DEVELOPMENT
OF
NIOBIUM DIFFUSION BARRIERS
FOR
ALUMINUM-CLAD URANIUM ALLOY FUEL ELEMENTS

By

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ABSTRACT

Nickel has been used as a diffusion barrier for Al-clad uranium alloy fuel elements, operating at 650°F in organic-cooled reactors. Advanced organic-moderated reactor (AOMR) concepts include operating temperatures up to 850°F. Since the interdiffusion of Al-Ni is 150 times faster at 850°F than at 650°F, an alternate diffusion barrier is required. Subsequent studies resulted in the selection of niobium.

Several techniques for bonding niobium to the U - 10 Mo fuel were investigated. After considerable development effort, electron beam vacuum deposition yielded adherent, nonporous, ductile coatings. Isostatic bonding, at 1050°C and 12,000 psi for 1 hr, also resulted in metallurgically bonded niobium on the major surfaces of U - 10 Mo fuel plates.

Roll-bonding achieved metallurgically bonded plates on small test specimens, but was never reproduced on full-size plates. Vapor phase deposition, by H₂ reduction of NbCl₅, was also partially successful, but not reproducible. Ultrasonic bonding has shown promise in spot welding tests. Plasma-spray coating, and electroplating in a fused salt bath, were also considered, but not actively evaluated.

I. INTRODUCTION

Aluminum-clad uranium alloy fuel elements were originally conceived for use in water-cooled reactors of relatively low power densities. The application of this system to organic-cooled reactors was extremely attractive, because of the negligible corrosion of aluminum in polyphenyls, as well as offering a cladding of low neutron-absorption cross section, good heat transfer characteristics, and an exceptional cost advantage, when compared with the more exotically clad fuel systems.

However, the rapid interdiffusion of uranium and aluminum at reactor temperatures requires the use of a diffusion barrier to prevent the formation of low-density, brittle intermetallics, which result in swelling and failure of the cladding. Nickel currently is being used at mean operating temperatures of 650°F (750°F peak).¹ With the prospects of operating temperatures of 800 to 900°F becoming a reality for organic moderated reactors, the value of Ni as a diffusion barrier became questionable. Diffusion data² revealed that Ni could prove unsatisfactory at these temperatures, since aluminum was shown to penetrate 0.001 in. of Ni some 150 times faster at 850°F than at 650°F. Therefore, a search for an alternate diffusion barrier was initiated.

As a result of a theoretical evaluation of the metallurgical properties of potential barrier metals, and of subsequent diffusion studies, niobium was selected for further investigation. Metallurgically, niobium was expected to be an excellent barrier, since it forms a solid solution with uranium with no intermetallics, and diffusion data reported by Peterson and Ogilvie³ indicated that the rate of diffusion ($D = 2 \times 10^{-13}$ cm²/sec at 500°C) would be negligible at reactor operating temperatures. Pertinent data on the niobium-aluminum system were quite limited, with only one intermetallic reported (though others were subsequently found).⁴ Diffusion couple studies subsequently indicated insignificant interdiffusion between aluminum and niobium, and that high-strength bonds could be attained.

With the general acceptance of niobium as the best choice for a barrier material in aluminum-clad uranium alloy fuel elements, the obvious question of how to apply the niobium barrier was raised. An investigation of various techniques for cladding the U-Mo fuel cores with a dense, adherent, uniform coating

of niobium, 0.001 to 0.002 in. thick, became the major development effort of the Uranium Alloy Fuel Element Process Development project. A total of six fabrication processes were investigated: roll bonding, vacuum plating, vapor phase deposition, isostatic pressure bonding, ultrasonic welding, and plasma spraying. Other techniques, including electroplating from fused salt baths, were considered, but not evaluated experimentally. It is the purpose of this report to discuss the equipment, procedures, and evaluations of the various methods that were investigated.

II. SELECTION OF NIOBIUM

Initial consideration of materials for a diffusion barrier was arbitrarily limited to metals having a thermal neutron cross section of less than 6 b and a melting point greater than aluminum. The physical properties of such metals (Table I), and their metallurgical relationships with both aluminum and uranium (Tables II and III), were then compiled;⁶⁻¹¹ and an evaluation was made, using known diffusion data, and applying the fundamentals of diffusion¹² for those systems without known diffusion coefficients.

The metals selected for further study, as a result of this theoretical evaluation, were beryllium, niobium, titanium, yttrium, and molybdenum. Beryllium was selected because it has the lowest thermal neutron cross section of any metal (0.0085 b), high thermal conductivity ($0.38 \text{ cal/cm/cm}^2/\text{sec}/^\circ\text{C}$), and forms no intermetallic with aluminum and only one with uranium. Metallurgically, it is an attractive barrier material; however, because of its cost, poor fabricability, lack of availability, and toxicity, it was not evaluated experimentally.

Niobium's neutron cross section (1.1 b) and thermal conductivity met the fuel element requirements; however, its principle advantages as a barrier were: (a) the formation of a solid solution with uranium (no intermetallics), with a very low rate of interdiffusion, and (b) the formation of a high-strength bond with aluminum, with but one known intermetallic compound.* Niobium was available as sheet for experimental studies.

Titanium had been shown to interdiffuse slowly with Al,¹⁰ and had excellent thermal conductivity ($0.41 \text{ cal/cm/cm}^2/\text{sec}/^\circ\text{C}$). Although it formed two intermetallics with Al and one with uranium, titanium was available, and it was considered worthy of further evaluation.

Yttrium was a potential barrier, because it had an acceptable thermal neutron cross section (1.2 b). However, since it was not readily available and was extremely expensive, experimental evaluation (as with Be) was withheld until evaluation of other selections was completed.

Molybdenum, with its high melting point of 2625°C and good compatibility with uranium, appeared worth trying, despite the formation of six intermetallic

*Subsequent studies have shown that three exist (see Reference 13)

compounds with aluminum. This dissimilarity in the system was expected to promote diffusion.

TABLE I
PHYSICAL AND NUCLEAR PROPERTIES OF
POTENTIAL DIFFUSION BARRIERS

Element	Cross ⁷ Section (b)	Structure ¹⁰	Melting ⁸ Point (°C)	Linear ⁸ Thermal Expansion (/°C)(x 10 ⁶)	Thermal ⁸ Conductivity (cal/cm/cm ² /sec/°C)
Al	0.23	fcc	660	22.9	0.53
M257*	0.23	fcc	643	24.5	0.47
M486*	-	fcc	651	23.8	0.32
U	-	ortho	-	20	0.07
	-	tetr	1133	-	-
	-	bcc	1133	-	-
U - 3.5 Mo	-	ortho	-	16.8	-
	-	tetr	-	-	-
	-	bcc	1135	-	-
U - 10 Mo	-	ortho	-	-	-
	-	bcc	1140	-	-
Be	0.0085	hcp	1280	12.3-13.3	0.38
Cr	2.5	bcc	1890	6.2	0.16
Cu	3.7	fcc	1083	16.5	0.94
Fe	2.4	bcc	1540	11.7	0.18
Mo	2.5	bcc	2625	5.3	0.35
Nb	1.1	bcc	2415	7.5 ⁶	0.13 ⁶
Ni	4.6	fcc	1455	13.3	0.22
Ti	5.6	hcp	1725	8.5	0.41
V	4.7	bcc	1740	8.3	0.074
Y	1.2	hcp	1490	10.6	0.029
Zr	0.18	hcp	1830	5.2	0.04

*M257 is an aluminum powder metallurgy (APM) alloy, consisting of 5 to 7% Al₂O₃ in aluminum. M486 is an APM alloy, made from a prealloyed powder of Al plus 7.8% Fe, 0.2% Cr, 0.2% Ti, 0.2% V, and 0.2% Zr.

