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PREPARATION, CLADDING, AND EVALUATION OF
TITANIUM-BORON DISPERSIONS

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PREPARATION, CLADDING, AND EVALUATION OF TITANIUM-BORON DISPERSIONS*

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and Donald E. Lozier

Powder dispersions of titanium-boron and titanium-boron carbide were prepared, clad, and evaluated for use as control materials.

Compacts possessing up to 95 per cent of theoretical density were prepared by a hot-pressing technique. The relatively low temperature of 1500 F was used to obtain the desired high density. There was no visible reaction between the boron dispersant and titanium.

Excellent metallurgical cladding of the titanium-boron dispersion with titanium was achieved by the use of both roll-bonding and gas pressure-bonding techniques. The rolling was performed at 1500 F and the pressure bonding was accomplished at 1600 F with a helium pressure of 10,000 psi for a time of 6 hr. The pressure-bonding technique produced a specimen with a more uniform boron dispersion and a better high-temperature-water corrosion resistance than were obtained through roll bonding.

Extruded titanium-boron dispersions were joined to hafnium and clad with Zircaloy 2 by a roll-bonding technique to determine in a preliminary way the feasibility of preparing clad composite control rods. Strong, relatively ductile bonds were obtained between all of the components by the roll-bonding process and postfabrication heat treatment.

INTRODUCTION

Titanium-boron dispersions were investigated as possible control materials. It was hoped that this material would combine the excellent high-temperature-water corrosion resistance of titanium with the broad thermal-epithermal neutron-absorption cross section of boron. The titanium powder is also attractive as a matrix material because of its availability, low cost, and low density.

The use of boron as a control material in long-life reactors is problematic. The boron absorbs neutrons by an n, α reaction and consequently is prone to extensive physical damage through irradiation. The absorption cross section of boron is primarily attributed to one isotope; boron-10. In naturally occurring boron, this isotope is present in an amount of approximately 18 per cent. The use of boron as a control material poses the question of the desirability of using the boron in the natural form or as concentrated in the isotope boron-10. Dispersions incorporating the boron-10 isotope require a

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smaller fraction of boron for the same blackness. This results in a more uniform, ductile, and corrosion-resistant dispersion than is obtained with a higher loading of natural boron. However, there is an indication that the boron-10 lattice is not capable of retaining the produced helium, and consequently, the material is more prone to damage by irradiation. This is to be anticipated because under prolonged irradiation the entire boron-10 lattice is subject to destruction. Since the boron-10 possesses a relatively high neutron-absorption cross section, self-shielding is present in materials of any appreciable thickness. This implies the burnup of the boron proceeds from the surface of a particle toward the center so that surface damage can also occur after a relatively short reactor life.

The use of natural boron appears to improve the physical stability of the boron under irradiation. Only a portion of the lattice is destroyed, and it is possible that the undamaged portion of the lattice is capable of retaining part of the released helium. There is also an indication that compounds of boron are more stable than the metal. However, larger amounts of boron are required in the natural form in order to obtain an equivalent cross section. Dispersions of higher boron loadings are more brittle and less corrosion resistant. Thus, the question of whether dispersions containing natural boron or enriched boron have superior properties must be solved by experiment.

This report combines several studies concerned with the development of a suitable titanium-boron control material. Several fabrication techniques were investigated in an attempt to select the technique capable of producing a natural-boron dispersion of high loading with optimum physical and mechanical properties.

Roll bonding was investigated as a method of joining the titanium-boron dispersion to hafnium. The hafnium portion of the rod would be used for shim control whereas the entire rod, hafnium and titanium-boron, would be utilized for reactor shutdowns. In such a control rod, the titanium-boron would be subjected to a relatively low burnup and might not suffer from radiation damage; however, a substantial saving of hafnium metal would be made.

PREPARATION AND CLADDING OF HOT-PRESSED TITANIUM-BORON POWDER COMPACTS

Compacts of titanium-boron were prepared by hot pressing mixed titanium and boron powders. The two-step pressing technique produced compacts of 95 per cent of theoretical density at a relatively low temperature. A low temperature was desirable to prevent reaction between the boron dispersant and the titanium matrix.

The pressed compacts were clad with titanium by a conventional roll-bonding technique and by gas-pressure bonding. In the pressure-bonding process, a bond is effected between the cladding and core without any appreciable deformation of the components. It was believed that a more uniform dispersion with improved physical and mechanical properties would be produced by this technique than by roll bonding. Specimens prepared by both methods were tested and evaluated to compare the products obtained by the two fabrication techniques.

Description of Materials

The materials used in this study were standardized so that a comparison could be made of specimens prepared by different fabrication techniques. The titanium selected analyzed 0.011, 0.003, and 0.15 w/o for hydrogen, nitrogen, and oxygen, respectively, and had a mesh size of minus 100 plus 250. The boron was prepared by the Fetterly process and had a mesh size of minus 100 plus 200. The B_4C was reactor-grade material sized to minus 100 plus 200 mesh. The particle size of each of the three materials was restricted to the same range to aid in producing a more uniform dispersion.

