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LABORATORY STUDIES OF Al-Ni-U BONDING-INTERIM REPORT

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by

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November 1, 1967

DECLASSIFIEDIntroduction and Summary

The purpose of this report is to summarize laboratory work concerning Al-Ni-U bonding. It was initiated by an analysis of the literature and hot die size bonding in particular.⁽¹⁾ A hot die size bond has three major deficiencies:

1. The presence of nickel in the bond has a small effect on neutron economy.
2. The bond offers virtually no secondary corrosion once the aluminum clad is penetrated by water.
3. The strength as well as the continuity of the bond are lowered by exposure to the reactor environment.

It is possible that one or more of the above deficiencies could be alleviated by adjusting the hot die size bonding conditions, but most likely at the expense of aggravating the other deficiencies. To date the HDSB process has been superbly engineered to yield a high quality bond before pile exposure.

Possible avenues for improvement of hot die size bonded fuel were surveyed. Areas for laboratory studies were then suggested.⁽²⁾ These areas included one to improve the secondary corrosion resistance of the bond, and another to provide a secondary corrosion barrier in the clad itself. A

[REDACTED]

third area was a study of the basic properties of the bond, especially the properties of the intermetallics in the bond.

Secondary corrosion resistance of the bond.

The secondary corrosion resistance of the bond could possibly be improved by thickening the nickel plate somewhat and increasing the Ni-U diffusion thickness. Thicker nickel-uranium diffusion may form an intermetallic layer of sufficient thickness and corrosion resistance to provide a secondary barrier to corrosion. The Al-Ni diffusion zone should always be minimized because it contains the intermetallic Ni_2Al_3 which is brittle and has low corrosion resistance.⁽³⁾ Thicker Ni-U diffusion will necessitate a slightly thicker nickel plate to prevent uranium penetration to the aluminum clad.

This work has not been started. It was planned to vary the nickel plate thickness (up to 1.5 mils maximum) and the amount of Ni-U diffusion. The resulting zone would be evaluated by bond strength and corrosion tests. Sections of the aluminum clad would be removed chemically and the protection determined in static autoclave tests.

Duplex aluminum components.

It is well known that Al-Si bonded elements have some degree of secondary corrosion resistance which is lent by the Al-Si layer. Theoretically the Al-Si layer is cathodic to the X-8001 which corrodes preferentially. An Al-Si layer can be introduced into a HDS bonded fuel if the layer is present in the can material.

Tubular components for the HDS process were fabricated by coextrusion in which the external material was X-8001 and the internal material Al-Si. The tubing was KVE size with a uniform 40 mils Al-Si and 15 mils X-8001. An excellent bond was achieved between the two materials, and it showed no

[REDACTED]

sign of deterioration during hot die sizing tests. Cladding dimensions satisfied the specifications for KVE external clad tubing.

Corrosion tests are planned for this type of tubing when chill cast X-8001 extrusion billet stock becomes available. The coextrusion techniques developed will probably be applicable to other aluminum alloy combinations.

High silicon aluminum alloys have been HDS bonded to unplated cores with some success. The above described tubing or similar tubing could also be bonded directly to unplated cores, thus eliminating the neutron absorbing nickel barrier. This presents an interesting possibility for a cladding system which would eliminate the major problems associated with nickel bonded HDS fuels:

1. A secondary corrosion barrier is contained in the clad tubing.
2. All high neutron absorbers are eliminated.
3. Bond degradation due to neutron irradiation is minimized.

Properties of the Al-Ni-U bond.

A better understanding of the bond may lead to improvements in the bond quality. Several studies were initiated to this end.

The chemistry of the bond itself is of interest. The electron microprobe was employed to investigate composition variation in the intermetallics and also the total depth of interdiffusion. Since the smallest available electron beam width is about 1 micron, a sample was specially prepared by thickening the diffusion layers substantially. This produced single intermetallic layers with thicknesses ranging from 0.7 to 2.0 microns. Even under these conditions, it was difficult to detect the presence of the intermetallic compositions which were metallographically present. The microprobe did, however, describe the total depths of interdiffusion rather well.

[REDACTED]

The properties of the intermetallic compounds in the bond are also of interest, especially if one or more of them is purposely thickened. It was planned to determine the corrosion resistance, thermal diffusivity, hardness, and ductility of each intermetallic. Attempts at forming massive samples of all four intermetallics were partially successful. Castings contained considerable shrink porosity. Forging closed the porosity and partially effected homogenization of the composition without producing cracking. Long time, high temperature anneals can be used to homogenize the structure and thus produce a pure, single phase intermetallic.

Discussion

Co-extrusion of duplex aluminum tubing.

Extrusion billet stock was induction melted under argon and cast into 3 1/2 inch diameter by 14 inch deep molds. The bottom seven inches were chilled by a water cooled coil, which eliminated secondary shrinkage in the middle of the casting.