TABLE II
METALLURGICAL PROPERTIES OF POTENTIAL DIFFUSION
BARRIERS WITH RESPECT TO ALUMINUM

Element	Maximum Solid Solubility ⁴ (25-500°C) (wt %)	Intermetallics ⁴	Diffusion Coefficient, D (500°C) (cm ² /sec)	Remarks
U	Nil	UAl ₂ , UAl ₃ , UAl ₄	400 x 10 ⁻¹⁰ *	Incompatible
Be	4	None	10 x 10 ⁻¹⁰ *	Excellent in theory, forms no intermetallics
Cr	0.21	9	-	Incompatible, forms 9 intermetallics
Cu	4	5	5 x 10 ⁻¹⁰ ¹²	Incompatible, forms 5 intermetallics, rapid rate of diffusion
Fe	35	5	0.1 x 10 ⁻¹⁰ ¹²	Questionable compati- bility, forms 5 inter- metallics, slow rate of diffusion
Mo	0.1	6 [†]	-	Questionable compati- bility, slow rate of diffusion expected, forms 6 intermetallics
Nb	-	1 or more	-	Compatibility unknown
Ni	0.1	4	0.27 x 10 ⁻¹⁰ [§]	Incompatible
Ti	0.24 [†]	TiAl, TiAl ₃	-	Very slow diffusion ¹⁰
V	0.37	5	-	Questionable compati- bility, forms 5 inter- metallics
Y	-	-	-	Compatibility unknown
Zr	0.1	9	-	Appears incompatible, forms 9 intermetallics

*Reference 5 (by extrapolation)

†Estimated, but not verified

§Reference 2 (by extrapolation)

TABLE III
METALLURGICAL PROPERTIES OF POTENTIAL DIFFUSION
BARRIERS WITH RESPECT TO URANIUM

Element	Maximum Solid ¹¹ Solubility (25-500°C) (wt %)	Intermetallics ¹¹	Remarks ⁹
Al	0.1	UAl ₂ , UAl ₃ , UAl ₄	
Be	0.3	UBe ₁₃	Excellent compatibility in theory, forms only 1 intermetallic
Cr	0.3	None	Excellent compatibility, forms no intermetallics
Cu	Nil	UCu ₅	Theoretically excellent compatibility, forms only 1 intermetallic
Fe	Nil	U ₆ Fe, UFe ₂	Compatibility probably good, eutectic at 725°C
Mo	0.2	None	Theoretically compatible, forms no intermetallics
Nb	15	None	Theoretically compatible, forms no intermetallics
Ni	Nil	7	Compatible, eutectic at 740°C
Ti	0.2	U ₂ Ti	Theoretically compatible, forms only 1 intermetallic, high MP
V	0.3	None	Theoretically compatible, forms no intermetallics, high MP
Y	Nil	-	Immiscible with U in liquid state ⁴
Zr	0.5	UZr ₂	Theoretically excellent compatibility, forms only 1 intermetallic

Diffusion couple studies were subsequently initiated to evaluate the selected materials. Tantalum and zirconium were also investigated. Tantalum appeared favorable, except for nuclear cross section; and zirconium appeared favorable only because of it. Since isostatic gas-pressure bonding was to be used for cladding the diffusion-barrier-coated uranium core with Al, the initial couples were prepared in the following manner.

Foils of Nb, Ta, Zr, Ti, and Mo were bonded in Al cladding at 1000°F and 8000 psi for 30 min. All foils were cleaned mechanically and rinsed in methyl alcohol. The Al was chemically cleaned, prior to assembly.

Specimens were examined metallographically, as-pressed and after isothermal heating for 30 and 90 hr at 1000°F. Photomicrographs of the Nb-Al, Mo-Al, Ti-Al, and Zr-Al bond areas are shown in Figure 1. The absence of diffusion in the Nb-Al and Ti-Al couples led to their selection for further study. Bend and peel tests confirmed this selection; whereas the Mo and Zr readily parted from the aluminum, the Nb and Ti never parted during bend tests, and peeled only with extreme difficulty. Shear tests, performed upon Nb-Al tensile specimens made by mechanical hot pressing at 1050°F for 1/2 hr, indicated bond strengths of 4500 psi.

In subsequent studies, a total of 50 ternary diffusion couples were prepared by mechanical hot pressing, instead of pressure bonding. These couples, consisting of 1-in. diameter aluminum capsules machined to receive a 0.580-in. diameter U - 10 Mo wafer (Figure 2a), were pressed at 6500 psi and 950 to 1070°F for 1 to 2-1/2 hr. The majority of these capsules were made with Nb; though Ni, Ti, and Mo were also investigated, to confirm the results witnessed in earlier diffusion trials. The specimens were examined as-pressed and after isothermal heating for 500, 1000, 2000, and 5000 hr at 1000°F. Evidence of Al-Nb diffusion was observed metallographically on the specimen maintained in test for 5000 hr (Figure 2b).

The selection of Nb, in preference to Ti and other metals evaluated, was verified by results reported elsewhere. Kittel¹⁴ reported that bond strengths of 4000 psi were consistently obtained between Nb and U, while Ti-U bonds were not of sufficient strength to be measured. Similarly, Be was shown to be undesirable, because of the formation of UBe_{13} that resulted in cracking and separation at the bond interface.

a. Nb-Al

b. Mo-Al

c. Ti-Al

d. Al-Zr-Al

Figure 1. Bond Zones of Diffusion Couples (isostatically pressed at 1000°F and 8000 psi for 30 min) After Isothermal Heating for 90 hr at 1000°F

a. Components

500 X
2088-H

b. Al-Nb Bond Zone After Isothermal Heating
for 5000 hr at 1000°F

Figure 2. Hot Die-Pressed Diffusion Couples

TABLE IV
TYPICAL ANALYSIS OF U - 10 Mo

Element	ppm	Element	ppm
Al	20	Si	1500
Be	<0.2	Sn	5
B	3	V	<2
Cd	2	Zn	<50
Ca	40	Ba	<3
Co	<1	Bi	<2
Cr	30	Li	<1
Cu	30	Ag	1
Fe	150	C	150,500
Mg	<1	N ₂	90,115
Mn	20	H ₂	54,58
Ni	50	Mo (%)	9.92,9.95
Pb	4		

TABLE V
ANALYSIS OF NIOBIUM FOIL*

Element	ppm	Element	ppm
C	30	Mn	<20
N ₂	110	Ni	<20
W	<100	Pb	<20
Al	20	Si	<50
Co	<20	Ti	<50
Cr	30	V	<20
Cu	30	Mo	80
Fe	<50	Sn	50
Mg	40	O ₂	170

*Analysis certified by Oregon Metallurgical Corporation

III. MATERIALS

The principal fuel alloy used in diffusion studies and in process development was U - 10% Mo. The alloy was vacuum induction melted in a magnesium zirconate-washed graphite mold, and bottom-poured into graphite molds. This melting and casting process has been discussed in detail by Stanley and Binstock.¹⁵ The alloy was cast as plates, 3 by 0.3 by 4 in., for rolling; as plates, 0.100 by 3 by 12 in., for isostatic pressure bonding, vacuum deposition, and ultrasonic bonding; and as rods, 0.32 in. in diameter, for vapor phase deposition. Chemical analyses, typical of the cast U - 10 Mo, are given in Table IV.