The powders for each dispersion were mixed for 18 hr with a camphor-methyl alcohol dispersing agent and cold pressed using a pressure of 50 tsi. This produced a green material with a density of approximately 85 per cent of theoretical. The specimens were then degassed in a fast-pumping vacuum system to a pressure of 1×10^{-3} mm of mercury at a temperature of 1100 F. The degassed specimens were sealed in MgO-smoked mild steel jackets by welding in an argon-filled tank. These compacts were pressed to a 30 per cent reduction in two steps at 1500 F. This hot press-forging operation increased the density of the material to the range of approximately 95 per cent of theoretical density, permitting all specimens to be machined by wet grinding on a surface grinder.

Evaluation of Hot-Pressed Compacts

Tensile testing was used for comparing various specimens. The tensile-specimen design illustrated in Figure 1 was used on hot-pressed specimens. Duplicate specimens of each dispersion were tested at 600 F in a protective atmosphere. Specimens of each composition except the 18.2 and 25.7 w/o B_4C dispersions were also tested at room temperature. The tensile data are presented in Table 1.

FIGURE 1. DIMENSIONS OF TENSILE SPECIMENS USED FOR TESTING CORE MATERIAL OF 9.6 AND 26 w/o BORON AND 12.9, 18.2, 25.7, AND 35 w/o B_4C IN TITANIUM

TABLE 1. TENSILE-STRENGTH DATA FOR TITANIUM-BORON AND - B_4C DISPERSIONS

Specimen	Testing Temperature, F	0.2 Per Cent Offset Yield Strength, psi	Tensile Strength, psi	Elongation In 1 In., per cent
Titanium standard	Room	69,900	78,400	(a)
Titanium standard	Room	59,900	71,000	5.0
Titanium standard	600	19,350	24,000	27.0
Titanium standard	600	17,590	22,900	25.5
Titanium-9.6 w/o boron	Room	53,100	56,500	(b)
Titanium-9.6 w/o boron	Room	53,150	56,900	1.5
Titanium-9.6 w/o boron	600	22,320	26,840	4.5
Titanium-9.6 w/o boron	600	29,240	33,800	2.0
Titanium-26 w/o boron	Room	(c)	25,200	1.5
Titanium-26 w/o boron	Room	(c)	29,630	1.0
Titanium-26 w/o boron	600	(c)	20,230	2.0
Titanium-26 w/o boron	600	(c)	17,110	2.0
Titanium-12.9 w/o B_4C	Room	(b)	13,070	(b)
Titanium-12.9 w/o B_4C	Room	54,050	55,600	1.5
Titanium-12.9 w/o B_4C	600	24,800	28,440	2.5
Titanium-12.9 w/o B_4C	600	24,000	28,130	3.0
Titanium-18.2 w/o B_4C	600	22,080	22,300	2.5
Titanium-18.2 w/o B_4C	600	22,400	22,540	1.5
Titanium-25.7 w/o B_4C	600	(c)	20,870	1.5
Titanium-25.7 w/o B_4C	600	(c)	18,800	2.0
Titanium-35 w/o B_4C	Room	(c)	16,450	0.5
Titanium-35 w/o B_4C	600	(c)	11,850	(b)
Titanium-35 w/o B_4C	600	(c)	10,800	1.0

(a) Broke in extensometer knife edge — no elongation measured.

(b) Broke outside gage marks.

(c) Specimen reached maximum load before 0.2 per cent offset was reached.

These data indicate that the unclad hot-pressed specimens are brittle as expected. The dispersion with the smallest amount of boron has the highest yield and ultimate strength at the elevated temperature. The specimens do not show any appreciable weakening effect in comparison with the titanium standard until the 35 w/o loading is reached.

Roll Bonding

The major portion of the cladding in this program was accomplished by the use of the pressure-bonding technique. For comparison, however, some roll-cladding tests were made utilizing the 9.6 w/o boron and 12.9 w/o B₄C dispersions. A 35 w/o B₄C specimen was also roll clad to obtain information on the feasibility of roll cladding a material containing a boron-compound loading of approximately 50 volume per cent.

The specimens were roll bonded by the conventional picture-frame technique. Mild steel packs with 2-in. -square inserts prepared from commercial-grade titanium were used. A compartmentalized titanium frame was used, permitting the cladding of four cores per pack. The inserts were machined from hot-rolled titanium, with the exception of the cover plates which were cold rolled the final 40 per cent to the desired thickness, vapor-grit blasted, annealed in a vacuum, and recleaned. Cores were prepared by grinding the hot-pressed compacts to the final size of 0.4 by 0.5 by 0.250 in.

The following cleaning procedure was used to prepare the inserts preparatory to assembly and roll bonding:

- (1) Scrub with steel wool in acetone
- (2) Wipe dry
- (3) Scrub with hot (180 F) Alconox solution
- (4) Rinse with hot (180 F) distilled water
- (5) Rinse with room-temperature distilled water
- (6) Rinse with hot (180 F) distilled water
- (7) Wipe dry immediately with a clean lint-free towel.

