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ELECTRON MICROSCOPICAL EXAMINATION OF
BONDS IN ZIRCALOY-2

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Arthur P. Young and Charles M. Schwartz

Electron microscopy was used to supplement metallographic studies of bonds between Zircaloy-2 interfaces. Treated surfaces before bonding, and bonded sections made by a variety of techniques were examined.

Electron micrographs of belt-abraded surfaces exhibited a consistent fine-scale roughness. Chemically pickled surfaces were nearly smooth regardless of prior treatment.

Chemically pickled samples and a zirconium oxide-coated sample pressure bonded at 1500 F and 10,000 psi had pitting at bond lines that could have been due to voids or to contaminant at the interface which etched out. The pitting was almost completely eliminated in one sample by pressing one hour at 500 F and 350,000 psi. This indicated that the bond-line pitting in these samples was due to voids at the interface.

Zircaloy-2 samples pressure bonded after coating with carbon, chromium, iron, nickel, or tin etched in relief along the bond line, indicating the presence of contaminant at the interface.

On the basis of the present investigation, it is proposed that grain growth across the interface in chemically pickled samples may have been inhibited by the presence of a thin contaminant film originally present on the Zircaloy surfaces. However, the poor grain-growth characteristics of chemically pickled samples may also be due in part to the surfaces being too smooth.

INTRODUCTION

In a study of gas-pressure bonding of Zircaloy-2, conducted at Battelle⁽¹⁾, it was important to find an inexpensive surface preparation that would yield consistently strong and corrosion-resistant metallurgical bonds. Several surface-preparation methods were tested. One method of evaluating the Zircaloy-to-Zircaloy and Zircaloy-to-core bonds obtained with the different surface preparations was metallographic examination of bond sections. It was found that carefully machined or belt-abraded Zircaloy-2 surfaces produced Zircaloy-to-Zircaloy bonds with nearly complete grain growth and very little evidence of contaminant at the bond interface. Other types of surface preparation, notably chemical polishing of Zircaloy-2 components, produced Zircaloy-to-Zircaloy bonds with incomplete grain growth and with apparent evidence of contaminant at the interface.

The cause of defective bonds in chemically pickled samples was not apparent from metallographic examination of bond sections. It was thought possible that a better understanding of the factors contributing to the formation of defective Zircaloy-to-Zircaloy bonds in gas-pressure-bonded samples might result from the use of other analytical methods to augment light microscopy.

(1) References at end of report.

The objective of the present investigation was to determine whether electron microscopy and electron diffraction could be used to gain a better understanding of Zircaloy-2 pressure bonding, particularly of chemically pickled samples. This report describes the experimental data and some theories about Zircaloy bonding resulting from the experimental work.

EXPERIMENTAL PROCEDURE

Sample Preparation

The Zircaloy-2 samples investigated in this study were prepared in a previous program on the development of techniques for the fabrication of flat-plate fuel elements by gas pressure bonding.⁽¹⁾ To evaluate the effect of the surface-preparation method on the bonding obtained by the process, Zircaloy-2 plates having mating surfaces prepared for bonding by various techniques were gas-pressure bonded in Ti-Namel containers in high-temperature autoclaves under 5,000 to 10,000 psi of helium. Excellent bonds were consistently obtained with some surface-preparation techniques, while with other techniques considerable variability in bonding was observed. Samples for the present investigation were selected for the most part from this latter group.

Microscopic Techniques

Metallographic specimens of Zircaloy-2 bond sections were prepared in the same manner for electron and light microscopy. Cathodic vacuum etching and chemical etching were compared on a bond section in which the bond line was intermittent and indistinct. The miscellaneous pitting resulting from cathodic etching made the bond line difficult to find in the electron microscope. Therefore, all of the electron micrographs of bond lines in this report were taken of samples which were chemically etched in a solution of 50 parts nitric acid, 50 parts glycerin, and 5 parts hydrofluoric acid.

Two types of replicas were used for electron microscopy. Platinum-shadowed carbon replicas were made by evaporating carbon on an intermediate thick plastic stripping from the sample surface, and then dissolving the plastic and shadowing the carbon replicas. Carbon-Formvar replicas were made by evaporating carbon on a plastic stripping in the same manner, and then backing the carbon with a thin Formvar film before dissolving the thick plastic. The shadowed carbon replicas were thinner and more contrasty than the carbon-Formvar replicas, and thus showed finer detail. However, the carbon-Formvar replicas had two advantages in this application. It was easier to determine whether material along the bond line etched out or was in relief in carbon-Formvar replicas. Secondly, the carbon-Formvar replicas generally held up over the whole specimen support screen. This was important in many instances in locating the bond line in the electron microscope.

Either positive or negative replicas could be made, the former by evaporating carbon on a cellulose nitrate impression of the sample surface, the latter by evaporating carbon on a cellulose nitrate stripping taken from an initial cellulose acetate

impression of the sample. In positive carbon-Formvar replicas fine microstructural features in relief appeared darker in the photographic print than the surrounding matrix; etched-out areas appeared lighter. This shading was reversed in negative replicas. Generally, replicas in which the bond line appeared darker than the matrix held up better along the bond line.