Niobium for roll bonding, isostatic bonding, and ultrasonic bonding was in the form of foil, 0.002 or 0.010 in. thick, that was rolled from electron beam melted ingots. Four-inch diameter ingots, weighing about 15 lb, were obtained from Temescal Metallurgical Corporation. Cold rolled strips were fabricated by cold pressing sections of the ingot to slabs, and then cold rolling to the required thicknesses without annealing. Fully annealed strip was purchased from Stauffer Metals Division of Stauffer Chemical Company. Typical analyses are given in Table V. The niobium used for vacuum plating was also from electron beam melted material. The niobium pentachloride used in vapor-phase plating was procured from Stauffer Chemical Company. Niobium powder was used in the plasma-flame spraying trials.

Type 1100 aluminum was used in the diffusion couple studies and as cladding for isothermal tests of the niobium coating. The cladding was a flat extruded tube with a rectangular internal cross section, and finned external surfaces of the configuration used on fuel plates fabricated for the OMRE Fourth Core.

IV. EQUIPMENT AND PROCEDURES

A. ELECTRON BEAM VACUUM DEPOSITION

Vacuum deposition of metals having a melting point below 1600°C has been accomplished, for many years, by heating the material to be deposited with a tungsten filament, while maintaining the system under a vacuum of $<10^{-5}$ mm Hg. Metals with high melting points and low vapor pressures are not amenable to this process, since the required temperature cannot be achieved and maintained for sufficient vaporization. These metals can be vaporized, however, by employing an electron beam as the source for heating.

A charge of the metal to be deposited is placed in a water-cooled copper crucible, and the electron beam is directed on it. The high energy beam brings the material under bombardment to the melting point in a matter of seconds, and evaporation occurs as it is superheated. The metal vapors are then deposited on everything they "see" (i.e., hidden areas, such as the interior of tubes or deep narrow cracks, would not be coated). The deposit, like electroplated Ni on uranium, is mechanical in nature, and metallurgical bonding must be subsequently promoted.

The Electron Beam Vacuum Deposition (EBVD) Program was contracted to Temescal Metallurgical Corporation, of Berkeley, California. The coating was done in a vacuum chamber, equipped with Phillips vacuum gauge, a viewing port, an electron-beam source, a water-cooled copper crucible, and a fixture for holding the plates to be coated. The chamber was evacuated by a 20-in. diffusion pump with a refrigerated baffle, and a Kinney 130 cfm mechanical pump. Prior to coating, the system was pumped to 7×10^{-5} mm Hg. During preheating of the plates, the pressure increased to about 10^{-4} mm Hg, and then dropped to about 3×10^{-5} mm Hg during a typical plating cycle.

The power source for the electron beam gun was rated at 30 kw, with variable voltage and amperage, to achieve the desired power density. Voltages of 6 to 8 kv and amperages of 2 to 3.5 amp were typical for coating runs. The niobium charge was melted in a water-cooled copper mold that was placed alongside, and about 3 in. from, the electron beam gun. The electron beam is not aimed directly into the crucible; instead, it is deflected magnetically into the crucible; and, in this way, the gun is out of sight of the niobium vapors.

In initial coating trials by EBVD, two plates were mounted in an egg beater type of fixture which rotated the plates about the longitudinal axis, coating one-half of the plate. The plates were then reversed in the fixture, and the other half coated. This fixture located the plates about 12 in. above the niobium source, in an inclined plane; so that, as the plates were rotated, all edges and corners, as well as the major surfaces, were in line of sight of the vapors. In more recent efforts, it was discovered that rotating the plates always resulted in some degree of porosity in the coating. New fixtures have been designed, and are now in use; in these, the plates are moved across the niobium source normal to the path of the vapors, without rotation. This means that separate plating runs are required for each of the major surfaces, as well as the ends and edges; however, the resultant coatings have been free from any porosity. This process will be discussed in detail in Section V.

B. ISOSTATIC PRESSURE BONDING

In this process, niobium foil is bonded to the surfaces of U-Mo fuel plates by applying gas pressure at elevated temperatures. The application of the isostatic gas pressure bonding process is being investigated, under contract with Sylcor Division of General Telephone and Electronics Laboratories, of Hicksville, New York. In the exploratory experiments, Sylcor completed a series of mechanical hot pressing trials that established conditions (12,000 psi pressure, 1050°C temperature, and 1 hr time) capable of producing a metallurgical bond between niobium and U - 10 Mo. A photomicrograph of the bond area, typical of the bonds produced by this technique and these conditions, is shown in Figure 3. A series of six U - 10 Mo plates were then clad with 0.002-in. niobium foil by isostatic gas pressing at the bonding conditions established. The following is an outline of the operations:¹⁶

- 1) Components (steel sheath, spacers, and U - 10 Mo plates) were vacuum outgassed at 900°C.
- 2) The niobium cladding and the core plates were cleaned by pickling in acid.
- 3) Three plate assemblies, separated by Aquadag-coated niobium spacers, were loaded into a single steel sheath. Two sheaths, containing a total of six plates, were assembled.

500X
2997-3

Figure 3. Nb/U - 10 Mo Bond Zone, Hot Pressed at 12,000 psi and 1050°C for 1 hr

- 4) The steel sheaths were evacuated, sealed, and hot isostatically pressed at 1050°C and 12,000 psi for 1 hr.
- 5) After pressing, the steel sheathing was stripped off, and the plates were separated without difficulty.

The fuel plates supplied to Sylcor were as-cast, normal U - 10 Mo, 0.1 in. thick. The edges and ends of the plates were machined to the required dimensions of 12.000 in. length and 2.645 in. width. The major surfaces of the plates were finished only by blasting with stainless steel grit. The niobium supplied to Sylcor was cold-rolled and vacuum-annealed strip, 0.010 in. thick by 3 in. wide, made from electron beam melted, reactor grade ingot. This strip was cold rolled by Sylcor to a thickness of 0.004 in., and then pickled to 0.002 in. thickness in 50% HNO₃ - 50% HF.

The isostatic gas pressure bonding was done in a cold wall pressure vessel having internal dimensions of 14-in. diameter by 60-in. length. The internal furnace has a hot zone, 5 in. in diameter by 48 in. long. The pressure vessel is rated at 15,000 maximum psi pressure with temperatures up to 1200°C.

C. ROLL BONDING

The roll bonding process employed the conventional picture frame technique. Components of the picture frame assembly are shown in Figure 4a. The external picture frame material was steel, either Type 1020 mild steel or TiNamel (a titanium-killed low-oxygen mild steel). Ferrous alloys form a eutectic with uranium at about 1350°F; therefore, a secondary internal picture frame was required, to prevent any Fe-U interaction or eutectic melting during hot rolling. Niobium was selected for this purpose in initial efforts. However, copper was subsequently used, because it was compatible with niobium, uranium, and steel at temperatures up to 1750°F, and could be readily removed from the core, using a cyanide leach. It was also readily available, and significantly less expensive than niobium. Two types of picture frames were used, as shown in Figure 4b, an integral frame, machined from plate stock, and a pieced-component frame, made up of individual side and end bars.