The specimens were cleaned by polishing each surface with a 600-grit paper. The compacts were then assembled immediately after the cleaning operation with care being taken to prevent any contamination of specimens or inserts. Clean rubber gloves were worn at all times by the personnel cleaning and assembling the compacts. Immediately upon assembly, the jackets were welded in a dry-argon-atmosphere tank. The packs were then heated to 500 C, evacuated to a pressure of 1×10^{-3} mm of mercury, and sealed.

The technique adopted for rolling was to reduce the specimens to an over-all 3-1/2-to-1 reduction at the rate of 20 per cent per pass. The packs were inverted and reversed after each pass. A rolling temperature of 1500 F was employed. After the last roll pass, the packs were cooled in air. Figure 2 shows a cross section of a titanium roll-clad specimen with a core of 12.9 w/o B₄C in titanium.

Figures 3, 4, and 5 show the dispersion and core-to-cladding interface of the specimens containing cores of 9.6 w/o boron, 12.9 w/o B₄C, and 35 w/o B₄C dispersions in titanium, respectively.

FIGURE 2. LONGITUDINAL CROSS SECTION OF A TITANIUM-CLAD TITANIUM-12.9 w/o B₄C DISPERSION

The specimen was rolled to a 3-1/2-to-1 reduction at 1500 F.

FIGURE 3. PHOTOMICROGRAPH OF A TITANIUM-CLAD TITANIUM-9.6 w/o BORON DISPERSION

Longitudinal cross section.

FIGURE 4. PHOTOMICROGRAPH OF A ROLL-BONDED TITANIUM-CLAD TITANIUM-12.9 w/o B₄C DISPERSION

Longitudinal cross section.

FIGURE 5. PHOTOMICROGRAPH OF A ROLL-BONDED TITANIUM-CLAD TITANIUM-35 w/o B₄C DISPERSION

The voids are the result of B₄C pullout during metallographic preparation.
Longitudinal cross section.

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Pressure Bonding

A pressure-bonding technique was utilized to clad with titanium dispersions of titanium-9.6 and 26 w/o boron and titanium-12.9, 18.2, 25.7, and 35 w/o B₄C. In this technique, the components to be bonded were sealed in an evacuated can and subjected to an inert-gas pressure at elevated temperature.

The hot-pressed titanium-boron dispersions were ground to a 0.500 by 0.500 by 0.100-in. size. Hot-rolled commercial-grade titanium was used as the cladding material. The titanium frames were machined to fit the core inserts with outside dimensions of 1.000 by 1.000 by 0.100 in. Cover plates of a 0.050-in. thickness were utilized. Several specimens were bonded in one operation. Each specimen was separated from the next by use of Ti-Namel spacers which were removed by acid pickling after bonding.

As-rolled 0.018-in. -thick Type 304 stainless steel was used as the can material. The cans were formed and sealed by arc welding. A stainless steel end plate (0.052 in. thick) sheared to size and containing a welded stainless steel evacuation tube was arc welded to each pressure-bonding can. The backup plates (0.123 in. thick) and the end plate (0.052 in. thick) for each container were sheared to size from as-rolled Type 304 stainless steel material. A typical pressure-bonding can arrangement is shown in Figure 6.

The stainless containers were pickled at 140 F in a solution consisting of 50 parts water, 48 parts nitric acid, and 2 parts hydrofluoric acid, and wire brushed to remove oxide residue formed during the welding of the cans.

The dispersion-core inserts and the mating surfaces of the clad components were metallographically polished and surface cleaned prior to the pressure-bonding operation. The polishing procedure for the dispersion-core inserts consisted of abrading all the surfaces under water with 80-, 180-, and finishing with 240-grit paper in order to remove the oxidized surfaces formed during the grinding operation and to produce smooth surfaces for effective bonding. The cladding components were abraded with 180- and finished with 240- grit paper.

No precleaning treatment was used on the Ti-Namel spacers and on the stainless steel backup and end plates. The core and cladding components were degreased with acetone and subjected to a series of washings and rinses as follows: 180 F Alconox solution wash, cold-water rinse, 180 F water wash, cold-water rinse, and a 200 F water wash followed by air drying. In all instances, the components were handled with clean rubber gloves during washing and rinsing. This was done in an effort to prevent recontamination of any surfaces during the cleaning cycles. After cleaning, the cores were given a low-temperature vacuum anneal and assembled immediately.

All components were carefully assembled with the use of clean rubber gloves, and the end plate, opposite the tube end, was immediately Heliarc welded to each can.

After welding of the final end plug, the assembly was immediately leak tested and evacuated for 24 hr. The specimens were evacuated to a pressure of 1×10^{-3} mm of mercury or less during this period. The evacuated can was then sealed and immediately placed in the high-pressure autoclave for pressure bonding.

