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THE BONDING OF MOLYBDENUM- AND
NIOBIUM-CLAD FUEL ELEMENTS

by

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THE BONDING OF MOLYBDENUM- AND NIOBIUM-CLAD FUEL ELEMENTS

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A solid-state bonding technique involving the use of gas pressure at elevated temperatures was utilized for the self-bonding of molybdenum and niobium. Bonding conditions and surface preparation as a function of the integrity of the bond achieved were evaluated for each material.

Optimum self-bonding of niobium was achieved by bonding parameters of 2100 to 2300 F at 10,000 psi for 3 hr with surfaces which had been prepared by etching in a nitric-hydrofluoric acid solution prior to bonding. The process as developed was used to prepare niobium-clad flat-plate- and rod-type fuel elements and flat-plate subassemblies. Niobium tubing was also fabricated by this technique.

Molybdenum self-bonding was most readily achieved by gas-pressure bonding at temperatures of 2300 to 2600 F at 10,000 psi for periods of 3 hr. With these bonding conditions a number of different surface preparations were satisfactory. Directional ductility of the molybdenum was encountered after bonding and methods to eliminate this were evaluated. Cross rolling with respect to the original rolling direction was shown to improve the ductility of molybdenum-clad specimens.

INTRODUCTION

Background

Molybdenum and niobium are promising structural and cladding materials for inert-gas-cooled and some liquid-metal-cooled high-temperature reactor applications.^{(1,2)*} Their most important property is high-temperature strength. At 2000 F, the tensile strength of niobium is approximately 9000 psi⁽³⁾, while molybdenum has a tensile strength of approximately 10,000 psi⁽⁴⁾. Temperatures of approximately 2000 F will be encountered in future reactors for space applications⁽⁵⁾, consequently, there is need for determining satisfactory methods for joining these materials.

An equally attractive property of these materials is their relatively low thermal-neutron-absorption cross section. Niobium exhibits no significant resonance peaks in the thermal or epithermal energy regions⁽⁶⁾ and molybdenum is also free of resonance peaks except for two in the epithermal region. In addition, both metals exhibit excellent resistance to attack by many purified inert gases and many liquid metals.⁽⁷⁾ These properties make molybdenum and niobium attractive in many types of high-temperature

*References are at end of report.

reactors as structural materials. Furthermore, it has been shown that both metals are compatible with many fissionable materials which indicates their desirability for use as fuel-element cladding materials.

Stringent requirements for nuclear fuel elements are numerous. It is necessary to produce high-integrity bonds between all cladding components for optimum heat transfer, corrosion resistance, and strength. Current reactor designs call for numerous complex fuel-element shapes with very accurate dimensional tolerances. There is a trend for these fuel elements to contain ceramic or cermet fuels so that high burnups can be achieved with greater dimensional stability.⁽⁸⁾ Unfortunately most fuel materials of this nature are extremely brittle which imposes restrictions on the fabrication processes which can be employed.

The desirability of employing molybdenum and niobium as cladding materials establishes a need for an effective process for bonding, cladding, and joining of molybdenum- and niobium-clad fuel elements. It is possible to join both of these materials by welding in a closely controlled atmosphere.^(2,9) The niobium is more easily welded because it does not become embrittled as readily during welding. Also, the room-temperature ductility of the molybdenum welds is sometimes difficult to obtain as a result of oxide precipitation along the molybdenum grain boundaries during the welding operation and the relatively high brittle-to-ductile transition of recrystallized molybdenum.⁽¹⁰⁾ Thin foils of both metals can be joined by ultrasonic spot welding; however, the process has not been proven applicable to relatively thick frame material.⁽⁹⁾

Since both molybdenum and niobium display a high affinity for oxygen and nitrogen^(10,11), it is necessary to protect them from atmospheric exposure during cladding by roll cladding or coextrusion. The temperature necessary to obtain bonding of these materials to themselves presents an additional problem. Oxidation-resistant materials normally employed as outer protective cans during cladding of metals that have high affinity for oxygen and nitrogen will readily alloy with the molybdenum and niobium at the required bonding temperature. In addition, the lower strength of the protective can materials at elevated temperatures will result in the can reducing much more than the molybdenum and niobium components⁽¹¹⁾; consequently, possible rupture of the protective can may occur or the fabricated fuel element will display poor dimensional properties. In an attempt to eliminate these problems, some work has been previously done on bonding of these materials by solid-state-diffusion processes involving the use of die pressures to obtain bonding⁽¹²⁾; however, none of those processes have been proven applicable for cladding fuel elements with molybdenum or niobium.

Many of the problems associated with conventional fabrication techniques for cladding with molybdenum and niobium can be avoided by pressure bonding of these elements with a high pressure applied to the cladding with an inert gas at elevated temperatures. Pressure can be applied directly on an edge-welded element or on a canned assembly.⁽¹³⁾ The edge-welding technique has the obvious advantage that no contamination of the specimen by the jacketing material is incurred; however, evacuation of this type of specimen is extremely difficult if an electron-beam welding unit is not available.

Jacketing the specimen offers a simple technique for evacuation and eliminates the need for fusion edge welding of the specimen to be bonded. By utilizing a jacketing material and appropriate spacers specimens of complex configurations, such as flat-plate subassemblies, can be fabricated in one step by this technique.

Pressure bonding is an attractive method of bonding brittle materials because a minimum amount of deformation is required. As a result, the possibility of extruding any of the hard, abrasive core particles through the cladding is minimized. In addition, the dispersion characteristics of dispersion-type cores are not altered during the bonding operation.

The program described in this report consisted of a study of pressure-bonding conditions of temperature, time, and pressure, a study of the surface preparation of surfaces for bonding, and an investigation of suitable barrier materials to prevent reaction between the specimen and bonding container. Discussion of limited study of edge-welded specimens is also included.

Materials

Initial investigations on the self-bonding of niobium were conducted with vacuum-arc-melted material procured from E. I. duPont de Nemours & Company, Inc. The niobium was supplied in sheet form with thicknesses of 0.010, 0.040, and 0.100 in. Later studies utilized electron-beam-melted material supplied by Temescal Metallurgical Corporation. This material was supplied in 3-in. -diameter ingots weighing approximately 10 lb each. Fabrication of these ingots into rod and sheet was accomplished at Battelle by cold forging and rolling without intermediate annealing.

In addition to the sheet and ingots described above, two sizes of niobium tubing were procured from Fansteel Metallurgical Corporation. Both a 0.175- and a 0.500-in. -OD tubing with a 0.015-in. wall thickness were required for the fabrication of slug-type elements in the final part of the study. Chemical analyses of the niobium utilized in this study are included in Table 1.

The major portion of molybdenum employed was obtained from the Fansteel Metallurgical Corporation. The arc-melted material was supplied in sheet form at thicknesses of 0.020, 0.040, 0.060, and 0.100 in. Later studies utilized molybdenum from General Electric Lamp Metals and Components Division. This was a powder-metallurgical product with high ductility at room temperature. Chemical analyses of both molybdenum products used are given in Table 2.

The uranium dioxide, uranium carbide, and dispersion cores were prepared at Battelle. These materials were sintered to near fully density with the exception of the uranium carbide cores which were supplied at approximately 60 per cent of theoretical density.

Gas-Pressure-Bonding Process

The gas-pressure-bonding process consists essentially of bonding materials through the action of high gas pressures at elevated temperatures. In order to be effective it is necessary to isolate the bond areas from the high-pressure environment, usually either by jacketing the assembly in a welded gastight envelope or by edge welding the assembly. The evacuation of assemblies prior to final sealing further increases the effectiveness of gas-pressure bonding since bond-surface contamination from entrapped air is minimized.

TABLE 1. AVERAGE CHEMICAL COMPOSITIONS OF NIOBIUM UTILIZED IN THESE STUDIES^(a)

Impurity	Amount of Impurity Present ^(b) , ppm		
	Arc Melted	Electron-Beam Melted	Tubing
Oxygen	320	120	339
Hydrogen	2.5	1	2.6
Carbon	30	40	130
Tantalum	620	1000	900
Nitrogen	69	40	150
Calcium	20	10	10
Copper	Trace	N.D.	N.D.
Chromium	10	N.D.	30
Iron	30	N.D.	400
Magnesium	Trace	Trace	Trace
Molybdenum	30	30	30
Nickel	30	N.D.	80
Silicon	100	N.D.	N.D.
Titanium	30	30	100
Zirconium	10	30	200

(a) DPH hardnesses for these materials after annealing were: arc melted, 98; electron-beam melted, 83; and tubing, 125.

(b) N.D. indicates element was not detected.

TABLE 2. AVERAGE CHEMICAL COMPOSITION OF MOLYBDENUM UTILIZED IN THESE STUDIES

Impurity	Amount of Impurity Present, ppm	
	Arc Cast	Powder
Oxygen	41	18
Hydrogen	2.2	1
Carbon	220	10
Nitrogen	20	20
Calcium	50	50
Chromium	50	10
Copper	10	10
Iron	30	40
Magnesium	Trace	Trace
Nickel	70	30
Silicon	30	10
Aluminum	50	10

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FIGURE 1. SECTIONAL VIEW OF A HIGH-PRESSURE COLD-WALL AUTOCLAVE WITH SPIRAL-GROOVED LINER

With the high gas pressure acting only on the exterior of the assemblies a state of compression is created, and this compression, coupled with a temperature high enough to lower sufficiently the compressive yield strengths of the materials, causes plastic flow of the bonding components. This material flow forces the mating faces of the bonding assembly into intimate contact, permitting diffusion to occur across the original interfaces and thus establishing the desired bond.

In order to attain sufficiently high gas pressures and temperatures, a cold-wall autoclave is required for the gas-pressure-bonding process.⁽¹⁴⁾ A cross-sectional drawing of a typical cold autoclave is shown in Figure 1. The body of this autoclave was machined from a billet of Type 410 stainless steel and equipped with modified Bridgman closures providing the necessary connections for pressure lines, thermocouples, and electrodes. A molybdenum-wound furnace is located in the center of the autoclave to provide the temperatures required for bonding. Bonding assemblies are placed within the furnace tube along with a refractory material such as sand, microquartz, or bubbled alumina which serves to minimize convection currents. Similar refractory material is also packed around the periphery of the furnace tube to minimize convective heat transfer from the furnace to the wall of the autoclave. Temperature control for temperatures up to 2400 F is maintained by the use of Chromel-Alumel thermocouples located at three points along the specimens. When temperatures above 2400 F are required platinum-platinum-rhodium or tungsten-rhenium thermocouples are employed. Helium is utilized as the pressurizing medium; pressure is increased to the maximum design value of 10,000 psi as the specimen is being brought to temperature.

The success of the gas-pressure-bonding process with a given material combination is dependent on the surface preparation prior to bonding and the proper combination of time, temperature, and pressure. Since only slight deformation occurs during the process it is necessary to remove all surface films and foreign matter prior to assembly. Such contaminants will not be disrupted during subsequent bonding.^(15,16) The combination of temperature and pressure must be such that sufficient plastic flow of material will occur to provide as nearly complete contact of the bonding surfaces as possible. It is only with such intimate contact that sufficient diffusion will occur to produce the high-integrity bonds desired in a reasonable length of time. Generally, the maximum pressure of the system is utilized in order that a lower bonding temperature or a shorter bonding time will be possible. Minimizing the temperature or time is advantageous in that excessive grain size and contamination can be avoided. Adjustment of these two parameters, however, must be within the conditions required to promote sufficient diffusion to establish the solid-phase bonds.

EXPERIMENTAL PROCEDURE

Specimen Preparation

Specimen Design

Evaluation of bonding parameters, surface preparations, and spacer materials were conducted with specimens consisting of two simple flat plates placed against each other. These plates measured 1-1/2-in. square and varied in thickness according to the fabrication history of the particular specimen. In general, these specimens were pressure

bonded in a container similar to that shown in Figure 2. Design and fabrication of such a container is described elsewhere in the literature.⁽¹⁴⁾

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FIGURE 2. DESIGN OF CONTAINER USED FOR PRESSURE-BONDED SPECIMENS

A limited number of specimens were prepared by fusion edge welding. These specimens were welded in a helium atmosphere while clamped tightly between copper cooling blocks. Evacuation of these elements was a formidable problem until very late in the program when an electron-beam welder was placed in operation. This permitted final welding of the element at a pressure below 10^{-4} mm of mercury.

