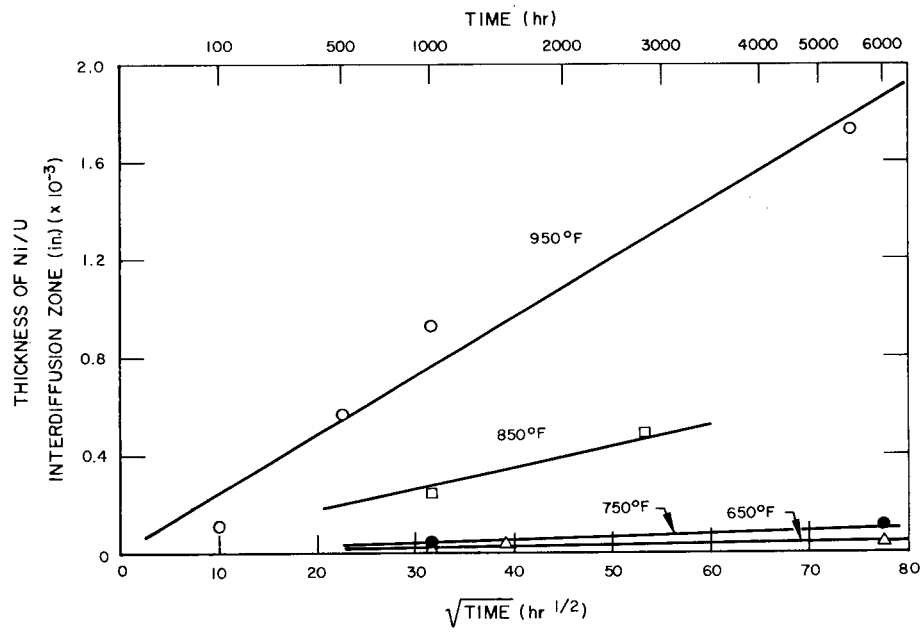
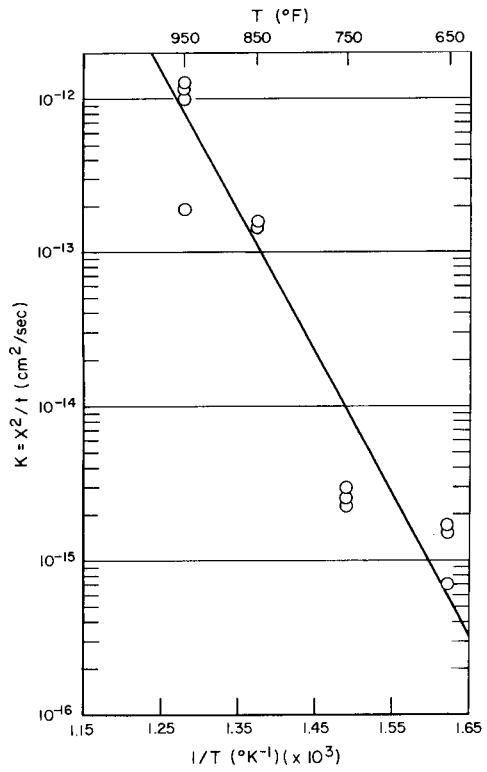Figure 12.   Diffusion Rates on Ni-U System

Figure 13.   Diffusion Coefficient vs 1/T for Ni-U Diffusion

Several Al/Ni/U diffusion couples were designed in such a way that the free nickel would be consumed, in order to observe the interaction between Al/Ni and Ni/U intermetallics. An example of this reaction is shown in Figure 14. The particular area depicted was located near the outer edge of the couple, where deformation occurred from the original hot pressing operation. The reaction products were very similar in appearance to those reported by Hanford.[2] Insufficient data were generated to compare with Hanford's, which indicated a slow decrease of Al_3Ni_2 layer by reaction with the U/Ni intermetallics.

## B. CYLINDRICAL FUEL ELEMENT OBSERVATIONS

1. Nickel Consumption Process

At 750°F, the electroplated nickel barrier layer was consumed almost completely by the Al/Ni reactions which yielded a series of intermetallic compounds, primarily Al_3Ni and Al_3Ni_2. Diffusion between nickel and uranium also occurred, but at a significantly lower rate.