In some samples the bond line could be easily seen in the light microscope but was quite indistinct in the electron microscope, because of the higher magnification and resultant loss in contrast. Positive identification of the bond line in the electron microscope was therefore in some instances quite difficult. It was found that the bond line could be positively identified by the following procedure: Parallel scratches bracketing the bond line were ruled on the metallographic sample and transverse scratches at intervals along the bond line. In the replica, the scratches and the bond line along with the underlying specimen screen wires could be seen in the light microscope as illustrated in Figure 1a. Figure 1b shows the same area in the original sample. A pencil sketch of an area such as that shown in Figure 1 could serve as a map showing the number of squares up and across from the intersection of scratches to a segment of the bond line. By locating the intersection of scratches in the electron microscope and counting squares according to the map the bond line could be located unambiguously. The gross wrinkling seen in the light micrograph, Figure 1a, does not affect the electron-microscope image.

EXPERIMENTAL RESULTS

Examination of Zircaloy-2 Surfaces Before Bonding

Since fine-scale surface roughness may affect bonding, the surfaces of Zircaloy-2 samples after various preparations were examined in the electron microscope. There were more local variations in the fine-scale roughness of machined surfaces than in belt-abraded surfaces. Figure 2 is typical of most of the areas examined in belt-abraded samples. There was no significant difference in the appearance of hot-rolled and cold-rolled belt-abraded samples. Figure 3 shows two quite different areas in a machined sample. Both types of surface finish were quite common in machined samples. If bonding is dependent on surface roughness, one might expect consistent results with belt-abraded samples, and it has been found that bonds with good integrity are obtained consistently with samples prepared by this technique.⁽¹⁾

Figure 4 shows a typical area in a cold-rolled sample. The bondability was generally very poor for cold-rolled Zircaloy.⁽¹⁾ This might be related in part to the fact that the cold-rolled surface was smoother on the average than machined or belt-abraded surfaces. However, other factors such as surface contamination also probably contributed to the failure of cold-rolled Zircaloy to bond well.

a. Replica

b. Sample

FIGURE 1. APPEARANCE IN THE REPLICA AND IN THE ORIGINAL SAMPLE OF RULED SCRATCHES USED TO LOCATE BOND LINE

The large-scale wrinkles in the replica do not affect the high-magnification image in the electron microscope. The sample shown, FP-2, is from a Zircaloy couple prepared with pickled components.

6500X

E5946D

FIGURE 2. TYPICAL SURFACE FOUND IN BELT-ABRADED ZIRCALLOY-2

This electron micrograph was made from a shadowed positive carbon replica. The Zircaloy-2 was belt abraded after hot rolling.

6500X

E5947B

6500X

E5947C

FIGURE 3. TWO TYPES OF SURFACE FINISH COMMONLY FOUND IN HOT-ROLLED ZIRCALOY-2 AFTER THE MACHINING SURFACE- PREPARATION TECHNIQUE

The electron micrographs were made from shadowed positive carbon replicas.

9000X

E5942B

FIGURE 4. TYPICAL SURFACE AREA IN COLD-ROLLED ZIRCALOY-2

The smooth surface of the cold-rolled material could account in part for poor bonding behavior. A shadowed positive carbon replica was used to make this electron micrograph.

Pickled surfaces were always smooth on a fine scale regardless of prior treatment. In going from hot-rolled to hot-rolled and machined, then to cold-rolled samples, pickling revealed a progressive lessening of definitive grain structure. This is illustrated in Figure 5. Samples of the type illustrated generally showed some localized pitting and lack of grain growth at the interface. At the time these samples were examined it was believed that lack of fine-scale roughness in pickled samples might contribute to poor bonding. In a subsequent investigation of the effect of surface roughness on bonding, annealed Zircaloy-2 specimens were surface machined with a shaper to 50-, 125-, 400-, and 1000-rms finishes. Complete grain growth with the absence of contaminant particles or voids was achieved across the bond interfaces in the 125-, 400-, and 1000-rms finished specimens. Grain growth across the bond interface in the 50-rms specimen was approximately 95 per cent and there were a few small areas containing particles and/or voids. There was some indication therefore that surface roughness above a minimum is desirable for good bonding.

To investigate the effect of pickling, apart from surface roughness, two annealed and belt-abraded Zircaloy-2 specimens, which would ordinarily bond well in that condition, were pickled for 5 sec at 100 F in a fresh solution of 45 parts nitric acid, 5 parts hydrofluoric acid, and 50 parts water. Presumably the surface roughness was largely preserved after the short pickle. However, the samples had a frosty appearance and some areas of discoloration. Lack of surface brightness and presence of visible films are common characteristics of samples immersed for short times in $\text{HF-HNO}_3\text{-H}_2\text{O}$ solutions. When bonded, these samples exhibited only about 20 per cent grain growth and a considerable amount of contaminant particles. Because of the greater contamination of these surfaces as compared with the usual pickled surface, the results of bonding these samples cannot be regarded as a definitive test to separate the effect of the smoothness of pickled surfaces as shown in Figure 5 from other possible effects of pickling such as contamination films and removal of worked layers.