Quantitative values of bond strengths for niobium self-bonds were obtained by employing a standard nonferrous tensile bar⁽¹⁷⁾ as shown in Figure 3. Bonding assemblies consisting of two abutting niobium rods were encased in a tubular jacket of Type 304 stainless steel. Each rod measured 1/2 in. in diameter by 2-1/4 in. long. Standards were prepared in the same manner by utilizing a 4-1/2-in.-long rod containing no bond. After completing the pressure-bonding cycle the rods were machined to the dimensions shown in Figure 3. Due to the inherent lack of ductility of molybdenum similar tests were not run on this material.

Cleaning and Assembly of Components

All molybdenum and niobium components were carefully cleaned by a standard degreasing process. Included in this cycle were successive scrubbing in acetone, methyl ethyl ketone, and ethyl alcohol. An additional ethyl alcohol rinse was provided to insure clean surfaces. If surface preparation requiring a pickling treatment was employed, the pickling was done just prior to the final ethyl alcohol rinse. Components were blown dry with filtered, compressed air to eliminate the pickup of lint associated with most drying materials. Rubber gloves were used throughout the cleaning and assembling operations.

Figure 4 shows the components of a typical specimen prepared for assembly. At assembly, the specimen is sandwiched between the two spacers and inserted into the

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FIGURE 3. DESIGN OF TENSILE SPECIMENS UTILIZED TO TEST BOND STRENGTH

1X

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FIGURE 4. COMPONENTS REQUIRED FOR AN EXPERIMENTAL PRESSURE-BONDING SPECIMEN

bonding container, the end plug positioned, and the final welds made by inert-gas-shielded arc techniques. Leak testing of the assembly was accomplished by pressurizing with helium followed by helium detection. After bonding, the ends of the container were cut off and the container and spacers were manually stripped from the specimen.

Testing Procedures

All specimens were subjected to extensive destructive testing. Coupons 1/4 in. wide were taken from both longitudinal and transverse directions in the specimens for metallographic examination, peel tests, and bend tests. Remaining sections of the specimens were used to make spot chemical analyses and for postbonding thermal and mechanical treatments. Niobium-clad fuel elements prepared later in the program were additionally evaluated by burst testing and thermal cycling.

Metallographic Examination

Cross-sectional samples of the specimens were removed for metallographic examination of bond quality and possible cladding-spacer reaction. Light microscopes with bright-field illumination were used with magnifications of 100, 250, and 500X. The samples were examined in the as-polished condition and after etching in a solution of 50 cm³ lactic acid-50 cm³ nitric acid-3 cm³ hydrofluoric acid for niobium and in a modified Murakami solution for molybdenum. Bond interfaces were examined for inclusions, separations, and extent of grain growth across the original interface. The base material was examined for the extent of recrystallization, excessive grain growth, and the presence of a second phase due to reactions with container or spacer materials included in many of the specimens between the can and cladding to prevent reaction.

Peel Tests of Bonds

Cross-sectional portions of the specimens were peel tested to determine the relative strength of the bonds. The bond strength was determined by driving a chisel into a V-notch which had been filed into the bond interface at the edge of the specimen. A good test was considered one in which rupture of the base material occurred instead of separation of the bond.

Bend Tests

Bend-test samples were prepared from each specimen to determine the ductility and relative bond strength after gas-pressure bonding. The bend tests were conducted by successively bending the sample through a 90-deg angle on dies with decreasing radii until failure occurred. The T-value for each test was equal to the radius of the die divided by the thickness of the sample. In many molybdenum specimens it was necessary to measure the angle of deflection before fracture due to the lack of ductility at room temperature. Specimens were examined to determine if any bond-line separation had occurred, which would indicate a weak bond.

Chemical Analysis

Periodic chemical analyses were performed to determine any change in composition of the cladding during bonding due to reactions with containers, spacers, or the autoclave atmosphere. Vacuum-fusion techniques were used to determine the oxygen and hydrogen contents; the micro-Kjeldahl technique was employed for nitrogen determination. Carbon contents were determined by analytical chemistry techniques, while all remaining elements were examined by spectrographic analysis.

Burst Tests

In the later stages of the program niobium-clad flat-plate fuel elements were prepared. The burst test was employed for a portion of the evaluation of these specimens. This test is described in detail elsewhere in the literature.⁽¹³⁾ Compartments of elements were burst tested in order to indicate the relative strength and ductility of the cladding and strength of the bond. In this test, one compartment of an element was subjected to increasing internal pressure until rupture of the cladding occurred. The pressure required to produce rupture and the amount of deflection of the cladding before rupture were recorded. It was also noted if any of the bonds between the cladding plates and the ribs of the picture frame failed during the test. In event of a bond failure the area was carefully marked and metallographic examination made in that area.

Thermal-Cycling Tests

Fuel elements containing uranium dioxide were thermal cycled between room temperature and 1800 F in 30-min intervals. Specimens were capsulated in Vycor with an argon atmosphere to minimize oxidation. Specimens were examined for changes in dimensions, configuration, bond quality, and grain size. Visual examination for obvious oxidation was also conducted.

STUDIES OF THE SELF-BONDING OF NIOBIUM

Bonding-Parameter Study

The gas-pressure-bonding operation is dependent upon successfully flowing the bonding surfaces into intimate contact, permitting diffusion and grain growth to occur across the original interface. To accomplish this the correct combination of time, temperature, and pressure must be determined. To insure that a minimum amount of contamination is introduced into the specimen and that excessive grain sizes are not encountered after bonding, it is desirable to hold the time and temperature to a minimum. It is obvious that to accomplish this the pressure must be held at a maximum or the design pressure of 10,000 psi.

Other work has shown that niobium softens rapidly above 1600 F^(11,18) and that recrystallization may initiate as low as 1425 F for high-purity material⁽¹⁹⁾. These data indicated that initial efforts for self-bonding should be made at temperatures near 1600 F

for relatively long periods of time and that further parameter studies should be determined from these results.

Previous studies on other materials had shown that the condition of the bonding surfaces had a pronounced effect on bonding.^(13,20) For initial studies it was decided that a shaper-finished surface should be relatively free of contamination and possess sufficient roughness to study the flow of the niobium at a given set of bonding parameters. Specimens prepared by the above technique were pressure bonded at temperatures of 1650 to 2200 F for times of 1 to 6 hr. Evaluations of specimens were based on metallographic examination, peel tests of bonds, bend tests, and composition analysis.

The results of the metallographic bond evaluations and bend- and peel-test results are shown in Table 3. Examination of these data indicated that bonding temperatures below 1900 F failed to produce even a mechanical bond between the niobium plates. Insufficient flow had occurred at these temperatures to close the macrovoids and to permit intimate contact. No evidence of recrystallization was noted, indicating that higher bonding temperatures would be required since recrystallization is believed to be a major prerequisite in solid-state bonding.⁽²¹⁾

Specimens bonded at temperatures between 1900 and 2100 F exhibit mechanical strength as indicated in Table 3. However, the presence of macrovoids was still detected in metallography even though recrystallization appeared complete. It is felt that at this point an increase in the operating pressure of 10,000 psi to some greater level would have been the most desirable technique for overcoming the resistance to flow. This would limit the contamination problem and minimize the grain size which increases rapidly at temperatures greater than 2000 F.^(1,22) However, since maximum design pressure of the autoclave was already being employed, it was necessary to increase the temperature to reduce the yield strength to a more favorable level.

As can be noted in Table 3, specimens bonded at temperatures of 2100 F or greater revealed sufficient flow to close macrovoids and produce mechanically strong bonds. In areas free of contamination excellent grain growth was obtained across the original interface. No separation at the bond interface could be initiated during either bend or peel tests.

Specimens bonded early in this study revealed very brittle behavior as evidenced by the bend-test results shown in Table 3. Chemical analyses for interstitial impurities were made to determine if any significant increase had occurred during the bonding operation. The results of these tests are summarized in Table 4. It was noted that significant quantities of hydrogen were introduced into the niobium during the bonding operation which could have a detrimental effect on the ductility.^(23,24) Changes in the composition levels of the other interstitials were deemed insignificant.

Other work has shown that hydrogen is readily removed by heating to 1800 F in vacuum.⁽²³⁾ To confirm the premise that the embrittlement stemmed from the hydrogen pickup, sections of each of the specimens were vacuum annealed at 1800 F for 1 hr at a pressure of 10^{-5} mm of mercury. Bend tests and hydrogen analysis for these specimens after annealing are given in Table 5. These results show that complete ductility was restored to the specimens by removal of the hydrogen during vacuum annealing. This treatment permits the salvage of specimens which would otherwise be useless due to the severe embrittlement; however, any postbonding heat treatments are undesirable and it was deemed necessary to eliminate the source of the hydrogen contamination.

TABLE 3. RESULTS OF TESTS ON SPECIMENS PREPARED FOR BONDING-PARAMETER INVESTIGATION

All surfaces were prepared by machining to 125 μ in., rms.

Bonding Conditions			Metallographic Examinations		Bend Test		V-Notch Test
Temperature, F	Time, hr	Pressure, psi	Bond Quality	Recrystallization	T-Value	Borderline Separation	Borderline Separation
1650	6	10,000	No bonding	None	>20	Complete	Complete
1750	6	10,000	No bonding	Spotty	>20	Complete	Complete
1800	6	10,000	No bonding	25 per cent	>20	Complete	Complete
1900	4	10,000	Macrovoids, no grain growth	75 per cent	>20	Partial	Complete
2000	3	10,000	Macrovoids, partial grain growth	Complete	<1 ^(a)	None	None
2100	1	10,000	Intimate contact, partial grain growth	Complete	<1	None	None
2100	3	10,000	Intimate contact, complete grain growth	Complete	<1	None	None
2200	1	10,000	Intimate contact, fair grain growth	Complete	<1	None	None
2200	3	10,000	Intimate contact, complete grain growth	Complete	<1	None	None

(a) These and subsequent specimens were bonded employing autoclave alteration as discussed on page 14.

TABLE 4. CHEMICAL ANALYSES FOR INTERSTITIAL ELEMENTS IN SPECIMENS PREPARED FOR BONDING-PARAMETER INVESTIGATION

Bonding Parameters			Net Changes in Content of Elements Shown During Bonding, ppm			
Temperature, F	Time, hr	Pressure, psi	Oxygen	Hydrogen	Nitrogen	Carbon
1650	6	10,000	0	+220	+20	+10
1800	6	10,000	+20	+196	+20	+10
1900	4	10,000	0	+202	+10	+10
2000	3	10,000	+40	+45	+50	+30
2100	3	10,000	+40	+56	+30	+30

TABLE 5. HYDROGEN CONTENTS AND BEND-TEST RESULTS AFTER VACUUM ANNEALING AT 1800 F

Specimens are the same as those reported in Table 4.

Specimen Bonding Temperature, F	Hydrogen, ppm	Bend Test, T-value
1650	1.2	<1 ^(a)
1800	<1	<1
1900	1.0	<1
2000	2.2	<1
2100	<1	<1

(a) Specimen could be bent 180 deg without cracking.

In an effort to trace the source of the hydrogen chemical analyses were obtained for the helium gas employed for the pressurizing medium. Table 6 shows the composition of the helium before and after use in the autoclave. It will be noted that there was an apparent pickup in water vapor during the bonding cycle. Further examination revealed that the refractory material employed in the autoclave to reduce convective currents could adsorb up to 3 per cent water vapor if exposed to moisture-laden air. Accordingly, all of the refractory material was removed and baked to remove all moisture. The material was then promptly sealed in airtight containers until used. As a further precaution an argon blanket was placed over the opening of the autoclave during all loading and unloading of the autoclave. A graphite crucible was included in the autoclave below the specimens which contained zirconium turnings which acted as a getter for any impurities within the autoclave gas. Specimens gas-pressure bonded after these revisions had been included in the autoclave showed excellent ductility as indicated in the latter portion of Table 3.