Literature showed that, after consumption of the free-nickel layer, the U/Ni and Ni/Al systems came in contact, and finally a ternary phase UNi_7Al_{13} was formed. The aluminum then reached the uranium alloy, and subsequently diffused into it, forming the UAl_3 intermetallic. At this point, the original U/Ni/Al system developed the following zones, in sequence: $U/UAl_3/UNi_7Al_{13}/$ $Al_3Ni_2/Al_3Ni/Al.$[6] The kinetics of the UAl_3 thickness growth, which is an essential parameter for determining the fuel element lifetime, depends on the final thickness reached by the intermediate layers, UNi_7Al_{13}, Al_3Ni_2, and Al_3Ni.

This study covered only the first step of the diffusion process (i.e., the period at which the nickel is completely consumed). Although the free-nickel layer lost continuity and started to vanish, on the 4000-hr exposed cylinder, the amount of aluminum that diffused into the fuel alloy was insufficient to permit detailed analysis.

Figures 15 through 18 show the initial bond and its development with the thermal exposure. The U/Ni diffusion zones generally increased. In the 4000-hr exposed cylinder, the layer of U/Ni intermetallics became continuous, and the resulting weakening of the bond strength was such that numerous areas of separation could be observed (see Figure 18c). Metallographic examination of the transverse specimens showed that a continuous separation between Al and Al_3Ni took place
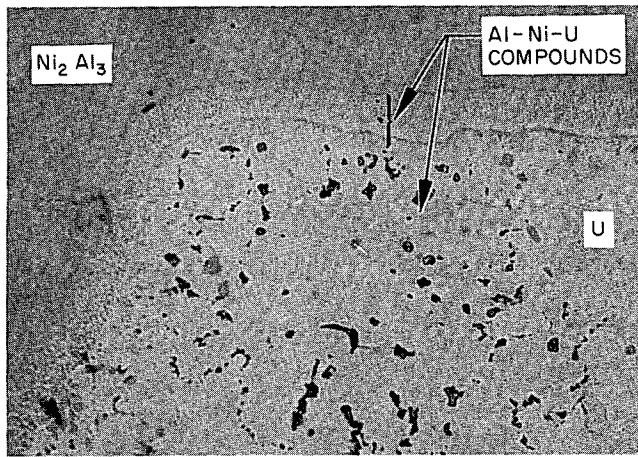
Figure 14. Ni_2Al_3 Reaction With
Ni-U Intermetallics