9000X

a. Hot-Rolled Material

E5945B

9000X

b. Material Hot Rolled and
Machined

E5955A 9000X

c. Cold-Rolled Material

E5944B

FIGURE 5. APPEARANCE OF TYPICAL ZIRCALOY-2 SURFACES PICKLED AFTER MECHANICAL TREATMENT

Pickling produces a surface that is smooth on a fine scale regardless of prior treatment. A successive loss of well-defined grain structure is apparent in the photographs shown here. Only in the hot-rolled material is the alpha clearly delineated. Surfaces of this type generally showed some pitting and lack of grain growth at the bond interface. These electron micrographs were made from shadowed positive carbon replicas.

For the determination of surface films present on Zircaloy-2 samples after various treatments, electron-diffraction studies were made of a number of samples shown in Table 1. It was evident from the results in Table 1 that chemical polishing of Zircaloy-2 left SnO_2 and metallic tin on the metal surface, confirming the results of previous work.⁽²⁾ The various pickling treatments used in this study either failed to remove the tin or oxidized the base metal. The results of the electron-diffraction study will be discussed further in relation to the microscopic examination of bond lines.

Examination of Pressure-Bonded Samples

Bond lines were examined in the electron microscope in four samples prepared with various surface treatments which had been held 4 hr at 10,000 psi and 1500 F. Sample numbers, surface treatment prior to bonding, and figure numbers are listed in Table 2. The bond line in Sample SP102, the hot-rolled, machined, and pickled sample, was continuous and easily visible at high magnification. The sample was etched out at the bond interface in either a nearly continuous furrow as shown in Figure 6a or in a row of pits as shown in Figure 6b. Metal shadowing in Figure 6b gave some idea of the depth of the pits. The replica was shadowed at approximately a 45-deg angle. In a negative replica the shadow cast by the pip from a hemispherical pit in the sample would be projected to a maximum distance of about 20 per cent of the diameter beyond the rim of the pip. Some of the pits in the sample area shown in Figure 6 were deeper and some were shallower than hemispherical pits.

The bond lines in Samples SP104 and SP126, both cold-rolled and pickled, were quite indistinct and not visible at all in many segments. Where the bond line was present it consisted generally of a row of discrete, nearly circular pits. Figure 7 shows segments of the bond line in Sample SP104. In some areas where grain growth across the bond interface occurred, the rows of pits along the bond line crossed grain boundaries, as shown in Figures 7a and 7b. In many of the grains across the interface there was no visible bond line. Figure 7c shows the bond line terminating at an interface grain boundary. The etching out and lack of distinction in the bond line as compared to etching in relief and sharp distinction of grain-boundary particles is evident in Figures 7b and 7c. The bond line in Sample SP104 was similar to the Sample SP126 bond line but even less distinct. Figure 8 shows a segment of the bond line in close juxtaposition to a grain boundary. The bond line fades out in the upper grain. The pitting along the bond line in these samples may have been due to contaminant etching out at the interface. However, the nature of the round, indistinct pits suggests that the etching out might be caused by crystal imperfections, most probably small voids.

In Sample SP114, which was cold rolled and hand abraded but not pickled, the bond line was visible only in certain areas. Contaminant of some sort was unmistakably present in these areas as a result of insufficient metal removal by hand abrading. Large precipitate particles were seen in the bond lines as in Figure 9a. In some areas both particles and shallow pits were seen in the bond line as in Figure 9b. In other areas the bond line was free of particles, but there was coarse precipitate in nearby grain boundaries as in Figure 9c. Figure 9d shows a typical grain boundary at some distance from the bond line. Whatever the impurity originally at the surface in this sample, some of it was evidently swept into boundaries between grains near the interface which were formed in the cold-worked material during the bonding cycle.

TABLE 1. ELECTRON-DIFFRACTION STUDY OF CHEMICALLY POLISHED ZIRCALOY -2 SURFACES

Sample	Surface Treatment		Phases Identified by Electron Diffraction
	Mechanical	Chemical	
1A	Machined	HNO ₃ -1 volume per cent HF polish plus H ₂ O rinse	Sn + SnO ₂
2A	Cold rolled	None	ZrO ₂ + Zr
3A	Abraded	None	Zr + diffuse bands
4A	Abraded	HNO ₃ -1 volume per cent HF polish plus H ₂ O rinse	Sn + weak Zr
5A	Abraded	As 4A plus HCl then HNO ₃ pickle and H ₂ O rinse	Sn + diffuse ZrO ₂ band
6A	Abraded	As 4A then anodic in HCl and H ₂ O rinse	ZrO ₂
7A	Machined	Pickled in 45 volume per cent HNO ₃ -50 volume per cent H ₂ O-5 volume per cent HF and then hot H ₂ O rinse	Very diffuse bands
8A	Machined	As 7A plus boiling NaOH treatment and hot H ₂ O rinse	ZrO ₂
9A	Machined	Repeat treatment 7A	ZrO ₂ + SnO ₂ + Sn
10A	Machined	Repeat treatment 8A	ZrO ₂
11A	Machined	Repeat 7A plus HCl pickle and then rinsed in H ₂ O	ZrO ₂ + SnO ₂
12A	Machined	Repeat 7A plus pickle in 5 volume per cent HCl and then H ₂ O rinsed	Sn