TABLE 6. CHEMICAL ANALYSIS OF HELIUM USED IN AUTOCLAVE

Impurity	Amount of Impurity Present, ppm	
	As Received ^(a)	After Bonding
Hydrogen	0.03	<20
Oxygen	None	<30
Nitrogen	2	<30
CO ₂	0.6	<20
CH ₄	0.01	<50
H ₂ O	None	300

(a) Analysis supplied by Bureau of Mines.

Surface-Preparation Study

The bonding-parameter study indicated that for simple flat-plate-type specimens satisfactory flow and self-diffusion could be obtained at 2100 F and 10,000 psi for 3 hr. However, during that investigation the shaper-finished bonding surfaces employed did not produce bonds of a satisfactory nature. Previous work has indicated the important role of proper surface preparation during gas-pressure bonding. (13-16) In view of the pronounced effect of surface preparation on bond quality demonstrated in those earlier studies on other systems, it was deemed necessary to determine the effects of various surface-finishing techniques on the niobium bond quality. Finishing techniques investigated included cold rolling, belt abrading, surface grinding, machining, and etching in both acidic and caustic solutions. In each case, previous experience obtained from earlier work was utilized to optimize each technique as applied to niobium. Pressure bonding was performed at 2100 F and 10,000 psi for 3 hr; specimens were bonded in containers so that evacuation of the assembly could be readily accomplished. Test results for these specimens are summarized in Table 7.

Cold-Rolled Surfaces

From a cost standpoint, the most desirable surface for bonding would be one which can be cleaned without metal removal. Specimens fabricated from carefully prepared cold-rolled stock showed very poor bonding as evidenced by the complete failure of the bond during peel testing. Metallographic examinations indicated the presence of continuous contamination along the bond interface. It is believed that the contamination is due to tenacious oxide surface films and to foreign particles which may be embedded in the surface during the cold-rolling operation.

Mechanical Surface Finishing

The results obtained with cold-rolled surfaces indicated it would be necessary to remove metal from the surface to produce a clean bonding surface. Experience obtained with other metal systems indicated that abrasive and machining techniques produced suitable bonding surfaces. Accordingly, surface grinding, belt-abrading, milling, and shaper finishing were thoroughly investigated.

Specimens were prepared by removing 0.002 in. per side by surface grinding under a coolant with various grades of silicon carbide. Examination of specimens bonded with niobium prepared in this manner revealed that severe contamination was present due to embedded grit. The relatively soft niobium readily picks up any foreign particles present and retains them in the surface.

Similar results were obtained with belt-abraded bonding surfaces. The abrading was conducted according to developed techniques under a flood of sulfonated oil which acted as both a coolant and lubricant. Although this technique was successful in eliminating embedded grit in Zircaloy⁽¹³⁾, it did not show any measurable improvement for niobium.

Milling and shaping were studied as typical machining operations which might be utilized to finish bonding surfaces. Due to the importance of using a lubricant during

TABLE 7. EVALUATIONS OF SURFACE-PREPARATION SPECIMENS

All specimens were pressure bonded at 2100 F and 10,000 psi for 3 hr.

Surface Preparation	Bend Test	V-Notch Test	Metallographic Examination
Cold-rolled surfaces	Partial separation	Complete separation	Continuous contamination in bond interface; little or no grain across bond interface
Abrasive finishing			
Surface grinding, 80 grit	Partial separation	Partial separation	Large pieces of embedded grit; little or no grain growth across bond interface
Surface grinding, 400 grit	Partial separation	Partial separation	Intermittent areas of contamination; scattered area of growth across bond interface
Surface grinding, 600 grit	Partial separation	Partial separation	Continuous occurrence of embedded grit; little or no grain growth across interface
Belt abrading, 40 grit	Partial separation	Complete separation	Badly contaminated with embedded grit; no grain growth across interface
Belt abrading, 60 grit	Partial separation	Partial separation	Badly contaminated with embedded grit; little or no grain growth across interface
Machining treatments			
Shaping, 60 μ in., rms	No separation	No separation	Light, continuous contamination; 50 per cent grain growth across an irregular interface
Shaping, 120 μ in., rms	No separation	No separation	Intermittent areas of contamination; grain growth in areas where contamination was absent
Shaping, 150 μ in., rms	No separation	No separation	Alternate areas of contamination and perfect bonding
Milling, 60 μ in., rms	No separation	No separation	Light, continuous contamination; 40 per cent grain growth across an irregular interface
Milling, 120 μ in., rms	No separation	No separation	Intermittent areas of contamination; grain growth in area where contamination was absent
Milling, 150 μ in., rms	No separation	No separation	Alternate areas of contamination and perfect bonding
Chemical treatments			
10 per cent HF in water	No separation	Partial separation	Light, continuous contamination; fair grain growth
Saturated NaOH	Partial separation	Partial separation	Continuous contamination with only 5 per cent grain growth
20 per cent HF in water	No separation	No separation	Very light present in most areas; 15 per cent grain growth

TABLE 7. (Continued)

Surface Preparation	Bend Test	V-Notch Test	Metallographic Examination
Chemical treatments (continued)			
95 per cent H_2SO_4 -4.5 per cent HNO_3 -0.5 per cent HF-18.8 g per liter Cr_2O_3	No separation	No separation	Light, continuous contamination; 5 per cent grain growth in scattered areas
Ryan's solutions ^(a)	No separation	No separation	Continuous contamination with only 5 per cent grain growth across interface
30 parts lactic acid, 10 parts HNO_3 , 10 parts HF	No separation	No separation	Discontinuous contamination along interface; 70 per cent or more grain growth
65 per cent HNO_3 -35 per cent HF	No separation	No separation	No evidence of appreciable contamination; grain growth across entire interface
Machining plus pickling			
Shaping, 60 μ in., rms, plus 65 per cent HNO_3 -35 per cent HF	No separation	No separation	Clean interface and complete grain growth across bond line
Shaping, 150 μ in., rms plus 65 per cent HNO_3 -35 per cent HF	No separation	No separation	No evidence of contamination and complete grain growth across bond interface

(a) Ryan's solutions consist of an aqueous solution of 10 per cent NaOH and 5 per cent potassium permanganate, followed by dipping in an aqueous solution with 15 per cent H_2SO_4 , 15 per cent HCl, and 10 per cent chromic acid.

machining⁽²⁵⁾, water-soluble oils and carbon tetrachloride were employed. Care was taken to employ sharp tools with feeds and speeds consistent with good machining practices. Surface roughness of each specimen was carefully controlled so that this variable might be better evaluated.

No apparent differences between shaped and milled surfaces of comparable surface roughness were observed. Specimens machined to surface roughness of 60 $\mu\text{in.}$, rms, showed evidence of light, continuous contamination along an irregular interface after bonding. Specimens with surface roughness of 150 $\mu\text{in.}$, rms, showed alternate areas of perfect bonding and no grain growth due to contamination. Apparently, the effective pressure at the peaks of the machined surface is quite high permitting extensive deformation into the opposite plate. As deformation occurs, any contamination present is pushed back into the trough of the machined surface causing alternate areas of no contamination and high contamination. The presence of contamination is attributed to niobium's tendency to seize and gall during machining, thereby allowing foreign matter to be trapped within the surface of the material. Material so entrapped could not be removed by standard cleaning procedures used prior to bonding.

These specimens demonstrate that surface roughness can play an important role in bond quality if machining is required to form a particular component of a fuel element. It has been shown that pickling the surface in the proper solution after machining produced bonds of excellent quality. This will be discussed in detail in the following section.

Chemical Surface Finishing

Mechanical surface treatments as described above failed to produce satisfactory bonding surfaces due to the entrapping of foreign particles during such operations. Also such treatments may not be applicable for such shapes as the inside diameter of a tube. This problem can be overcome by employing chemical surface-finishing techniques, provided, of course, that the proper pickling solution is employed.

The chemical treatments investigated are summarized in Table 7. Each treatment employed was selected on the basis that it had been successfully used for some cleaning application with niobium.^(11,18,26,27) Special efforts were made to prevent formation of residue on the surfaces during pickling which might interfere with subsequent bonding.

Results of the specimens prepared for this investigation showed that in general acidic etching reagents produced surfaces which could be bonded with good mechanical strength. However, of the etching solutions employed only the solution consisting of 65 parts HNO_3 -35 parts HF produced surfaces which yielded consistently sound metallurgical bonds after gas-pressure bonding. It is believed the reason for the success obtained with this pickling solution is that it dissolves all known oxides of niobium and also etches the base metal.⁽²⁷⁾ Figure 5 shows the type of bond which can be obtained by this technique. It was found that the removal of 0.001 in. per side was sufficient to produce satisfactory bonding surfaces; this could be accomplished in approximately 1 min at a temperature of 120 F.

Figure 6 is presented to demonstrate the pronounced effect of proper surface preparation on pressure bonding of niobium. The specimen, in this case, consisted of a composite of four cold-rolled platelets. The two center platelets were pickled in a solution of 65 parts HNO_3 -35 parts HF, whereas the two other plates were only degreased

100X

N59713

FIGURE 5. EXAMPLE OF TYPICAL NIOBIUM SELF - BOND OBTAINED WITH PROPERLY PREPARED SURFACES

100X

N61093

FIGURE 6. PHOTOMICROGRAPH SHOWING THE PRONOUNCED EFFECT OF PROPER SURFACE PREPARATION

Specimen consisted of a composite of four plates. The two inner plates were etched in a solution of 65 parts HNO_3 -35 parts HF, while the outer plates were only degreased prior to bonding.

and cleaned after cold rolling. Note that the two outer interfaces exhibit heavy contamination while the central bond shows no contamination. This contrast indicates the degree of contamination still present on the surfaces of cold-rolled niobium even after a thorough degreasing and cleaning. It should also be noted that only one of the mating faces in the outer bonds was initially contaminated.

As previously discussed, surface-preparation studies showed that machined surfaces produce erratic bonding results and as such are not suitable for use. However, it is sometimes necessary to fabricate a given shape by machining before pressure bonding is conducted. It was therefore necessary to evaluate a combination surface preparation of machining followed by pickling in the 65 part HNO_3 -35 part HF solution. As can be noted in Table 7 excellent results were obtained. Figure 7 shows the bond quality attainable with niobium surfaces that were pickled after machining. This is particularly important when piece-component fuel elements are being prepared.

In order to evaluate the integrity of the niobium self-bonds obtained with the optimum surface preparation, tensile tests were performed on both bonded specimens and a set of annealed niobium control specimens. Results of these specimens are tabulated in Table 8. All specimens were tested in a Baldwin-Southwark tensile-testing machine at a strain rate of 0.05 per min. Note that 2100 F appears to be the very minimum bonding temperature at this pressure. Figure 8 shows a comparison of a bonded specimen and a control specimen after tensile testing. Note the similar location and appearance of fracture indicating no evidence of weakness at the bond interface.

TABLE 8. TENSILE-TEST RESULTS

Strain rate was 0.05 per min.

Bonding Conditions			Ultimate Strength, psi	Reduction in Area, per cent
Temperature, F	Time, hr	Pressure, psi		
2000	3	10,000	15,000	--
2100	3	10,000	44,000	92
2300	3	10,000	41,000	89
2100	3	(a)	42,000	91

(a) Control specimen was annealed at 2100 F for 3 hr but contained no bond.

Study of Bondline Voids

Although perfect metallurgical bonds can be obtained as indicated in Figures 5 through 7, there are frequent instances where small, isolated voids remain at the original interface; Figure 9 shows a representative area from a bond of this type. It is evident that the presence of these voids did not impair grain growth across the original bond interface since they appear within the grains. Such an effect has also been observed during solid-phase bonding of copper.⁽²⁸⁾ In copper this can be overcome by increasing the pressure at a given temperature indicating that the effective pressure for small-void closure must be greater than that necessary to initiate normal deformation^(28,29). Apparently at bonding temperatures the driving force for grain growth is so great that insufficient time is provided to permit the large excess of vacancies to be absorbed by the grain boundaries.⁽³⁰⁾ Once contained within a grain, the removal of the void must be completed by the relatively slow process of diffusion.