1. 250X   3135-1-6   2. 500X   3169-4-1

a. OD
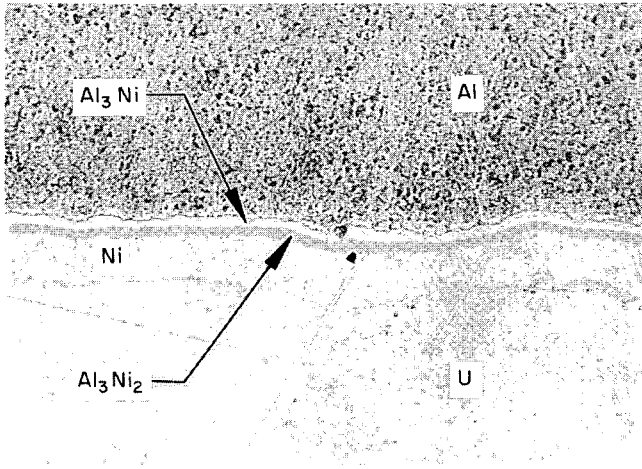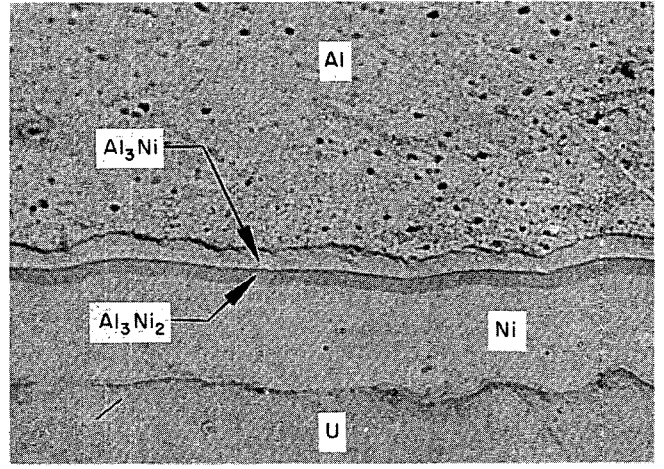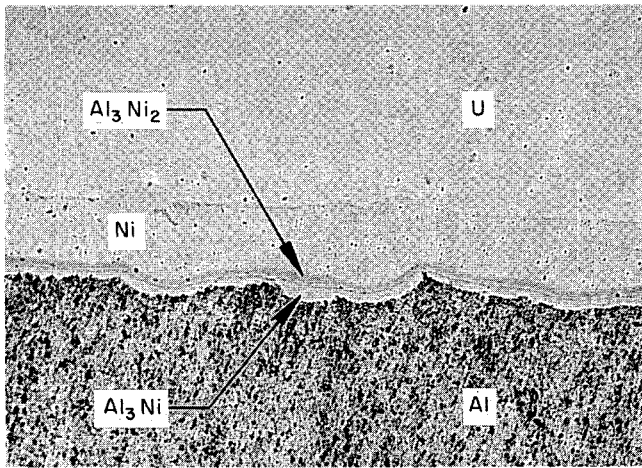
1. 250X   3135-1   2. 500X   3169-5-2
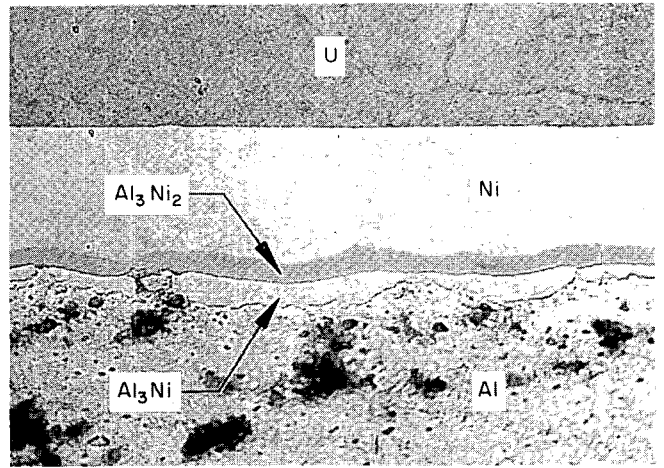
b. ID

Figure 15. Control Cylinder (After Pressure Bonding Process)
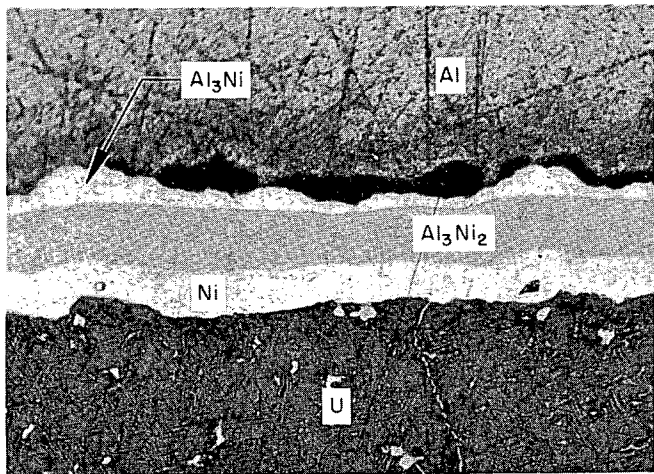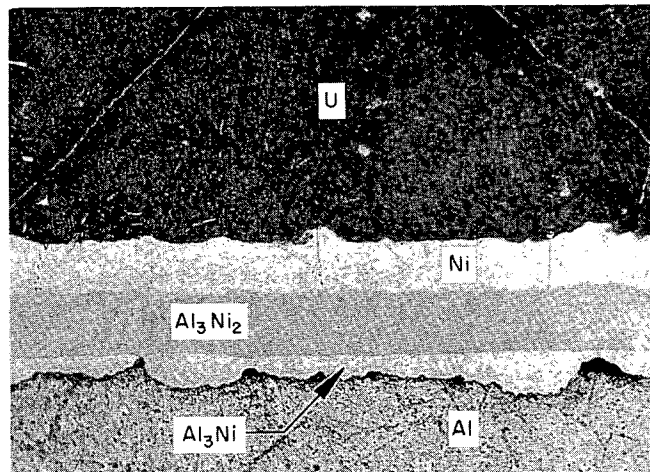
a. OD 250 X 3129-6-3