TABLE 2. DESCRIPTION OF BONDED ZIRCALOY -2 SAMPLES EXAMINED

Sample	Surface Treatment Before Bonding	Figure Number
SP102	Hot rolled and machined, pickled in HNO ₃ -1 volume per cent HF (boiling)	6
SP104	Hot rolled and machined, cold rolled (3 to 1), pickled in (1) HNO ₃ -1 volume per cent HF (boiling), (2) 10 volume per cent HCl (5 min at 125 F), and (3) 10 volume per cent HNO ₃ (5 min at 120 F)	7
SP126	Hot rolled and machined, cold rolled (3 to 1), pickled in (1) 5 volume per cent HF-45 volume per cent HNO ₃ -50 volume per cent H ₂ O (100 F) and (2) 15 per cent NaOH (boiling)	8
SP114	Hot rolled and machined, cold rolled (3 to 1), hand abraded with 180-grit silicon carbide paper under water, not pickled	9

a. Negative Carbon-Formvar
Replica

b. Shadowed Negative Carbon-
Formvar Replica

FIGURE 6. BOND LINE IN ZIRCALOY-2 SAMPLE PRESSURE BONDED AFTER HOT ROLLING, MACHINING, AND PICKLING IN BOILING HNO_3 -1 HF SOLUTION

In Figure 6b, where the platinum vapor deposited at a 45-deg angle did not strike the replica surface, the shadows are transparent. The length of the shadow indicates the height of elevation in the negative replica corresponding to the depth of pits in the bond line. Sample SP102, pressure bonded 5 hr at 1500 F and 10,000 psi, is shown in these electron micrographs.

a. Segments of Bond Line Showing Grain Growth Across Interface

The arrows indicate the position of the bond line.

5000X

E6008B

b. Another Interface Area

Notice the clearly delineated grain-boundary particles etched in relief and the rounded off, poorly defined bond-line pits. The arrows indicate the position of the bond line.

5000X

E6008E

c. Termination of Bond Line

Notice that the bond line at lower right does not cross the grain boundary.

5000X

E6007B

FIGURE 7. BOND LINE IN ZIRCALLOY-2 SAMPLE PREPARED FOR BONDING BY HOT ROLLING, MACHINING, COLD ROLLING, AND PICKLING

The sample shown, SP104, was pressure bonded 4 hr at 1500 F and 10,000 psi. These electron micrographs were made from shadowed positive carbon replicas.

FIGURE 8. FAINT BOND LINE IN ZIRCALOY-2 SAMPLE PREPARED FOR BONDING BY HOT ROLLING, MACHINING, COLD ROLLING, AND PICKLING

Specimen SP126, pressure bonded 4 hr at 1500 F and 10,000 psi, is shown. The row of bond-line pits is nearly parallel with a grain boundary extending across the interface. This electron micrograph was made from a shadowed positive carbon replica.

5000X

E6010A

- a. Large Contaminant Particle
at Interface

5000X

E6012C

- b. Fine Particles and Pits at
Bond Line

5000X

E6012E

- c. Grain Boundary With Coarse
Precipitate Adjacent to
Pitted Bond Line

5000X

E6013C

- d. Typical Grain Boundary Some
Distance From Bond Line

FIGURE 9. BOND LINE AND GRAIN-BOUNDARY AREA IN ZIRCALOY-2 SAMPLE PREPARED FOR BONDING BY HOT ROLLING, MACHINING, COLD ROLLING, AND HAND ABRADING

The sample shown, SP114, was bonded 4 hr at 1500 F and 10,000 psi. These electron micrographs were made from shadowed positive carbon replicas.

A series of samples prepared from cold-rolled and annealed Zircaloy-2 sheet by belt abrading or by pickling in NaOH or H₂SO₄ was examined. These samples were beta treated after bonding by holding 5 min at 1850 F. The list of samples examined is shown in Table 3. Samples FP-1, FP-4, and FP-7, all belt abraded, showed very little bond line visible microscopically. Only FP-10 of the belt-abraded samples had a bond line which could be located definitely in the electron microscope. The visible segments in the bond line were quite short. Figure 10 shows two bond-line segments in this sample. Areas such as those shown were rare in this sample. In most areas the bond line was not visible. The bond line was etched out in both areas shown, being in the shape of a long shallow furrow in Figure 10a and a furrow with somewhat deeper pits in Figure 10b.