100X

N69304

FIGURE 7. TYPICAL BOND OBTAINED BETWEEN SURFACES THAT HAVE BEEN MACHINED AND THEN ETCHED IN 65 PARTS HNO_3 -35 PARTS HF

100X

N59712

FIGURE 9. PRESSURE-BONDED NIOBIUM SPECIMEN SHOWING SMALL VOIDS CONTAINED COMPLETELY WITHIN GRAINS

1X

RM15939

FIGURE 8. TENSILE-TESTED CONTROL AND PRESSURE-BONDED SPECIMENS

Top specimen was machined from annealed rod, while lower specimen was machined from rod that was bonded from two shorter pieces of rod. Note similarity in fracture and ductility.

This theory was somewhat substantiated by high-temperature, vacuum heat treatments. Specimens containing voids were annealed for 1, 3, and 8 hr at 3600 F at a pressure 10^{-5} mm of mercury. Examination of these specimens showed that the size and number of voids were decreased as the annealing time was increased indicating a diffusion-dependent process.

Since the results of the previously described experiment proved only that the apparent voids could be removed by diffusion it was deemed necessary to substantiate that the apparent voids were not contaminants which would diffuse away in a similar manner. Flat-plate specimens with bonding surfaces properly cleaned by pickling and with as-rolled surfaces were bonded at 2100 F and 10,000 psi for 3 hr. After bonding, the specimens were sectioned and one-half of each was examined in the as-bonded condition while the other section was cold rolled 25 per cent and annealed at 2100 F for 1 hr to produce recrystallization of the niobium. Examination of the as-bonded sections revealed a significant amount of contamination in the as-rolled specimen and only occasional contamination or voids within the grains of the pickled specimen. After the cold-rolling and recrystallization treatment, the contamination was still present in the bond line of the as-rolled specimen. The bond line could not be detected in the pickled specimen after this treatment; consequently, it is apparent that the spherical areas within the grains are in fact voids and not contamination.

The results of these experiments would indicate that some niobium grains should be expected to contain voids when bonded under these conditions. As previously mentioned, this problem was overcome in copper by applying greater pressure during the bonding cycle. Unfortunately, due to the design limitations the equipment used in this study higher pressures could not be explored. The procurement of an autoclave for higher operating pressures is being considered; such equipment would permit using high pressures at high temperatures to achieve metallurgical bonding with virtually any ultra-high-strength materials.

Investigation of Spacer Materials

The role of the spacer between the can and specimen was discussed earlier. Additional uses for spacers include separators between specimens and the formation of channels in flat-plate sub-assemblies when the latter are being bonded in a one step operation. These uses point up the obvious requirements for a spacer, namely, non-reactive with the niobium and one that can be easily removed by chemical means if it is being used to form a coolant channel.

Numerous metallic and ceramic materials were employed as spacers or spacer coatings in the program. Since this study was conducted simultaneously with the bonding parameter investigation, some materials were employed at the lower bonding temperatures which could not be considered at higher temperatures. All materials and bonding conditions are included in this report since the compatibility data may be useful in other applications. Table 9 summarizes the results of these investigations. Spot chemical analyses made for specific elements are given in Table 10.

TABLE 9. RESULTS OF THE INVESTIGATION OF SPACER MATERIALS FOR NIOBIUM

Spacer Material	Bonding Conditions			Bend Test, T-value	Peel Test ^(a)	Metallographic Examination
	Temperature, F	Time, hr	Pressure, psi			
Copper	1650	6	10,000	<1	Easily separated	Small diffusion zone formed
Ti-Namel	1650	6	10,000	<1	Easily separated	Small diffusion zone formed
Fecral	1750	6	10,000	<1	Easily separated	No apparent reaction
	1800	6	10,000	2.5	Easily separated	Very slight reaction
	1900	4	10,000	9	Easily separated	Small diffusion zone formed; presence of second phase detected
	2100	3	10,000	>20	Separable	3-mil diffusion zone; heavy occurrence of second phase
Iron	1800	6	10,000	2.5	Easily separated	1-mil diffusion zone formed
	2100	3	10,000	9	Difficult to separate	3-mil diffusion zone formed; second phase present
Nickel	1750	6	10,000	<1	Easily separated	Small diffusion zone formed
	1800	6	10,000	2.5	Separable	0.8-mil diffusion zone
Type 304 stainless steel	1800	6	10,000	<1	Separable	1.5-mil diffusion zone
	2000	3	10,000	2.5	Separable	3-mil diffusion zone; appearance of a second phase
	2100	3	10,000	2.5	Separable	3-mil diffusion zone; heavy second phase near zone
	2300	3	10,000	>20	Difficult	Severely alloyed; heavy second phase throughout
Type 304L stainless steel	2100	3	10,000	1.5	Separable	3-mil diffusion zone; little second phase apparent
Molybdenum	2100	3	10,000	2.5	Easily separated	Slight interdiffusion
	2300	3	10,000	9	Difficult	Appreciable alloying
Tungsten	2100	3	10,000	2.5	Easily separated	Slight alloying
Tantalum	2100	3	10,000	1	Separable	Slight interdiffusion
	2300	3	10,000	2.5	Difficult	Appreciable alloying
Carbon	2000	3	10,000	1	Very easily separated	Carbide formation near surface
	2100	3	10,000	9	Very easily separated	Minimum of 3-mil layer of carbides formed
Hard-lime window glass	2100	3	10,000	20	Very difficult to remove	General precipitate throughout structure
Vycor	2100	3	10,000	20	Very difficult to remove	General precipitate throughout structure
Alumina	2100	3	10,000	<1	Difficult	General precipitate throughout structure
Titania	2100	3	10,000	>20	Difficult	General precipitate throughout structure
Alumina plus titania	2100	3	10,000	9	Difficult	General precipitate throughout structure
Magnesia	2100	3	10,000	>20	Easily removed	General precipitate throughout structure
Enamel ^(b)	2100	3	10,000	9	Difficult	Grain-boundary precipitate
Uranium dioxide	2100	3	10,000	<1	Easily removed	No reaction
	2400	3	10,000	<1	Easily removed	No reaction

(a) A measure of how readily the spacer can be removed from the niobium.

(b) Composition of enamel is 9.8 per cent calcium oxide-26.4 per cent silica-6.4 per cent alumina-57.4 per cent barium oxide.

TABLE 10. CHEMICAL ANALYSIS FOR IMPURITIES INTRODUCED BY SPACER MATERIALS DURING BONDING

All specimens were bonded 3 hr at 10,000 psi at the temperatures shown.

Spacer Material	Bonding Temperature, F	Impurity Analysis	
		Element	Net Change in Base Material, ppm
Iron	2100	Iron	+300
	2300	Iron	+1100
Molybdenum	2100	Molybdenum	+150
	2300	Molybdenum	+1000
Tungsten	2300	Tungsten	+1000
Type 304 stainless steel	2100	Iron	+300
		Chromium	+400
		Nickel	+100
		Carbon	+225
		Carbon	+100
Type 304L stainless steel		Carbon	+500
Graphite	2100	Oxygen	+50
Uranium dioxide	2100	Uranium	Nil
		Oxygen	Nil
	2300	Uranium	Nil
		Oxygen	+50
		Uranium	Nil
Silica	2100	Silicon	+100
		Oxygen	+1200
		Oxygen	+900
Magnesia		Oxygen	+600
Alumina	2100	Oxygen	+2200
Hard-lime window glass	2100	Oxygen	+900
Vycor	2100	Oxygen	

Metallic Materials

In general the metallic spacers or barriers did not prove completely successful in this application. At temperatures to 2100 F Type 304 stainless steel showed only limited reaction with the niobium as had been found by others.⁽³¹⁾ However, the presence of a second phase was noted around the periphery of the niobium, especially in the grain boundaries. This precipitate was caused by the diffusion of carbon from the stainless steel into the niobium. A noticeable reduction in quantity of precipitate was noted when Type 304L (low carbon) stainless steel was employed. This material might be acceptable at 2100 F since the niobium is the diffusing atom, thereby leaving the base metal's chemical composition unaltered.

Molybdenum, tungsten, and tantalum might also be employed if sufficient pickling, probably 2 mils per side, could be tolerated after bonding. Of these, molybdenum and tungsten are most favorable since they are easily removed by pickling in dilute nitric acid.⁽³²⁾ The chemical properties of tantalum are so similar to those of⁽¹¹⁾ niobium that selective pickling is not possible.

Other metallic spacers failed to produce any encouraging results. Diffusion zones formed between the materials and the adverse effect of many on the ductility of the niobium rendered them unsuitable. Many of these materials may find use as barriers at lower temperatures or under less stringent conditions.

Nonmetallic Materials

The severe alloying problems encountered with metal spacers made it necessary to investigate the use of nonmetallics as spacers or barriers to reaction between a metallic spacer and the specimen. The materials were employed in either the solid form as a spacer or were sprayed, brushed, or flame-coated onto a material with desirable chemical properties.

Graphite was employed at bonding temperatures to 2100 F. This material was effective in preventing reaction between molybdenum spacers and the niobium specimen; however, when coated on Ti-Namel the graphite diffused so rapidly into the Ti-Namel that the barrier was completely dissipated during the bonding cycle and spacer-specimen alloying occurred. The graphite has a low solubility in niobium^(33,34); however, the diffusion rate is sufficient at this temperature to allow the carbon to move rapidly into the niobium and to precipitate out as a carbide phase⁽³⁴⁾. The presence of the carbide phase reduces the ductility of niobium to an unacceptable level for cladding applications.

From thermodynamic considerations many of the refractory oxides appeared to be stable against niobium up to 2300 F.^(35,36) However, earlier work has shown that reactions with high-purity niobium and some refractory oxides occur below temperatures predicted from thermodynamic data.⁽³⁷⁾ Similar results were obtained with most oxides employed in this program.

As seen in Table 10, the oxides investigated, with the exception of uranium dioxide, caused large increases in oxygen contents and caused severe embrittlement of the niobium. Explanation of this phenomenon apparently is that the free energy for the solution of oxygen into the niobium at bonding temperatures is less than the free energy of formation of most of the refractory oxides so that the actual reaction involved can be

written

where MO represents a stoichiometric oxide and $\text{MO}_{<1}$ represents an oxide with oxygen content something less than stoichiometric. For this reaction to be true the free energy of formation of MO must be less than that of NbO or Nb_2O_5 . This reaction could progress to the solubility limit of oxygen in niobium at the bonding temperature, which is given as 0.52 w/o⁽³⁸⁾. Upon cooling to room temperature the oxygen would be rejected from the solid solution and precipitated in the form of an oxide since the room-temperature solubility is essentially nil. In this way oxygen could be introduced and would account for the increased amounts of oxygen contamination observed.

Uranium dioxide was completely successful when employed in sintered form as a spacer. This material is relatively expensive, however, and techniques for applying it as a coating will have to be developed if it is to be employed extensively in pressure bonding of niobium. A cursory investigation was conducted to determine the feasibility of flame spraying the uranium dioxide onto a Ti-Namel base. A 3-mil-thick coating with the characteristic olive color of U_3O_8 was obtained; adherence of the coating was not uniform. Efforts to reduce the U_3O_8 to UO_2 by hydrogen reduction were partially successful, although some powdering of the coating occurred during the reduction treatment. This technique shows promise and further studies should yield an economical process for readily coating spacers with uranium dioxide.

PREPARATION OF NIOBIUM-CLAD FUEL ELEMENTS

Having established the conditions necessary for achieving satisfactory niobium self-bonds, investigations into the cladding of ceramic and cermet nuclear fuels were initiated. The general fuel-element shapes considered in this study were the flat-plate and rod-type elements. Ceramic cores of uranium dioxide and uranium carbide, high-loaded cermets or uranium dioxide and niobium, and dispersion cores containing 15 volume per cent uranium dioxide in a niobium matrix were successfully clad with niobium.