b. ID · 250 X 3127-7

Figure 16. Cylinder Exposed 1000 hr at 750°F
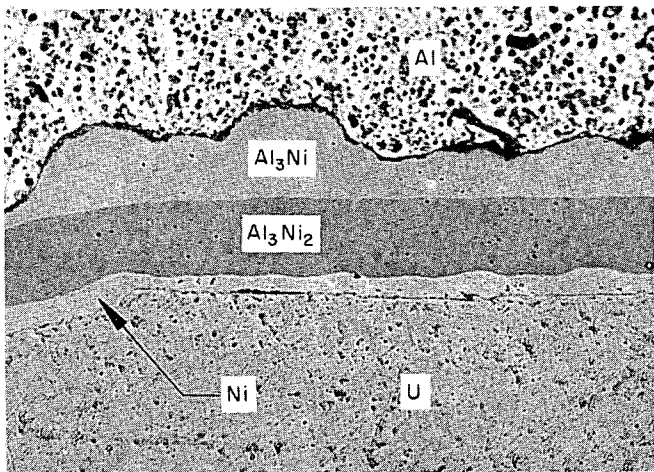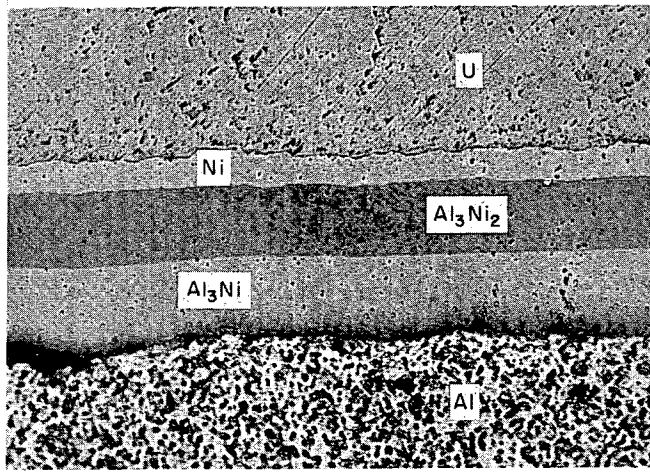
a. OD 250 X 3232-2-2

b. ID 250 X 3232-2-3

Figure 17. Cylinder Exposed 2000 hr at 750°F

a. OD
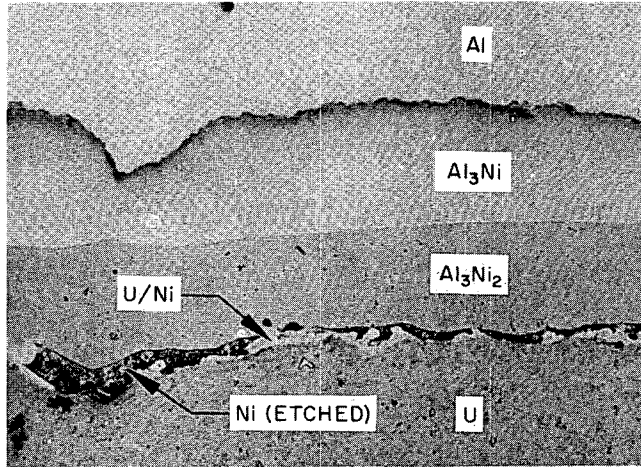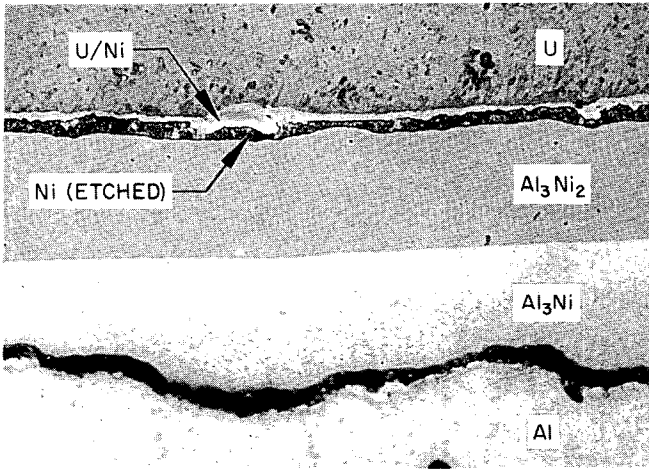
250 X
3517-2-4

