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CORROSION RESISTANT BRAZING ALLOYS FOR ZIRCALOY

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Final Report

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by

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CORROSION RESISTANT BRAZING ALLOYS FOR ZIRCALOY

ABSTRACT

The objective of this program was the development and evaluation of filler metals suitable for the brazing of Zircaloy for service in high temperature water.

More than 60 experimental alloys and a few commercial alloys were used to prepare brazements of simple design for exposure in an autoclave to 600° or 680°F water. Brazing was performed in a purified atmosphere of helium. From the results of these tests several alloys were selected for extensive study which included induction, furnace and torch brazing characteristics, and tensile and shear strengths. Metallography of the joints as brazed and after corrosion testing is shown.

A number of alloys were obtained which had good corrosion resistance in elevated temperature water. Outstanding among these was one which used Zircaloy 2 as base metal and 4 or 5% beryllium as the alloying constituent. This alloy had excellent flow characteristics, good strength, withstood corrosion well, and caused no attack on or erosion of the base metal.

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CORROSION RESISTANT BRAZING ALLOYS FOR ZIRCALOY

I. INTRODUCTION

This is the final report covering work performed from 10 May 1956 to 9 July 1957, under AEC Principal Contract AT-11-1-Gen-14, Subcontract 73-(14-401), Westinghouse Atomic Power Division to Armour Research Foundation. A summary report was previously issued on June 1, 1956 which covered work that was done between 9 May 1955 and 9 May 1956.

The object of this project was to devise satisfactory brazing alloys and techniques for joining Zircaloy to Zircaloy where the brazement is to be subjected to high temperature water. Ideally, the brazed joint would have corrosion resistance equal to that of the base metal and mechanical properties sufficient to give a good margin of safety for likely applications. While for a given use, the mechanical or physical properties may be critical, the sine qua non is corrosion resistance, and principal effort has been a study of the latter property.

The mechanisms of corrosion and corrosion resistance in high temperature water are not sufficiently known to predict from theory whether a given alloy will corrode in a specified high temperature water environment. There is some evidence indicating that (1) protection is generally ascribable to surface films, (2) galvanic effects play a small part in determining corrosion rate, (3) crevice corrosion is slight, (4) the manner in which hydrogen is discharged may determine breakdown time, and (5) at high temperatures the corrosion rate and breakdown time are highly temperature dependent. For the most part, however, it is necessary to rely upon a somewhat empirical approach to the problem. Even if the corrosion resistance of a brazing alloy could be predicted, this would not guarantee the performance of the brazement, since composition of the filler metal and adjacent base metal may both be altered to an indeterminate extent by the joining operation.

The experimental program, therefore, was to prepare brazing alloys with as wide a range of composition as possible within the known limitations, to make brazements of simple geometry with these alloys, and to conduct

screening tests of these brazements in water at 680°F. From those tests several promising alloys were selected for more intensive study. A few commercial alloys were tested, but a large majority of the alloys were of experimental composition selected on the basis of information available as to binary phase relationships, impurity effects on the corrosion of Zircaloy, and known brazing characteristics with zirconium. Elements such as boron and cadmium were excluded as being generally undesirable in a reactor environment. In all, more than 60 different alloys were used to prepare brazements which were corrosion tested. Alloys which were discussed in the summary report are not discussed here unless further work was done with them.

II. MATERIALS

The Zircaloy 2 used in these brazing experiments was supplied by WAPD from ingots 5Y511, 5Y425, F2396 and others, and was of reactor grade, in the form of plate approximately 3 in. wide x 1/4 in. thick. Before use, these plates were surface ground on one side to completely remove scale and oxygen-contaminated metal. A small amount of Zircaloy 3A was also supplied from ingot E306.

Zircaloy 2, 3/4 inch thick, was utilized for fabrication of irradiation shear specimens and tensile bars.

Compositions of the alloys used in this investigation appear in Table I. These are nominal compositions but are believed to be, with few exceptions as noted, quite close to the actual composition.

For the preparation of zirconium-base brazing alloys, Zircaloy 2 was used rather than zirconium, although the alloying elements present in Zircaloy are not listed in the nominal compositions. Aside from this, the metals used were of the highest purity readily available.

Details of alloy preparation and measured melting temperatures for several promising alloys will be found in Appendix A.

Chemical analyses were performed on alloys which were found to be promising from the corrosion standpoint. Because of the presence of many interfering elements and the uncommon elements analyzed, these analyses were

by no means always routine, and it may be assumed that the accuracy was sometimes less than in better standardized determinations.

The analyses obtained for various melts are shown in Table II.

Unless otherwise noted, alloys will be referred to by nominal composition. The majority of alloys listed in Table I were discussed in the summary report of June 1, 1956.

III. EXPERIMENTAL PROCEDURES

A. Alloy Preparation

Two melting procedures were used for the preparation of alloys. The first was to induction heat in alundum crucibles under a bell jar with a helium atmosphere. The second method, used with the more reactive and refractory metals, was to arc melt with a tungsten electrode, a water-cooled copper crucible, and a helium atmosphere.

In recent induction melting of alloys which have shown promise, the additional precaution was taken to melt under argon which was first passed through a liquid nitrogen trap and then over titanium sponge at about 900°C. The argon liquefies at the boiling point of nitrogen, so that very effective drying is obtained as the gas bubbles through its own liquid phase. These precautions may be unnecessary, but they can perhaps be justified because of the known lowering of the corrosion resistance of Zircaloy when contaminated by small amounts of interstitials, especially nitrogen.

B. Brazing

1. Induction Brazing

All of the corrosion test specimens were made as single lap joints 1/2 to 3/4 inch long x 1 inch wide. These were cut at the midpoint of the 1 inch dimension and one piece was used for metallographic examination, while the other was corrosion tested. The brazes were made using 0.003 in. molybdenum shims for spacing; 0.001 in. molybdenum shims were also used with the more promising alloys. The arrangement for these brazes is shown in Figure 1.

The majority of brazes were made by placing the filler metal outside of the joint and allowing it to flow in by capillary attraction. Preplacing of the alloy in the joint was tried in a few tests with some of the better alloys. In most cases this was difficult to do because alloys with sufficient ductility to roll to sheet were the exception rather than the rule. Kanigen brazes were made both with coating and with externally placed alloy which had been deposited as heavy plate, stripped from the base, and broken into pieces of suitable size.

All brazes, both induction and furnace, were made in an inert atmosphere (of helium) without the use of any flux. This was made possible by the fact that zirconium-base alloys at brazing temperatures absorb surface oxidation films rapidly to leave a clean metal surface quite suitable for flow and bonding of the filler metal.

The practice of passing high purity tank helium first through a liquid nitrogen cold trap and then over titanium sponge heated to approximately 900°C was adopted after observing that flow of some alloys was not satisfactory.

The corrosion specimens were induction heated. This was almost mandatory, since many alloys of unknown brazing characteristics were used, and control of the heating cycle was necessarily by visual observation. Also, the inductive method was capable of fast heating and cooling, so that diffusion effects could be minimized.

The specimen, specimen supports, and induction coil were all covered by a bell jar which could be evacuated to less than 1 micron pressure (0.1 to 0.2 micron was commonly obtained). Pressures were measured with an ionization gage manufactured by the National Research Corporation. The system was twice evacuated and refilled with helium before heating was started.

The standard procedure for making a braze for corrosion testing was as follows. The two strips of Zircaloy were etched in a solution containing 57% H_2O, 35% conc. HNO_3, and 5% HF solution, by volume. This was done to remove worked metal, which lowers the corrosion resistance of Zircaloy. Next, the two pieces were clamped together, a suitable quantity of brazing alloy was placed adjacent to the lap, and the assembly was placed on Vycor tube supports holding it in the induction coil. The bell jar was then

positioned, and the system was evacuated to less than 1 micron. Helium was admitted until a pressure of approximately 1 atmosphere was reached, and the system was again evacuated, and finally refilled with helium to slightly above atmospheric pressure. The specimen was then heated until filler metal flow was observed, after which it was allowed to cool before removing the bell jar.

To save autoclave space the base metal ends were trimmed from the joint. The specimens were then cut in half and identified with an electric engraver. The fillets were also trimmed from some specimens. One half of each specimen was set aside for metallographic examination and the remaining half was prepared for corrosion testing. This was done by lap grinding the edges so that corrosion effects could be more readily observed. These specimens were also briefly etched in the solution mentioned above.

Some shear tests were performed on specimens induction brazed with one of the better alloys, namely Zr-5% Be. The specimen in these tests consisted of a Zircaloy 2 bar 1/4 in. thick x 1 in. wide x 3 in. long to which was brazed a small block of Zircaloy 2, 1/4 in. thick x 1 in. wide x 5/16 in. long. The fillets were removed from the braze and one end of the Zircaloy bar was ground parallel to one edge of the Zircaloy block. The specimen was then held in a massive steel fixture and the Zircaloy block was sheared off by a compressive load, longitudinally applied by means of a Baldwin-Southwark tensile machine. Cleaning and induction braving of these shear specimens was done in a manner similar to the corrosion specimens discussed above.

Three standard 1/2 inch diameter tensile bars were also made using Zr-5% Be filler metal. Three-inch-long bars of 3/4 in. diameter were machined from Zircaloy 2 plate. The ends of these bars were ground and lapped in a plane perpendicular to the axis of the bars. Brazing was accomplished by placing the lapped surfaces of two bars together in a vertical position. Two small molybdenum ears were spot welded on opposite sides of the lower bar slightly below the lapped surfaces. The filler metal was inserted behind the ears adjacent to the joint so that flow into the joint area would occur during the brazing operation. Two of the tensile bars were spaced by means of two short lengths of 3 mil tungsten wire placed at the opposite edges of the joint while no spacer was used for the third tensile bar.

After the bars were induction brazed in an atmosphere of pure helium, they were machined to standard size and tensile tested.

The final group of induction brazed specimens consisted of five sets (approximately 18 per set) of specially designed single lap joints for irradiation exposure studies. Dimensions of these specimens and the clamping arrangements for the brazing operation are shown in Figure 2. The 7/16 in. tongue of Zircaloy, which lies directly below the short molybdenum spacer, was removed after brazing along with any excess filler metal. The most promising alloys, namely, Zr-4% Be, Kanigen, Cu-20% Pd-3% In, Ni-20% Pd-10% Si and Ni-30% Ge-13% Cr were used in these specimens.

The irradiation-shear specimens will be tested by WAPD to determine the effects of irradiation on corrosion resistance and strength.

The Kanigen specimens were made from Zircaloy stock with a one-mil plate. The diffusion process as described in experimental results with Kanigen (Section IV-A, Part 5d) was employed to secure an adherent and blister-free deposit of Kanigen on the specimen. All the other specimens were made with flowed filler metal. The Zr-4% Be alloy flowed readily and formed good appearing specimens. Use of the Cu-20% Pd-3% In, Ni-20% Pd-10% Si, and Ni-30% Ge-13% Cr alloys was more difficult due to their poor flow characteristics. Base metal erosion also occurred with use of the above three alloys.

Some of the specimens were radiographed. However, the results were misleading since what appeared to be voids on the radiograms actually could be eroded areas.

2. Furnace Brazing

A limited amount of furnace brazing was carried out during the year with a few selected filler metals which performed well in earlier work. The specimens consisted of pairs of Zircaloy 2 sheet strips 6 inches by 1 inch wide by 0.070 inch thick, wired together to form an inverted T-section 6 inches long. A weighed amount of filler metal (~0.5g) was placed at one end of the specimen adjacent to the junction of the two members. The assembly was placed in the

cold zone of a retort which was then sealed and evacuated. High purity helium was admitted until atmospheric pressure was reached. The system was again evacuated and refilled with helium to slightly above atmospheric pressure and a flow of helium was maintained. The specimen was next pushed into the hot zone and allowed to remain for 10 or 15 minutes depending on the alloy used. Specimens for furnace brazing were cleaned prior to brazing in the same manner as described for the corrosion specimens.

A number of impact specimens were also furnace brazed with the same alloys used for the T-specimens. Zircaloy 2 of the size required to make standard impact specimens was not available so a four-pound charge of Zircaloy 2 was melted by the nonconsumable electrode arc process. The charge for this melt consisted of pieces of sheet which had been rolled from 1/4 in. stock. The resultant ingot was forged to a slab which allowed the making of multiple width half-length impact specimen stock. Two multiple width pieces were butt brazed with each of the desired filler metals to form a brazement from which five impact bars could be machined. The brazing procedure for these impact specimens was similar to that of the T-specimens.

A design for a furnace-brazed, dynamic corrosion test specimen was agreed upon between ARF and WAPD representatives. Members for such specimens were machined at ARF and shipped to WAPD for brazing and testing.

3. Torch Brazing

Only a small amount of work was done on the torch brazing of Zircaloy 2. Procedure followed included the coating of the Zircaloy with a liberal quantity of a fluoride-containing brazing flux (Handy and Harman Special Handy Flux for Titanium). The two pieces were spaced with a three-mil shim and tightly clamped to maintain this spacing. Both Zircaloy members were heated simultaneously with a double-tipped oxyacetylene torch. When the braze area was at temperature, the flame was directed at the filler metal to get quick melting and flow. The flame-brazed specimens were corrosion tested in the same manner as the induction-brazed bars.