The designs of the picture frame and other components were based upon the desired dimensions of the bonded plate. In seven preliminary bonding trials, a sub-size picture frame assembly (0.102 in. thick by 1.440 in. long by 2.625 in. wide) was used for U - 10 Mo core fillers that were machined from cast plates on hand. In rolling these assemblies to a 3:1 reduction, the final plate thickness was about 0.033 in. In subsequent work, all components were designed to attain a niobium-clad plate of the dimensions specified for an OMRE Fourth Core plate (0.102 by 2.645 by 12.000 in.), using a 3:1 reduction during hot rolling. The fillers for these assemblies were machined to 0.300 in. thick by 4.250 in. long by 2.600 in. wide, in a variety of end configurations to determine the best design for dimensional control. The fillers and the mating end pieces were machined with squared ends, partial radii, full radii, 60° tapers, and 45° tapers. The 45° taper, shown in Figure 4b, proved to be the only acceptable design. The niobium cover plates were reduced from 0.010 in. to 0.003 to 0.004 in. thickness during hot rolling.

The steel picture frames were designed with border widths of about 1-1/2 in., to minimize camber in the core during rolling. The other components were designed to mate with the U - 10 Mo core and the picture frame, to prevent uncontrolled spreading of the core during rolling and to prevent rupture of the niobium cover plate during initial rolling passes. A roll bonding assembly, just prior to welding of the top cover plate, is shown in Figure 4c.

7500-51511A

a. Components of Picture Frame Assembly

7500-51511B

b. Internal Picture Frames and U - 10 Mo Fillers

7500-51511D

c. Assembly, Prior to Welding

Figure 4. Roll Bonding

The steel cover plates were welded to the steel picture frame, using an inert gas shielded tungsten arc. Since oxidation of the U-Mo fuel core during welding would prevent bonding, a number of welding conditions were evaluated. These included the use of air and water-cooled copper chill blocks, to prevent overheating of the core, and welding in inert atmosphere glove boxes, using argon from bottles or a liquid argon source, to eliminate or minimize oxidation. The welds were required to be leaktight when checked with a Veeco leak detector capable of detecting a leak of 10^{-10} cc/sec. The welded picture frame assemblies were evacuated 12 hr prior to sealing and roll bonding. The roll bonding cycle consisted of a prescribed preheat, followed by a series of hot rolling passes, with intermediate reheats between passes. Table VI summarizes the various rolling conditions that were investigated.

D. VAPOR PHASE DEPOSITION

Niobium had been deposited successfully on UO_2 by hydrogen reduction of the pentachloride, so that the basic technology of this process had been explored.¹⁷ The reactivity of uranium alloys with a by-product of the reduction reaction presents a number of difficulties. These difficulties were not present in the application of the process to niobium coating of UO_2 . However, the U-Mo alloy must be protected from chloride attack by a nonporous metallic undercoating, such as copper, nickel, or chromium. The major effort of this task was aimed at demonstrating the feasibility of depositing niobium on copper-plated U - 10 Mo fuel specimens.

The procedures and the equipment for the reduction of niobium pentachloride have been fully described elsewhere,¹⁸ and will not be detailed in this report. A schematic of the gas flow system is presented in Figure 5a. Argon purge gas was passed through a zirconium chip-loaded furnace, and hydrogen gas was passed through a palladium thimble gas purifier. Gas flow was metered, both to a halide reservoir and to the main reaction vessel. The gas streams could be preheated by 6-in. immersion heaters incorporated into the lines. The halide reservoir was a 2-neck Pyrex flask, heated by an electric heating mantle. The gas line leading from the halide reservoir to the reaction chamber was wrapped with heating tape, to prevent premature condensation of the halide and consequent blocking of the line. The Vycor reaction vessel (Figure 5b) consisted of an inner cylindrical chamber (inside which the cylindrical fuel specimen was

TABLE VI

ROLLING SCHEDULES EVALUATED FOR BONDING NIOBIUM
TO U - 10 Mo PLATES BY THE ROLL BONDING PROCESS

Method	Temperature (°F)	Preheat Time (hr)	Reductions* (%)
1	1450	1	10, 17, 22, 12, 13, 8
2	1450	1	11, 25, 12, 13, 19.1, 10.7, 10
3	1450	1	18, 18, 13, 15, 15, 9, 7, 5, 6
4	1450	1-1/2	11, 19, 17, 16, 12, 8, 7, 6 30-min. post-rolling anneal
5	1500	1	24, 21, 14, 15, 17 30-min. post-rolling anneal
6	1500	1	19, 19, 16, 17, 10, 10 1-hr post-rolling anneal
7	1600	1	22, 22, 17, 16
8	1400	1	22, 20, 14, 14
9	1600	2	41, 25, 10
10	1900	1-1/2	38, 38, 16 1-1/2-hr post-rolling anneal
11	1450	1-1/2	18, 18, 15, 11, 16
12	1200	1/2	5, 1, 4, 3, 3, 4, 4, 5, 4, 1

*Reheats between passes were as follows:

30 min after first pass
25 min after second pass
20 min after third pass
20 min after fourth pass
15 min after each succeeding pass

a. Schematic of Gas Flow

7500-1867A

b. Reaction Vessel and Test Specimen Support

Figure 5. Vapor Phase Deposition

placed), surrounded by an annular gas mixing space. The halide-carrier gas mixture (coming from the halide reservoir and hydrogen purifier) entered the annular space, then passed to the inner reaction chamber through a series of perforations or slots in the inner chamber. These openings were positioned around the cylindrical fuel specimen. The fuel specimen was positioned at the axial center of the reaction chamber by BeO rods which protruded into depressions at either end of the U-Mo slug. The gas mixture exited from the inner reaction chamber by passing along a water-cooled finger to a liquid seal bubbler. A dust trap and/or scrubber vessel and a hydrogen gas burner completed the system. The fuel specimen was heated by induction heating with a 10-kc, 15-kw Tocco motor-generator set.

Reduction of the pentachloride by hydrogen begins at a very slow rate, at approximately 600°C, and becomes very rapid at temperatures in excess of 1000°C. Consideration of the U-Cu eutectic temperature dictated that the reaction temperature be limited to <850°C. For the purpose of this feasibility study, satisfactory deposition rates were achieved at ~750°C. The coated fuel specimen was generally held at 650°C for 1/2 hr, then cooled to room temperature at a rate of ~50°C/min.

The niobium pentachloride used in this work was purchased from Stauffer Chemical Company, and analyzed 99.6% minimum Nb on a metal-to-metal basis. Oxygen content was less than 2000 ppm, and additional purification of the pentachloride was not found to be necessary. Hydrogen was purified by passing it through a palladium thimble gas purifier (Milton Roy Company) at ~400°C, and argon purge gas was passed through a zirconium chip furnace at 700°C prior to use.

In initial trial runs, niobium films, approximately 0.0001 in. thick, were successfully deposited on solid copper specimens. However, in subsequent runs, using copper-plated U-Mo specimens, it was apparent that the copper plate was not protecting the U-Mo substrate from attack by the reduction atmosphere. A major effort of this program became, by necessity, the evolution of plating techniques for applying a porosity-free coating of copper. The main emphasis was placed on the electrodeposition of copper from either a cyanide or sulfate bath. In some instances, a copper flash coat was obtained in a cyanide bath, followed by plating a 2-mil coat in a sulfate bath. The latter procedure had previously been found to produce satisfactory copper plate on uranium metal.

It was necessary to plate to a 2-mil thickness, in order to produce a coating which was nonporous enough to prevent the formation of volatile uranium chlorides during the subsequent niobium pentachloride reduction step.

In some instances, the copper-plated U-Mo was heat treated in an argon atmosphere for ~24 hr at 1500°F, in an effort to promote diffusion bonding between the uranium alloy and copper.