250 X
3517-3-3

b. ID, Showing Continuous Layer
of U/Ni
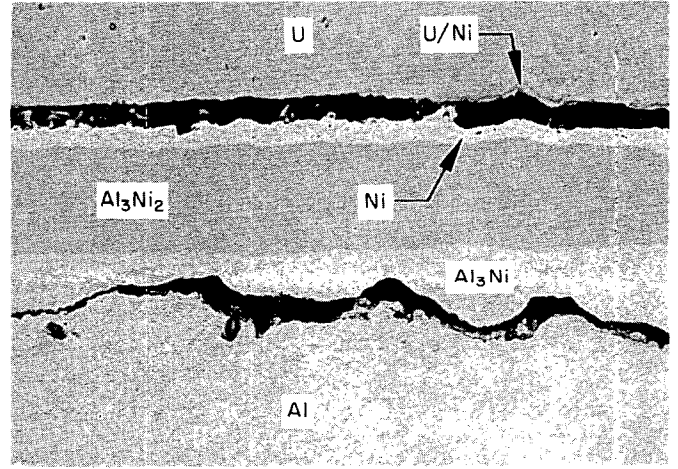
250 X
3464-3-2

c. ID, Showing Separation Caused by
Bond Weakening

Figure 18. Cylinder Exposed 4000 hr at 750°F

TABLE I

NICKEL CONSUMPTION IN CYLINDRICAL FUEL ELEMENTS

	Thickness of Free-Ni Layer* (in.) (x 10^3)		Thickness of Ni Consumed[†]	
	Electroplated	Final	(in.) (x 10^3)	%
ID				
Control Cylinder Fabrication	1.40	1.32	0.08	5.7
1000-hr Exposed Cylinder	1.63	1.11	0.52	31.9
2000-hr Exposed Cylinder	1.52	0.75	0.77	50.6
4000-hr Exposed Cylinder	1.49	0.40 §	1.09	73.2
OD				
Control Cylinder Fabrication	1.22	1.11	0.11	9.0
1000-hr Exposed Cylinder	1.16	0.66	0.50	43.0
2000-hr Exposed Cylinder	1.21	0.47	0.74	61.0
4000-hr Exposed Cylinder	1.07	0.12**	0.95	88.8

*These thicknesses correspond to the cylindrical surfaces without including the cylinder ends, where the original nickel thicknesses were greater.
†Calculated on the basis of the nickel content on the measured intermetallics.
§Average thickness; the nickel layer was continuous; in no area did the Al/Ni intermetallic contact the uranium.
**Average thickness, assuming an even nickel distribution over the entire interface; the nickel layer was discontinuous; the Al/Ni intermetallic was in contact with U/Ni intermetallic in 51% of the perimeter inspected.

at the inner Al/Ni interface. It is postulated that the aluminum cladding plastically adapted itself to the ID of the uranium cylinder while at temperature. Upon cooling to room temperature, the differential contraction between the aluminum and uranium resulted in the observed separation of the cladding. The Ni barrier, which has a thermal expansion similar to that of U, remained attached to the fuel. The gap was not continuous at the outer Al/Ni interface, but the unbonded areas were as frequent as the bonded ones.

The inspection of the longitudinal specimens showed an effect of the longitudinal differential expansion of the aluminum and the Ni/U system. A relative displacement of both phases was observed metallographically by the position of adjacent patterns in the irregular interface. However, the uniform growth of the intermetallic phases at the OD and ID indicated that, at the soaking temperature and pressure, the contact between nickel and cladding was sufficient to permit diffusion. The observed separations and relative displacements were a result of weakening of the bond strength during the thermal exposure, which resulted from substantial growth of the brittle intermetallic layers. At the top and bottom faces of the uranium cylinder, the free longitudinal expansion of the aluminum cladding created a clearance between nickel and aluminum, wide enough to prevent the aluminum migration. The diffusion layers did not increase in thickness, as on the cylindrical surfaces.