C. Corrosion Testing

Corrosion tests were carried out in a standard type of stainless

steel 347 autoclave produced by Autoclave Engineers, Incorporated. Temperature was regulated by a Wheelco controller with a Limitrol safety device. A check of the operating conditions was obtained from a pressure gage. Distilled water was used as the corrosive medium, and the air was carefully bled from the system at the start of each run. The specimens were immersed in the water and were contained in a basket of stainless steel screen. Temperatures of 600 or 680°F were used in all tests, and each specimen was tested to complete failure (separation of the joined pieces) or to at least 1200 hours exposure time. The specimens were examined at intervals varying from 24 to several hundred hours.

The brazements which survived the 1200-hour test were broken apart when possible to permit examination of the brazed area. Those which could not be broken were sectioned and examined metallographically.

IV. EXPERIMENTAL RESULTS

The results will be presented under the following headings: A. Corrosion of Induction-Brazed Joints; B. Shear Strength; C. Tensile Strength; D. Furnace-Brazed T-Joints; E. Furnace-Brazed Impact Bars; and F. Torch Brazing.

A. Corrosion of Induction-Brazed Joints

Of the large number of alloys investigated during the first year of effort on this program five alloys warranted further study as discussed in the summary report of June 1, 1956. Work during the current year was concentrated on these five alloys, plus some investigation of new compositions. The new compositions will be discussed first. All brazements made with these compositions were three-mil spaced and corrosion tested in 680°F water.

1. Copper-Base Alloys

One of the five alloys that warranted further study was Cu-20% Pd-3% In. This was the only alloy of the five that was ductile and could be rolled into sheet; however, its use caused erosion of the base metal. An attempt was made to reduce this erosion by the addition of Zircaloy to the brazing alloy.

One such composition was Cu-20% Pd-3% In-7% Zr 2. This alloy formed a relatively thick joint as seen in Figure 3, and extensive erosion occurred in the base metal at the fillet. After exposure of 1212 hours, the brazement was broken apart and was found to be unattacked except for a thin corrosion line around the edges (Figure 4).

Another composition with increased Zircaloy content, Cu-20% Pd-3% In-37% Zr 2, was investigated. (Figure 5). This also resulted in erosion of the base metal. After 1212 hours of exposure the specimen was unattacked except for a small area at one corner near the filler (Figure 6).

Analysis of the original Cu-20 Pd-3 In alloy revealed that the In content was only 1.74%. In the belief that a higher indium content might reduce the erosion of the base metal a nominal Cu-18.5% Pd-4.5% Ir alloy was prepared (analysed 5.07 In). Use of this alloy resulted in a thin joint as seen in Figure 7, but erosion of the base metal again occurred. Only a small amount of corrosion occurred in this sample during 1212 hours of exposure (Figure 8).

A Cu-20% Pd-3% In-3% Ni-3% Fe braze (Figure 9) sustained no corrosion damage during 1212 hours of exposure (Figure 10); however, erosion of the base metal occurred during brazing.

Flowed joints could not be made with Cu-20% Pd-3% Ni-3% Fe-3% Sn; however, two brazements were made by preplacing the alloy. A representative structure is shown in Figure 11. Virtually no corrosion occurred during 1212 hours in the autoclave (Figure 12).

Erosion of the base metal occurred with the use of Cu-20% Pd-3% In-7% stainless steel 347 (Figure 13) but there was no corrosion during 1212 hours of high temperature water exposure as shown in Figure 14.

No further work was done with the above five alloy variations; however, all were corrosion resistant and additional work with a view to reducing their erosion characteristics would be in order.

Two other copper-base alloys investigated were Cu-2% Be and Cu-4% Be. Both are commercially available alloys and these were used for brazing. Structures obtained with these alloys are shown in Figures 15 and 17. Both alloys were tested for 1349 hours after which the Cu-2% Be alloy was found to be 60% corroded (Figure 16) and the Cu-4% Be was unattacked. The unattacked structure is shown in Figure 18. The dark areas are regions that did not fill during the brazing operation. Erosion of the Zircaloy occurred near the fillet during brazing with both of the alloys; however, the erosion was much more severe with the Cu-2 Be alloy. It should be noted that the Cu-4 Be alloy brazed below the transformation temperature of the Zircaloy 2. A WAPD representative reported that the high temperature water corrosion resistance of Zircaloy is lowered when the material is in the transformed state; hence, any corrosion resistant brazing alloy which flows below the transformation temperature is of particular interest. Lack of time prevented further investigation of this alloy although it is promising enough to deserve further attention.

It was stated in last year's report that three joints brazed with Cu-3.5% P were under test, one of which failed after 830 hours. A second specimen had parted after 1235 hours while the third was found to be completely attacked after 1235 hours.

2. Aluminum-Base Alloys

The Al-3% Ni alloy formed a satisfactory brazement (Figure 19) but failed after 98 hours of exposure. The filler metal of this specimen remained in one piece after failure and its microstructure is shown in Figure 20. Apparently the dark-etching material which is adjacent to the Zircaloy (Figure 19) is more susceptible to corrosion than the remainder of the filler metal. Brazements made with Al-55% Ge (Figure 21) and Al-20% Si (Figure 22) failed in 911 hours. An Al-1% Be brazement (Figure 23) failed in 1349 hours. An Al-2% Be alloy was also made but not used. The final aluminum-base alloy investigated had a nominal composition of Al-35% Ge-10% Zr. A brazement made with this alloy is shown in Figure 24. After 712 hours of corrosion testing this sample was removed and sent to WAPD for further testing. At that time it was noted that the filler metal was corroding.

3. Zirconium-Base Alloys

Two new zirconium-base alloys were tested during the year. Zr-10% Fe-10% Cr alloy formed the braze shown in Figure 25. After 1235 hours of exposure the specimen was broken apart and found to be unattacked although one end had not completely brazed (Figure 26). A Zr-35% Al-3% Be specimen (Figure 27) failed after 98 hours of exposure.

4. Miscellaneous Filler Metals

Complete melting did not occur when Ti-30% Al-5% Be was used. The structure of this sample is shown in Figure 28. The specimen was sent to WAPD for further testing after 712 hours of exposure to water. At that time the sample had been slightly attacked.

A specimen brazed with Au-1.5% Be alloy was also sent to WAPD after 712 hours in water. This alloy had excellent flow characteristics and formed a smooth fillet. The specimen appeared to be attacked at the base metal-filler metal interface. As can be seen from the microstructure in Figure 29, brazing occurred below the transformation temperature of the Zircaloy.

Attempts to braze with Nb-4% Be were unsuccessful due to its high melting point.

A Ag-1% Be alloy was also prepared but never tried.

5. Alloys Previously Selected as Promising

The five alloys that were selected for further study at the conclusion of the first year's work on this project are: (1) Ni-30% Ge-13% Cr, (2) Cu-20% Pd-3% In, (3) Ni-20% Pd-10% Si, (4) Kanigen, and (5) Zr-5% Be. Duplicate three-mil and one-mil brazements made with these alloys were corrosion tested in 600° and 680°F water to determine consistency of results.

In addition, cuboid samples of the five filler alloys were corrosion tested in 600° and 680°F water and 750°F steam, and their weight determined at periodic intervals. The 600° and 680°F evaluations were started at Armour Research Foundation; shortly thereafter these samples were transferred to WAPD along with the samples for 750°F testing. Preliminary data were too fragmentary to indicate any trend.

a. Ni-30% Ge-13% Cr

Ten duplicate three-mil spaced brazements were made with this alloy for testing at 680°F. Four of these specimens failed within 207 hours due to poor filling. The remaining six specimens were broken apart after 1212 hours of exposure, and it was found that only one of the specimens was almost completely brazed while the others varied from 5 to 50% brazed. No corrosion was evident in any of these samples (Figure 30). In spite of the fact that most of the specimens had brazed poorly, all were difficult to break apart. Two more one-mil spaced specimens (Figure 31) were prepared for 680°F testing along with six specimens, four spaced 3 mils and two spaced 1 mil, for 600°F. After 410 hours, one of the 680° specimens had failed as did a three-mil, 600° brazement after 564 hours. The remaining specimens were sent to WAPD for continued testing after 564 hours for the 600°F specimens and 712 hours for the one 680°F specimen.

This alloy, of the five selected for extensive study, appears to be the least promising. Its flow properties are the poorest, and it tends to alloy with the base metal to an extent that results in an eroded area at the fillet. The alloy melts between 1090° and 1120°C.

b. Cu-20% Pd-3% In

This alloy alone among the promising alloys has sufficient ductility to permit rolling into thin sheet; thus, it can be preplaced if necessary. Severe erosion occurs in the fillet area during the brazing operation and this area is extensively attacked if it is not removed prior to corrosion testing. The alloy by itself is very corrosion resistant. A small rolled sample was subjected to 3511 hours in 680°F water with no change in appearance except for a slight darkening of the surface. The microstructure of this alloy after corrosion testing is shown in Figures 32 and 33. Figure 32 shows the complete cross section of the rolled material while Figure 33 shows one edge. The layer of metal at the surfaces of the sample did not result from corrosion but may be material which received a greater amount of cold work during the rolling operation.

Nine duplicate three-mil spaced brazements were made for 680°F water testing. The flow characteristics of this alloy are poor, so two of the samples were made with preplaced alloy for comparison purposes. The fillets were removed from the samples prior to corrosion testing to eliminate their effect on any corrosion in the interior of the sample. Prior to the conclusion of the test a number of the specimens appeared to be attacked in regions where the filler metal was thicker than normal. After 1374 hours the specimens were broken apart and were found to be unattacked except for a thin corrosion line around the exposed edges of the filler metal. No difference was noted between the preplaced and the flowed alloy samples. Complete filling did not occur in all the samples as seen by the dark regions in Figure 34.

One-mil spaced brazements (Figure 35) were also made for testing in 600° as well as 680°F water. The fillets were left intact on these specimens to determine if a lesser amount of fillet corrosion would take place at the lower temperature. The 680° samples were removed from test after 1349 hours, and the 600° samples after 1279 hours. After the samples were broken open, it was noted that all had suffered some attack near the fillet; elsewhere they were free of corrosion. The fillet areas on all the samples were moderately corroded but no difference could be seen in the degree of attack in the 600° specimens compared to those at the higher temperature. Figure 36 and 37 show the appearance of these samples after 600° and 680°F test, respectively. Four 3-mil samples that were being tested at 600°F have been sent to WAPD for the completion of testing. At the time of shipment (854 hours) three of the samples appeared relatively unattacked while the fourth had heavy fillet attack.

A number of three-mil spaced brazements were also made using Zircaloy 3A as the base metal (Figure 38). No corrosion was evident in the interior of these specimens after they were removed from 680°F water testing at the completion of 1361 hours of exposure. Very extensive and severe attack occurred in the fillets of the samples, and this attack extended down the sides adjacent to the fillet as seen in Figure 39. Fillet attack was much more severe in the Zircaloy 3A brazements than in the Zircaloy 2 brazements. Experimentation with variations in composition of this alloy has been discussed earlier.

The melting range of this alloy is approximately 975° to 1050°C.

c. Ni-20% Pd-10% Si

Less metal erosion and fillet attack occur with this alloy (melting range 1035° to 1050°C), than with either of the two previously discussed alloys. The alloy is brittle; hence, it cannot be rolled and must either be preplaced as a powder or flowed into the joint area. The flow properties of the alloy are rather poor, and careful technique is required in order to obtain good joints. An adherent black coating of corrosion product forms on the surface of the alloy shortly after exposure to high temperature water.

Eleven duplicate 3-mil brazements were prepared and subjected to 680°F water. The specimens were broken apart for examination after 1355 hours of exposure. All the specimens were found to exhibit a peculiar type of attack not found in the earlier specimens made with this alloy nor in later specimens. This attack extended from the fillet into the interior of the brazement and consisted of a network of unattacked filler metal surrounding attacked regions as shown in Figure 41. The remainder of each specimen was completely unattacked. None of these specimens filled entirely during the brazing operation (Figure 40). No explanation for this type of attack is offered but it appears to have started at the fillet and proceeded into the joint. The fillet area itself was not badly attacked and erosion of the base metal was not heavy.

Additional specimens with one-mil spacing (Figure 42) were tested at 600° and 680°F for 1279 and 1349 hours, respectively. A moderate amount of attack occurred around the fillets but the interiors were free of corrosion as seen in Figure 43 and 44. The 680° brazements suffered slightly more corrosion around the fillets than the 600° specimens, but this difference was minor.

An additional set of three-mil spaced brazements which was under test at 600°F is being completed at WAPD. At the time of shipment the specimens had been exposed for 854 hours and they all appeared sound. WAPD is also testing in 750°F steam a set of three-mil spaced brazements that were prepared at ARF.