FIGURE 6. CAN ASSEMBLY FOR PRESSURE BONDING

In a trial run, a specimen that had been subjected to a temperature of 1600 F at 10,000 psi for 4 hr exhibited spotty bonding, so the balance was pressure bonded for 6 hr. In pressure bonding, the temperature and helium gas pressure were increased together and held for 6 hr. The specimens were all furnace cooled under pressure to room temperature. After pressure bonding and stripping of the stainless steel can, the composites were pickled in a solution of 52 parts water and 48 parts nitric acid in order to remove the Ti-Namel spacers from between the clad specimens.

Metallographic examination of the clad specimens in the as-pressure-bonded condition indicated that good bonding had occurred. In addition, metallographic examination indicated that the core inserts had undergone slight densification with no apparent change in dispersion characteristics as a result of the pressure-bonding operation. The average reduction in thickness after pressure bonding was 3 per cent. No edge effects or uneven surfaces were evident in the clad specimens after pressure bonding. Typical sections of the pressure-bonded specimens are shown in Figures 7 through 10. It should be mentioned that the voids in the photomicrographs resulted from pullout during metallographic preparation.

To evaluate the mechanical properties of the specimens, bend testing was used. All specimens subjected to bend testing failed before a 90-deg bend was achieved. However, examination of the bend-test specimens revealed that good core-to-cladding bonding was achieved, since the diffusion interfaces formed seemed to be stronger than the base-core materials. Photomacrographs of the as-pressure-bonded and bend-tested specimens are shown in Figures 11 through 16. Although some of the ruptures occurred in the vicinity of the core-cladding interface, the actual ruptures occurred in the core and not along the original core-cladding interface.

Corrosion Tests

The as-rolled and pressure-bonded specimens were corrosion tested in 680 F pressurized water (specified resistivity greater than 1 megohm-cm) in a 1-liter Type 316 stainless steel autoclave. The pressure-bonded specimens measured 1 by 1 by 0.2 in. and contained dispersion cores measuring 0.5 by 0.5 by 0.1 in., whereas the roll-bonded specimens had a core measurement of 1.75 by 0.4 by 0.070 in. The latter specimens had a top and bottom cladding thickness of 0.017 in. Comparing the heat treatments, the pressure-bonded specimens were held at 1600 F for 6 hr and slow cooled in the high-pressure autoclave, whereas the roll-bonded specimens were rolled at 1500 F and were at temperature for approximately 2 hr and air cooled.

The corrosion resistance of all specimens was measured by a standard technique of defecting the cladding, using a 0.040-in. hole drilled through one cladding face and halfway through the core, as shown in the tested specimen in Figure 17. Another hole was drilled through one edge of each specimen, not touching the core, by which the specimens were suspended.

50X

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FIGURE 7. BOND INTERFACE BETWEEN TITANIUM AND A DISPERSION OF 26 w/o BORON IN TITANIUM

Pressure bonded for 4 hr at 1600 F and 10,000 psi of pressure for experimental studies. A machined core insert from a hot-pressed compact was used. Particle size of dispersant is minus 60 plus 80 mesh.

50X

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FIGURE 8. BOND INTERFACE BETWEEN TITANIUM AND A DISPERSION OF 12.9 w/o B₄C IN TITANIUM

Pressure bonded for 6 hr at 1600 F and 10,000 psi of pressure. A surface-ground core insert from a hot-pressed compact was used. Particle size of dispersant is minus 100 plus 200 mesh.

Bond Interface Between Titanium and a Dispersion of 18.2 w/o B_4C in Titanium

Bond Interface Between Titanium and a Dispersion of 25.7 w/o B_4C in Titanium

FIGURE 9. BOND INTERFACES FORMED AFTER PRESSURE BONDING FOR 6 HR AT 1600 F AND 10,000 PSI OF PRESSURE

Surface-ground core inserts from hot-pressed compacts were used. Particle size of dispersants is minus 100 plus 200 mesh.

Titanium

Dispersion

Bond Interface Between Titanium and a Dispersion of 26 w/o Boron in Titanium

Titanium

Dispersion

Bond Interface Between Titanium and a Dispersion of 35 w/o B_4C in Titanium

FIGURE 10. BOND INTERFACES FORMED AFTER PRESSURE BONDING FOR 6 HR AT 1600 F AND 10,000 PSI OF PRESSURE

Surface-ground core inserts from hot-pressed compacts were used. Particle size of dispersants is minus 100 plus 200 mesh.

5X

Etched

N41935

FIGURE 11. AS-PRESSURE-BONDED (TOP) AND BEND-TESTED (BOTTOM) DISPERSION SPECIMENS OF 26 w/o BORON IN TITANIUM CLAD WITH TITANIUM

Pressure bonded for 6 hr at 1600 F and 10,000 psi of pressure.