The data in Table I indicate the rate of consumption of the electroplated nickel. The OD barrier, which was thinner than the ID barrier on the four cylinders, was practically consumed after 4000 hr of treatment. The remaining unreacted nickel did not constitute a continuous layer after this exposure. It was concluded that the pressure bonding process, plus the 4000-hr exposure at 750°F, consumed a thickness of 1 mil of electroplated nickel barrier. The net consumption of Ni for each exposure is indicated in Figure 8.

2. Al-Ni Diffusion Reactions

The thickness growths of the Al_3Ni and Al_3Ni_2 phases were measured, at both the OD and the ID surfaces of the cylinders. The results, shown in Table II, are accompanied by calculated thicknesses of aluminum and nickel required to produce the Al_3Ni and Al_3Ni_2 intermetallics. In comparing the calculated and measured thicknesses, it was observed that no volume increase would be expected to result from the diffusion process during thermal exposure. This

TABLE II

BOND DEVELOPMENT IN CYLINDRICAL FUEL ELEMENTS

	Measured Thicknesses		Calculated Thicknesses of Consumed Metal		Calculated Total Al/Ni Consumed	Measured Thickness of Al/Ni Intermetallics
	Al_3Ni	Al_3Ni_2	Ni	Al		
ID						
Control Cylinder	0.16	0.18	0.08	0.26	0.34	0.34
1000-hr Cylinder	0.51	1.33	0.52	1.39	1.91	1.84
2000-hr Cylinder	1.38	1.63	0.77	2.34	3.11	3.01
4000-hr Cylinder	2.08	2.20	1.09	3.35	4.44	4.28
OD						
Control Cylinder	0.24	0.22	0.11	0.36	0.47	0.46
1000-hr Cylinder	0.58	1.22	0.50	1.34	1.84	1.80
2000-hr Cylinder	1.37	1.52	0.74	2.26	3.00	2.89
4000-hr Cylinder	2.03	1.78	0.95	3.00	3.95	3.81

NOTE:
    All thicknesses in 10^{-3} inch
    Densities: For Al   : 2.71 g/cc
   For Ni   : 8.90 g/cc
            For Al_3Ni : 3.98 g/cc
            For Al_3Ni_2: 4.78 g/cc

conclusion assumed that the measurement statistics were adequate, that the adopted values for phase densities were precise, and that the electroplated nickel barrier and extruded aluminum cladding were of zero porosity. Dimensional inspection was in agreement with this conclusion, in that no significant dimensional changes occurred.

In addition to these high-aluminum phases, another phase was formed at specific and consistent locations in the cylinders. The new phase (AlNi and/or AlNi$_3$, according to the Al-Ni phase diagram) appeared as an agglomeration of dark gray grains which grew at the expense of the Al$_3$Ni and the Al$_3$Ni$_2$, but only in zones where the intermetallics had no further contact with the aluminum cladding during the soaking treatments. The growth of the new intermetallic progressed until all the Al$_3$Ni vanished, producing a nucleate and discontinuous formation in the 1000-hr exposure specimens and a continuous band in the 2000-hr exposure specimens, as shown in Figure 19. The 4000-hr exposure specimens showed depletion of Al from the Al$_3$Ni$_2$ phase after the Al$_3$Ni phase was consumed. The appearance of the low-aluminum phases was observed only at both ends of the exposed cylinders, where a separation between the uranium and the aluminum end plugs could occur by differential expansion during the annealing. When this separation occurred, insufficient aluminum was available to promote growth of the high-aluminum phases, which induced their transformation to the low-aluminum phases. The first phase to undergo this transformation was the richest in aluminum, Al$_3$Ni.

The insufficient contact between fuel and end plug under the heat treatment conditions was substantiated by the calculation of the total amount of aluminum which migrated from the plug to the bond. Table III indicates the aluminum migration in milligrams of aluminum per in.^{2} of bonded areas, for both the cylindrical surfaces and the annular ends, calculated from the intermetallic thickness on those areas. Less aluminum migrated from the end plugs, due to poor contact.