With Zircaloy 3A as base metal, two sets of two specimens (1-mil and 3-mil) were prepared for 680°F exposure. The microstructure of one of the 3-mil brazements is shown in Figure 45. Metallographic examination of

both 1-mil samples revealed that they had pressure welded together in many places and what filler metal was present was extremely thin. Internally, all the samples were in excellent condition at the conclusion of 1255 hours of exposure with the exception of one sample, which showed slight attack at one corner near the fillet. The fillet attack on these brazements was relatively light. No difference was noted in the degree of attack on the Zircaloy 3A compared to Zircaloy 2. The one- and three-mil brazements are shown respectively in Figures 46 and 47. The dark, grainy structure seen near the fillets in the above figures represents fracture through the base metal and not attack.

d. Kanigen (Ni-7% P)

"Kanigen" is a proprietary name (General American Transportation Company) for a chemically deposited coating of nickel containing about 7% phosphorus. The alloy in chunk form is glass brittle but in normal use it could be preplaced in the joint by depositing on the pieces to be brazed. Thin joints can be obtained by limiting the thickness of the deposit; however, if the mating surfaces are not true, voids could result. Flowed brazements have been made with this alloy but with some difficulty because of rather poor flow properties. No erosion of the base metal occurs during the brazing operation using either deposited or flowed Kanigen. Fillet attack during the 680°F water corrosion test is also nil with Kanigen. When Kanigen is plated in the normal manner as given in appendix A, a relatively nonadherent film is produced on the surface of the Zircaloy.

This nonadherent film allows plating solution to be trapped below the plate as was found after examination of ten brazed specimens subjected to 680°F water for 1200 hours. These ten brazements, each with one mil of deposited Kanigen on each surface, all appeared sound at the start of the test although a number of them contained some small voids. A typical microstructure is given in Figure 48. Of the ten specimens only one was completely unattacked; the others exhibited filler metal attack ranging from slight to 100 per cent (Figure 49). All of the corroded areas contained a green residue believed to be nickel salts left from entrapped plating solution. Considerable work was devoted to the problem of securing an adherent Kanigen deposit on the Zircaloy and thus

eliminating any opportunity for plating solution to be trapped below the deposit. After investigating many variations of the plating procedure the following successful method was adopted. The Zircaloy is first etched to give a surface as oxide-free as possible and immediately thereafter given a 15-second flash coat of nickel. A thin coat of Kanigen is next deposited over the specimen (about 10 to 15 minutes) and diffused into the surface. This diffusion treatment consists of heating the specimen slowly in inert atmosphere to 840°C and holding at temperature for two hours (time is not critical). If the Kanigen coat has diffused properly, scratching the surface with a sharp object will cause no cracking or flaking. The desired thickness of Kanigen is finally deposited over the surface thus prepared.

The microstructure of a Kanigen brazement prepared as above is given in Figures 50 and 51. While a good braze was obtained, a number of small, totally enclosed voids were present in the filler metal (Figure 51). This specimen was tested for 1321 hours in 680°F water and found to be perfect (Figure 52). Additional brazements were prepared (one-mil deposit on each surface) for testing at 600° and 680°F and these samples were transferred to WAPD after respective times of 854 and 640 hours. No corrosion was evident at the time of shipment. WAPD is also testing in 750°F steam, a set of 3-mil spaced specimens brazed at ARF with flowed filler metal.

Another set of Kanigen specimens for 680°F testing using Zircaloy 3A base material gave a microstructure as shown in Figure 53. These samples were also sent to WAPD after 640 hours and they also were free of attack.

A piece of Kanigen alloy was also corrosion tested for 3379 hours at 680°F. The only visible change was a slight darkening of the surface. No layer of corrosion product can be detected at the edge of the sample as Figure 54 attests.

The melting range for the Kanigen (Ni-7% P) is approximately 880° to 1060°C. The eutectic composition lies at 880°C and 11% P. Attempts were made to secure such a composition by adding phosphorus to Kanigen alloy powder, but without success.

e. Zr-4 to 5% Be

This alloy appears to be by far the best alloy developed during

this program. Its major drawback is lack of ductility but this is more than compensated by excellent wetting and flow properties. In this respect the lower beryllium composition might be slightly superior; otherwise, the pertinent properties are unaffected by this variation in beryllium content. There is no noticeable erosion or attack of the base metal during brazing, and a smooth fillet is formed. A limited amount of shear and tensile data indicate good mechanical properties. The difficulty of breaking apart specimens after corrosion testing is a further indication. The alloy has a melting range of approximately 970° to 990°C which is lower than the four alloys discussed above.

The corrosion resistance is consistently excellent in the hot water tests. A white adherent film forms on the fillet and any other exposed filler metal shortly after exposure to hot water. This film is less adherent when brazing Zircaloy 3A than when brazing Zircaloy 2.

One drawback to the use of this alloy could be its possible toxicity. Not much is known about the toxicity of beryllium alloys but pure beryllium and beryllium salts are very toxic and great care must be taken to avoid inhalation or ingestion of such materials, especially during the preparation and melting of the alloy as the stage of greatest danger.*

The first set of specimens brazed with this alloy consisted of nine 3-mil spaced brazements for 680°F corrosion testing. With one exception, which is illustrated in Figure 55, these specimens could not be broken apart in the filler metal after 137½ hours of exposure. Two other brazements fractured in the base metal rather than in the filler metal. Three of the samples were cut in half transversely and examined microscopically (Figures 56, 57 and 58). A very thin layer of corrosion product can be seen at the exposed edge in these three specimens. Two specimens with rather heavy fillets are shown in Figure 59, after removal from the autoclave. The thin layer of corrosion product which is present on the fillets of all these specimens can be seen in this photograph.

None of these nine specimens showed any sign of attack other than the surface film.

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* See The Metal Beryllium, Edited by D. W. White, Jr. and J. E. Burke, Chap. XII, ASM, Cleveland, 1955.

Attack was also absent from a set of one-mil specimens that were exposed for 1279 hours at 600°F and 1349 hours at 680°F. A typical microstructure for the one-mil spaced braze can be seen in Figure 60. The fracture surfaces of these specimens are shown in Figures 61 and 62 for 600° and 680°F exposures, respectively. A considerable amount of effort was required to break the samples apart and the specimen at the left in Figure 62 suffered some deformation of the base metal in the process.

A set of three-mil spaced brazements had also been under test in 600°F water when the set was sent to WAPD for continued testing. At that time, after 854 hours of test, no evidence of attack was noticed. A set of three-mil specimens was also prepared at ARF for 750°F steam exposure at WAPD.

Two rather thick brazements resulted when three-mil spaced specimens were made with Zircaloy 3A base metal. The microstructure of one brazement is seen in Figure 63. No corrosion occurred during 1361 hours of exposure at 680°F; however, as noted earlier, the film of corrosion product formed on the fillet was not as adherent as that formed on Zircaloy 2 base metal. Fracture occurred through the filler metal when the specimens were broken open, and this resulted in a rough surface as shown in Figure 64. Note that one specimen did not completely fill during brazing.

One of the early heats of this alloy was a nominal Zr-6% Be which analyzed about 2.5% Be and had a low melting range of 870° to 885°C. This heat of alloy was made from a much more impure grade of beryllium than that used for subsequent melts, and this may account in some part for the low melting range. Analysis of the melt revealed nothing unusual except a possible high copper content (one sample analyzed a 0.72% Cu while another analyzed 0.06% Cu). Two 3-mil brazements for 680°F testing made with the above melt were exposed for 1212 hours, then broken open. Neither had been attacked and both broke rather easily in smooth fractures at the filler metal-base metal interface. The fractured surfaces are shown in Figure 65.

B. Shear Strength

Only a small amount of mechanical testing of brazes was done during this program, and this was done not with the object of developing design data,

but rather to demonstrate usable strength and to help guide the research effort.

The area of braze first tested was approximately 1/2 in. x 1 in., but it was found that there was a tendency for the base strip to bend, and the area was therefore reduced to 1/4 in. x 1 in.

Shear data reported in last year's summary report are repeated in Table III.

During the current year only one set of shear specimens was prepared. This set was three-mil spaced and brazed with the Zr-5% Be alloy (analyzed 5.30% Be). Results are in Table IV.

C. Tensile Strength

A limited number of tensile bars were butt brazed using the same Zr-5% Be alloy as was used to obtain the above shear data. Results of the tensile tests are listed in Table V.

D. Furnace-Brazed T-Joints

T-joints were furnace brazed with Kanigen, Ni-20% Pd-10% Si, and Zr-4% Be. The Kanigen used was not deposited on the Zircaloy but was allowed to flow from a 0.5 gram sample placed at one end of the T.

Two T-joints were made with the Kanigen alloy: one at 950°C and the other at 978°C. Both specimens were in the hot zone for ten minutes. Flow of one inch was obtained at 950°C while a two-inch flow with a fairly heavy fillet was obtained at 978°C. A slight amount of base metal attack also occurred on the latter specimen at the point where the filler metal was placed.

Flow was obtained along the full six-inch length of two T-joints brazed with Ni-20% Pd-10% Si alloy. One specimen was held for 15 minutes at 1022°C while the other was held for 10 minutes at 1048°C. A 1 1/2 in. flow was obtained on a third specimen brazed 10 minutes at 1022°C. Little filleting occurred on these specimens. Base metal erosion took place as with the Kanigen. Use of Zr-4% Be yielded the best appearing T-joints. Two specimens were brazed, one at 985°C and the other at 995°C for 15-minute intervals. Complete flow

was obtained on both specimens and smooth, heavy fillets were formed on both sides of the junction between the Zircaloy strips. No base metal attack resulted. Specimens brazed with this Zr-4% Be alloy can be allowed to remain in the furnace hot zone for a longer time than the above two alloys since its use does not result in any base metal erosion. Figure 66 shows one of the T-joints brazed with the Zr-4% Be alloy.

E. Furnace-Brazed Impact Bars

Brazed Charpy impact bars were prepared with the same alloys as were used on the T-joints. Standard size bars were machined from 3-mil spaced brazed slabs. No V-notch was machined in these specimens since the filler metal represents a metallurgical notch. For comparison purposes a number of unbrazed V-notched Charpy bars were also prepared. Room temperature and 550°F were selected as the test temperatures.

The Kanigen specimens were held for 20 minutes at 990°C. Two of these specimens were broken during machining; examination revealed that these specimens were well brazed and contained no voids. This indicated a low impact strength for Kanigen brazes and this was later borne out by the Charpy tests.

Three of the Ni-20% Pd-10% Si impact bars were also broken during machining but in this case the cause was due to incomplete filling (under 50%). Upon completion of the impact tests it was found that the remaining two specimens were only 75% brazed. Unfortunately, in both cases the Charpy bars had been placed in the impact machine with the unfilled area opposite the side that was struck; thus the effect of the unfilled area was magnified. Brazing was done at 1060°C for 15 minutes.

No difficulty was encountered with the specimens brazed with the Zr-4% Be alloy, which were held for 20 minutes at 995°C.

Results of the impact tests are given in Table VI. Testing was done on a Sonntag Universal Impact Machine, using the 0 to 50 ft-lb range.

The impact strengths of the Zr-4% Be brazements are much superior to those of the other alloys. Furthermore, at room temperature, the impact strength of the brazed specimens is no lower than that of unbrazed specimens containing a V-notch. Photomacrographs of the fractured specimens are shown in Figures 67 through 70.

F. Torch Brazing

Torch brazing was attempted with both the Cu-20% Pd-3% In and Zr-4% Be alloys.

Results with the Cu-base alloy were fairly successful; this alloy melted easily and flowed rapidly into the joint. One specimen, after it was broken apart, revealed that a sound joint had been obtained although a number of small flux inclusions were present. Heavy fillet attack occurred shortly after the start of 680°F corrosion testing of two torch-brazed specimens. These samples were sent to WAPD after 302 hours of test.

All attempts to torch braze with the Zr-4% Be alloy were unsuccessful. An oxide coating appeared to form around the alloy and flow did not occur.

V. DISCUSSION AND SUMMARY

Further work on the development and evaluation of filler metals for brazing Zircaloy to Zircaloy, the joints to be corrosion resistant in 680°F water, has been completed.

The results of this year's work have largely borne out the findings reported for the previous year, as regards the more promising brazing alloys. The all-around superiority of Zircaloy-4% Be became more incontrovertibly evident with respect to the properties tested. The tensile strength at room temperature and the impact strength at room temperature and 500°F are both remarkably high for butt-brazed joints prepared with this alloy. The flow properties are quite good, although there is a slight tendency for liquation, which might be eliminated by a small adjustment of the composition, if desirable for a particular application. Unfortunately, information as to the effects of irradiation on brazements prepared with Zr-4% Be probably will not be available for some time. Results of test exposures to 750°F steam and to dynamic corrosion conditions are also unavailable at this time. Therefore, the present evaluation must still remain provisional. However, there seems to be reasonable ground for optimism concerning the potential utility of this filler metal for the field of application intended.

The Ni-7% P (Kanigen) alloy has been found to yield brazements with excellent corrosion resistance, but the mechanical properties of these joints are relatively poor. Therefore, it would seem that this filler metal might best serve the function of a seal rather than structural joining. The experiments which have been made with plated Kanigen as a filler suggest that, properly plated, this material might be useful as a protective coating for use in high temperature water. In order to apply dependable coating, careful plating procedures must be followed, including diffusion treatment of a thin preliminary coat. The flow characteristics of bulk Kanigen on Zircaloy are not particularly good, and it seems likely that improvement in this respect would be obtainable if the phosphorus content could be increased.