Another variation on the copper plating procedure was the deposition of a 1-mil layer of copper by vacuum deposition, followed by electrodeposition of an additional 1 mil of copper.

Surface treatment of the U-Mo, prior to copper deposition, generally included outgassing for 24 hr at 1500°F and 1 μ pressure, followed by grit blasting and ultrasonic cleaning in an absolute alcohol bath. U-Mo fuel specimens used in this study were cylindrical in shape, 0.32 in. in diameter by 1-1/2 in. long.

E. ULTRASONIC BONDING

Ultrasonic roll bonding has been used to bond an aluminum alloy (X-8001) to cermet cores consisting of U_3O_8 dispersed in an X-8001 matrix.¹⁹ In this process, overlapping seam welds are made over the surfaces of the fuel element, using an ultrasonic roller-type continuous seam welder. With this in mind, samples of U - 10 Mo and niobium foil were submitted to Aeroprojects Inc., of West Chester, Pennsylvania, for feasibility studies. Spot welds were successfully made, using a 600-w ultrasonic spot welding machine. However, there has been no further experimental evaluation, using the roll bonding technique.

F. OTHER PROCESSES

Two other processes for applying Nb to U - 10 Mo were also considered: plasma spraying, and electroplating in a fused salt bath.

Plasma spraying of niobium powder was tried in air. However, during the process of spraying, the U - 10 Mo was overheated and oxidation occurred. Further work was discontinued, because of the high costs involved in obtaining the inert atmosphere equipment required for spraying, and since the probability of obtaining nonporous coatings in the range of 0.002 in. thickness, even under ideal conditions, were believed to be remote.

A literature survey failed to reveal any successful techniques for electrodepositing dense adherent niobium. However, a technique had been developed for depositing titanium on stainless steel in a fused salt bath. An investigation of this process for plating niobium was considered; but no action has been taken, since Nb had never been deposited, and since the vendor had no experience or capability for handling uranium.

V. EVALUATION PROCEDURES

A. MECHANICAL TESTS

The mechanical strength of bonds was determined by peel and/or chisel tests and by tensile tests. Bonds obtained by roll bonding and isostatic pressure bonding were evaluated primarily by simple peel or chisel tests, since most of these specimens were not bonded on the edges and the overlapping niobium foil provided convenient starting points. These were qualitative tests only; with good bonds, the niobium could not be separated from the core; while, with poor bonds, the niobium was readily peeled.

Tensile tests were made on specimens coated by vacuum deposition and pressure bonding. Tensile specimens, as shown in Figure 6, were prepared by cementing 1-in. square niobium-coated coupons between two aluminum I-beam sections, using epoxy resin. The tensile

Figure 6. Tensile Specimen After Testing Bond Strength of Niobium-Coated U - 10 Mo (Specimen failed in epoxy cement — coated coupon is shown intact on adapter at left)

machine gripped each I-beam section and pulled the specimen in tension. All tests were at room temperature. This test also proved to be qualitative, rather than quantitative; in that, in all but one test, the failure occurred in the epoxy cement, rather than in the Nb/U-Mo interface.

B. ULTRASONIC TESTS

The Nb/U-Mo bonds were evaluated by ultrasonic through-transmission techniques, using equipment manufactured by Automation Industries. The principal components were an Immerscope, an Ultragraph, and transducers, and a water tank that was custom built for test work of this nature. The transmitting transducer was located 3-3/4 in. above the surface of the plate and 4-3/8 in. above the receiving transducer. The plate, which was immersed in water, was scanned by a spot focused on an area, 3/16 in. in diameter, on the top surface of the plate. Three scans were run on each plate at three different amplifications. The amplifications, or gain settings, were 1.1, 1.05, and 1.02 times the gain necessary to receive a signal of 90% of saturation

from a 0.375-in. thick aluminum test standard. The received 5-Mc signals were amplified and traced on the Ultragraph. A photograph of a plate, as traced on the Ultragraph, is shown in Figure 7. All plates were ultrasonically tested after

Figure 7. Ultrasonic Scan of Niobium-Clad U - 10 Mo Plate, Using Through-Transmission Technique at 5 Mc, 1.5 Gain (Plate was isostatically bonded at 1050°C and 12,000 psi for 1 hr — dark area indicates poor bond)

the niobium was bonded to the U-Mo core. Additional tests were made after pressure bonding in the finned aluminum cladding, and at intervals during thermal cycling or isothermal heating.

C. ACID TESTS

Since niobium is insoluble in 70 vol % HNO_3 , and U - 10 Mo reacts vigorously with it to form a distinctive greenish residual (uranyl nitrate), acid tests were devised to determine the presence and extent of porosity in coatings. These tests were used primarily to evaluate coatings applied by vacuum plating, and also as a test of vapor phase coatings. Gross porosity, which was prevalent in initial vacuum plating efforts, was readily detected by a spot test. As the process was refined and the coatings became more impervious, the acid was run along the entire length of the plate. The acid was then blotted with a highly absorbent paper — any areas of uranium reaction were revealed by a staining of

the paper. This technique not only located areas of porosity, but effectively established the degree of porosity as well. If porosity was not immediately detected by these tests, the acid was allowed to remain on the coating for a period of 3 hr, and the specimen was again checked.

D. ISOTHERMAL HEATING TESTS

Isothermal heating tests were used as the final test of the effectiveness of the niobium coating as a diffusion barrier. Niobium-coated plates that were not sectioned for metallographic or other destructive evaluation were isostatically pressure bonded in finned aluminum cladding of the configuration used for OMRE Fourth Core loading.²⁰ Metallographic evaluations were made in the as-pressed condition, and after heating the plates isothermally for extended periods, to establish the behavior of the bond with time. Most of the plates were held at 1000°F as an accelerated test. However, 900°F tests were also used, since it was more typical of expected reactor temperatures. Initially, these tests were carried out in an air furnace at atmospheric pressure. Later, all heating was done in a retort that was pressurized at 400 psi to simulate reactor conditions. All plates were inspected weekly for the visual "blistering" that results from the formation of U-Al intermetallic compounds.

250 X
2642-1-2

a. After Isostatic Bonding
(On the right, the Nb
has shown preferential
adherence to the Al;
on the left, to the
U - 10 Mo)

250 X
2553-1-2

b. After Isothermal Heating for 1131 hr at 1000°F (The compound
found only on the U - 10 Mo side of the Nb is thought
to be UAl_4)

Figure 8. U - 10 Mo Coupon With 0.001 in. Nb Coating and Al Cladding

VI. RESULTS AND DISCUSSION

A. ELECTRON BEAM VACUUM DEPOSITION

A total of 55 U - 10 Mo coupons and plates were coated with niobium during the evaluation of this process. In the first series, 15 coupons, 1 by 2 by 0.1 in., were coated as a preliminary feasibility study. It was demonstrated that niobium could be vacuum-coated on U-Mo in a uniform adherent layer. During evaluation, however, discontinuities in the coating were observed metallographically, and subsequent isothermal heating revealed U-Al interdiffusion. Bond areas of aluminum-clad coupons are shown in Figure 8.