At the cylindrical surfaces of the cylinders, both on the OD and ID, the growth of the high-aluminum intermetallics progressed at essentially equal rates. This was true, even though some metallographic specimens showed a definite gap between aluminum and bond, because apparently, under the pressure and temperature of the thermal exposure, sufficient contact occurred between the cladding and diffusion zone to promote formation of the high-aluminum intermetallics.
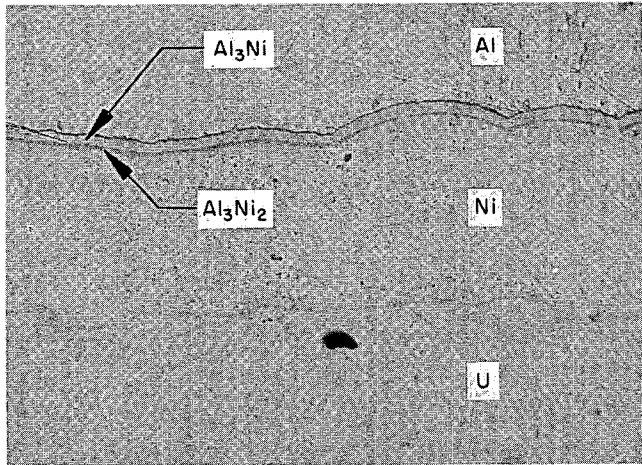
a. Control Cylinder
250X
3752-1
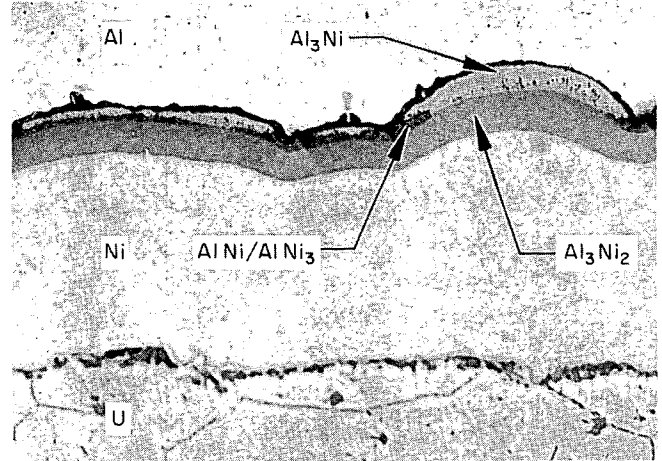
b. 1000-hr Exposed Cylinder
250X
3301-2-4
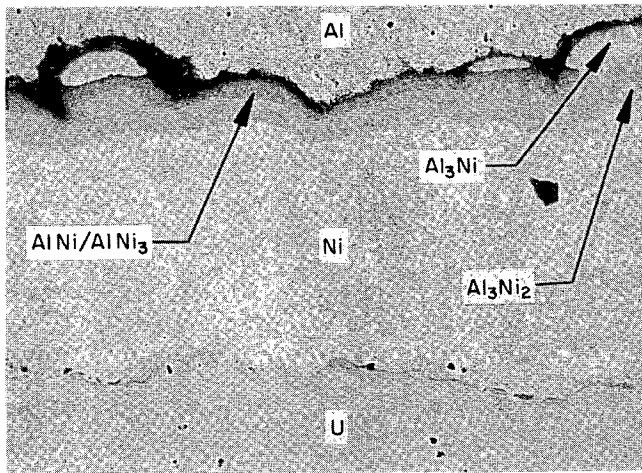
c. 2000-hr Exposed Cylinder
250X
3301-1-2
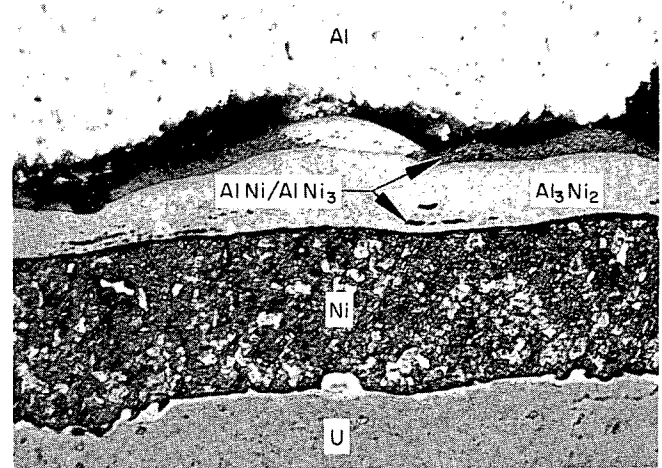
d. 4000-hr Exposed Cylinder
250X
3454-2-3