Both Ni-20% Pd-10% Si and Cu-20% Pd-3% In must be considered difficult to use successfully because of flow characteristics and the tendency to wash out the base metal. On the other hand, should the Zr-4% Be alloy exhibit some unexpected shortcoming to bar its use, either of these two alloys could very likely be modified in composition so as to be serviceable. This would require further research and evaluation.

Although corrosion resistant brazements have been prepared with Ni-30% Ge-13% Si, unexplained failure has also been observed during recent work. For this reason, and because this alloy does not appear to have any particular property to recommend it in preference to the alloys mentioned above, this alloy is considered the least promising of the five.

Among the new alloys which were subjected to preliminary tests, some promise was shown by Cu-4% Be and Au-1.5% Be. Fillet corrosion occurred, however, in the case of Cu-4% Be, and a tendency to wash out base metal during brazing was also observed. Both alloys brazed below the Zircaloy 2 transformation temperature. Testing of the Au-1.5% Be alloy has not yet been completed, but hairline attack may have been occurring at the filler metal-base metal interface. There is a possibility that this might be prevented by plating a barrier layer such as nickel or Kanigen on the base metal before brazing. A factor which must be considered, however, is that neutron capture by gold results in the formation of mercury, which would be undesirable.

No success was achieved with new Al-base alloys, and this field is not presently considered promising.

Since several alloys containing beryllium have been discussed in this report, it might be wise to remind those who may be working with such alloys that there is a toxicity hazard with which they should familiarize themselves before proceeding.

VI. LOGBOOKS AND CONTRIBUTING PERSONNEL

All data reported here are recorded in Armour Research Foundation Logbooks C-5576, C-4873, C-5040, C-5138, C-4872 and C-6358.

The following persons contributed directly to the work on this project: O. T. Barnett, Assistant Manager; H. Schwartzbart, Supervisor; B. P. Schofield, Research Chemical Engineer; J. B. McAndrew, Research Metallurgist; J. Miller, Associate Electrochemist; R. Necheles, Assistant Metallurgist; and W. Heitman, T. Niemczyk, C. Christensen, A. Masschelin, and J. Sillivan, Technicians. Metallographic work was done under the supervision of E. J. Klimek.

Respectfully submitted:

ARMOUR RESEARCH FOUNDATION OF
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Approved by:

W. Rostoker, Asst. Manager
Metals Research Department

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TABLE I

NOMINAL COMPOSITIONS OF BRAZING ALLOYS

Alloy No.	Nominal Composition, wt. %
1	71 to 73 Ag-27 to 29 Cu (BAg-8)
2	6.75 to 7.50 P-Bal. Cu (B CuP-2)
2-3	3.5 P-Bal. Cu
2-5	5.0 P-Bal. Cu
3	6.8 P-Bal. Ni (Kanigen)
4	99 Al-1 Ni
5	60 Pd-40 Ni
6	94 Pd-6 Si
7	70 Ni-20 Pd-10 Si
8	60 Ag-30 Cu-10 Si
9	75 Cu-15 Ag-5 Sn-5 P
10	70 Cu-15 Ag-10 Sn-5 P
11	Al-Hot dip coating
12	60 Ag-30 Cu-10 Sn
13	Au
14	57 Ni-30 Ge-13 Cr (G.E. 75)
15	70 Ni-20 Cr-10 Si (G.E. 81)
16	90 Pd-10 Nb
17	90 Nb-10 Pd
18	76 Al-24 Pd
19	Ni-3.4 P
20	50 In-50 Nb
21	79 Zr-21 Cu
22	62.5 Cu-37.5 Au
22-A	Ni-47.5 Cu-2 B-0.5 Li
23	90 Ag-10 In
24	60 Ag-27 Cu-13 In
25	85 Ag-15 Mn
26	90 Au-10 Co

TABLE I (CONT.)

NOMINAL COMPOSITIONS OF BRAZING ALLOYS

Alloy No.	Nominal Composition, wt. %
27	83 Zr-17 Ni
28	73 Zr-27 Ni
29	75 Zr-15 Ni-10 Sn
30	80 Pd-20 Sn
31	77 Cu-20 Pd-3 In
32	Sn (foil)
33	88 Al-12 Si
34	95 Zr-5 Be
34 C-34 J	94.75 Zr-5.25 Be
34 D-34 K	94.50 Zr-5.50 Be
34 E-34 L	94.25 Zr-5.75 Be
34 F-34 N	94 Zr-6 Be
34 M	97.5 Zr-2.5 Be
34 O	96.5 Zr-3.5 Be
34 Q	96 Zr-4 Be
34 R	97 Zr-3 Be
35	80 Zr-10 Fe-10 Pd
36	60 Zr-30 Fe-10 Mn
37	80 Zr-10 Fe-10 Cr
38	82 Ni-18 In
39	54 Ni-36 In-10 Pd
40	80 Zr-15 Pd-5 Nb
41	70 Zr-15 Fe-15 Mn
42	Al-6.2 Cu
43	60 Ni-40 In
44	80 Zr-10 Fe-10 Sn
45	46 Nb-44 Ni-10 Zr
46	46 Nb-44 Ni-10 Si
47	48.6 Nb-46.4 Ni-5 Si

TABLE I (CONT.)

NOMINAL COMPOSITIONS OF BRAZING ALLOYS

Alloy No.	Nominal Composition, wt. %
48	48.6 Nb-46.4 Ni-5 Pd
49	46 Nb-44 Ni-10 Pd
50	77 Cu-18.5 Pd-4.5 In
51	40 Cu-20 Pd-3 In-37 Zr-2
52	70 Cu-20 Pd-3 In-7 Zr-2
53	71 Cu-20 Pd-3 In-3 Ni-3 Fe
54	71 Cu-20 Pd-3 Ni-3 Fe-3 Sn
55	70 Cu-20 Pd-3 In-7 Stainless Steel 347
56	Cu-2 Be
57	Cu-4 Be
58	Al-1 Be
59	Al-2 Be
60	Ag-1 Be
61	Nb-4 Be
62	Al-55 Ge
63	Al-3 Ni
64	Au-1.5 Be
65	Al-20 Si
66	62 Zr-35 Al-3 Be
67	65 Ti-30 Al-5 Be
68	55 Al-35 Ge-10 Zr

NOTE: All alloys containing zirconium were made using Zircaloy 2 as the source of the zirconium.

TABLE II

ANALYZED COMPOSITIONS OF BRAZING ALLOYS

Alloy No.	Nominal Composition, wt %	Analyzed Composition
2-3	Cu-3.5 P	3.11 P
7	70 Ni-20 Pd-10 Si	18.81 Pd-8.89 Si (Melt 1) 19.48 Pd-9.75 Si (Melt 2)
19	Ni-3.4 P	3.36 P
31	77 Cu-20 Pd-3 In	76.95 Cu-21.39 Pd-1.74 In (Melt 1) 19.70 Pd-1.78 In (Melt 2)
34	95 Zr-5 Be	4.39 Be (Melt 1) 4.81 Be (Melt 2)
34 C	94.75 Zr-5.25 Be	4.48 Be-0.16 Cu 4.00 Be (Recheck)
34 D	94.50 Zr-5.50 Be	5.37 Be-1.09 Cu
34 E	94.25 Zr-5.75 Be	3.08 Be-0.26 Cu
34 F	94 Zr-6 Be	2.61 Be-0.06 Cu 2.19 Be-0.71 Cu (Recheck)
34 J	94.75 Zr-5.25 Be	5.94 Be
34 K	94.50 Zr-5.50 Be	5.30 Be
34 L	94.25 Zr-5.75 Be	6.33 Be
34 M	94 Zr-6 Be	6.37 Be
34 N	97.5 Zr-2.5 Be	2.04 Be
34 O	96.5 Zr-3.5 Be	3.57 Be
34 P	95.5 Zr-4.5 Be	1.30 Be 4.82 Be (Recheck)
34 Q	96 Zr-4 Be	3.93 Be
34 R	97 Zr-3 Be	2.99 Be
50	77 Cu-18.5 Pd-4.5 In	18.68 Pd-5.07 In
51	40 Cu-20 Pd-37 Zr-2-3 In	18.69 Pd-3.28 In
52	70 Cu-20 Pd-7 Zr-2-3 In	20.52 Pd-3.69 In
53	71 Cu-20 Pd-3 In-3 Ni-3 Fe	19.68 Pd-3.45 In-3.49 Fe-3.28 Ni
54	71 Cu-20 Pd-3 Sn-3 Ni-3 Fe	18.89 Pd-3.09 Fe-3.38 Ni
55	70 Cu-20 Pd-3 In-7 Stainless Steel 347	20.30 Pd-0.93 In-3.84

TABLE III

SHEAR DATA (FIRST YEAR)

Filler Metal	Area in. x in.	Load, lb (3000 lb/min. loading rate)	Ultimate Shear Stress, psi
Ni-30% Ge-13% Cr	0.250 x 0.967	4,750	19,600
Ni-20% Pd-10% Si	0.244 x 0.963	5,350	22,800
Cu-20% Pd-3% In	0.268 x 0.993	4,700	17,700
Zr-5% Be	0.270 x 0.987	9,000	>34,000*

* Poor braze - estimated 40% of area unbrazed.

TABLE IV

SHEAR STRENGTHS OF Zr-5% Be* BRAZEMENTS

Specimen No.	Area in. x in.	Load, lb	Ultimate Shear Stress, psi
1**	0.324 x 1.084	15,400	43,875
2	0.309 x 1.047	18,200	56,175
3	0.358 x 1.078	20,200	52,325
4	0.329 x 1.062	19,400	55,875
5	0.348 x 1.059	18,800	50,950
6	0.311 x 1.078	17,400	51,950

* Analyzed composition - 5.30% Be

** One small area in this specimen was not brazed.

TABLE V

TENSILE STRENGTH OF Zr-5% Be* BRAZEMENTS

Specimen No.	Spacing, W Wire	Diameter, in.	Tensile Load lb	Ultimate Tensile Strength, psi
1**	None	.500	7,850	40,050
2**	3-mil	.504	7,250	36,250
3	3-mil	.504	7,450	37,250

* Analyzed composition - 5.30% Be

** Small void present

TABLE VI

IMPACT STRENGTH OF FURNACE-BRAZED ZIRCALOY 2 CHARPY BARS

Brazing Alloy (3-mil spacing)	Test Temperature, °F	Impact Strength, ft-lb
Ni-20% Pd-10% Si*	R. T.	0.5
Ni-20% Pd-10% Si*	550	0.5
Kanigen (Ni-7% P)	R. T.	0.5
Kanigen (Ni-7% P)	R. T.	0.2
Kanigen (Ni-7% P)	550	0.5
Zr-4% Be	R. T.	2.7
Zr-4% Be	R. T.	6.2
Zr-4% Be	R. T.	8.5
Zr-4% Be	550	8.5
Zr-4% Be	550	5.0
Unbrazed, V-notch	R. T.	3.7
Unbrazed, V-notch	R. T.	5.7
Unbrazed, V-notch	R. T.	5.2
Unbrazed, V-notch	550	15.5
Unbrazed, V-notch	550	33.2
Unbrazed, V-notch	550	14.0

* Only 75% of specimen was brazed.

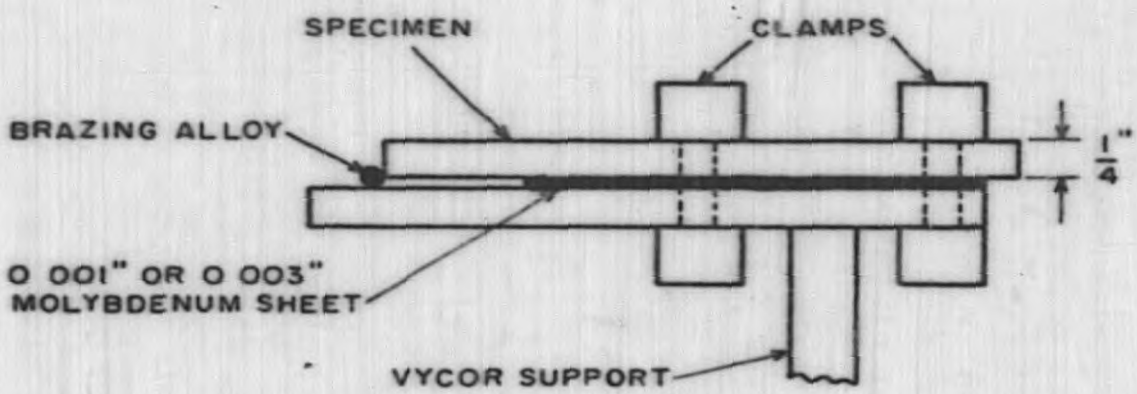


FIG. 1 - CLAMPING ARRANGEMENT FOR BRAZEMENTS.