The second series consisted of 15 plates, 0.100 by 2.645 by 12.000 in., to determine the feasibility of coating plates of typical OMRE Fourth Core dimensions, rather than coupons. All of these plates were coated with about 0.001 in. of niobium, using the inclined, rotating paddle wheel, or egg beater fixture described in Section IV. A typical niobium-plated core is shown in Figure 9, along with components for isostatic pressure bonding. The apparent seam at the midpoint is the area of overlap of coating that occurred when the plate was turned end-for-end in the fixture, since only one-half was plated at one time. The principle evaluation of this series of plates was isothermal heating tests, after pressure bonding in aluminum cladding. The behavior of the plates was erratic; some plates were heated at 1000°F for as long as 2857 hr before "blistering" due to U-Al intermetallic formation, while others failed as early as 198 hr. Figure 10a shows the localized U-Al areas resulting from porosity in the plate that failed at 198 hr. Figure 10b is a cross section through a blister. Figure 10c shows continuous bonding in an area of the same plate that was free from porosity. Figure 11 is a photograph of a plate that exhibited general overall blistering. It was apparent, from the behavior of these plates, that the niobium coatings were porous; and that, during isostatic pressure bonding, the aluminum cladding was extruded through the pores into contact, or near contact, with the U-Mo, nullifying the effectiveness of niobium as a diffusion barrier.

In view of this porosity problem, the third and fourth series of plates were processed with the objective of determining the effect of surface preparation and processing variables on the quality of the niobium coating. The acid test, described in Section IV-E, was devised as a means of determining the extent of porosity. It proved to be a very effective technique, and it was soon determined

7500-51518

Figure 9. U - 10 Mo Plate, As-Coated With Niobium by Electron Beam Vacuum Deposition
(Aluminum components for isostatic bonding to finned aluminum cladding are also shown)

PHOTOGRAPHED AT 5.5X
REDUCED TO 2.1X

a. Cross Section of Plate

PHOTOGRAPHED AT 100X
REDUCED TO 59X
2614-6-6

b. Cross Section Through Blister Area, Showing Extent of Cladding Consumption During UAl_4 Formation (Note that, at one point, only 0.002 in. of cladding remains)

c. Cross Section Through Good Bond Area, Showing Continuous Niobium Barrier

PHOTOGRAPHED AT 100X
REDUCED TO 59X
2614-6-5

Figure 10. Plate Which Exhibited Blisters After 198 hr at 1000°F
(Dark areas extending into cladding are UAl_4)

7500-51543H

Figure 11. Typical Blistering Found in Center of Plates After Isothermal Testing

7500-51603A

Figure 12. Edge Failure in Finned Aluminum Cladding Caused by Al-U Contact — Rupturing Increased by Oxidation of Exposed Uranium (Failures were predominantly in this region)

that the quality of the coating (i. e., the degree of porosity) was drastically affected by the surface condition of the plate. In the continuing evaluation, plate surfaces were prepared by: (1) grit blasting only; (2) grinding to 80 to 120 rms μ -in. finish, using 60-grit abrasive belts; and (3) belt grinding to 10 to 20 rms μ -in. finish, using 320-grit belts. Spot and smear acid tests indicated that grit blasted surfaces were always porous, that 60-grit finished surfaces showed only slight response to the acid test, and that 320-grit finishes were nonporous. In subsequent isothermal tests, however, it was revealed that blistering or failure occurred most frequently at the edges, as shown in Figure 12. These results, along with metallographic studies, indicated that coating thickness and quality was not under control at the edges and corners, although the major surfaces appeared to be satisfactorily coated.

At this time, it was decided that the most expeditious solution to the problems of achieving porosity-free, uniformly thick, dense coatings of niobium was by conducting a Research and Development program to systematically evaluate the variables that could affect quality. This program, as carried out by the vendor, is described in the following paragraphs.²¹

1. Substrate Preparation and Precleaning Techniques

Coatings were made on plate material with a grit blast finish, an 80-grit polish finish, and a 320-grit polish finish. With all other coating variables the same, satisfactory results were never obtained on the plain grit blast finish, but were obtained on both the 80- and 320-grit polished material. The coatings on 320-grit polished material had a better appearance, although no distinction could be made between coating performance in the 3-hr acid test.

The U - 10 Mo plates were kept packaged in an inert atmosphere until just prior to processing, to avoid excessive oxidation. Each plate was then scrubbed with water and pumice cleanser until the water wet the surface. The plate was dried and placed in the vacuum system, where it was bombarded with an electron beam, heating it to a temperature of approximately 800°C, to remove any volatile surface contamination. This procedure permitted the subsequent deposition of adherent, acid-impervious coatings.

2. Rate of Niobium Deposition

The rate of deposition of niobium was varied, by raising and lowering the substrate above the source of evaporant. The evaporation source was optimized

by bombarding the niobium pool with the maximum amount of power that could be focused into a given size molten pool without fusing the water-cooled copper crucible which contained the pool. A stable, reproducible condition was obtained with 25 kw into a 1-3/4-in.-diameter molten pool. This power setting and geometry were used throughout the program.

Runs were made at distances of 12 and 6 in. above the source. At the 12-in. distance, 0.002 in. of niobium was deposited in 30 min; at the 6-in. distance, 0.002 in. was deposited in 8 min. The samples made at 12 in. showed very slight visible attack by 70% nitric acid after 2 hr. The samples coated at 6 in. showed no visible attack after the same time interval, but evidenced a very slight discoloration under 600X magnification.

3. Angle of Incidence of Impinging Niobium Vapor Molecules

One of the most important coating variables turned out to be the angle of incidence of the impinging vapor molecules. Samples were mounted on a cylindrical surface whose axis of symmetry was located 12 in. above the source. Five samples were mounted, one each at angles of 0, 10, 20, 30, and 40° from a plane parallel to the source plane. After a standard run, the samples reacted as follows to the 70% nitric acid:

- a) The 40° sample showed immediate attack by the acid.
- b) The 30 and 20° samples showed slight attack, and hence porosity, after a 3-hr exposure to the 70% nitric acid, with the 30° sample somewhat more heavily attacked than the 20° sample.
- c) Neither the 10° nor the 0° sample showed any porosity after the 3-hr exposure.

Following this experiment, subsequent evaporation was performed so that no part of the sample was exposed to molecular impingement at greater than 15° from the normal.

4. Pressure During Evaporation Process

The pressure in the vacuum tank during evaporation did not appear to be an important variable, as long as the evaporation was conducted at less than 5×10^{-5} mm Hg. However, the residual vapor present in the tank during evaporation did prove to have an extremely important effect, and pointed up the

necessity for maintaining a high degree of vacuum tank cleanliness, in order to achieve successful results. In coating some of the samples, excellent results obtained on one side could not be reproduced when the sample was turned over for coating on the other side. This was caused by evaporation of contaminant molecules from the tank walls during the evaporation, and their subsequent deposition onto the back side of the sample during coating. These contaminants were evidently not removed by the degree of cleaning provided when the specimen was turned over for coating of the contaminated side. The following paragraph outlines an experiment which indicated this condition.

Three identical samples, two of which had been cleaned with wet polish, were placed in the vacuum system for coating. All were heated to 800°C by electron bombardment, and then coated with 2 mils of niobium in a standard run. The samples were then removed, and one of the two previously cleaned samples was again scrubbed with wet polish on the uncoated surface. All three samples were then put back in the vacuum system, precleaned by heating at 800°C, and a 2-mil coat was placed on the previously uncoated side. This second side of all three samples was then subjected to 70% nitric acid for 2 hr. The sample which had had its second side recleaned, presumably removing the evaporated contaminants, was superior in acid resistance. This experiment was duplicated several times, and yielded the same results. A careful cleaning of the tank, and an extremely careful selection of the materials exposed to temperature during the process, overcame this difficulty.