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FIGURE 12. AS-PRESSURE-BONDED (TOP) AND BEND-TESTED (BOTTOM) DISPERSION SPECIMENS OF 12.9 w/o B_4C IN TITANIUM CLAD WITH TITANIUM

Pressure bonded for 6 hr at 1600 F and 10,000 psi of pressure. The rupture parallel to the cladding is contained in the core rather than in the core-to-cladding interface.

FIGURE 13. AS-PRESSURE-BONDED (TOP) AND BEND-TESTED (BOTTOM) DISPERSION SPECIMENS OF 18.2 w/o B₄C IN TITANIUM CLAD WITH TITANIUM

Pressure bonded for 6 hr at 1600 F and 10,000 psi of pressure. The rupture parallel to the cladding is contained in the core rather than in the core-to-cladding interface.

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FIGURE 14. AS-PRESSURE-BONDED (TOP) AND BEND-TESTED (BOTTOM) DISPERSION SPECIMENS OF 25.7 w/o B_4C IN TITANIUM CLAD WITH TITANIUM

Pressure bonded for 6 hr at 1600 F and 10,000 psi of pressure. The rupture parallel to the cladding is contained in the core rather than in the core-to-cladding interface.

FIGURE 15. AS-PRESSURE-BONDED (TOP) AND BEND-TESTED (BOTTOM) DISPERSION SPECIMENS OF 26 w/o BORON IN TITANIUM CLAD WITH TITANIUM

Pressure bonded for 6 hr at 1600 F and 10,000 psi of pressure. The rupture parallel to the cladding is contained in the core rather than in the core-to-cladding interface.

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FIGURE 16. AS-PRESSURE-BONDED (TOP) AND BEND-TESTED (BOTTOM) DISPERSION SPECIMENS OF 35 w/o B_4C IN TITANIUM CLAD WITH TITANIUM

Pressure bonded for 6 hr at 1600 F and 10,000 psi of pressure.

FIGURE 17. TITANIUM-ROLL-CLAD 35 w/o B₄C DISPERSION IN TITANIUM BEFORE AND AFTER CORROSION TESTING 1 DAY IN 680 F WATER

The corrosion results are summarized in Table 2. From these results, the following conclusions can be made:

- (1) Roll-bonded and pressure-bonded samples containing boron and B₄C are both corrosion resistant at loadings of 12.9 w/o or less.
- (2) At high loadings, the pressure-bonded samples are more resistant than those which are roll bonded. After 21 days of exposure, the thickness increase and weight change on a pressure-bonded 35 w/o B₄C sample was comparable with that obtained after only 1 day of exposure on a similar roll-bonded sample. Apparently, pressure bonding results in a more uniform dispersion, whereas roll bonding may produce stringers which could allow a continuous path for attack.
- (3) Corrosion resistance decreases as loadings increase. Dispersions of 9.6 w/o boron and 12.9 w/o B₄C survived up to 77 days of exposure with no evidence of corrosion. However, as the amount of the loadings increased, thickness and weight change of samples increased accordingly. At the higher loadings, there is more chance of the particles touching one another. Since corrosion occurs around or at the edge of the particles, this would allow a continuous path for attack. This effect is shown in the photomicrographs in Figures 18, 19, and 20. The areas shown are cross sections near the intentional defect. There is little attack around the particles in the 12.9 w/o B₄C sample. However, in the 18.2 and 25.7 w/o B₄C samples, attack has occurred around or at the edge of the particles and the grinding and polishing operations appear to have dislodged some of the particles resulting in voids.

TABLE 2. CORROSION RESULTS OBTAINED IN 680 F WATER ON TITANIUM-CLAD BORON AND B₄C DISPERSIONS IN TITANIUM

Samples Contained a 0.040-In.-Diameter Defect Drilled Halfway Through the Core

Dispersion in Core, w/o	Bonding Method	Exposure Time, days	Thickness Increase at Defect, mils	Remarks
9.6 boron	Roll	77	None	Little or no attack in core
9.6 boron	Roll	77	None	Little or no attack in core
9.6 boron	Pressure	21	None	Little or no attack in core
26 boron	Pressure	35	9	Some attack in core
26 boron	Pressure	35	10	Some attack in core
12.9 B ₄ C	Roll	77	None	Little or no attack in core
12.9 B ₄ C	Roll	77	None	Little or no attack in core
12.9 B ₄ C	Pressure	35	None	Little or no attack in core
12.9 B ₄ C	Pressure	35	None	Little or no attack in core
18.2 B ₄ C	Pressure	35	4	Some attack in core
18.2 B ₄ C	Pressure	35	3	Some attack in core
25.7 B ₄ C	Pressure	35	18	Severe attack in core
25.7 B ₄ C	Pressure	35	22	Severe attack in core
35 B ₄ C	Pressure	21	25	Severe attack in core
35 B ₄ C	Pressure	21	25	Severe attack in core
35 B ₄ C	Roll	1	20	Severe attack in core
35 B ₄ C	Roll	1	20	Severe attack in core

FIGURE 18. PHOTOMICROGRAPH OF TITANIUM-CLAD 12.9 w/o B_4C DISPERSION IN TITANIUM AFTER 35 DAYS OF EXPOSURE IN 680 F WATER

Cross section near defect.