Melt stock for the X-8001 castings was excess X-8001 rails. Al-Si melt stock was thermal samples taken from the pots on the Al-Si casting line. The Al-Si charge was calculated to produce an alloy of 10.5 wt.% Si.

Castings were machined to the coextrusion billet components shown in Figure 1. The billet components were chemically etched and cleaned before assembly. After assembly, the interface at the billet ends between the two components was electron beam welded in vacuum. The assembled and welded billet was preheated to 400°C for 2 hours and lubricated with Aqua Dag before extrusion. Tooling was lubricated with a mixture of Bentonite grease and lead powder.

The extrusion constant was 12 tons/in² and the extrusion ratio was 21/1. Ram speed was 30 inches per minute.

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Two identical extrusions were made. Both extrusions had excellent surface finish inside and outside. The dimensions of the tubing were very uniform and well within specifications for KVE external clad tubing. Each extrusion yielded 8 feet of good tubing and 1 foot of extrusion defect at each end. Tubing dimensions are given in Table I. Photomicrographs of the tubing cross section in Figures 2 and 3 show the bond between the two components and also the disposition of the second phase particles in each alloy. The distribution of the second phase particles in the X-8001 alloy is not acceptable for good corrosion resistance. Future extrusion billets will be made up with chill cast X-8001 having an acceptable dispersion. The bond between the two alloys showed no signs of deterioration during hot die sizing tests.

Present plans call for this duplex alloy tubing to be corrosion tested concurrently with single alloy tubing also being fabricated by PNL. The coextrusion technique developed here could also be used to fabricate tubing components containing other alloys or more than two alloys.

TABLE I

Dimensions of Coextruded Tubing

	<u>Outside Diameter</u>	<u>Inside Diameter</u>
Head (In defect-No X-8001)	1.573-1.577	1.465-1.466
Middle	1.573-1.576	1.466
Tail (In defect-I.D. enlarged)	1.570-1.583	1.465-1.497

Die Diameter: 1.578
Mandrel Diameter: 1.470
Container Diameter: 3.040
Extrusion Ratio: 21/1

FIGURE 1

Coextrusion Billet--Duplex Alloy Tubing

100 X

250 X

FIGURE 2

Duplex Alloy Tube - Longitudinal Section

Note the excellent bond, and the distribution of second phase particles in each alloy.

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FIGURE 3

Duplex Alloy Tube - Transverse Section

Note the excellent bond, and the distribution of second phase particles in each alloy.

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100 X

Electron microprobe analysis of a hot die size bond.

The smallest available electron beam width is about 1 micron. In hot die size bonds, the Al-Ni layer width is normally about 1 micron and Ni-U layer width is slightly smaller. In order to increase the sensitivity of the microprobe, the diffusion layers were thickened substantially by extending the time and temperature during the end bonding step. This resulted in single intermetallic layer thicknesses ranging from 0.7 to 2.0 microns. The structure of that bond is shown in Figure 4.

Several traces across the bond were made with the microprobe. Generally very smooth diffusion gradients were observed showing total diffusion widths of 4 to 14 microns for Al-Ni diffusions and 6 to 10 microns for Ni-U diffusion. Metallographically, the Al-Ni intermetallic layers measured from 2 to 3.5 microns and the Ni-U layers measured 1 to 1.5 microns. These numbers show that the total diffusion is considerably wider than the intermetallic layer widths. This is somewhat surprising in view of the fact that the solid solubility of these metals in each other is less than 1% (except for Ni which dissolves 10% Al). Part of the wide difference in widths can be explained by a smearing of the microprobe trace caused by:

- 1) The large beam size in relation to the diffusion width, and 2) The large topographical variations encountered by the electron beam as it penetrates into the sample. If diffusion widths were much larger, the smearing action would be proportionately reduced, but the sample would be even less typical of a hot die size bond.

It is significant to note that the microprobe generally did not reveal the presence of intermetallic compounds, even though they were metallographically observable. This is again attributable to smearing of the data.

Typical microprobe traces are shown in Figures 5 and 6.

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FIGURE 4

Structure of Specially Prepared End Bond - 500 X

Al-Ni Diffusion

Ni-U Diffusion

FIGURE 5

Electron Microprobe Trace At Typical Location

Ni-U Diffusion

Al-Ni Diffusion

FIGURE 6

Electron Microprobe Trace at Typical Location

DECLASSIFIEDPreparation of intermetallic compounds

In order to measure the properties of the intermetallics appearing in HDS bonds, one must first prepare the intermetallics in a comparatively massive form. Pure, single phase intermetallics are usually difficult to form because they often exist over narrow composition ranges. Of the four intermetallics, Al_3Ni , Al_3Ni_2 , Ni_5U , and NiU_6 ; only Al_3Ni_2 has an appreciable composition range (5%). All but one (Ni_5U) are formed by peritectic reactions during solidification. Peritectically formed alloys are difficult to homogenize since solid state diffusion must be relied upon.