Figure 19. Bond Conditions Between Fuel Cylinder and Aluminum End Plug

TABLE III

ALUMINUM MIGRATION FROM CLADDING TO BOND IN
CYLINDRICAL FUEL ELEMENTS
(mg Al/in.^{2} of bonded area)

	Zones of Piqua Fuel Cylinder	
	Cylindrical Surfaces	Annular Ends
After Pressure Bonding	13.9	9.8
After 1000-hr Annealing	60.7	36.9
After 2000-hr Annealing	102.3	53.2
After 4000-hr Annealing	141.2	66.4

IV. CONCLUSIONS

The experimental work performed on the Al-Ni-U system, using the diffusion couple technique, and the results of the investigation of the fuel cylinder bond quality, served as a basis for the following conclusions and general observations:

a) The penetration of aluminum into nickel followed a parabolic relationship with time. The penetration, x, can be calculated from the equation $x = \sqrt{K_1 t}$, where t is the time and K_1 is the penetration coefficient. K_1 is a function of temperature, as shown in Figure 9. These data are in reasonable agreement, but slightly lower than data reported by others.[2]

b) The nickel penetration data generated by the diffusion couple technique were slightly higher than those produced during the cylinder bond study. The maximum discrepancy was 20%. This disagreement was attributed to the cylindrical geometry of the specimens and the bond interface displacement resulting from differential thermal expansion between fuel and cladding.

c) A low-aluminum phase ($AlNi$ or $AlNi_3$) nucleated at the Al_3Ni/Al_3Ni_2 interface when the supply of additional free aluminum into the system was restricted due to void formation or separation between the intermetallics and aluminum. The growth of the low-aluminum phase progressed at the expense of the Al_3Ni until all this phase was consumed, then consumption of the Al_3Ni_2 phase began.

d) The interdiffusion rate of uranium and nickel also followed the parabolic relationship with time. The diffusion zone growth can be calculated from the equation $x = \sqrt{K_2 t}$, where x is the diffusion zone thickness and K_2 is the diffusion coefficient, which is a function of temperature, as shown in Figure 13.

e) A reaction was observed between the Al/Ni/U intermetallic system and the uranium alloy after complete consumption of the free-nickel layer between Al/Ni and Ni/U intermetallics. This reaction appeared to propogate rapidly into the uranium alloy.

REFERENCES

1. T. K. Bierlein and D. R. Green, "The Diffusion of Uranium Into Aluminum," HW-38982 (October 6, 1955)

2. D. R. Green, "Preliminary Data on U/Ni/X-8001 Aluminum Alloy Diffusion," HW-56513 (June 20, 1958)

3. C. L. Angerman, "Metallographic Studies of Al-Ni-U Bonds in Nuclear Fuel Elements," Reprinted from Transactions Quarterly, 54, No. 3 (September 1961)

4. Frank A. Rough and Arthur A. Bauer, "Constitution of Uranium and Thorium Alloys," BMI-1300 (June 2, 1958)

5. W. L. Fink and L. A. Willey, "Al-Ni Aluminum-Nickel," Metals Handbook, 1948 Edition (The American Society for Metals, Cleveland, Ohio) p 1164

6. F. Brossa et al., "Study of Nickel as a Diffusion Barrier Between Uranium and Aluminum," European Atomic Energy Community - Euratom, 17F (May, 1962)

7. O. Gamba, "Al-Ni Diffusion Reaction," NAA-SR-TDR-7871 (October 30, 1962)

8. Samuel Storchheim, "Aluminum-Nickel Alloy Zone Formation During Solid State Reaction," SEP-165 (June 7, 1954)

9. Norbert Muller, "Untersuchungen uber die Diffusion in den Systemen Uran-Zirkon und Uran-Nickel," Z. Metallkunde, Bd. 50 (1959) p 652

10. E. Garrett, G. V. Alm, and M. H. Binstock, "Hot Pressure Bonding of OMR Tubular Fuel Elements," NAA-SR-5120 (July 30, 1960)

11. Samuel Storchheim et al., "Solid State Bonding of Aluminum and Nickel," SEP-132 (July 8, 1953)