FIGURE 19. PHOTOMICROGRAPH OF TITANIUM-CLAD 18.2 w/o B_4C DISPERSION IN TITANIUM AFTER 35 DAYS OF EXPOSURE IN 680 F WATER

Cross section near defect.

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100X

As Polished

N41992

FIGURE 20. PHOTOMICROGRAPH OF TITANIUM-CLAD 25.7 w/o B₄C DISPERSION IN TITANIUM
AFTER 35 DAYS OF EXPOSURE IN 680 F WATER

Cross section near defect.

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ROLL BONDING COMPOSITE ZIRCALOY 2-CLAD SPECIMENS OF
HAFNIUM AND EXTRUDED TITANIUM-BORON

A study was conducted to determine the feasibility of fabricating composite sub-scale control-rod specimens incorporating a core of titanium-boron joined by a metallurgical bond to hafnium. It was planned to utilize an extrusion process for the breakdown of the titanium-boron dispersion. It was anticipated that extrusion would produce a dense product of uniform dispersion at a low relative cost. The extruded titanium-boron dispersion and wrought hafnium were then to be joined and clad with Zircaloy 2 by roll bonding.

Description of Materials

The boron-dispersion material used for roll-bonding studies was received from the Bettis Laboratories in the form of extruded-powder bar stock containing 3.8 and 20 w/o boron-titanium. Metallographic examination of both materials revealed that the dispersant was nonuniform in size and was nonuniformly dispersed throughout a matrix of alpha titanium plus a minute amount of a needlelike constituent believed to be titanium hydride. In addition, a considerable amount of porosity was observed in the matrix. Typical transverse and longitudinal sections are shown in Figures 21 and 22 for the as-extruded 3.8 and 20 w/o boron-titanium dispersions, respectively. The longitudinal sections of both dispersion materials exhibit slight directionality. It should be noted that the voids in Figure 21 and subsequent photomicrographs resulted from pullout during metallographic preparation.

For the 3.8 w/o boron-titanium dispersion material the dispersant particle size varied from 400 to 16 mesh. Particle sizes of 400 to 20 mesh were observed in the transverse and longitudinal specimens of the material having the 20 w/o boron addition.

Reactor-grade Zircaloy 2 and hafnium metal were used for the roll-bonding studies.

Preparation and Assembly of Components for Roll Bonding

Longitudinal specimens 0.180 by 0.400 by 0.600 in. were machined from the as-extruded dispersion materials. During machining, a considerable amount of the dispersed boron particles was torn out and, as a result, metallographic surface preparation of the core components appeared necessary. All surfaces of each dispersion specimen were abraded under water with 80- and 240-grit paper until satisfactory surfaces for bonding were attained.

Hafnium end attachments 0.180 by 0.200 by 0.400 in. were machined from hot-rolled-plate material and surface prepared in the same manner as the dispersion specimens. The Zircaloy 2 cladding components and Ti-Namel frames and covers were used in the as-machined condition.

FIGURE 21. TITANIUM-3.8 w/o BORON DISPERSION

Transverse and longitudinal sections of
as-extruded stock.

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50X

Transverse Section

N41944

50X

Longitudinal Section

N41945

FIGURE 22. TITANIUM-20 w/o BORON DISPERSION.

Transverse and longitudinal sections of
as-extruded stock.

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The machined and abraded specimens were degreased in acetone and subjected to a series of washings and rinses as follows: 180 F Alconox-solution wash, cold-water rinse, 180 F water wash, cold-water rinse, and a 200 F water wash followed by air drying. In all instances, the components were handled with clean rubber gloves during the wash cycle. This was done in an effort to prevent recontamination of any of the surfaces during the cleaning cycle. After cleaning, the components were immediately assembled.

All components were carefully assembled with the use of clean rubber gloves and immediately loaded into a controlled-atmosphere weld tank for welding the Ti-Namel packs. The manner in which the cladding components were assembled in the Ti-Namel frames is shown in Figure 23. Each pack contained one dispersion-core insert from each of the two dispersion materials. After welding, each pack was unloaded from the welding tank, leak tested, and immediately evacuated for 24 hr until a pressure of 1×10^{-3} mm of mercury was reached in the pack. The evacuated pack was then sealed and immediately placed in a furnace previous to roll bonding.

FIGURE 23. ASSEMBLY OF CLADDING COMPONENTS FOR ROLL-BONDING STUDIES

Roll Bonding

The sealed packs were fabricated at 1450 and 1550 F. Reductions of 20 per cent per pass were employed with a total over-all reduction of 3 to 1. The packs were preheated for 45 min and annealed for 20 min between passes and after the last pass prior

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to air cooling. In order to reduce end effects, the packs were inverted and reversed after each roll pass.