Several techniques were considered. Powder metallurgical techniques were rejected because the aluminum and uranium oxides present in the powders cannot be hydrogen reduced. Diffusion couples were rejected because they cannot produce thick enough layers in finite time. Vacuum melting was chosen as the primary fabrication step. Vacuum arc button melting was chosen on the basis of convenience and a high cooling rate which minimizes segregation during cooling. Three buttons of each intermetallic composition were prepared using 99.9% pure melt stock. Two buttons of each alloy were subjected to further homogenization treatments. The other buttons are being held in reserve.

One set of buttons was homogenized 100 hours at 15°C below their respective melting points in evacuated quartz capsules. The second set of buttons was forged to about 60% reduction at 25 to 50°C below their melting points. Forging was done in thick walled stainless steel capsules (Figure 7) which minimized tensile stress and subsequent cracking. Each capsule was preheated one hour before forging.

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Capsule Material - 300 Series Stainless Steel

FIGURE 7

Forging Capsule For Arc Melted Buttons

All of the annealed buttons had large grain size and an undesirable amount of porosity (left over from solidification shrinkage). As expected, the Ni_2Al_3 button was single phase and the other buttons showed small amounts of another phase (see Table II). The forged buttons had relatively small grains and no porosity. All, but the Ni_2Al_3 which is reputedly very brittle, proved to be forgable. There was predominately intergranular cracking in the Ni_2Al_3 button. Most of the compositions would have benefited from an additional high temperature homogenization anneal after forging. A summary of the characteristics of the fabrication buttons is given in Table I. The corresponding microstructures are presented in Figure 8, 9, 10, and 11.

It appears that the most satisfactory fabrication method for all the intermetallics is forging or extrusion followed by a high temperature homogenization anneal. A somewhat less severe forging reduction should be used for the brittle Ni_2Al_3 . These methods will yield material satisfactory for corrosion, thermal diffusivity, and mechanical property tests.

ACKNOWLEDGEMENT

The following people made significant contributions to the work cited in this report:

G. S. Allison - Extrusion of duplex aluminum clad tubing.

W. I. Clark - Electron microprobe analysis of HDS bond.

TABLE II

Characteristics of Fabricated Intermetallic Compounds

	<u>AS CAST</u>	<u>ANNEALED</u>	<u>FORGED</u>
NiAl_3	Microstructure--Cored Shrink Porosity--High	Microstructure--Single Phase small inclusions are possibly oxides Porosity--High XRD--single phase NiAl_3 Grain size--Large	Microstructure--Some second phase in grain boundaries Porosity--None XRD--one strong peak from unidentified second phase. Grain size--Moderate
Ni_2Al_3	Microstructure--Single phase Shrink Porosity--Moderate	Microstructure--Single phase Ni_2Al_3 Porosity--Moderate XRD--Pure Ni_2Al_3 Grain size--very large	Microstructure--Single phase Ni_2Al_3 Porosity--None XRD--Pure Ni_2Al_3 Grain size--Small Intergranular cracking perpendicular to forging direction.
Ni_5U	Microstructure--Single phase Shrink Porosity--Low	Contaminated during annealing due to breakage of quartz capsule.	Microstructure--Stringers of second phase concentrated mainly at grain boundaries. Porosity--None XRD--Indeterminable pattern Grain size--very large
NiU_6	Microstructure--Two phase Shrink Porosity--Low	Microstructure--Some widely dispersed inclusions Porosity--Low XRD--one very weak, unidentifiable peak, other- wise pure NiU_6 Grain size--very large	Microstructure--Two phase Porosity--None XRD--Single phase NiU_6

NOTE: XRD = X-Ray Diffraction

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As Cast - 500 X
As Polished

Annealed 100 hrs. at 840°C-500 X
0.5% HF Etch

Forged 56% at 800°C - 250 X
0.5% HF Etch

FIGURE 8

NiAl₂ Microstructures

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As Cast - 500 X
As Polished

Annealed 100 hrs. at 1315°C - 500 X
0.5% HF Etch

Formed 61% at 1075°C - 250 X
92HCl, 8HNO₃ Etch

FIGURE 2

Ni₂Al₃ Microstructures

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As Cast - 500 X
As Polished

Annealed 100 hrs. at 1290°C-500 X
Electrolytic- H_3PO_4 bath.
Capsule broke during anneal, button
grossly contaminated.

Forged 65% at 1250°C - 250 X
Electrolytic Etch - H_3PO_4 Bath

FIGURE 10

Ni_3U Microstructures

Ni₃ Microstructures

FIGURE 11

Forged 55% at 765°C - 250 X
Electrolytic Etch-H₃PO₄ Bath

As Cast - 500 X
As Polished

Annealed 100 hrs. at 775°C-500 X
Electrolytic-H₃PO₄ Bath

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2. Letter from R. S. Kemper to H. F. Tew dated March 23, 1967. "Development Work on Al-Ni-U Bond System."
3. A. J. Bradley and A. Taylor, "An X-Ray Analysis of the Nickel-Aluminum System."