Etching out occurred along the bond lines in all of the pickled samples. The bond lines were similar in appearance in all of these samples. However, the coarseness and continuity of the bond line pitting depended on the pressure-bonding conditions. Higher temperatures and pressures resulted in finer pitting. Figure 11 shows the bond lines in FP-2 and FP-3, the pickled samples bonded 4 hr at 1500 F and 10,000 psi. These pictures are not typical of the appearance of the entire bond line but represent areas where the bond line was most prominent. In many areas there was no visible pitting along the bond line. The bond line was also intermittent in Samples FP-5, FP-6, FP-8, and FP-9. Figure 12a, a light micrograph of Sample FP-5, shows a segment of the bond line. Figures 12b and 13a are electron micrographs of the bond lines in Samples FP-5 and FP-9, respectively. The pitting in Samples FP-11 and FP-12, bonded at 1500 F and 5000 psi, was continuous along the bond line. Figure 13b is an electron micrograph of the bond line in Sample FP-12.

The bond lines in all of the beta-treated FP series of samples were similar in appearance. All had pits which varied considerably in depth, as evidenced by the difference in shading in unshadowed carbon-Formvar replicas, as shown in Figure 13b, or in the variation in the shadow length in metal-shadowed carbon replicas, as shown in Figure 11a. Apparently, the interface defects, contaminant, or crystal imperfections responsible for bond-line pitting were present in all of these samples and persisted during the beta anneal.

Effect of Contaminants on Pressure Bonding

Since the etching out along the bond line might be due to contamination, the individual effect of known contaminants on bonding was assessed. Prior to bonding, both surfaces of annealed and beta-abraded Zircaloy samples were coated with carbon, chromium, iron, nickel, niobium, tin, titanium, and zirconium oxide. The oxide layer was formed at 700 C in a controlled oxygen atmosphere. The other layers were applied by vacuum deposition. Weighed amounts of material to produce layers in a certain thickness range were evaporated. Since evaporation was not generally complete the thickness of the evaporated layers was known only approximately. The approximate thickness of the applied layers is shown in Table 4.

The coated samples were bonded 4 hr at 1500 F and 10,000 psi in a multiple-type specimen can with an uncoated belt-abraded sample as a control. Illustrations of the bonds obtained are shown in Figures 14 through 19. Comparison between the uncoated

TABLE 3. ZIRCALOY -2 SAMPLES EXAMINED AFTER A BETA HEAT TREATMENT OF 5 MIN AT 1850 F FOLLOWING PRESSURE BONDING

Sample	Surface Preparation ^(a)	Pressure-Bonding Conditions			Figure Number
		Time, hr	Temperature, F	Pressure, psi	
FP-1	Belt abraded	4	1500	10,000	--
FP-2	Pickled, NaOH rinse	4	1500	10,000	11a
FP-3	Pickled, H ₂ SO ₄ rinse	4	1500	10,000	11b
FP-4	Belt abraded	4	1450	10,000	--
FP-5	Pickled, NaOH rinse	4	1450	10,000	12
FP-6	Pickled, H ₂ SO ₄ rinse	4	1450	10,000	--
FP-7	Belt abraded	4	1400	10,000	--
FP-8	Pickled, NaOH rinse	4	1400	10,000	--
FP-9	Pickled, H ₂ SO ₄ rinse	4	1400	10,000	13a
FP-10	Belt abraded	4	1500	5,000	10
FP-11	Pickled, NaOH rinse	4	1500	5,000	--
FP-12	Pickled, H ₂ SO ₄ rinse	4	1500	5,000	13b

(a) The samples were cold rolled and annealed before the surface preparation. The chemically treated samples were pickled in a HNO₃-1 volume per cent HF bath and rinsed in a cold H₂SO₄ or cold NaOH bath.

TABLE 4. APPROXIMATE THICKNESS OF APPLIED SURFACE LAYERS TO ANNEALED BELT-ABRADED ZIRCALOY -2

Material	Nominal Thickness on Each Surface, A
Zirconium oxide	500
Titanium	500-1000
Iron	500-1000
Chromium	500-1000
Tin	500-1000
Nickel	500-1000
Carbon	200
Niobium	Thin ^(a)

(a) Several niobium evaporations were made. A small amount was evaporated each time before filament burnout.

FIGURE 10. VISIBLE BOND LINE IN ZIRCALOY-2 SAMPLE PREPARED FOR BONDING BY COLD ROLLING, ANNEALING, AND BELT ABRADING AND GIVEN POSTBONDING BETA HEAT TREATMENT

This sample was pressure bonded 4 hr at 1850 F and 5000 psi and then annealed 5 min at 1850 F. Sample FP-10, shown here, was the only belt-abraded sample bonded and heat treated under these conditions in which the bond line could be located. These electron micrographs were made from negative carbon-Formvar replicas.

FIGURE 11. AREAS IN WHICH THE BOND LINE WAS MOST PROMINENT IN ZIRCALOY-2 SAMPLES PREPARED FOR BONDING BY COLD ROLLING, ANNEALING, AND PICKLING IN HNO_3 -1 VOLUME PER CENT HF

Both samples were pressure bonded 11 hr at 1500 F and 10,000 psi and then annealed 5 min at 1850 F. Only an intermittent bond line could be found in these samples. In many areas there was no visible pitting along the bond line. These electron micrographs were made from a shadowed negative carbon (FP-2) and a negative carbon-Formvar replica (FP-3).