Both edge-welded specimens and specimens in containers were pressure bonded in this study. Evacuation and sealing techniques were developed which permitted the edge-welded specimens to be evacuated prior to bonding.

Flat-Plate-Type Specimens

Machined Frame Design

Specimens of this design were prepared by cold rolling niobium stock to the thickness of the core-insert frame plus one cover plate. This plate was integrally machined to produce two channels the depth of the core inserts along the length of the specimen. The two channels were separated by a 0.100-in.-wide rib in the center of the specimen. Niobium inserts were machined to be placed at each end of each row of cores and also

0.100-in.-wide pieces were made to be placed between each core. The remaining cover plate was fabricated from cold-rolled material 0.015 in. in thickness. In this arrangement each core is surrounded with cladding so that an individual compartment is formed; this is an ideal situation for retention of fission gas and also localizes the ill effects which would result if the cladding should develop a leak during operation. The components required for such an element are shown in Figure 10.

All specimens of this type contained sintered uranium dioxide fuel inserts and were fusion edge welded to produce a container for bonding. To permit evacuation of these elements a technique developed for evacuating Zircaloy-clad fuel elements was employed.⁽¹³⁾ In this method a 0.025 by 2-in. projection is machined on the end of the element as shown in Figure 10. A groove 0.015 in. deep and 0.060 in. wide was machined into the surface of the element to provide a channel for the evacuation of the entrapped gas. The elements were fusion welded in a helium-atmosphere tank on all sides so that only the end of the evacuation extensions remained open.

For evacuation, the extension of the edge-welded element was connected to a vacuum manifold by means of an adapter and a rubber hose. The specimen was evacuated to less than 1μ and then sealed by resistance-upset welding at the center of the evacuation extension. The specimen was then disconnected from the vacuum manifold and the tip of the extension was additionally sealed by helium-shielded arc welding to insure a gastight seal.

Although this technique did produce evacuated, pressure-tight specimens, the resistance sealing technique severely embrittled the niobium in the extension since it was conducted in air. This technique of sealing should be considered only as a technique for use when electron-beam welding equipment is not available.

Initially these specimens were bonded at 2100 F and 10,000 psi for 3 hr. A typical bonded specimen of this type is shown in Figure 11. The specimen is shown as it was taken from the autoclave; the light stain visible was easily removed by a light vapor blast and bright pickle. Note that the evacuation stem fractured through the resistance seal when being removed from the autoclave, indicating the localized embrittlement which occurs during the sealing operation.

Tables 11 and 12 summarize the results of the burst tests conducted on individual compartments and metallographic examinations of bonds, respectively. The results of the burst tests indicated excellent bond strength, compartment integrity, and cladding ductility at all bonding temperatures. Figure 12 shows a specimen of this type after burst testing. Note the ductility of the niobium cladding and that all failures were through the cladding and not across a bond. The depressions noted in three of the compartments were caused by relocation of the testing jig after bursting of the compartment had been accomplished.

Metallographic examinations revealed that although excellent cover plate-to-frame bonds were obtained, the vertical-type bonds between the ribs and frames were not of equivalent quality when bonding was conducted at 2100 F. These bonds contained voids with some lack of grain growth. As the bonding temperature was raised to lower the compressive yield strength of the niobium, the size and frequency of the voids were reduced until at 2400 F good vertical-type bonds could be obtained. Figure 13 demonstrates a typical cover plate-to-frame bond obtained in these specimens. Figure 14 shows a vertical-type bond obtained at 2400 F.

7/8X

N69220

FIGURE 10. COMPONENTS REQUIRED FOR AN EDGE-WELDED, MACHINED-FRAME SPECIMEN

1X

N67814

FIGURE 11. MACHINED-FRAME SPECIMEN TAKEN DIRECTLY FROM THE AUTOCLAVE AFTER BONDING

The light stain on the upper portion of the element was easily removed by a light vapor blasting.

TABLE 11. BURST-TEST RESULTS OBTAINED WITH MACHINED-FRAME-TYPE SPECIMENS

All specimens were fusion edge welded prior to bonding; all bonding was conducted for 3 hr at 10,000 psi.

Bonding Temperature, F	Number of Compartments Tested	Intercompartmental Leakage	Average Burst Pressure, psi	Average Cladding Deflection, mils
2100	2	None	1300	80
2200	4	None	1400	55
2300	8	None	1300	78
2400	4	None	1300	70

TABLE 12. METALLOGRAPHIC OBSERVATIONS ON MACHINED-FRAME-TYPE SPECIMENS

All bonding was conducted for 3 hr at 10,000 psi.

Bonding Temperature, F	Evaluation of Cover Plate-to-Frame Bonds	Evaluation of Vertical-Type Bonds	Core-Cladding Reaction
2100	Excellent grain growth, small isolated voids within grains	Numerous, large, isolated voids; 70 per cent grain growth	None
2200	Excellent grain growth, few small voids present within grains	Large isolated voids; 80 per cent grain growth	None
2300	Excellent grain growth with little evidence of voids	Small, isolated voids, 85 per cent grain growth	None
2400	Excellent grain growth; very small voids in scattered areas	Voids nearly eliminated, 100 per cent grain growth	None

1X

RM16262

FIGURE 12. MACHINED-FRAME SPECIMEN AFTER BONDING
AND SUCCESSFUL BURST TESTING

150X

N66607

FIGURE 13. TYPICAL COVER PLATE-TO-FRAME BOND OBTAINED BY PRESSURE
BONDING AT 2400 F AND 10,000 PSI FOR 3 HR

150X

N66603

FIGURE 14. TYPICAL VERTICAL-TYPE BOND OBTAINED BY PRESSURE
BONDING AT 2400 F AND 10,000 PSI FOR 3 HR

As pointed out previously, the raising of the bonding temperature is not the most desirable technique for producing more flow. It is felt that if the application of higher pressures could be employed, a bonding temperature of 2100 F would be adequate. By increasing the bonding temperature there is greater danger of contaminating the niobium with residual interstitials in the autoclave gas. With increased bonding temperature, however, the impurity level as shown in Table 13 was maintained low enough to prevent embrittlement of the niobium as shown by the burst-test results in Table 11.

TABLE 13. RESULTS OF CHEMICAL ANALYSES FOR INTERSTITIAL IMPURITIES IN EDGE-WELDED SPECIMENS

All bonding was conducted for 3 hr at 100,000 psi.

Bonding Temperature, F	Net Changes in Content of Impurities Shown During Bonding, ppm			
	Oxygen	Nitrogen	Carbon	Hydrogen
2100	160	20	10	50
2200	190	100	0	2
2300	140	120	100	82
2400	200	100	130	90

Piece-Component Frame Design

Although the machined frame design facilitates assembly and welding, significant material losses are encountered during machining such an element. For example, to machine a reference element 3 ft long containing 11 rows of 0.250 by 0.100-in. fuel a materials loss of 3.07 lb of niobium in each element would be encountered. Since it is conceivable that 3600 such fuel plates might be used in a core loading, it is evident that a loss of 11,000 lb of niobium or \$655,000 might be realized.

It is evident that such material losses must be reduced for an economic fuel element. Such reductions can be accomplished by employing a frame composed of strip components. In this design the side plates, end plates, longitudinal and cross ribs are fabricated separately so that no waste material is encountered in the formation of channels. The technique represents only a slight increase in machining costs while greatly reducing material losses. Figure 15 shows the components required for a specimen of this type readied for assembly.

Specimens of this type are more difficult to edge weld than those of the machined frame design; however, as shown in Figure 16 successful preparation of specimens by this technique is possible. Figure 17 shows the same design after bonding within a container. In general, better dimensional control is obtained with specimens bonded within a container, since the container acts as a jig during assembly and bonding to hold the components in the proper position.

Excellent results were obtained with these specimens. As seen in Table 14, strong bond and good ductility were obtained as evidenced by the burst test. Figure 18 shows an edge-welded piece-component specimen after burst testing. Examination of cross sections made through such burst-tested elements showed no evidence of separation of the

1/2X

N69221

FIGURE 15. ASSEMBLY OF A PIECE-COMPONENT SPECIMEN TO BE PRESSURE BONDED IN A CONTAINER

1X

RM15588

FIGURE 16. EDGE-WELDED PIECE-COMPONENT ELEMENT AFTER PRESSURE BONDING

1X

N66812

FIGURE 17. PIECE-COMPONENT ELEMENT AFTER PRESSURE BONDING IN A BONDING CONTAINER

1X

RM15874

FIGURE 18. RESULTS OF BURST TESTING A TYPICAL PIECE-COMPONENT, PRESSURE-BONDED SPECIMEN

Lower compartment was compressed by the testing jig when the upper compartment was tested.

cover plate from the frame due to the applied stress. A typical cross section of a burst-tested element is shown in Figure 19.

TABLE 14. BURST-TEST RESULTS ON PIECE-COMPONENT SPECIMENS

All specimens were bonded at 10,000 psi for 3 hr.

Bonding Temperature, F	Number of Compartments Tested	Intercompartmental Leakage	Average Burst Pressure, psi	Average Cladding Deflection, mils
2100 ^(a)	2	None	1200	72
2100 ^(b)	2	None	1700	59
2200 ^(a)	2	None	1300	65
2300 ^(a)	2	None	1300	60

(a) Edge-welded specimens.

(b) Specimens were bonded within a container.

Metallographic examinations indicated results similar to those of the machined frame design described in Table 12. At bonding temperatures of 2300 F sufficient flow was obtained to produce excellent cover plate-to-frame bonds as shown in Figure 20; acceptable vertical-type bonds were also obtained. No evidence of reaction between the uranium dioxide cores and the niobium cladding was observed at any of the bonding temperatures studied.

The thermal stability of both types of flat-plate specimens was studied. The specimens were encapsulated in Vycor in an argon atmosphere to minimize oxidation during thermal cycling. The test comprised 25 cycles, each cycle consisting of 30 min at 1830 F and 30 min to room temperature. No evidence of dimensional changes could be detected and metallographic examination revealed no change in microstructure and no evidence of core-to-cladding reaction in either type of flat-plate specimen.

Flat-Plate Subassembly

Conventionally, flat-plate fuel assemblies are formed by first fabricating the individual fuel elements and then joining them by brazing or welding to form multiplate structures. The many operations involved in this process increase both cost and the problems of quality control in fuel-assembly fabrication. Successful application of the one-step gas-pressure-bonding technique would offer improvement in both of these areas.

To show the feasibility of such a technique, a subassembly 5.5 in. in length consisting of three fuel plates separated by 0.070 by 1.000-in. coolant channels was produced. Each fuel plate was constructed from a piece-component frame as described in the previous section. The coolant channels were formed by two strips of niobium on each side of the uranium dioxide spacers which were later removed by pickling. Forty-nine individual components were required to form this one subassembly. The assembly of this specimen is shown schematically in Figure 21.

FIGURE 19. CROSS-SECTIONAL VIEW OF A PIECE-COMPONENT ELEMENT AFTER BURST TESTING

Note that no bond separation occurred at the corner of the core.

FIGURE 20. TYPICAL COVER PLATE-TO-FRAME BOND OBTAINED IN PIECE-COMPONENT SPECIMENS AT 2300 F AND 10,000 PSI FOR 3 HR

FIGURE 21. SCHEMATIC DRAWING SHOWING THE CONSTRUCTION OF A FLAT-PLATE, PIECE-COMPONENT SUBASSEMBLY

After gas-pressure bonding at 2100 F and 10,000 psi for 3 hr, the bonding container was stripped from the specimen and the uranium dioxide spacers were pickled out; a 180 F solution of 50 parts HNO_3 and 50 parts water was used. The resulting subassembly is shown in Figure 22.

Excellent dimensional control was obtained in this specimen. Variations in dimensions of the coolant channels were equivalent to the ± 0.001 -in. tolerances of the uranium dioxide spacers. Width and thickness measurements indicated the specimen fell within a ± 0.003 -in. tolerance in the as-bonded condition.

Metallographic examination made on the ends of the specimens revealed bonds comparable to those obtained in earlier elements at this bonding temperature. No indication of bonding separation was noted in any of the 15 bond interfaces examined.