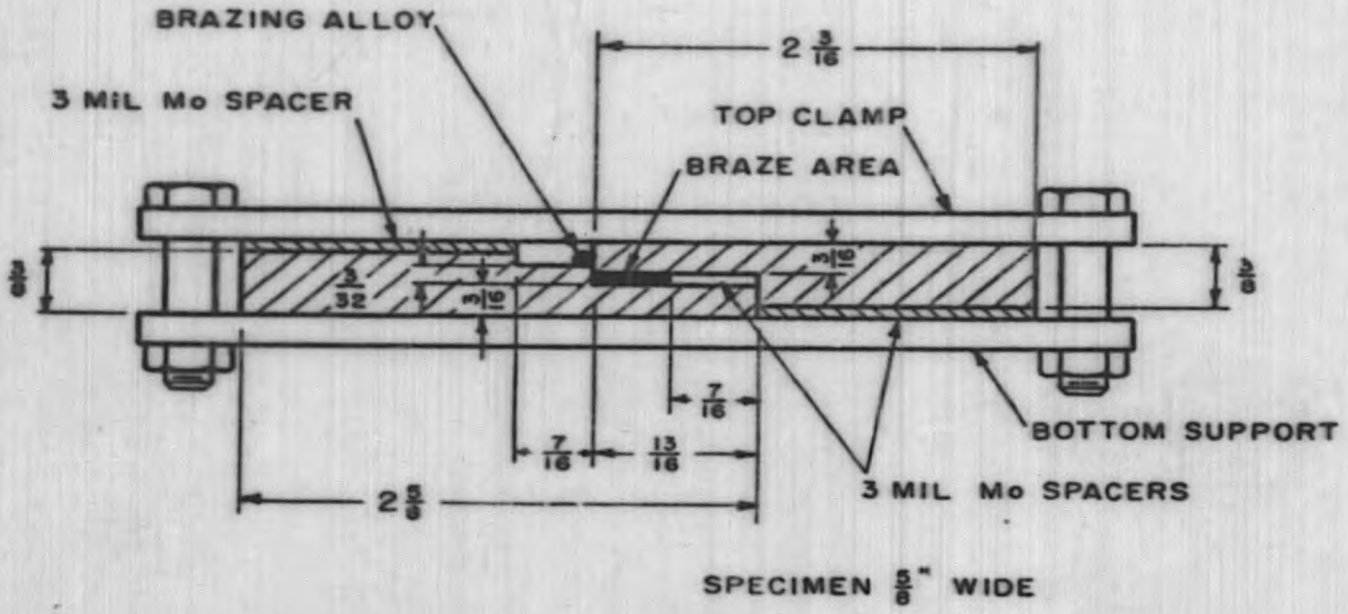
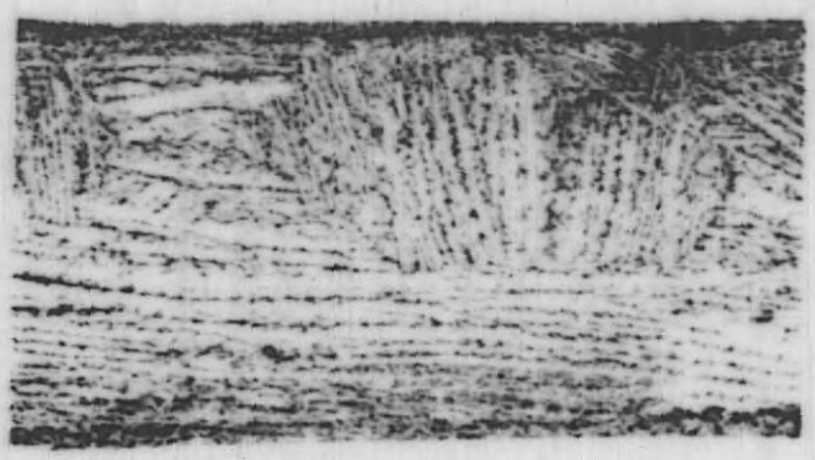


FIG. 2 - ZIRCALOY TO ZIRCALOY IRRADIATION SHEAR SPECIMEN.



Mag. No. 13060 Mag. X 150

Micro No. 13986

Figure 3 - Microstructure of 3-Mil Spaced Brazement with Cu-20% Pd-3% In-7% Zr 2 Filler Metal.

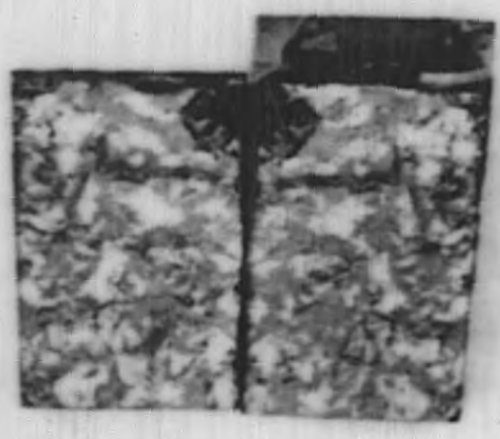
Mag. No. 13597 Mag. X 2 1/2

Figure 4 - Appearance of the Above Brazement After 1212 Hours of Exposure in 680°F Water.

Neg. No. 13042 Mag. X 150

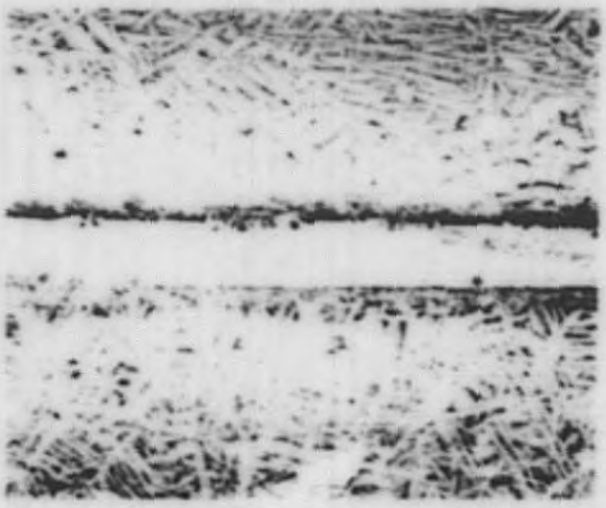
Micro No. 13985

Figure 5 - 3-Mil Spaced Brazement with Cu-20% Pd-3% In-37% Zr 2 Filler Metal.



Neg. No. 13596 Mag. X 2 1/2

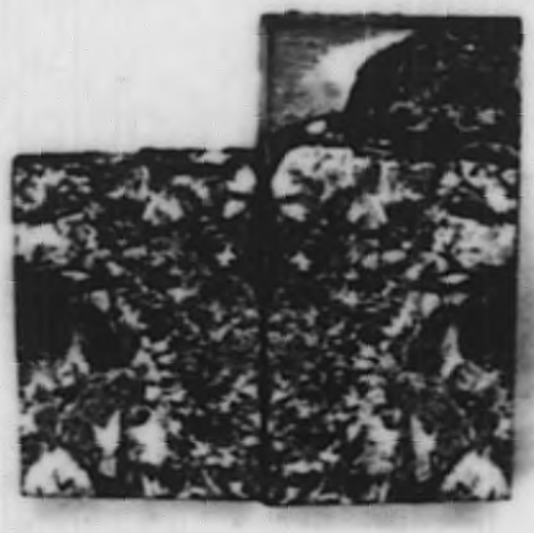
Figure 6 - Appearance of Above Brazement Broken Apart after 1212 Hours in 680°F Water.



Neg. No. 13014 Mag. X 150

Micro No. 13983

Figure 7 - Structure of 3-Mil Spaced Brazement with Cu-18.5% Pd-4.5% In Filler Metal.

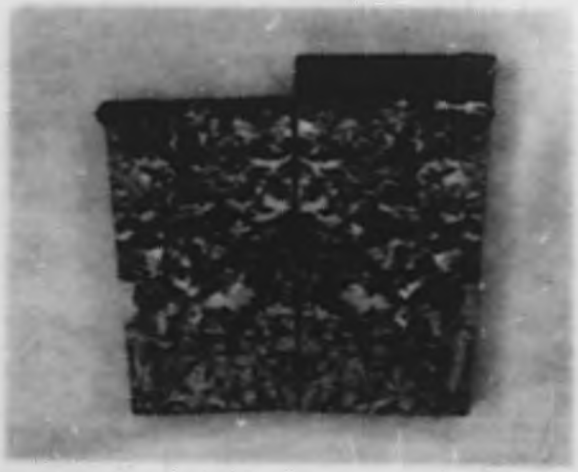


Neg. No. 13598 Mag. X 2 1/2

Figure 8 - Appearance of Above Brazement After 1212 Hours of Exposure.

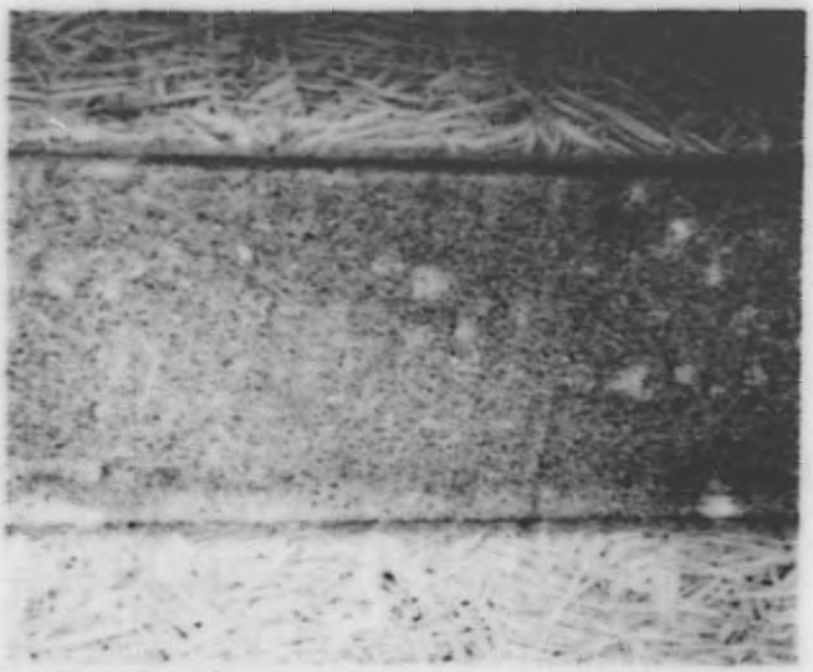
Neg. No. 13041 Mag. X 150
Micro No. 13987

Figure 9 - Microstructure of 3-Mil Spaced Brazement with Cu-20% Pd-3% In-3% Ni-3% Fe Filler Metal.



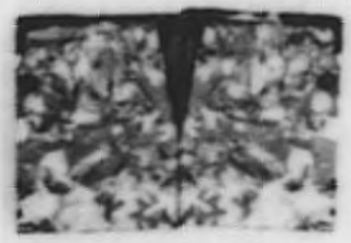
Neg. No. 13611 Mag. X 2 1/2

Figure 10 - Appearance of Above Brazement Broken After 1212 Hours in 680°F Water.

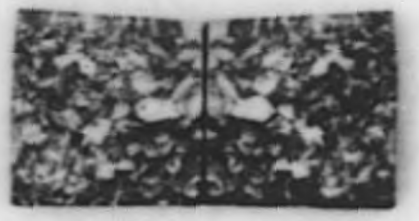


Neg. No. 13040 Mag. X 150
Micro No. 13984

Figure 11 - Microstructure of 3-Mil Spaced Brazement Using Cu-20% Pd-3% Ni-3% Fe-3% Sn Filler Metal.

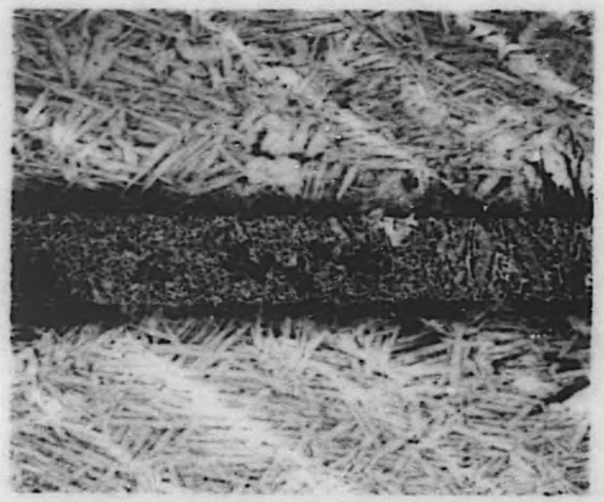


Neg. No. 13603 Mag. X 2 1/2



Neg. No. 13604 Mag. X 2 1/2

Figure 12 - Appearance of Brazements with Above Filler Metal After 1212 Hours of Exposure to 680°F Water.