250X

RM10408

7500X

E6102A

a. Light Photomicrograph

b. Electron Micrograph Made From
Shadowed Negative Carbon Replica

FIGURE 12. BOND LINE IN ZIRCALOY-2 SAMPLE PREPARED FOR BONDING BY COLD ROLLING, ANNEALING, PICKLING IN HNO_3 -1 VOLUME PER CENT HF, AND RINSING IN NaOH

The sample shown, FP-5, was bonded 4 hr at 1450 F and 10,000 psi and annealed 5 min at 1850 F. The bond line was only intermittently visible in this sample.

4000X

E6090C

4000X

E6087B

a. Bond Line in Sample FP-9

b. Bond Line in Sample FP-12

FIGURE 13. BOND LINES IN TWO ZIRCALOY-2 SAMPLES PREPARED FOR BONDING BY COLD ROLLING, ANNEALING, PICKLING IN HNO_3 -1 VOLUME PER CENT HF, AND RINSING IN H_2SO_4

Sample FP-9 was bonded 4 hr at 1400 F and 10,000 psi, while Sample FP-12 was bonded 4 hr at 1500 F and 5,000 psi. Both samples were annealed after bonding for 5 min at 1850 F. Continuous pitting along the bond line was observed in Sample FP-12. Both electron micrographs were made from negative carbon-Formvar replicas.

250X

RM10780

a. Light Photomicrograph

5000X

E6155A

b. Electron Micrograph Made From
Positive Carbon-Formvar Replica

FIGURE 14. BOND LINE IN ANNEALED BELT-ABRADED ZIRCALOY-2 SAMPLE
WITH INTERFACE INTENTIONALLY CONTAMINATED BY A LAYER
OF VACUUM-DEPOSITED IRON

The dark line along the bond line in the replica denotes etching in relief.

250X

RM10774

a. Light Photomicrograph

5000X

E6156A

b. Electron Micrograph Made From
Positive Carbon-Formvar Replica

FIGURE 15. BOND LINE IN ANNEALED BELT-ABRADED ZIRCALOY-2 SAMPLE
WITH INTERFACE INTENTIONALLY CONTAMINATED BY A LAYER
OF VACUUM-DEPOSITED TIN

The bond line in the replica is etched in relief.

250X

RM10778

a. Light Photomicrograph

7000X

E6498C

b. Electron Micrograph Made From
Carbon-Formvar Replica

FIGURE 16. BOND LINE IN ANNEALED BELT ABRADED ZIRCALOY-2 SAMPLE
WITH INTERFACE INTENTIONALLY CONTAMINATED BY A LAYER
OF VACUUM-DEPOSITED CHROMIUM

250X

RM10770

a. Light Photomicrograph

9000X

E6501D

b. Electron Micrograph Made From
Carbon-Formvar Replica

FIGURE 17. BOND LINE IN ANNEALED BELT-ABRADED ZIRCALOY-2 SAMPLE
WITH INTERFACE INTENTIONALLY CONTAMINATED BY A LAYER
OF VACUUM-DEPOSITED NICKEL

The dotlike bond line evident in the photomicrographs was revealed in
the electron micrograph as a series of particles etched slightly in relief.

250X

RM10574

5000X

E6503E

a. Light Photomicrograph

b. Electron Micrograph Made From
Positive Carbon-Formvar Replica

FIGURE 18. BOND LINE IN ANNEALED BELT-ABRADED ZIRCALOY-2 SAMPLE WITH INTERFACE INTENTIONALLY CONTAMINATED BY A LAYER OF VACUUM-DEPOSITED CARBON

The thin carbon layer (200 Å) only partially blocked grain growth across the interface.

250X

RM10781

5000X

E6229A

a. Light Photomicrograph

b. Electron Micrograph Made From
Positive Carbon-Formvar Replica

FIGURE 19. BOND LINE IN ANNEALED BELT-ABRADED ZIRCALOY-2 SAMPLE WITH INTERFACE INTENTIONALLY CONTAMINATED BY A LAYER OF OXIDE APPLIED BY HEATING AT 700 C IN OXYGEN

While the oxide layer inhibited grain growth across the interface, there was little evidence of either pitting or precipitate at the bond line.

and the coated samples indicated that all the coatings inhibited grain growth across the bond interface. The titanium- and niobium-coated samples contained almost no contaminant or voids at the bond interface, and it was not possible to positively identify the bond line in these samples in the electron microscope. Light micrographs with polarized light of the iron-, tin-, and chromium-coated samples are shown in Figures 14a, 15a, and 16a. Electron micrographs of the iron- and tin-coated samples in Figures 14b and 15b show the boundary layer etched in relief. The difference in elevation between the bond-line structure and the matrix was not very pronounced in the chromium-coated samples, as can be seen in Figure 16b. The bond line was more sharply delineated than was generally the case in samples which were pitted along the bond line. In the chromium-coated sample a second phase which etched at nearly the same rate as the matrix was probably present. The bond line in the nickel-coated sample was dotlike, as can be seen in Figure 17a. An electron micrograph, Figure 17b, shows that the dots were particles which etched slightly in relief. Figure 18 shows that the carbon-coated sample had a thin nearly continuous interface layer, which etched in relief.