5. Post-Heat Treatment of Coated Samples

It was hoped that a post-heat treatment of the coated samples would provide a better bonding of the coating to the substrate without deteriorating the acid resistance of the film structure. Two samples were placed in the furnace and given a standard cleaning and coating. Following the completion of the coating, the beam was focused on one sample, and the temperature was raised to approximately 1000°C for 1 hr. The samples were then subjected to an acid test, and the post-heated sample showed immediate visual porosity. Since the adhesion was not markedly improved, no further runs at other temperatures were tried.

6. Substrate Temperature

Initially, no attempt was made to control the substrate temperature during evaporation. Since some noticeable cooling of the sample occurred during

a. Discontinuity and
Contaminants at Bond
Interface Area Where
Ultrasonic Test
(Figure 7)
Indicated
Poor Bond

250 X
3042-1

b. Typical Bond Interface

500 X
3042-5

Figure 13. U - 10 Mo Plates, Isostatic Press Bonded at 1050°C
and 12,000 psi for 1 hr

coating (from the starting condition of about 800°C, resulting from the precleaning), a substrate heater was installed. This heater maintained the samples at a constant temperature, and yielded very acid-impervious, yet ductile, films.

Although cold substrate samples were also impervious to nitric acid, the workability of the ductile coating is felt to be a significant advantage, particularly with respect to subsequent handling and working on the plates.

The electron beam vacuum plating process and equipment was modified, by the vendor, to incorporate the optimum plating conditions discussed in the preceding paragraphs. In the current process, the plate is preheated to about 1300°F by passing it through a radiant heater and conveying it across an opening, 4 in. long by 3 in. wide, located 6 in. above the niobium source. With this design, the angle of impingement is less than 15° to the normal, to eliminate or minimize porosity; and, at a traverse speed of 0.4 in./min, a uniform coating, 0.002 in. thick, is deposited. A series of normal U-Mo plates has been processed, to demonstrate that reproducible coatings can be achieved. Evaluation, to date, indicates that the resultant coatings are adherent and ductile, and are apparently of high quality. However, in a 3-hr immersion in 70% HNO₃ some porosity was detected. Since vacuum plating is by "line of sight" only, it is probable that this isolated porosity in the coating is due to surface porosity in the as-cast U-Mo plate. Several of the plates submitted for coating were rejected for this reason. U-Mo plates now being processed have been cast oversize, to allow about 0.010 in. to be ground from each surface to eliminate surface porosity. Enriched fuel plates for a test fuel element are now being coated by electron beam vacuum coating.

B. ISOSTATIC PRESSURE BONDING

Niobium foil was isostatically pressure bonded to six U-10 Mo plates, by Sylcor, at bonding conditions of 1050°C and 12,000 psi for 1 hr.²² Ultrasonic tests indicated that bonding was generally consistent over the major surfaces of all six plates. One unbonded area was detected in one plate, as shown in Figure 7. A metallographic section, taken through this defect area, confirmed the presence of discontinuities and contaminants. Figure 13a is a photomicrograph of this defect area. This was the only unbonded area found, and it was believed due to faulty surface cleaning. Metallographic examination showed that

interfacial diffusion, indicative of metallurgical bonding, was achieved. A typical bond interface, showing the diffusion zone, is shown in Figure 13b.

In addition to bond evaluation, the effects of isostatic bonding at 1050°C upon grain size and γ -phase stability of U - 10 Mo were also evaluated metallographically. Average grain size was observed to be ASTM 3 to 4. There was no evidence of the $\alpha + \epsilon$ phase being greater than that observed in as-cast specimens.

Tensile tests, to evaluate the Nb/U-Mo bond strength, were performed by attaching 1-in. square specimens to special tensile adapters with epoxy resins. Room temperature tests showed that the bond strengths exceeded that of the epoxy resin; since all failed in the epoxy resin, not in the bond, in the range of 415 to 1170 psi. As further evidence of significant bond strength, peel tests could not remove the niobium.

The initial effort has established the feasibility of isostatically bonding niobium to U - 10 Mo. Bonds achieved on the major faces were excellent, and have met all requirements. The problem of bonding the edges is yet to be resolved; but the edges can be covered, even though bonding is not achieved.

Since wrought niobium foil is used, this process principally offers a diffusion barrier, free of pinholes and other discontinuities, and therefore a complete barrier between the aluminum and uranium. Secondly, the bond is metallurgical, and free of intermetallics; and initial results indicate that it is readily obtained between clean components.

This development is continuing. In the next phases, the vendor will isostatically bond niobium foil to 15 normal U-Mo plates to: (1) establish reproducibility of the process, and (2) evaluate various techniques for covering the edges of the plates with niobium.

C. ROLL BONDING

Initial efforts to roll-bond niobium to U - 10 Mo indicated that this process was feasible. In rolling 7 sub-size plates, at 1550°F, to a 3:1 reduction, 3 were bonded over 95% of the major surface area. A photomicrograph of the bond, shown in Figure 14, reveals a diffusion zone indicative of a metallurgical bond. Two more of these plates were bonded over some 60% of the surface area, while two were unbonded. The lack of bonding in these plates was believed to be due to oxidation of the fuel cores, as a result of overheating while welding the picture frame.

500X
1874-3C

Figure 14. Nb/U - 10 Mo Bond Zone, Roll Bonded
at 1500°F, Using 3:1 Reduction

However, scaling the process up to full-size OMRE-4 type plates was never successfully achieved. A total of 42 picture frame assemblies were rolled, during which such fabrication variables as rolling temperature, mill reductions, cleaning, and assembly procedures were investigated. This series resulted in localized and inconsistent bonding that could not be correlated with any of the processing variables. The bonding ranged from poor, in which case the niobium could be peeled off, to excellent, in which the niobium could not be chiseled off. One observation, common to all plates, was that any bonding that did occur was always in the center of the plate, and never only around the edges. Another observation was that unbonded areas of the U-Mo core were always discolored or coated by some contaminant. This contamination was never eliminated by, or correlated with, any particular cleaning, assembly, or fabrication variable. One possible source of contamination was in the fuel itself, due to outgassing at the rolling temperatures employed. In subsequent laboratory tests, in which components used in roll bonding were heated to temperatures above 1600°F in vacuo, a surface film was deposited on all samples in contact with the U - 10 Mo specimen. Several combinations were run, excluding one of the component materials in each case. In every test, the surfaces in contact with the U - 10 Mo, regardless of the material involved, were contaminated.

D. VAPOR PHASE DEPOSITION

The deposition of niobium on U - 10 Mo by hydrogen reduction of niobium pentachloride is feasible, if the U - 10 Mo is protected by an adherent continuous copper coating. The niobium coating deposited on copper tubing, as shown in Figure 15, was only about 0.001 in. thick; however, it was shown to be free from

BF
ETCHANT: 2g CrO_3 - 0.5g NaCl - 2.5 ml HNO_3
2.5 ml H_2SO_4 - 95 ml H_2O

500X
3044-2

Figure 15. Niobium, Vapor Plated on Copper by Hydrogen Reduction of NbCl_5

any porosity, when acid-tested in 70% HNO_3 . Deposition of niobium on copper-plated U - 10 Mo, however, was never successful, because of porosity or other discontinuities in the copper-plating that allowed the reducing atmosphere to react with the U - 10 Mo substrate. This reaction always formed volatile chlorides that blistered and ruptured the copper plating.