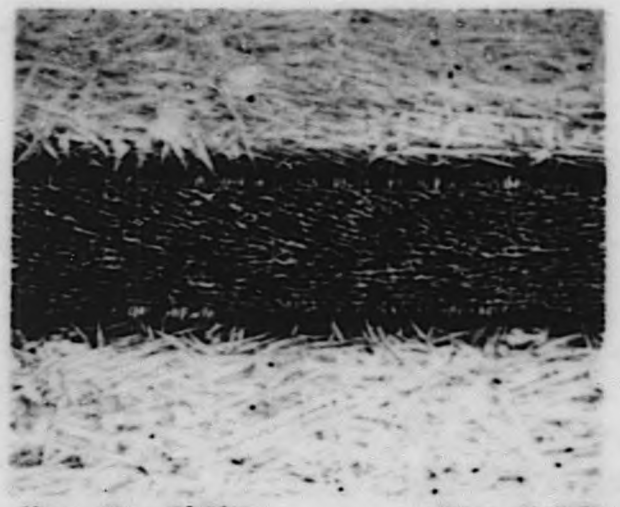
Neg. No. 13043 Mag. X 150

Micro No. 13043

Figure 13 - Microstructure of 3-Mil Spaced Brazement with Cu-20% Pd-3% In-7% Stainless Steel 347 Filler Metal.

Neg. No. 13607 Mag. X 2 1/2

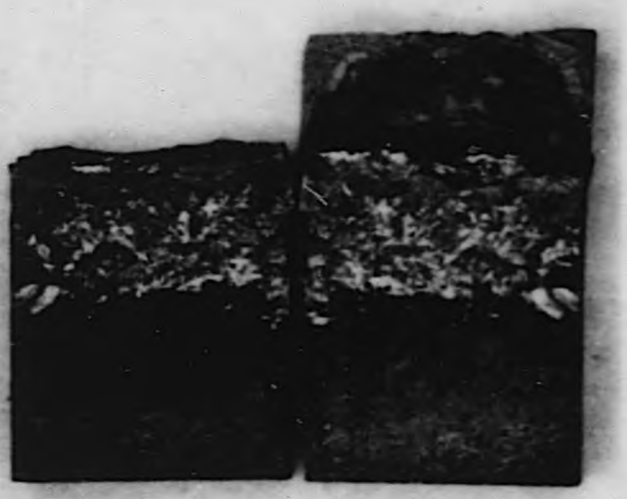
Figure 14 - Appearance of Above Brazement After 1212 Hours in 680°F Autoclave.



Neg. No. 14043 Mag. X 150

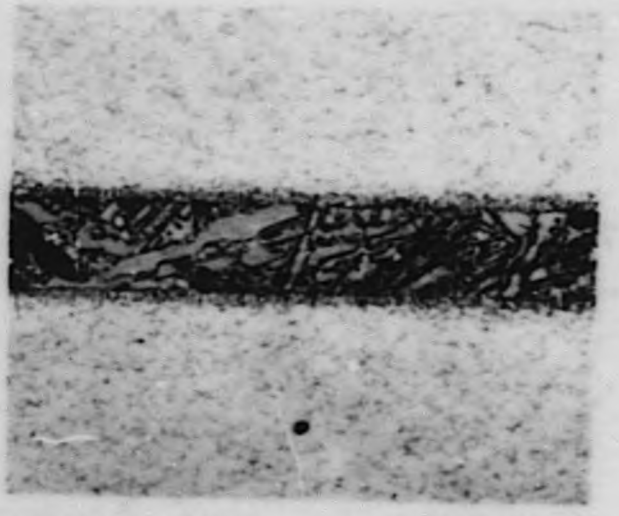
Micro No. 06503

Figure 15 - Structure of 3-Mil Spaced Brazement Made with Cu-2% Be Filler Metal.



Neg. No. 14226 Mag. X 3

Figure 16 - Appearance of Above Brazement After 1349 Hours of Exposure to 680°F Water.

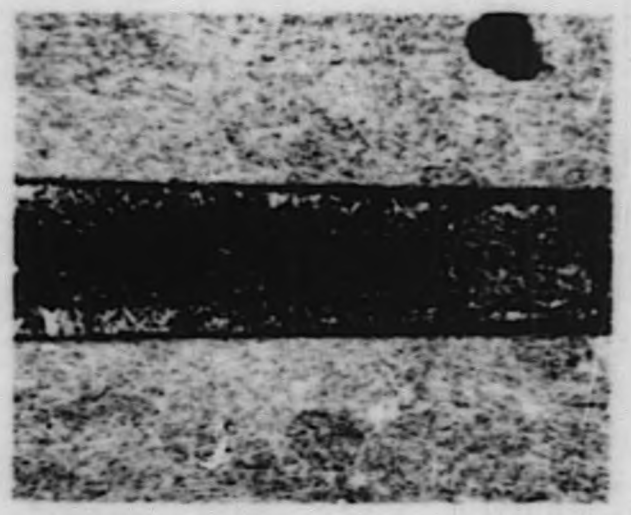


Neg. No. 14044 Mag. X 150
Micro No. 06504

Figure 17 - Structure of 3-Mil Spaced Joint Brazed with Cu-4% Be Filler Metal.

Neg. No. 14226 Mag. X 3

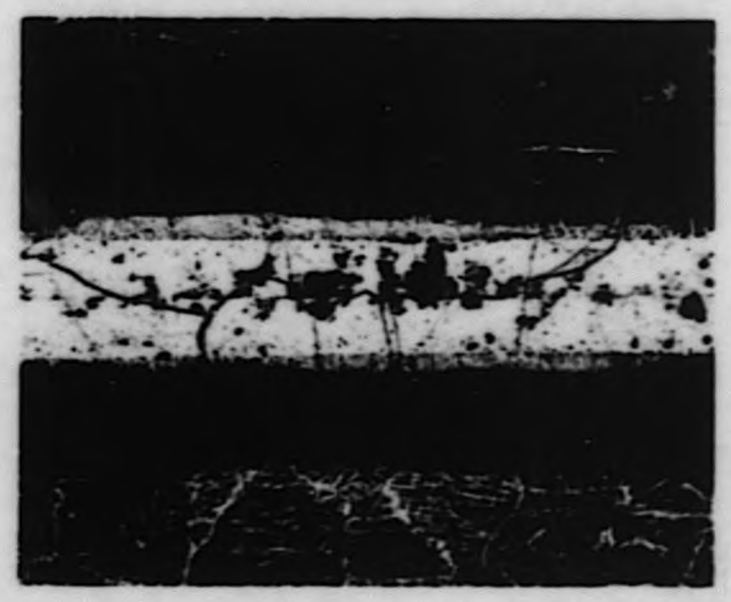
Figure 18 - Appearance of Above Specimen After 1256 Hours of Corrosion Testing in 680°F Water.



Neg. No. 14306 Mag. X 50

Micro No. 14014

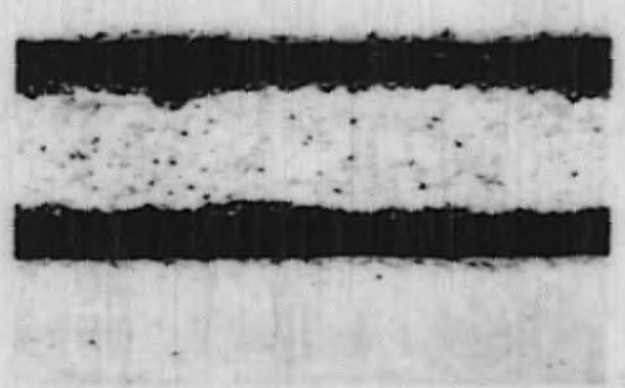
Figure 19 - Structure of 3-Mil Spaced Joint Brazed with Al-3% Ni Filler Metal.



Neg. No. 14281 Mag. X 75

Micro No. 07160

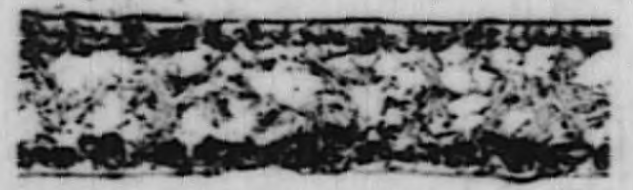
Figure 20 - Above Specimen After Failure from 98 Hours of Exposure to 680°F Water. Filler metal remained in one piece.



Neg. No. 14164 Mag. X 150

Micro No. 14006

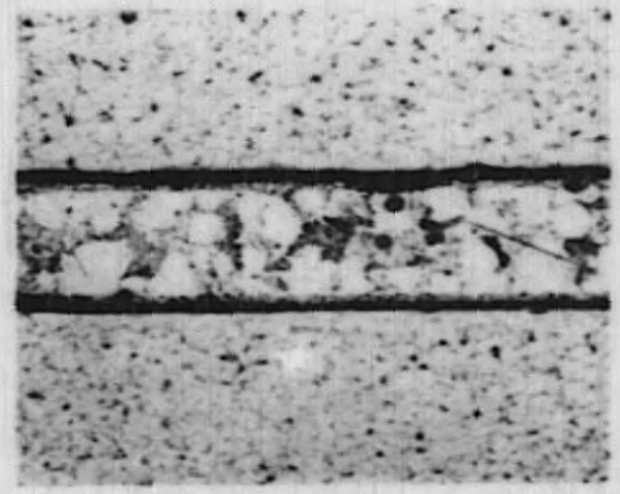
Figure 21 - Structure of 3-Mil Spaced Brazements with Al-55% Ge Filler Metal.



Neg. No. 14166 Mag. X 150

Micro No. 14007

Figure 22 - 3-Mil Spaced Brazement Made with Al-20% Si Filler Metal.



Neg. No. 14046 Mag. X 150

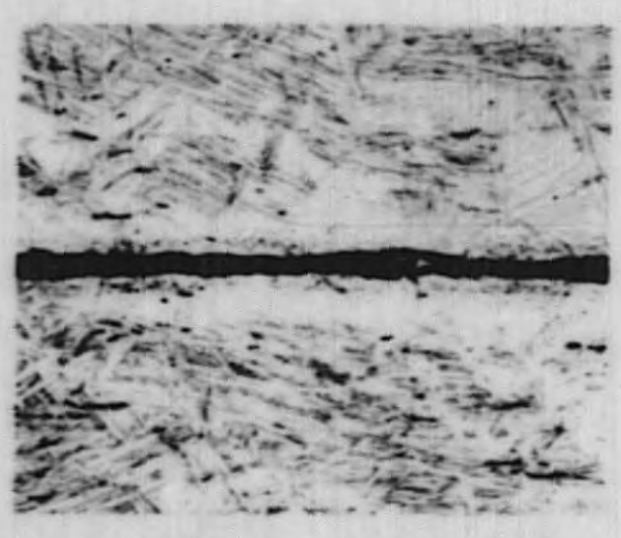
Micro No. 06505

Figure 23 - Structure of 3-Mil Spaced Brazement with Al-1% Be Filler Metal.

Neg. No. 14257 Mag. X 150

Micro No. 14011

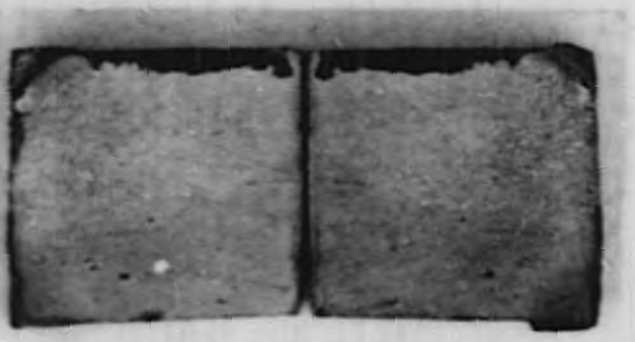
Figure 24 - Microstructure of 3-Mil Spaced Brazement with Al-35% Ge-10% Zr Filler Metal.



Neg. No. 12481 Mag. X 150

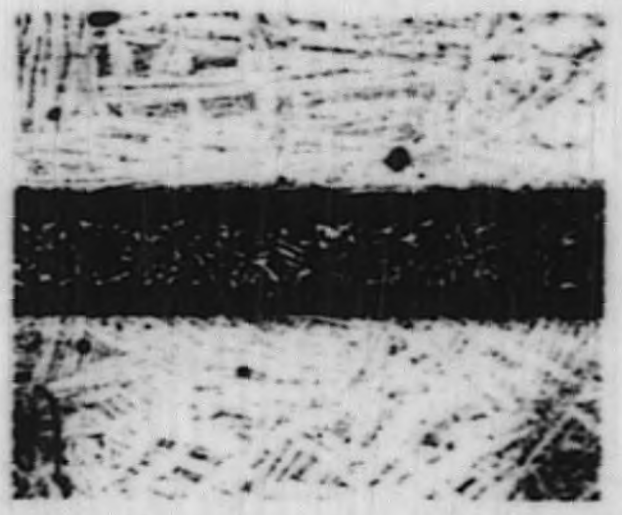
Micro No. 13977

Figure 25 - 3-Mil Spaced Joint Brazed with Zr-10% Fe-10% Cr Filler Metal.



Neg. No. 12796 Mag. X 3

Figure 26 - Appearance of Above Specimen After 1235 Hours of Corrosion Testing.