Rod-Type Fuel Elements

Elements Clad With Niobium Tubing

Niobium clad rod-type elements were prepared containing uranium dioxide, uranium carbide, and cermets with both high and low loadings of uranium dioxide in niobium. These specimens were prepared by placing the cores into a 0.5-in. -diameter niobium tube. Closure of the 0.015-in. -thick-wall niobium tubing was accomplished by placing niobium end caps in each end, and sealing with an electron-beam welder. One-quarter-in. -thick end caps were used so that a portion of end cap next to the fuel would be unaffected during welding and could be utilized for bonding studies.

In general excellent dimensional control was obtained with all specimens. Results of metallographic examinations of these specimens are summarized in Table 15. As shown in the table excellent bonding was obtained between the niobium end caps and the niobium tubing. As was expected, intimate contact was achieved between the uranium dioxide cores and niobium cladding but no evidence of interaction was observed.

Elements containing niobium-uranium dioxide cermet cores showed excellent promise. In all cases bonding was observed between the niobium cladding and the niobium contained within the cores. Figures 23 and 24 show the bond obtained in an element with a high uranium dioxide loading in the core. Elements of this type offer excellent thermal-conductivity properties and may be resistant to swelling during irradiation testing.

The third type of core material employed was uranium carbide. Specimens were bonded at 2100 and 2400 F to determine the effect of bonding temperature on the diffusion zone formed between the core and cladding. It was anticipated that a diffusion zone would be formed since uranium carbide is thermodynamically unstable against niobium. (39)

Figures 25 and 26 show the typical diffusion zones formed at 2100 and 2400 F between niobium and uranium carbide. Note the relatively narrow widths of these diffusion zones even at 2400 F. The lack of severe reaction as seen here may be significant if this fuel system is ever employed. Additional work will be required with this fuel system to determine quantitatively the long-time compatibility of niobium and uranium-carbide at various probable reactor-operating temperatures.

N66811

FIGURE 22. NIOBIUM-CLAD FLAT-PLATE SUBASSEMBLY PREPARED BY GAS-PRESSURE BONDING

Specimen was prepared from 49 individual components. Channels were formed by removing spacers by pickling after bonding at 2100 F and 10,000 psi for 3 hr.

TABLE 15. RESULTS OF METALLOGRAPHIC EXAMINATIONS CONDUCTED ON ROD-TYPE FUEL ELEMENTS

All specimens were bonded at 10,000 psi for 3 hr.

Core Material	Bonding Temperature, F	Core-Cladding Bond	End Cap-Tube Bond
Uranium dioxide	2100	None; intimate contact	Excellent grain growth; numerous voids within grains
	2300	None; intimate contact	Excellent grain growth; very few voids present in interface
Uranium dioxide plus 20 volume per cent niobium	2100	Fair bonding obtained; evidence of bond-line contamination	Excellent grain growth; small voids present
	2200	Good bonding obtained; only scattered areas of no grain growth	Excellent grain growth; very few voids present
	2300	Excellent bonding obtained	Excellent grain growth; very few voids present
Uranium dioxide plus 85 volume per cent niobium	2300	Excellent bonding obtained	Excellent bonding
Uranium carbide ^(a)	2100	No apparent reaction; intimate contact	Evidence of uranium carbide in interfaces
	2200	No apparent reaction; intimate contact	Good bonding; only few areas with uranium carbide
	2300	Complete bonding obtained, diffusion zone 0.0002 in.	Evidence of uranium carbide in some areas
	2400	Complete bonding obtained, diffusion zone 0.0004 in.	Evidence of uranium carbide in many areas

(a) Green pressed cores were used which readily powdered into the bond interfaces.

FIGURE 23. TYPICAL INTERFACE FORMED BETWEEN NIOBIUM CLADDING
AND A NIOBIUM-URANIUM DIOXIDE CERMET CORE

FIGURE 24. HIGHER MAGNIFICATION OF THE INTERFACE SHOWN
IN FIGURE 23

500X

N67030

FIGURE 25. INTERFACE FORMED BETWEEN NIOBIUM AND URANIUM CARBIDE AFTER PRESSURE BONDING AT 2300 F and 10,000 PSI FOR 3 HR

500X

RM16585

FIGURE 26. INTERFACE FORMED BETWEEN NIOBIUM AND URANIUM CARBIDE AFTER PRESSURE BONDING AT 2400 F AND 10,000 PSI FOR 3 HR

1.5X

N69223

FIGURE 27. ASSEMBLY OF ROD-TYPE ELEMENT CLAD WITH NIOBIUM SHEET

2X

RM16090

FIGURE 28. SPECIMEN SHOWN IN FIGURE 27 AFTER GAS-PRESSURE BONDING AT 2100 F AND 10,000 PSI FOR 3 HR

Elements Clad From Niobium Sheet

Due to the limited availability of niobium tubing in certain sizes and amount, the current cost, and the fact that many niobium-base alloys with cladding potentials cannot be formed into tubing, investigations were conducted to determine the feasibility of producing rod-type elements starting with sheet stock. This technique would offer several very desirable features in that the formation of the tubing and the cladding of the fuel are combined into one operation, and in addition many alloys could be employed as cladding materials even though they cannot be formed into tubing by conventional means.

Several specimens were prepared using 0.015-in. -thick annealed sheet to form the cladding. The mating edges of the formed niobium sheet were tapered so that overlapping could be achieved and still maintain a uniform diameter in the bonded tubing. This niobium was formed around sintered uranium dioxide pellets with the required niobium end plugs and inserted into a Type 304 stainless steel tube, sealed, and pressure bonded. Figure 27 shows the required components for such a specimen and the assembly technique employed.

Figure 28 shows an isometric view of such a specimen after pressure bonding. Note the uniform diameter that has been achieved. Micrometer measurements showed the tubes to be round within ± 0.002 in. Satisfactory bonding was also achieved although not of the usual quality obtained. This is no doubt due to the filing operation employed to taper the specimens. More carefully controlled machining operations would produce improved results.

The economics of such a system can be seen at a glance. The quoted current price for annealed niobium tubing with a 0.500-in. OD and 0.015-in. -thick wall is \$17.50 per foot. The corresponding price of 0.015-in. -thick niobium sheet necessary to produce 1 ft of the reference-size tubing is \$76.70 per lb. The cost of tapering the edges for the lap joint should be approximately \$0.20 on a production basis, so that the cost of tubing by this technique might cost only \$8.75. Since pressure-bonding costs would be comparable for prefabricated and sheet formed tubing, a saving of \$8.75 or 50 per cent in material costs might be realized on each 1-ft-long fuel element.

This technique appears quite attractive for many applications. Since this investigation was rather cursory in nature, it is believed that a more detailed analysis of the problem should be conducted. Such an investigation should demonstrate whether niobium or niobium-base-alloy tubing can be economically prepared by this technique.

SUMMARY OF NIOBIUM-BONDING STUDIES

The gas-pressure-bonding technique can be utilized to achieve high-integrity solid-phase self-bonds with niobium. The structure, mechanical and physical properties of the bond areas are consistent with those of the parent metal when proper surface preparation and bonding parameters are employed.

Bonding-parameter investigations showed that the minimum conditions for bonding were 2100 F and 10,000 psi for 3 hr. Higher temperatures, up to 2400 F, were studied and showed somewhat improved bonding especially in the vertical-type bonds.

Surface preparation of the niobium was found to have a significant influence on the subsequent bond characteristics. Of the many methods that were investigated, including various chemical treatments, grit abrasion, and machining, only a treatment with a pickling solution made up of 65 parts nitric acid and 35 parts hydrofluoric acid consistently resulted in satisfactory bonding.

Investigations were conducted to determine the nature of the voidlike structure along some bond interfaces after pressure bonding. High-temperature vacuum heat treatments and cold-rolling experiments were conducted. Results of these tests showed conclusively that there were in fact voids and not inclusions present in the original interface.

An investigation to determine a suitable spacer material to form coolant channel in subassemblies revealed that only uranium dioxide could be considered completely successful. Metallic materials, such as stainless steel, Fecral, molybdenum, and tungsten, alloyed readily with the niobium during bonding. Ceramic materials, such as alumina, magnesia, silica, and glass, embrittled the niobium by raising the oxygen content to an unacceptable level.

Fabrication of compartmented niobium-clad flat-plate fuel elements was successfully accomplished. Bond strength, compartment integrity, and cladding ductility were shown by burst testing to be satisfactory. Both machined and piece-component frame design were bonded as was a subassembly consisting of three flat-plate, compartmented, fuel elements separated by integral coolant channels.

Niobium-clad rod-type elements containing uranium dioxide, uranium carbide, and uranium dioxide-niobium cermet were fabricated. No evidence of core-cladding interaction was noted when uranium dioxide cores were employed. Small diffusion zones of 0.0005 in. were noted between the niobium and uranium carbide after bonding at 2400 F. Good bonding was obtained between the niobium cladding and niobium contained within the cermet cores.

The simultaneous fabrication of rod-type elements from niobium sheet stock and uranium dioxide pellets was successfully accomplished. The edges of the sheet were tapered so that lapping could be accomplished while still maintaining a uniform diameter. Pressure-bonded specimens showed excellent dimensional control, well within normal commercial tolerances.

STUDIES ON THE SELF-BONDING OF MOLYBDENUM

Bonding-Parameter Study

As previously discussed the gas-pressure-bonding operation is dependent upon successfully flowing the bonding surfaces into intimate contact, permitting diffusion and grain growth to occur across the original interface. Accordingly, an investigation was conducted to determine the optimum bonding parameters of time, temperature, and pressure required to accomplish self-bonding of molybdenum.

Other work has shown that molybdenum softens rapidly at temperatures above 1600 F.⁽⁴⁰⁾ The minimum temperature for the initiation of recrystallization is given as 1650 F. These data indicated that initial efforts for self-bonding studies should be made at 1650 F which is above the initial recrystallization temperature and in the range where softening occurs.

Previous studies had shown that the surface condition of materials to be bonded had a pronounced effect on bonding. Since proper surface-preparation techniques were not yet developed for molybdenum it was necessary to employ the most promising surface-finishing technique during these studies. A technique developed at Battelle for cleaning molybdenum surfaces prior to welding was used. This preparation consisted of etching for 30 sec in a 140 F solution of 95 parts H₂SO₄, 4.5 parts HNO₃, 0.5 part HF, and 18.8 g per liter Cr₂O₃. Specimens prepared by this technique were pressure bonded at temperatures of 1650 to 2200 F for times of 1 to 6 hr to determine the effect of bonding conditions on the properties of the bond achieved. Evaluation of the specimens was based on metallographic examination and bend tests.

The results of the metallographic bond evaluations and bend tests are presented in Table 16. Examination of these data indicated that bonding temperatures below 2200 F failed to produce mechanical bonding between the molybdenum plates. Insufficient flow had occurred at these temperatures to close macrovoids and permit intimate contact during the bonding cycle. Incomplete recrystallization was also observed at these temperatures, indicating higher bonding temperatures would be required.

TABLE 16. RESULTS OF TESTS ON MOLYBDENUM SPECIMENS PREPARED FOR BONDING-PARAMETER STUDY

Surfaces were cold rolled and pickled^(a), unless otherwise indicated.

Bonding Parameters			Metallographic Examination		Bend Test,
Temperature, F	Time, hr	Pressure, psi	Bond Quality	Recrystallization	Bondline Separation
1650	6	10,000	No bonding	None	Complete
1750	6	10,000	No bonding	Spotty	Complete
1800	6	10,000	No bonding	Spotty	Complete
2100	3	10,000	No bonding	80 per cent	Complete
2200	3	10,000	Macrovoids, 5 per cent grain growth	90 per cent	Complete
2300	3	10,000	Intimate contact, 5 per cent grain growth	100 per cent	Partial
2300 ^(b)	3	10,000	Large voids present Good bonding away from voids	100 per cent	Partial
2400 ^(b)	3	10,000	Macrovoids present, 10 per cent grain growth	100 per cent	None
2450	3	10,000	Intimate contact, 10 per cent grain growth	100 per cent	None
2450 ^(b)	3	10,000	Small voids, 10 per cent grain growth	100 per cent	None
2600 ^(b)	3	10,000	Intimate contact, 95 per cent grain growth	100 per cent	None

(a) Pickled in 95 per cent H₂SO₄ - 4.5 per cent HNO₃ - 0.5 per cent HF - 18.8 g per liter Cr₂O₃.