The oxide-coated sample had a layer of extraordinarily large grains on either side of the bond interface. This is apparent in Figure 19a, a light micrograph taken under polarized light. The oxide layer inhibited grain growth across the bond interface. However, there was very little evidence of either pitting or precipitate in relief along the bond line. Where either did occur the bond line was etched out as shown in Figure 19b. The etch figure resembled that seen in pickled samples. It should be noted that the pits in Figure 19b appear lighter than the matrix because the replica is a positive. The pits are darker in a negative replica (Figure 6a).

Effect of Ultrahigh Pressure on Zircaloy Bonds

In the samples which etched in relief along the bond line there was undoubtedly contaminant at the bond interface. In the case of etching out along the bond line an ambiguity in interpretation resulted, since the etching out could be due either to voids or to a contaminant which etched more rapidly than the matrix. It was possible that this ambiguity could be resolved by applying pressure to the sample much higher than the original bonding pressure. Since high-pressure apparatus was available, two samples, one which was pitted and another which etched in relief along the bond line, were subjected to high pressure. The apparatus used was a tungsten carbide right-circular-cylinder die and plunger. The sample, having a thermocouple welded to it, was embedded in pyrophyllite and then was pressed for 1 hr at about 500 F and 350,000 psi. One of the samples pressed was FP-12 (Table 3). The bond line in this sample was particularly prominent in the light microscope, as shown in Figure 20a. The electron microscope showed that this sample was pitted. The other sample pressed was the tin-coated sample shown in Figure 15. Figure 20b shows a polished section of Sample FP-12 after the application of high pressure. The bond line was visible only in short segments as shown. Since the bond line before pressure was as prominent everywhere as the area shown in Figure 20a, there was no question that the added pressure had a large effect on the bonding of this sample. On the other hand, there was no observable effect of high pressure on the bond line in the tin-coated sample. The interpretation of the results of the electron-microscope investigation and the high-pressure experiment on Zircaloy-bonded samples is presented under "Discussion".

150X

L6917 150X

N57143

a. As-Bonded Interface

b. After Application of High Pressure

FIGURE 20. EFFECT OF APPLICATION OF ULTRAHIGH PRESSURE ON PRESSURE-BONDED ZIRCALOY-2

The sample shown, FP-12, was cold rolled, annealed, pickled in HNO_3 -1 volume per cent HF, and rinsed in H_2SO_4 before bonding for 4 hr at 1500 F and 5000 psi. The pressure application of 1 hr at 350,000 psi and 500 F markedly decreased the bond-line pitting.

Examination of a Zircaloy-Niobium Pressure Bond

A sample in which Zircaloy-2 had been pressure bonded to niobium was examined in the electron microscope. The sample had been bonded 4 hr at 1500 F and 10,000 psi. The diffusion zone at the Zircaloy-niobium interface was from 10 to 20 μ wide and consisted of three bands, as shown in Figure 21. There was no indication of pitting along any of the boundaries in the diffusion zone.

The broadest band in the diffusion zone was on the Zircaloy side. This band had a fine Widmannstätten pattern characteristic of titanium or zirconium alloys which are not rich enough in the alloying element to stabilize the beta on slow cooling. The band on the Zircaloy side presumably was a two-phase region on cooling. The nodular structure could denote a second phase which was not well delineated by the etch. At the bonding temperature this band was probably beta prime, that is, a solid solution of zirconium in niobium. The etching rate in this band was much lower than in the zirconium-rich band, resulting in a high step between the second and third bands. The replicas generally split along this boundary. The height of the step is indicated by the length of the shadow in the center band. Toward the bottom of the picture there is a fold in the replica along the boundary between the second and third bands.

The electron micrograph of the Zircaloy-niobium bond indicates how it is possible to distinguish bands in a diffusion zone which is too narrow to resolve into individual bands in the light microscope.

FIGURE 21. DIFFUSION ZONE IN NIOBIUM-ZIRCALOY-2 SAMPLE
PRESSURE BONDED 4 HR AT 1500 F AND 10,000 PSI

This electron micrograph was made from a shadowed
positive carbon replica.

DISCUSSION

This research was initiated to determine why occasional bonds produced by the pressure-bonding process with improperly prepared surfaces had the appearance of being incomplete. As seen metallographically, the bond lines sometimes appeared contaminated, and in some segments no grain growth across the bond line was apparent. This type of behavior was especially prevalent when pickled surfaces were used, even though such surfaces should be quite clean aside from a thin oxide film. The same behavior was noted when the surfaces were prepared by metallographic techniques before bonding. Although one would expect that these two types of surfaces would be especially clean, the observation might, nevertheless, indicate the presence of contamination or of unclosed voids. The objective of the program reported here was to determine whether it was possible to distinguish between these two possibilities.