Many variables were introduced into the U-Mo surface cleaning procedure, in an effort to obtain a Cu protective layer which was both adherent and nonporous, ranging from grit blasting (which tended to give an adherent coating that was porous) to polishing with 400-grit cloth (which tended to give a nonporous coating that was not adherent). Even combinations of grit blasting, followed by Cu plating, polishing with 400-grit cloth, and replating, was attempted. A nonporous adherent coating, when achieved, was never reproducible. The use of a Ni flash as a base for the Cu plating also failed to provide an adherent coating.

A possible source of experimental difficulty may have been introduced by the method used for test specimen heating during niobium vapor phase plating. Test specimens were heated by induction, thereby achieving high temperatures in the copper undercoat, relative to the U-Mo substrate, and possibly introducing thermal stresses which lead to blistering. Also, the geometry of the test specimens (0.32-in. diameter slugs) was such that differences in the thermal expansion coefficients of the U-Mo substrate, copper undercoat, and the niobium deposits were magnified, and possibly led to spalling of the plate.

Many techniques appeared to hold promise, as several specimens were made which had coatings that were essentially nonporous and adherent. The duplication of these coatings, despite an effort to reproduce previous experiments to the closest detail, was never achieved.

E. ULTRASONIC BONDING

In a limited feasibility investigation, it was demonstrated that a 0.002-in. niobium diffusion barrier could be bonded to U - 10 Mo core material by the ultrasonic welding technique.²³ The welding evaluation was conducted, using a 600-w ultrasonic spot welding machine. The resulting welds were strong enough to cause nugget pullout or parent metal failure in a peel test. Metallographic examination (Figure 16) of one ultrasonic spot weld indicated sound bonding, with

MAG - 500X

Figure 16. Ultrasonic Bond Between 0.002-in.
Niobium Foil and U - 10 Mo Core Material
(Photomicrograph supplied by Aeroprojects, Inc.)

no interface discontinuities, no material cracking or dispersion of the uranium into the diffusion barrier, and negligible deformation of the niobium foil.

The extension of the ultrasonic technique, from spot welds to overlapping seam welds, has not been investigated; and such an investigation is not considered to be warranted, at this time.

VII. CONCLUSIONS AND RECOMMENDATIONS

Of the techniques evaluated for applying a niobium barrier on U-Mo alloy fuel, for the fabrication of aluminum-clad, niobium-bonded, U-alloy fuel elements, two have been shown to be feasible and practical processes. The two are: (a) isostatic gas pressure bonding, and (b) electron beam vacuum deposition. Two techniques, vapor phase reduction plating and roll bonding, have limited potential, in that feasibility has been demonstrated; but the processes have not shown reproducibility or adaptability to production techniques. Three additional techniques: ultrasonic bonding, plasma spraying, and fused salt plating, do not show any immediate application.

Niobium can be bonded to U-Mo plates by isostatic gas pressing at 1050°C (1900°F) temperature and 12,000 psi pressure for 1 hr. This process has two major advantages: (a) the achieving of metallurgical bonds between niobium and the U-Mo fuel, and (b) assurance of a diffusion barrier free from pinholes, porosity, or other discontinuities. Additional work is required to establish optimum bonding conditions, to demonstrate that reproducible bonding can be achieved, and to develop techniques for bonding the edges. The process is adaptable to production quantities. Continued development of this process is recommended for any application where refractory metals must be bonded.

It has been demonstrated that niobium coatings can be applied by electron beam vacuum deposition. The current development efforts indicate that dense, adherent, ductile, and porosity-free coatings are feasible. However, process control, to assure reproducibility, is required. The process is practical, and adaptable to production quantities. Additional effort is required to evaluate and/or develop techniques for achieving a metallurgical bond. It is recommended that this process be further developed for numerous other reactor applications in which refractory metal or ceramic coatings must be applied.

Roll bonding of niobium to U-Mo is believed to be feasible; however, an acceptable process has not been developed to assure reproducible results. Because of the high costs of machined components and the relative complexity of the process, it is believed that roll bonding cannot be economically competitive with isostatic pressure bonding or electron beam vacuum deposition. Further development of this process is not recommended.

Vapor phase deposition of niobium by the hydrogen reduction of niobium pentachloride is not a practical method of applying a niobium barrier on metallic uranium alloys. While dense, porosity-free niobium films were deposited (in very thin films) on occasional specimens, the process is not a reproducible one, nor is it adaptable to the coating of plates for either development or production quantities. It may have potential application for hollow tubes or similar shapes. However, in view of the advantages of electron beam vacuum deposition or iso-static bonding processes, further effort is not recommended at this time.

REFERENCES

1. M. H. Binstock, "Fuel Element Development for Piqua OMR," NAA-SR-5119 (June 30, 1960)
2. G. V. Alm, "Nickel Bonding of Aluminum Clad OMR Metallic Core Fuels, Current Status," NAA-SR-Memo-3662 (March 20, 1959)
3. N. L. Peterson and R. E. Ogilvie, "Diffusion Studies in the Uranium-Niobium (Columbium) System," Transactions of the Metallurgical Society of AIME, 218 (June 1960)
4. Max Hansen, Constitution of Binary Alloys (McGraw-Hill Book Company, Inc., New York, 1958)
5. J. W. H. Clare, "A Review of Diffusion in Aluminum," Metallurgia 57 (June 1958) p 344
6. E. L. Francis, "Niobium Data Manual," IGR-R/R-304
7. G. Friedlander and J. Kennedy, Nuclear and Radiochemistry (John Wiley and Sons, Inc., New York, 1955)
8. C. A. Hampel, Rare Metals Handbook (Rheinhold Publishing Company, New York, 1954)
9. A. B. McIntosh, J. S. Broadley, and K. Q. Bagley, "Some Factors Influencing the Compatibility of Metals with Sodium, Potassium, and Uranium," R + DB (c) TN-31 (1959)
10. Metals Handbook (American Society of Metals, Cleveland, Ohio, 1948)
11. F. A. Rough and A. A. Bauer, Constitutional Diagrams of Uranium and Thorium (Addison Wesley Publishing Company, Inc., Reading, Massachusetts, 1958)
12. Smithells, Metal Reference Book (Butterworth Scientific Publications, Vol. 2, Second Edition, London, England, 1955)
13. U. V. Baron and E. M. Savitskii, "Structure and Properties of Niobium-Aluminum Alloys," Russian Journal of Inorganic Chemistry 6, No. 1 (January 1961)
14. J. H. Kittel, "Layer Formation by Interdiffusion Between Some Reactor Construction Metals," ANL-4937 (June 17, 1949)
15. J. A. Stanley and M. H. Binstock, "Development and Production of Uranium 10 wt % Molybdenum As-Cast Slugs for HNPF Physics Experiment," NAA-SR-4874 (April 1960)
16. L. Scheinhartz, General Telephone and Electronics Laboratories, private communication

REFERENCES (Continued)

17. Final Report Contract AT(30-1)-2264, November 15, 1958, through November 14, 1959, NUMEC-NYO-2801
18. J. M. Blocher et al., "Fluidized-Bed Coating of UO_2 Powder With Niobium and Other Elements," BMI-1440, (July 6, 1960)
19. "A Program to Study the Feasibility of and Develop an Apparatus for the Ultrasonic Roll Bonding of Fuel Plates," CEND-93 (December 1960)
20. G. V. Alm, M. H. Binstock, and E. E. Garrett, "Hot Pressure Bonding of OMR Fuel Plates," NAA-SR-3583 (November 15, 1959)
21. H. Smith, Temescal Metallurgical Corporation, private communication
22. L. Scheinhartz, General Telephone and Electronics Laboratories, private communication
23. H. L. McKaig, Aeroprojects, Inc., private communication