(b) Machined to 125 μ in., rms, before pickling as in (a).

Specimens bonded between 2300 and 2450 F showed metallurgical bonding and good mechanical strength as indicated by bend tests. Varying degrees of grain growth across the original interface were observed in this temperature range. Metallographic examinations revealed that complete recrystallization had occurred but that insufficient flow had prevented complete intimate contact if a roughened molybdenum surface was used. Such a specimen is shown in Figure 29. Note that although satisfactory bonding was achieved at some areas, other areas exhibited macrovoids which were not closed during pressure bonding. As previously mentioned, such bonding indicates that adequate temperature has been provided but insufficient pressure has been applied to produce the required flow for closures of macrovoids. However, since maximum design pressure of the present autoclave was already being used, it was necessary to increase the temperature to reduce the yield strength to a more favorable level.

As can be noted in Table 16, specimens bonded at temperatures over 2450 F revealed improved flow had occurred and macrovoids had been closed. Figure 30 shows the bond interface after bonding at 2450 F. Note that the interface is straight and no evidence of macrovoids can be seen.

Results of the bonding-parameter investigation established that flat-plate-type specimens could be moved into intimate contact by bonding at temperatures of 2300 F and 10,000 psi for 3 hr if smooth bonding surfaces were employed. When roughened surfaces, such as machined surfaces, were used it was necessary to increase the bonding temperature to 2450 F or higher to produce sufficient flow to close all macrovoids.

Surface-Preparation Study

The bonding-parameter study indicated that minimum satisfactory conditions for flow and diffusion were 2300 F and 10,000 psi for 3 hr. However, during that investigation the surface preparation employed, namely a cleaning solution of 95 parts H_2SO_4 , 4.5 parts HNO_3 , 0.5 part HF , and 18.8 g per liter of Cr_2O_3 , failed to produce bonds of a satisfactory nature. As discussed earlier in this report, surface preparation has a pronounced effect on the quality of bond obtained, therefore, a number of surface-conditioning techniques were investigated. These included cold rolling, belt abrading, surface grinding, machining, and etching in both caustic and acidic solutions. Pressure bonding was conducted on these surface-preparation specimens at 2300 or 2450 F depending upon the surface roughness of the bonding surfaces. Specimens with relatively rough surfaces required a higher bonding temperature to produce sufficient flow to close macrovoids. However, the lowest possible bonding temperature was employed in all instances in an effort to retain ductility in the bonded specimen. Specimens were generally bonded in containers to facilitate evacuation of the assembly; a limited number of specimens were prepared by fusion edge welding. Results of this investigation are presented in Tables 17 and 18.

Cold-Rolled Surfaces. From a cost standpoint, the most desirable surface for bonding would be one which is cold rolled and cleaned without metal removal. Specimens fabricated from carefully cold-rolled stock showed very poor bonding as evidenced by the complete failure of the bond during bend testing. Metallographic examinations indicated the presence of continuous contamination along all the bond interface. Consequently, this surface-conditioning technique did not warrant further study.

FIGURE 29. PRESSURE-BONDED MOLYBDENUM SPECIMEN IN WHICH ALL MACROVOIDS WERE NOT CLOSED

Specimen was bonded at 2300 F and 10,000 psi for 3 hr.

FIGURE 30. PRESSURE-BONDED MOLYBDENUM SPECIMEN IN WHICH ALL MACROVOIDS WERE CLOSED

Specimen was bonded at 2450 F and 10,000 psi for 3 hr.

TABLE 17. EVALUATION OF MOLYBDENUM SPECIMENS WITH NONCHEMICALLY TREATED SURFACES

All specimens were pressure bonded at 2300 F and 10,000 psi for 3 hr, unless otherwise noted.

Surface Preparation	Bend Test	Metallographic Examination
Cold-rolled surfaces	Complete separation	Heavy, continuous contamination in bond interface
Abrasive finishing		
Surface grinding, 80 grit	Complete separation	Heavy contamination due to embedded grit
Surface grinding, 400 grit	Complete separation	Heavy contamination due to embedded grit
Surface grinding, 600 grit	Complete separation	Light, continuous contamination
Belt abrading, 40 grit	Complete separation	Heavy contamination and large voids
Belt abrading, 60 grit	Complete separation	Heavy contamination and small voids
Machining treatments		
Shaping, 60 μ in., rms	Partial separation	Little contamination but large, elongated voids
Shaping, 125 μ in., rms	Partial separation	Little contamination but large, spherical voids
Shaping ^(a) , 60 μ in., rms	No separation	Very little contamination and no voids
Shaping ^(b) , 125 μ in., rms	No separation	Very little contamination and no voids
Thermal treatments		
Vacuum treated at 1600 F	No separation	No evidence of voids or contamination
Hydrogen treated at 1100 F	No separation	No evidence of voids or contamination

(a) Pressure bonded at 2450 F and 10,000 psi for 3 hr.

(b) Pressure bonded at 2600 F and 10,000 psi for 3 hr.

TABLE 18. EVALUATION OF MOLYBDENUM SPECIMENS WITH CHEMICALLY TREATED SURFACES

All specimens were pressure bonded at 2300 F and 10,000 psi for 3 hr, unless otherwise noted

Pickling Solution	Bend Test	Metallographic Examination
95 per cent H_2SO_4 - 4-1/2 per cent HNO_3 - 0.5 per cent HF - 18.8 g per liter Cr_2O_3	Partial separation	Evidence of light continuous contamination
95 per cent H_2SO_4 - 4-1/2 per cent HNO_3 - 0.5 per cent HF - 18.8 g per liter Cr_2O_3	No separation	Light contamination with 10 per cent grain growth
Saturated sodium hydroxide	Complete separation	Continuous bond-line contamination
20 per cent HF in water	Complete separation	Heavy contamination and no bonding
Ryan's solution ^(b)	Partial separation	Evidence of very little contamination
Nitric acid under kerosene	No separation	Clean interface with good bonding
50 per cent HNO_3 in water ^(c)	Complete separation	Contaminated interface with no bonding
50 per cent HNO_3 in water ^(d)	No separation	Clean interface with good bonding
25 per cent HNO_3 in water ^(e)	Complete separation	Contaminated interface with no bonding

(a) Pressure bonded at 2450 F and 10,000 psi for 3 hr.

(b) For composition see Footnote (a) in Table 7.

(c) Residue was formed during pickling and could not be removed.

(d) Residue was not formed during pickling.

(e) Residue cannot be prevented from forming and cannot be removed.

Mechanical Finishing. Earlier pressure-bonding studies have indicated that machining and abrasive finishing techniques are suitable for the surface preparation of certain materials. (13,14,20) Accordingly, surface grinding, belt abrading, and shaper finishing were investigated as possible surface preparations for molybdenum.

Specimens were prepared by grinding 0.002 in. per side from the bonding surface with various grades of silicon carbide. The grit size was varied between 80 and 600 to insure the effect of surface roughness did not affect the bond quality. A water-soluble oil was used as a coolant and lubricant during grinding. Examination of these specimens revealed that severe contamination of the bonding surface had occurred due to embedding of grit during grinding. Bend tests showed these bonds to be weak; results are tabulated in Table 17.

Similar results were obtained when bonding surfaces were belt abraded prior to pressure bonding. The abrading was conducted according to developed techniques under a flood of sulfonated oil which acted as both a coolant and lubricant. Uneven metal removal was encountered during these treatments as tearing rather than clean metal removal occurred.

Shaper finishing was investigated as a typical machining operation which might be employed to finish bonding surfaces. A water-soluble oil was used to minimize oxidation and to act as a lubricant during machining. Care was taken to use sharp tools with feeds and speeds consistent with good machining practice. Surface roughness of each specimen was carefully controlled so that this variable might be better evaluated.

Table 17 gives an evaluation of these specimens. Note that the only apparent effect of surface roughness is that as the surface roughness is increased, it is increasingly difficult to bring the surfaces into complete intimate contact. In areas where intimate contact was achieved excellent bonding could be seen. This technique was shown suitable in a specimen bonded at 2600 F to insure sufficient flow as can be seen in Figures 31 and 32.

Chemical Finishing Techniques. The most desirable surface-finishing technique is a chemical etch since it is so readily adapted to production. An investigation was therefore conducted to determine if chemical surface preparations were satisfactory. Etching solutions were employed that were known to attack the molybdenum or were established as cleaning solutions for some other application. (2,41,42) The chemical etchants used and the corresponding bonding results are given in Table 18.

Results of the specimens prepared for this investigation showed that acidic etching reagents produced surfaces which could be bonded with good mechanical strength. However, the bonding achieved was inconsistent, even within a given specimen. This inconsistency in the bonding is attributed to the fact that during the pickling operation residues are formed on the surfaces of the molybdenum; these residues have the characteristic brown and blue hues of the molybdenum oxides. Subsequent cleaning treatments used after pickling failed to completely remove these residues.

The etching reagent that produced the best surfaces for bonding consisted of concentrated nitric acid covered with a layer of kerosene. The nitric acid and kerosene are completely nonreactive and immiscible and the kerosene forms a floating layer on the heavier nitric acid. Specimens pickled in this manner showed very little residue on the

FIGURE 31. EXAMPLE OF EXCELLENT MOLYBDENUM SELF-BONDS THAT CAN BE ACHIEVED BY PRESSURE BONDING

FIGURE 32. HIGHER MAGNIFICATION OF BOND AREA SHOWN IN FIGURE 31

molybdenum surfaces. Apparently the kerosene acts as a blanket and retards the formation of the oxide films on the molybdenum and produces a more desirable bonding surface. This surface-preparation technique produced the most satisfactory surfaces for self-bonding of molybdenum.

Investigation of Spacer Materials

Numerous metallic and ceramic materials were studied as spacers or spacer coatings to prevent reaction between the stainless container and the molybdenum. Materials were evaluated for use at 2300 and 2450 F during a normal bonding cycle. Specimens bonded at higher temperatures were bonded as edge-welded specimens to eliminate eutectic reactions between the molybdenum and jacketing materials. Table 19 summarizes the results of these investigations.

Metallic Materials. In general, metallic spacers as reaction barriers did not prove satisfactory in this application. At 2300 F Ti-Namel, stainless steel, and all other nonrefractory metals reacted severely with the molybdenum.

Niobium, tantalum, and tungsten could be separated from the molybdenum after bonding at 2450 F. However, extensive interdiffusion occurred with these materials and they alloyed with the molybdenum at the outer surfaces during bonding.