In an effort to further improve the properties of the various bonds formed during roll bonding at 1550 F, a postfabrication heat treatment was investigated. This pack was roll bonded in the same manner as the other packs, with the exception that after the final anneal the pack was furnace cooled to 800 F and then air cooled. After removal of the Ti-Namel jacket, the roll-bonded specimen was annealed at 2300 F for 3 hr in a helium-controlled atmosphere, furnace cooled, and vapor-grit blasted. The high-temperature diffusion anneal in the beta-phase region of the zirconium-hafnium system was used to increase the amount of diffusion between hafnium and Zircaloy 2. A 12 per cent reduction at 1000 F was then used to work the titanium-to-hafnium and the Zircaloy 2-to-titanium bonds in the alpha region. This hot-working treatment was followed by vapor-grit blasting and alpha vacuum annealing for 24 hr at 1000 F.

Radiographs were made of the roll-bonded specimens to locate the composite core and to determine the core configuration. The specimens were then sectioned for metallographic inspection and test evaluation.

Evaluation and Testing of Roll-Clad Specimens

The roll-bonded specimens were evaluated by metallographic inspection for bond uniformity and integrity. Hardness and bend tests were conducted to obtain a relative measure of bond strength.

The results of the metallographic inspection are discussed below for each specimen and individual bond interface. In most instances, a photomicrograph is used to illustrate the type of bond that was formed. The following discussions do not include the specimens roll bonded at 1450 F because metallographic examination revealed that some of these specimens possessed discontinuous bonding.

Specimens roll bonded at 1550 F and not given the postfabrication anneal were bend tested. All specimens failed before a 90-deg bend was achieved. Hardness data were obtained across the bond interface, and Knoop hardness numbers (100-g load) are shown adjacent to some of the photomicrographs. Since no significant difference in hardness values was observed at the hafnium-Zircaloy 2 bond interface for the as-roll-bonded specimens, the values are not reported.

Titanium-Boron-Zircaloy 2 Interface

Excellent metallurgical bonds with a relatively thick diffusion interface were obtained during roll cladding the Zircaloy 2 cover material and the two titanium-boron dispersions at 1550 F. Figures 24 and 25 illustrate that diffusion was relatively extensive. The rolling temperature of 1550 F was above the transformation temperature for alloys between about 2 and 80 w/o titanium in zirconium, and it is for this reason that diffusion was rapid, and that there was a transformed-beta structure in the diffusion zones, having a high hardness.

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FIGURE 24. PHOTOMICROGRAPH OF TITANIUM-3.8 w/o BORON DISPERSION-ZIRCALOY 2 INTERFACE

Average diffusion-interface thickness is 1.93 mils. Knoop hardness numbers (100-g load) for the diffusion zones and matrices are shown adjacent to the photomicrograph.

FIGURE 25. PHOTOMICROGRAPH OF TITANIUM-20 w/o BORON DISPERSION-ZIRCALOY 2 INTERFACE

Average diffusion-interface thickness is 1.90 mils. Knoop hardness numbers (100-g load) for the diffusion zones and matrices are shown adjacent to the photomicrograph.

Metallographic examination revealed bonds of good integrity and continuity along the bond interfaces, except where a large boron particle or a large number of closely spaced small boron particles were at the bond interface during fabrication. It was apparent that good bonding can be achieved by roll cladding at 1550 F if the boron-particle size is relatively small and the particles are well dispersed.

The hardness values obtained in the diffusion interface adjacent to the photomicrographs in Figure 24 and 25 are higher than for either the core or the cladding; however, the values are not so high as to indicate any compound formation at the interface, but rather are indicative of a transformed-beta structure.

Metallographic examination of the bend-tested specimens revealed that in areas where the boron particles in the dispersion matrix had segregated at the diffusion interface rupture took place during bending between the two diffusion layers and progressed along this interface for some distance. However, in areas where the dispersion of boron particles was more uniform and smaller in size, rupture occurred in the core matrix, leaving the core-cladding diffusion zone intact.

The extent of diffusion produced by the postfabrication heat treatment between the titanium-boron dispersion and the Zircaloy 2 cladding, as can be seen in Figures 26 and 27, was considerably more extensive than for the as-roll-bonded specimens. Since the diffusion-annealing temperature, 2300 F, was above the transformation temperature for all titanium-zirconium alloys, a transformed-beta structure was produced in the diffusion zones as well as in the matrices of the core and the cladding. No attempt was made to determine the diffusion-interface thickness.

The strength of the diffusion interface in comparison to the strength of the core was improved by the postfabrication heat treatment, as indicated by metallographic examination of the bend-tested specimens. There was no separation between the core and the cladding for the titanium-3.8 w/o boron specimen, and only slight separation for the titanium-20 w/o boron specimen.

Titanium-Boron-Hafnium Interface

Excellent metallurgical bonds with a large diffusion interface were obtained during roll cladding at 1550 F between the hafnium end attachments and the two titanium-boron dispersions. Photomicrographs of two of these bonds are shown in Figure 28. It will be noted that the appearance of the bond interface between titanium and hafnium is practically identical to that between titanium and Zircaloy 2, as illustrated in Figures 24 and 25. This strongly suggests that the constitutional diagram for the hafnium-titanium system and that for the zirconium-titanium system are of the same type, including a minimum in the alpha-beta transformation region. No trace of an intermetallic-compound layer can be seen.