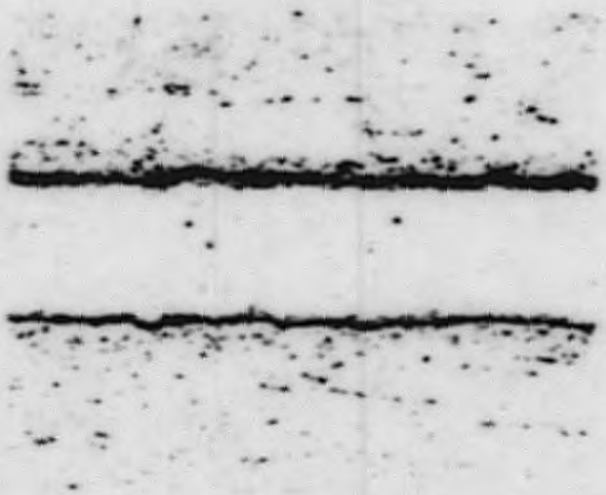


Neg. No. 14260 Mag. X 150
Micro No. 14013

Figure 27 - Microstructure of 3-Mil Spaced Brazement Using Zr-35% Al-3% Be Filler Metal.

Neg. No. 14259 Mag. X 150
Micro No. 14010

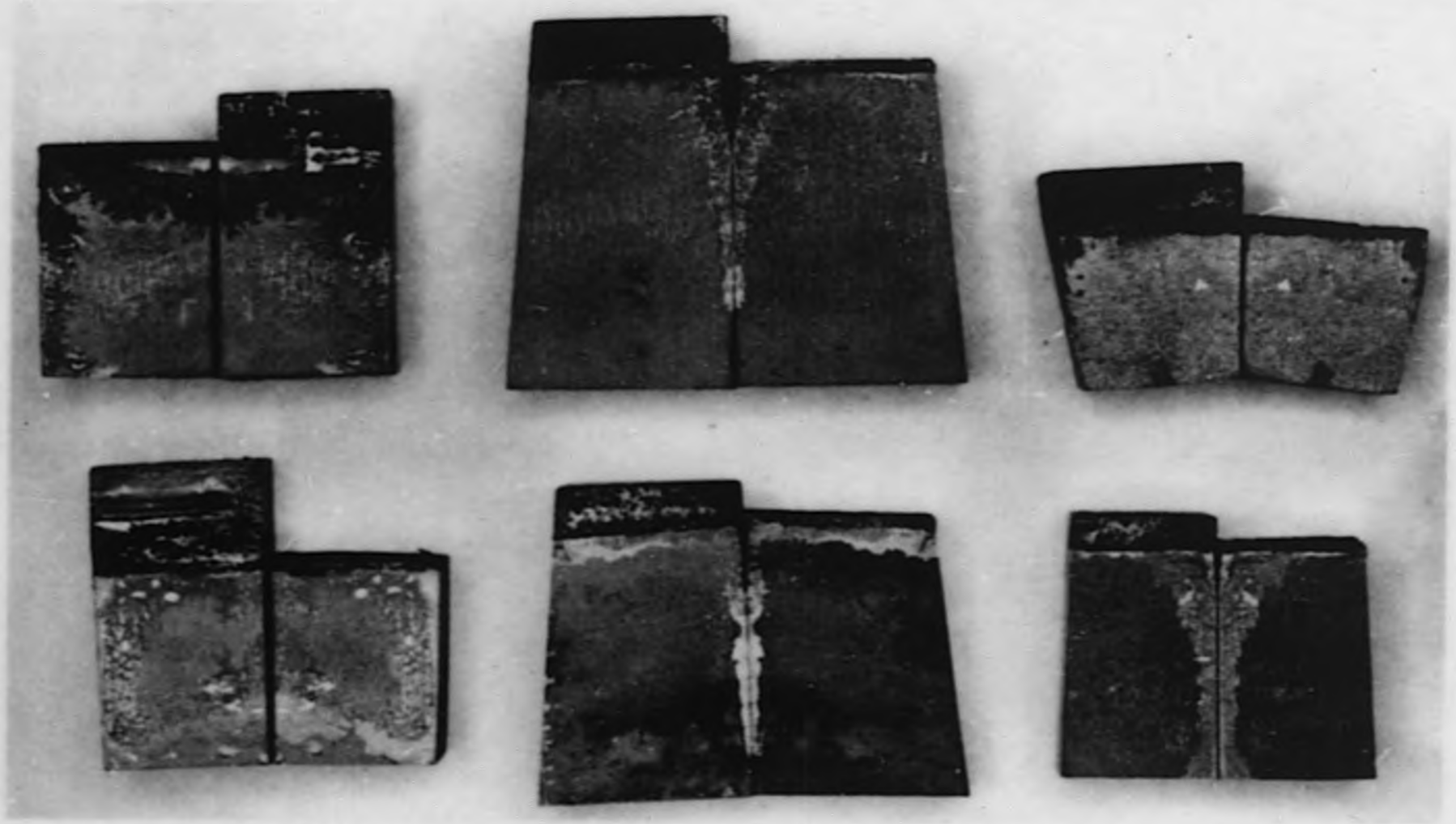
Figure 28 - Structure of 3-Mil Spaced Brazement with Ti-30% Al-5% Be Filler Metal.



Neg. No. 14256 Mag. X 150

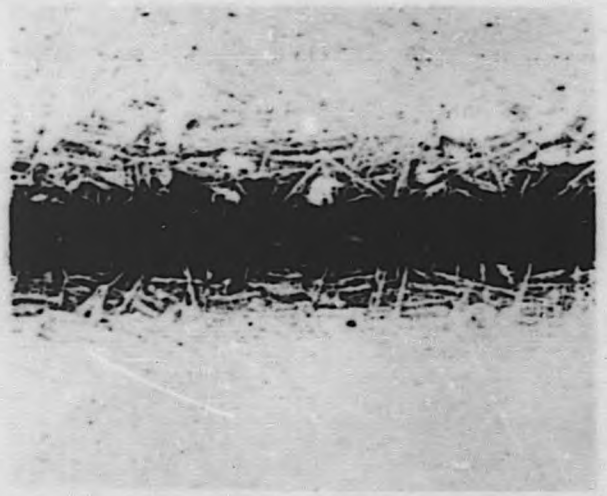
Micro No. 14009

Figure 29 - Microstructure of 3-Mil Spaced Joint Using Au-1.5% Be Filler Metal.



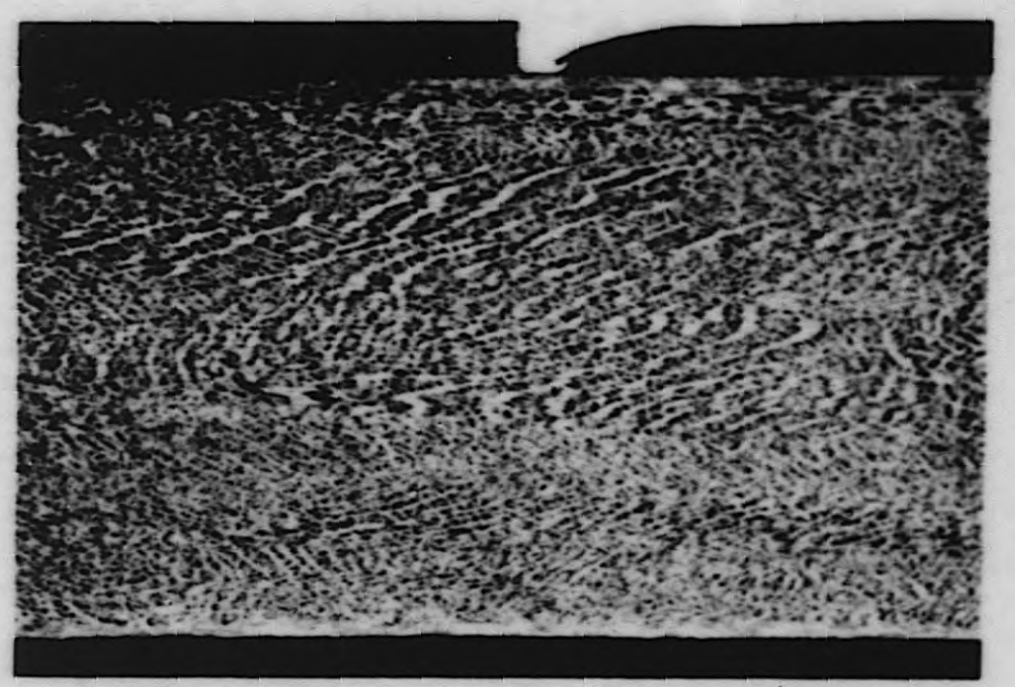
Neg. No. 13600 Mag. X 2 1/2

Figure 30 - 3-Mil Spaced Brazements with Ni-30% Ge-13% Cr Filler Metal After 1212 Hours of Corrosion Testing in 680°F Water.



Neg. No. 14258 Mag. X 150
Micro No. 14012

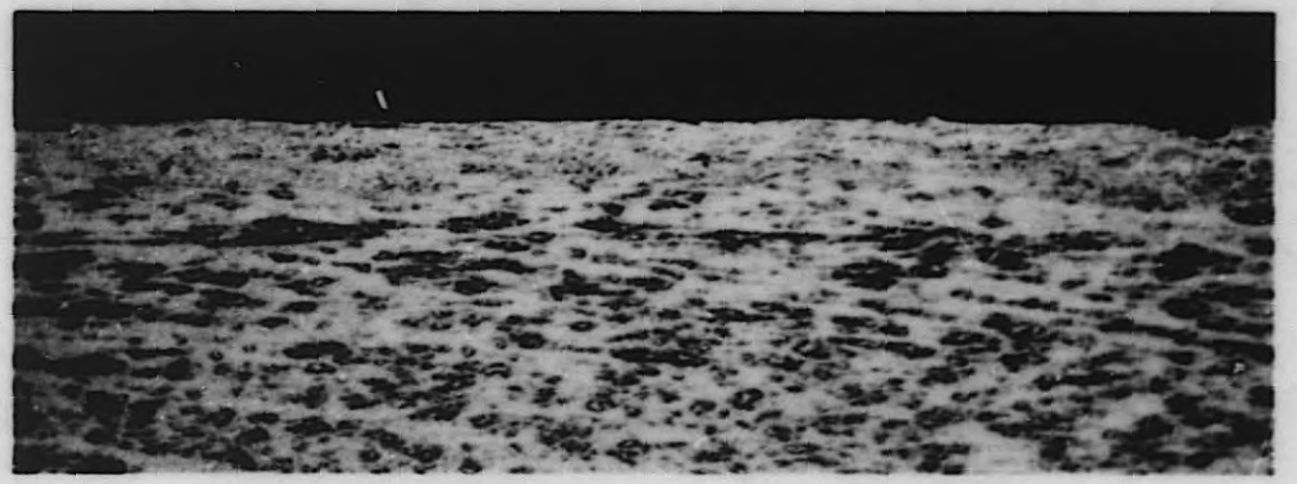
Figure 31 - 1-Mil Spaced Brazement Made with Ni-30% Ge-13% Cr Filler Metal.



Neg. No. 13824 Mag. X 150

Micro No. 14003

Figure 32 - Cross Section of Rolled Cu-20% Pd-3% In Alloy After 3511 Hours of Exposure in 680°F Water.



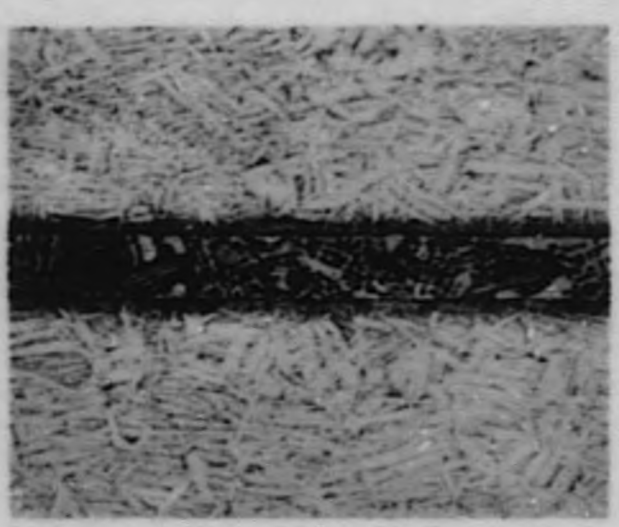
Neg. No. 13825 Mag. X 500

Micro No. 14003

Figure 33 - One Edge of Above.