The most satisfactory metallic material for bonding at 2300 F was found to be chromium. This material was electroplated onto Ti-Namel spacers for this application. Figure 33 shows a typical diffusion zone formed between the molybdenum and the chromium at 2300 F. The reaction zone measured only 0.0008 in. and could be readily removed by pickling to produce an unalloyed molybdenum surface. In some applications such a diffusion zone may be desirable, however, since this formation of such diffusion

FIGURE 33. DIFFUSION ZONE FORMED BETWEEN CHROMIUM AND MOLYBDENUM AT 2300 F

TABLE 19. RESULTS OF THE INVESTIGATION OF SPACER MATERIALS FOR MOLYBDENUM

Spacer Material	Bonding Conditions			Peel Test ^(a)	Metallographic Examination
	Temperature, F	Time, hr	Pressure, psi		
Copper	1650	6	10,000	Easily separated	1.5-mil diffusion zone was formed
Ti-Namel	1650	6	10,000	Easily separated	Small reaction zone was formed
	1750	6	10,000	Easily separated	1-mil diffusion zone was formed
Iron	1800	6	10,000	Separable	1.5-mil diffusion zone was formed
Nickel	1800	6	10,000	Easily separated	1-mil diffusion zone was formed
	2100	3	10,000	Separable	2-mil diffusion zone was formed
Type 304 stainless steel	2100	3	10,000	Separable	2-mil reaction zone was formed
	2300	3	10,000	Very difficult to separate	Severe alloying had occurred
Niobium	2100	3	10,000	Separable	Small reaction zone formed
	2300	3	10,000	Difficult to separate	Extensive alloying had occurred
Tantalum	2300	3	10,000	Difficult to separate	Extensive alloying had occurred
Tungsten	2300	3	10,000	Difficult to separate	Extensive alloying had occurred
Carbon on Ti-Namel	2300	3	10,000	Very difficult to separate	Carbon had diffused into the Ti-Namel allowing Ti-Namel to react with the molybdenum
Carbon on molybdenum	2300	3	10,000	Easily separated	Only slight evidence of second phase
Carbon on Type 304 stainless steel	2300	3	10,000	Difficult to separate	Carbon diffused into the stainless steel allowing reaction to occur
Hard-lime window glass	2300	3	10,000	Easily removed	No apparent reaction
	2400	3	10,000	Easily removed	No apparent reaction
Vycor	2300	3	10,000	Easily removed	No apparent reaction
Alumina	2300	3	10,000	Difficult to remove	Embedded in surface but did not appear to react
Titania	2300	3	10,000	Difficult to remove	Possible formation of second phase
Alumina plus titania	2300	3	10,000	Difficult to remove	Embedded in surface but did not appear to react
Magnesia	2300	3	10,000	Difficult to remove	Reaction zone formed
Enamel ^(b)	2300	3	10,000	Separable	No apparent reaction
	2400	3	10,000	Separable	No apparent reaction
Uranium dioxide	2300	3	10,000	Separable	No apparent reaction

(a) A measure of how readily the spacer can be removed from the molybdenum.

(b) Composition given in Footnote (b) in Table 9.

zones has been shown to greatly increase the oxidation resistance of the molybdenum^(2,10). Higher bonding temperatures which produce the most consistent molybdenum bonds result in more extensive diffusion of the chromium.

Nonmetallic Materials. The severe alloying problem encountered with metal spacers made it necessary to investigate the use of nonmetallics as spacers or barriers to prevent reaction between the container and the specimen. The materials were employed in either the solid form as a spacer or were sprayed, brushed, or flame-coated onto a material with desirable physical and chemical properties.

Graphite was employed as an effective barrier to reaction between the molybdenum and metallic spacers. The diffusion of carbon into the molybdenum is quite slow at bonding temperature so that carbon pickup is held to an acceptable level. Graphite coatings were most successfully used on niobium or molybdenum spacers; ferrous base materials were found unsuitable as a substrate since the graphite coating diffused into the spacer and was rapidly dissipated, so that spacer-specimen alloying could occur.

Refractory oxides were investigated as spacer materials. Thermodynamic data indicated these materials should not be reduced by the molybdenum during pressure bonding^(35,36). As discussed previously these data cannot be applied directly to the pressure-bonding application, as in many instances the oxides did react quite readily with the molybdenum. Uranium dioxide, uranium dioxide diluted with 21 per cent alumina, and silica were satisfactory materials in that they showed no evidence of reacting with the molybdenum specimens. Flame-sprayed alumina and alumina with titania additions were not completely satisfactory in that some oxygen was given up to the molybdenum during the bonding cycle.

Hard-lime window glass, Vycor, and a complex enamel of 9.8 w/o CaO, 26.4 w/o SiO₂, 6.4 w/o Al₂O₃, with the balance BaO showed no appreciable reaction with the molybdenum. Although these materials appear to be satisfactory as spacer materials they are extremely difficult to produce to correct tolerances. Their use may be impractical unless an inexpensive technique for coating these materials onto metallic spacers can be developed.

Ductility Investigation

Molybdenum specimens pressure bonded at 2300 F or higher do not retain room-temperature ductility in any direction except those parallel with the original rolling direction. This loss of ductility renders the material useless as a cladding material in that catastrophic failures could be encountered with essentially no deflection of the cladding.

It should be pointed out that many molybdenum specimens which showed no ductility at room temperature could be bent 45 deg or more when testing was conducted in boiling water. Obviously this indicates that the ductile-to-brittle transition temperature for molybdenum may have been raised above room temperature by the pressure-bonding cycle.

The ductile-to-brittle transition is characteristic of body-centered-cubic materials^(9,10,43). The transition is due to a sharp increase in the yield strength and a

corresponding reduction in ductility over a narrow range of temperatures. The range of temperatures at which transition actually occurs is dependent primarily on purity, microstructure, and deformation rate during testing.⁽⁴³⁾ Of these three variables the first two represent likely causes for the increase in the ductile-to-brittle transition from below room temperature to over 200 F after pressure bonding.

The effect of purity on the brittle behavior was investigated. Chemical analyses were made to determine if any increase in impurity content had occurred during bonding. The result of these tests are tabulated in Table 20. It can be noted that in most specimens only small increases in the interstitial elements were encountered. However, due to the low solubility of these elements at room temperature only small amounts are required to form precipitates in the grain boundaries.^(44,45) Such precipitates weaken the grain boundaries and promote intergranular fracture. During the course of pressure bonding the material is held at temperatures where significant amounts of contaminants can be dissolved; however, the low cooling rate obtained in the autoclave permits rejection of the interstitials from solid solutions and precipitates are formed in the grain boundaries.⁽⁴⁶⁾

Heat-treatment experiments were conducted to determine if these interstitial compounds could be redissolved and held in solution. Specimens were capsulated in Vycor with an argon atmosphere to minimize oxidation. The specimens were then solution treated at 2100 F for 1 hr and quenched to room temperature. Examination of microstructures indicated that no apparent change had been achieved by the solution heat treatment. Bend tests revealed no improvement in ductility had been obtained by this treatment.

Since pressure-bonded molybdenum usually retained its room-temperature ductility in the original rolling direction, investigations were conducted to determine if cross rolling might improve the ductility in the transverse direction. Such treatments have been successfully used to eliminate the directional properties of cold-rolled sheet. Specimens were prepared which were cold rolled prior to bonding at 90 deg to the original rolling direction for various amounts of reduction. Table 21 shows the treatments employed. Note that the observed objective was not obtained and that at certain critical reductions all ductility was lost. At greater reductions the retention of ductility after bonding shifted from the original rolling direction to the new rolling direction, indicating the approach would not be satisfactory.

Recrystallization, which is necessary in the pressure-bonding process, raises the ductile-to-brittle transition temperature because a given amount of impurity element can form a more continuous network of grain-boundary films.⁽⁹⁾ This effect is more pronounced as grain size is increased.⁽⁴⁷⁾ Working the molybdenum breaks up the grain-boundary films that cause brittle failure through the grain boundaries.⁽⁹⁾ Accordingly, it should be possible to cold roll the molybdenum after pressure bonding and restore a portion of its ductility.

To test this premise several pressure-bonded molybdenum specimens with directional ductility were selected. These specimens were rolled without jacketing at 700 F across the original rolling direction with 10 and 25 per cent reductions. Heating was accomplished in an argon atmosphere to minimize oxidation of the molybdenum. The specimens were quenched immediately after rolling to further reduce oxidation.

TABLE 20. CHANGES IN INTERSTITIAL IMPURITIES DURING PRESSURE BONDING OF EDGE-WELDED SPECIMENS

All bonding was conducted for 3 hr at 10,000 psi.

Bonding Temperature, F	Net Changes in Content of Impurities Shown During Bonding, ppm			
	Oxygen	Nitrogen	Carbon	Hydrogen
2100	+10	0	0	0
2300	+8	0	+10	0
2450	+10	+10	+10	0
2600	+20	+10	+30	0

TABLE 21. EFFECT OF CROSS ROLLING ON THE DIRECTIONAL DUCTILITY OF PRESSURE-BONDED MOLYBDENUM

Reduction, per cent	Bend Deflection in Original Rolling Direction, deg	Bend Deflection in New Rolling Direction, deg
Before bonding		
0	90	0
10	60	0
25	15	0
50	0	45
65	0	90
After bonding		
0	90	0
10	90	15
25	75	45

Results of these tests showed that 10 per cent reductions were insufficient to restore ductility to the molybdenum. Reduction of 25 per cent, however, resulted in a material which could be bent greater than 45 deg over a sharp die at room temperature.

This treatment offers promise for cladding cermet-type cores which have some ductility. The molybdenum self-bonds and the core-to-cladding bonds could be produced by the gas-pressure-bonding process. After bonding the light reduction at low temperatures would be employed to restore ductility of the cladding and also to increase its physical properties.⁽²⁾ Since a semiductile core would be employed, the rolling procedure should not fragment the core.

SUMMARY OF MOLYBDENUM-BONDING STUDIES

The gas-pressure-bonding technique can be utilized to achieve high-integrity solid-phase self-bonds with molybdenum. Bonding can be satisfactorily achieved by employing either jacketed or edge-welded specimens to obtain the required pressure differential between the bonding surfaces and the helium gas.

Bonding parameters studied showed that the minimum conditions for bonding were 2300 F and 10,000 psi for 3 hr. Higher temperatures, up to 2600 F, were studied and showed improved flow characteristics and bonding, especially when properly cleaned machined surfaces were employed.

Satisfactory surface preparations for the molybdenum were developed. Machining, and pickling in nitric acid solutions were successfully employed in surface preparation. Abrasive techniques and certain chemical treatments were found to be unsatisfactory.

An investigation to determine a suitable spacer material that would act as a barrier to reaction with the container revealed that only ceramic-type materials could be used. Silica, uranium dioxide, hard-lime window glass, Vycor, and certain enamels showed no evidence of reaction at temperatures up to 2450 F. Graphite appeared suitable as a barrier at temperatures to 2300 F. Metallic materials generally alloyed severely with the molybdenum during bonding. Chromium appeared promising as a barrier at temperatures up to 2300 F where only a small diffusion zone was formed between the chromium and molybdenum.

Molybdenum specimens prepared on this program possessed ductility only in the original rolling direction after bonding. Cross rolling the bonded specimen to a 25 per cent reduction was found to restore ductility at room temperature. Cross rolling prior to bonding failed to improve the directional properties obtained after pressure bonding. Solution heat treatments after bonding also failed to improve the room-temperature ductility of the molybdenum.

CONCLUSIONS

The feasibility of obtaining self-bonding with molybdenum and niobium by the gas-pressure-bonding process has been established. Bond strengths obtained by this technique have been shown to be as strong as the base material.

In the case of niobium, no detrimental effects on the properties of the material were encountered. The fabrication of rod- and flat-plate-type fuel elements and flat-plate subassemblies demonstrated the flexibility of the pressure-bonding process and the ability of niobium to be used as a fuel-element cladding material.

Cladding of rod-type elements with niobium sheet stock was a most unique achievement. The technique may be of great importance in the fabrication of niobium-clad rod-type elements. It has even greater promise as a technique for cladding rod-type fuel elements with some of the recently developed high-strength niobium-base alloys. Many of these materials cannot be fabricated into tubing by conventional means but can be rolled into sheet form. Providing the alloy has sufficient ductility to be formed around the core material, the fabrication of the tubing and cladding of the element could be accomplished in one step as was demonstrated for unalloyed niobium.

Molybdenum has the undesirable feature of losing a portion of its room-temperature ductility during the process of recrystallization during bonding at high temperatures. This can be overcome in part with a 25 per cent warm reduction by rolling across the original rolling direction after recrystallization or bonding has occurred. This greatly limits the choice of core materials, however, since it would be required that the core material have at least semiductile properties. This would permit the bonding of certain cermet but would eliminate the use of such desirable fuels as uranium carbide, uranium dioxide, and uranium nitride.

This problem cannot be overcome with unalloyed molybdenum if room-temperature ductility is a necessary feature unless the current technology is greatly advanced. However, at the present time a number of molybdenum-base alloys have been developed with ductile-to-brittle transitions well below room temperature. By substituting such an alloy for unalloyed molybdenum as the cladding material it might be possible to produce pressure-bonded fuel elements with excellent mechanical properties which could embody all types of fuels.

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