By an examination of the photomicrographs, it appears that brittle bonds were the result of rapid cooling from the beta temperature which caused transformation of beta to alpha at lower temperatures. The hardness values given with the photomicrographs in Figure 28, obtained across the diffusion zone, are higher than for the core or the cladding; however, the values are not high enough to indicate any compound formation at the interface.

Dispersion

Zircaloy 2

100X

N40788

FIGURE 26. PHOTOMICROGRAPH OF TITANIUM-3.8 w/o BORON DISPERSION-ZIRCALOY 2 INTERFACE

Specimen was given the postfabrication heat treatment.

Dispersion

Zircaloy 2

100X

N40792

FIGURE 27. PHOTOMICROGRAPH OF TITANIUM-20 w/o BORON DISPERSION-ZIRCALOY 2 INTERFACE

Specimen was given the postfabrication heat treatment.

Photomicrograph of Titanium-3.8 w/o Boron Dispersion-Hafnium Interface;
Average Diffusion-Interface Thickness Is 2.10 Mils

Photomicrograph of Titanium-20 w/o Boron Dispersion-Hafnium Interface;
Average Diffusion-Interface Thickness is 1.16 Mils

FIGURE 28. BOND INTERFACES BETWEEN DISPERSIONS AND HAFNIUM END ATTACHMENTS

As roll clad at 1550 F with a 3-to-1 reduction. Knoop hardness numbers (100-g load) for the diffusion zones and matrices are shown adjacent to the photomicrographs.

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During bend testing, ruptures were produced in the hafnium, leaving the bond interface intact. This suggests that the bond is relatively strong and is not brittle.

Metallographic examination of the bond interfaces between the two dispersion materials and the hafnium end attachments after the postfabrication heat treatment revealed that the amount of diffusion was considerably greater than for the as-roll-bonded specimens. Typical bond interfaces after the postfabrication heat treatment are shown in Figure 29. A transformed-beta structure was produced in the diffusion zones as well as in the matrices of the core and the cladding by the high-temperature diffusion anneal. No attempt was made to determine the diffusion-interface thickness.

Metallographic examination of the bend-tested specimens indicated that the strength of the diffusion interface was not affected. For the specimens containing cores of the two dispersion materials, rupture during bending occurred through the titanium-boron core, leaving the titanium-hafnium diffusion interface intact to the hafnium.

Zircaloy 2-Hafnium Interface

Roll cladding at 1550 F produced a Zircaloy 2-hafnium bond with a minimum amount of diffusion. The bond interface is shown in Figure 30. No significant change in hardness was observed across the hafnium-Zircaloy 2 interface.

Metallographic examination of the bend-tested specimens revealed that rupture occurred at the bond interface. This indicates that the interface is weak or that a poor metallurgical bond is produced during roll cladding at 1550 F.

Excellent metallurgical bonding with a comparatively large diffusion zone was achieved by the postfabrication heat treatment of specimens roll clad at 1550 F. Due to the high-temperature diffusion anneal, which was probably in the beta region for all zirconium-hafnium alloys, a transformed-beta structure was produced in the diffusion zones as well as in the matrices of the core and the cladding, as observed by metallographic inspection (Figure 31). Evidently extensive diffusion has occurred; however, it is not evident because of the lack of structural or etching differences in alloys of the zirconium-hafnium system.

Metallographic examination of the bend-tested specimen revealed that considerable improvement in properties was achieved by the postfabrication heat treatment. Direct rupture between the Zircaloy 2 covers and hafnium end attachments occurred during bending without the slightest evidence of bond separation.

SJP:DLK:ESH:GWC:MAG:DEL/vcz

Photomicrograph of Titanium-3.8 w/o Boron Dispersion-Hafnium Interface

Photomicrograph of Titanium-20 w/o Boron Dispersion-Hafnium Interface

FIGURE 29. BOND INTERFACES BETWEEN DISPERSIONS AND HAFNIUM END ATTACHMENTS

Roll clad at 1550 F with a 3-to-4 reduction and given the postfabrication heat treatment of furnace cooling to 800 F and then air cooling to room temperature. This was followed by an anneal at 2300 F for 3 hr in a helium atmosphere and furnace cooling.

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FIGURE 30. PHOTOMICROGRAPH OF BOND INTERFACE BETWEEN ZIRCALOY 2 AND HAFNIUM END ATTACHMENT

As roll clad at 1550 F with a 3-to-1 reduction.

FIGURE 31. PHOTOMICROGRAPH OF BOND INTERFACE BETWEEN ZIRCALOY 2 AND HAFNIUM END ATTACHMENT

Roll clad at 1550 F with a 3-to-1 reduction and given the postfabrication heat treatment.

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