The electron micrographs of Zircaloy samples which had been chemically pickled before pressing showed an etching effect resulting in small pits (of the order of $1\ \mu$ or less in size) along the bond line. The bond lines were free of precipitate particles such as appeared in grain boundaries. Segments of the bond line where pitting did not occur were etched no deeper than a normal grain boundary. The fact that destructive bend tests rarely showed any bond weakness indicated that the interface bonds were comparable in rupture strength to normal grain boundaries.

In an attempt to learn whether contamination was the cause of observed effects, machined Zircaloy surfaces were purposely contaminated with most of the materials which might normally be found on the surfaces of specimens prepared for bonding, including carbon, chromium, iron, nickel, oxygen, and tin. In every case, except that of oxygen, the bond line in the purposely contaminated samples had a different appearance from those between uncontaminated surfaces. Some of the added contaminant remained at the bond line, leaving compounds which etched in relief, not as pits. From this it would be inferred that these contaminants were not normally present to any appreciable degree in chemically pickled samples.

The oxygen-contaminated surfaces exhibited the same etching patterns as pickled material, with approximately the same size etch pits, although it was evident that the amount of oxygen added was far in excess of that normally present on zirconium surfaces.

The results of the studies suggest quite strongly that the etching effect in chemically pickled samples is not a result of contaminant remaining at the interface after bonding. The only type of coating giving the same etching effect as chemically pickled surfaces is oxygen, which dissolves in alpha zirconium at the bonding temperature.

The high-pressure experiment supports strongly the idea that the etching effect is related to voids. In this experiment, samples were put in a Bridgman-type apparatus and heated to a temperature of 500 F for a period of 1 hr under a pressure of 350,000 psi. The sample chosen was one in which bond-line etching effects were especially prominent. Examination after the test was completed showed that the bond then appeared nearly clean. This result makes it likely that the etching effect was due to voids which closed under the effect of high pressure.

The next consideration is the mechanism for this closure. Calculations were made using Bridgman's formula for the closure of holes, and the results led to the conclusion that voids of the size observed would not be closed by a deformation process at the applied pressure. For that reason it is believed that the process is a diffusional one in which vacancies diffuse from the surface of the void to vacancy sinks at a distance from the void, possibly to neighboring grain boundaries or to other areas in the interface boundary itself. Barnes⁽³⁾ closed previously formed voids by the application of pressure to copper-nickel diffusion couples. Even though the pressure was much lower and the voids much larger in the Barnes experiment, similar mechanisms in collapsing the voids in the two systems might well be operative.

The effect of the high pressure in increasing the rate of void closure is thought to be that of causing a higher concentration gradient for vacancy diffusion from the surface of the void to the sink some distance away. No attempts to confirm this hypothesis by numerical calculations have been made because of the lack of good data on the self-diffusion coefficient and the energy of vacancy formation in zirconium.

Thus there is a strong probability from this work that voids exist at the interface in pressure-bonded chemically pickled and oxide-coated samples. Voids would normally be expected to be caused by incomplete closure of rough mating surfaces. The fact that voids are not generally present in relatively rough machined samples but are present in chemically pickled samples indicates that void formation in pressure-bonded samples may in some instances be more closely related to the film originally present on the surface than to the surface roughness.

The other apparent defect of bonds is the fact that grain growth does not seem to occur to any great extent across the original interface. The best explanation for this observation appears to be that the contaminating layers on surfaces do not diffuse away until recovery and recrystallization on either side of the interface are nearly complete. When this has happened the configuration with a relatively low-energy interface boundary is quite stable and there is little driving force for grain growth across the interface.

CONCLUSIONS

It is possible by electron microscopy to examine the fine-scale roughness of Zircaloy-2 samples after various surface preparations. In examining sections of bonded samples, electron microscopy is useful in delineating the shape of microstructural features along the bond line and in determining whether relief etching or etching out occurs along the bond line.

Determination of the exact nature of bonding in Zircaloy-2 requires a detailed examination of samples at various stages during bonding. Some conclusions about the probable nature of Zircaloy-2 bonding derived from the present investigation are as follows:

- (1) Pressure-bonded chemically pickled and also oxide-coated belt-abraded samples sometimes have voids at the bond interfaces.

- (2) Voids formed in samples pressure bonded in the alpha persist after a short-time beta anneal.
- (3) Vapor-deposited layers of carbon, chromium, iron, nickel, niobium, tin, and titanium on belt-abraded samples inhibited grain growth across the bond interface in samples pressure bonded in the alpha temperature range.
- (4) There was a contaminant layer but no indication of voids at the bond interface in the pressure-bonded carbon-, chromium-, iron-, nickel-, and tin-coated samples. There was no positive indication of either voids or contaminant in the niobium- and titanium-coated samples.

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