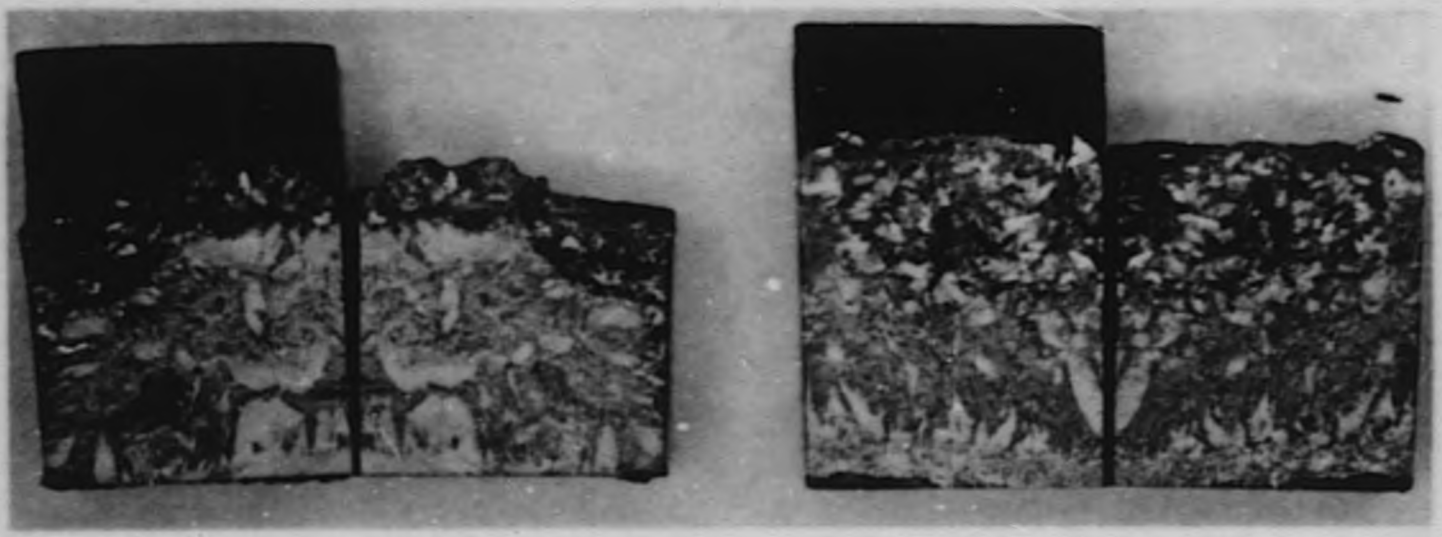
Neg. No. 13186 Mag. X 3

Figure 34 - Appearance of 3-Mil Spaced Brazements with Cu-20% Pd-3% In Filler Metal After 137½ Hours of 600°F Corrosion Testing.



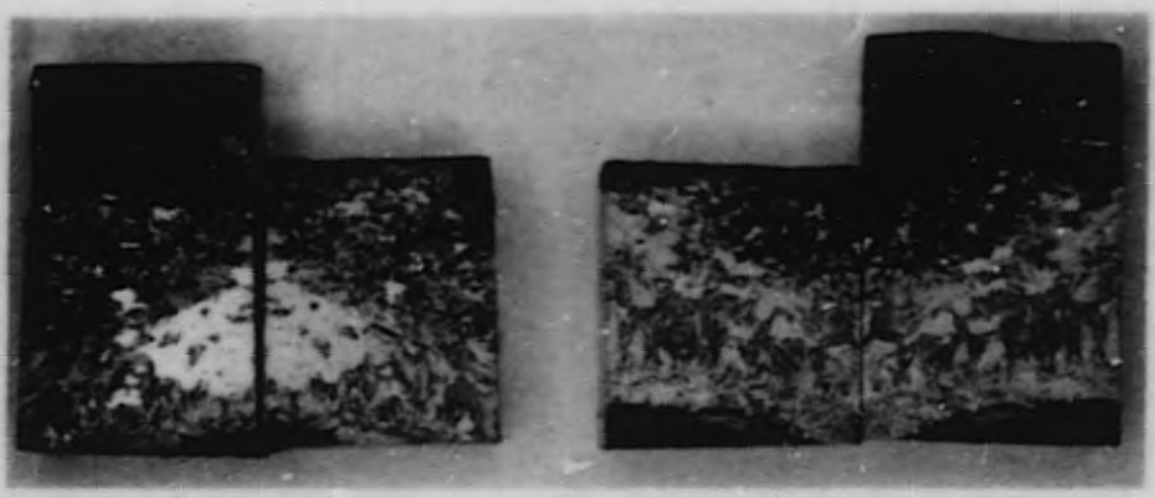
Neg. No. 14045 Mag. X 150
Micro No. 06501

Figure 35 - 1-Mil Spaced Joint Brazed with Cu-20% Pd-3% In Filler Metal.



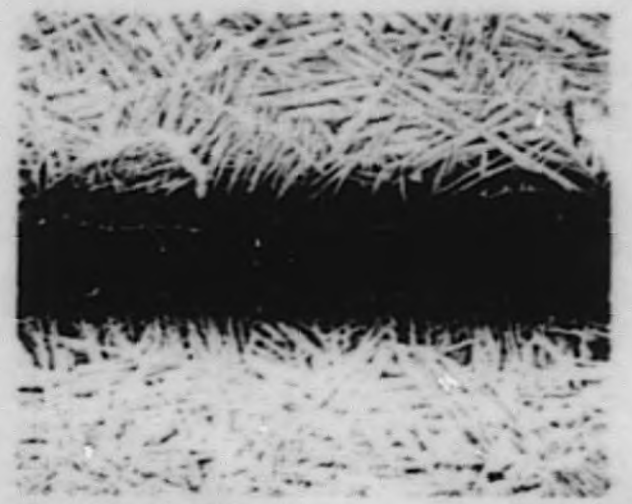
Neg. No. 14230 Mag. X 3

Figure 36 - Appearance of 1-Mil Spaced Brazements Brazed with Above Alloy After Exposure to 680°F Water for 1349 Hours.



Neg. No. 14275 Mag. X 2 1/2

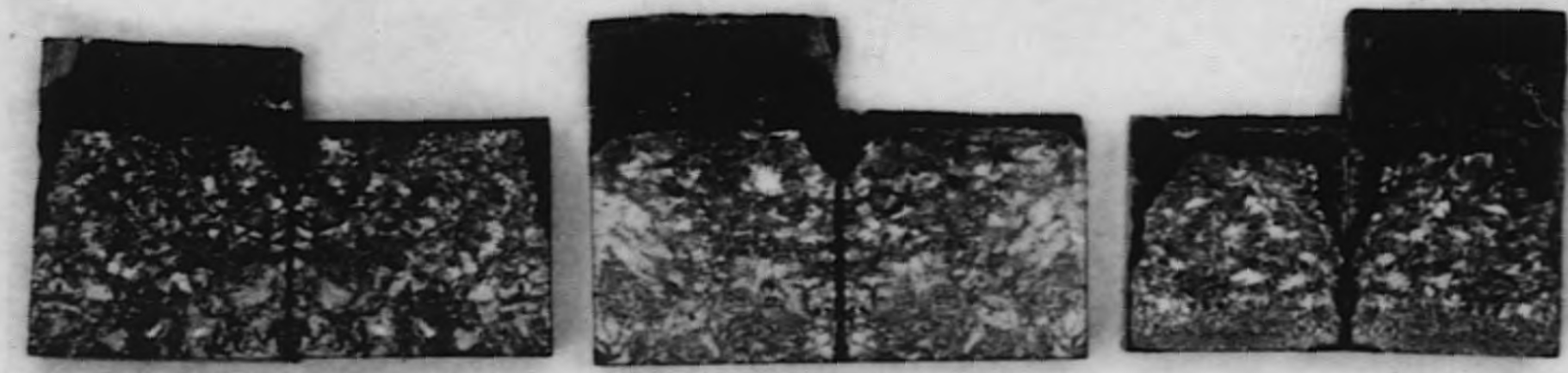
Figure 37 - Appearance of 1-Mil Spaced Brazements with Cu-20% Pd-3% In Filler Metal After 1279 Hours in 600°F Water.



Neg. No. 13821 Mag. X 150

Micro No. 14002

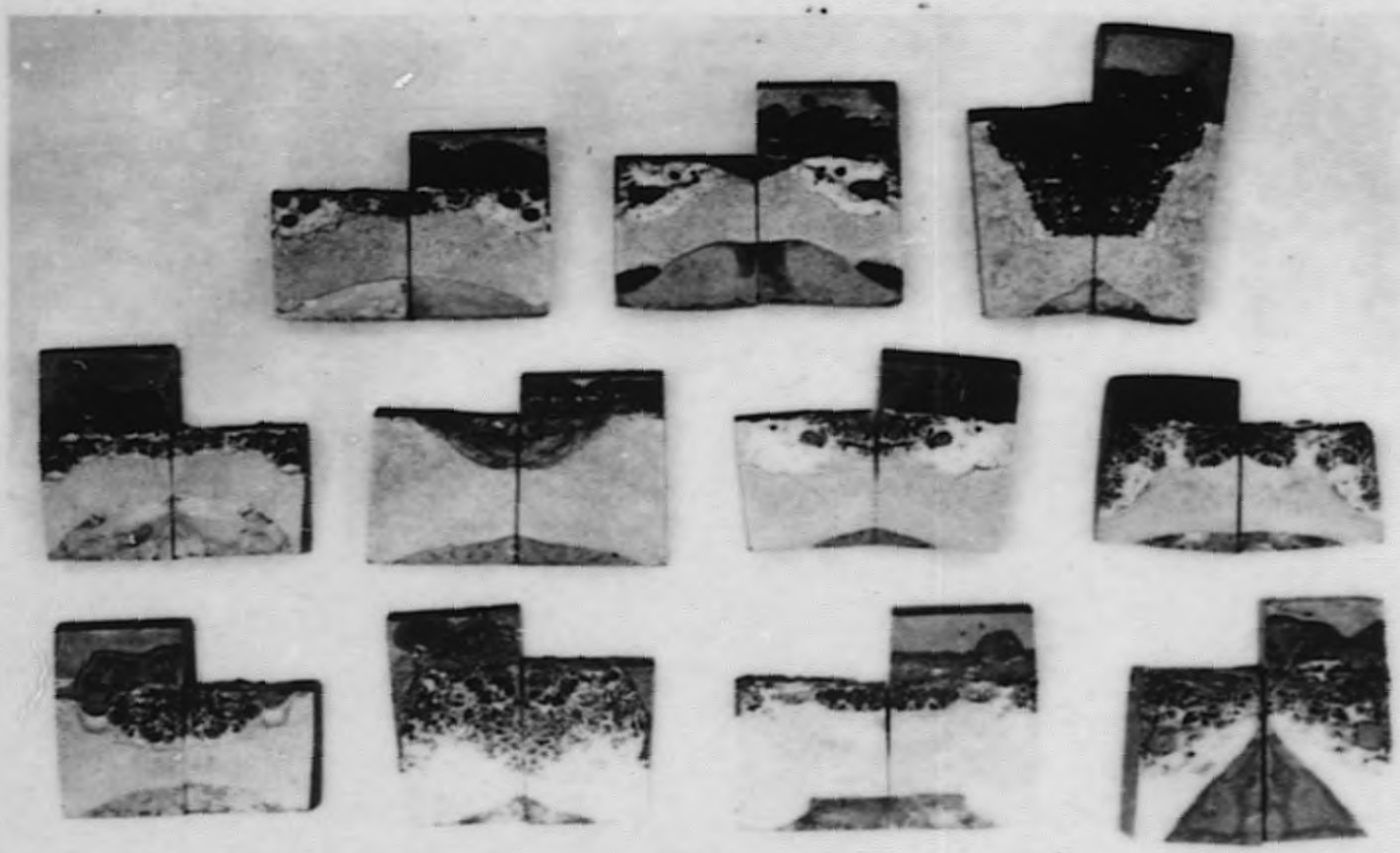
Figure 38 - Microstructure of 3-Mil Spaced Brazement with Cu-20% Pd-3% In Filler Metal. Base metal is Zircaloy 3A.



Neg. No. 14228 Mag. X 3

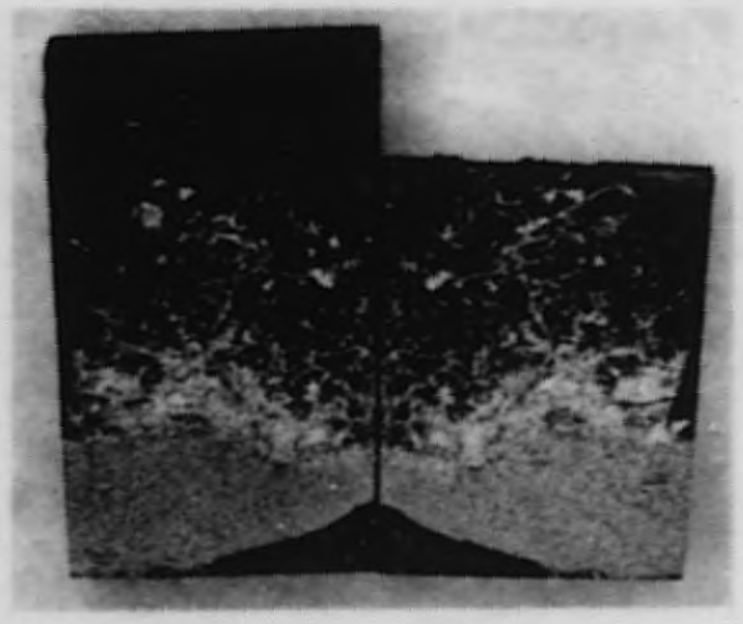
Figure 39 - Appearance of 3-Mil Spaced Brazements Made with Cu-20% Pd-3% In Filler Metal After Exposure to 680°F Water for 1361 Hours.

Zircaloy 3A was used as base metal.



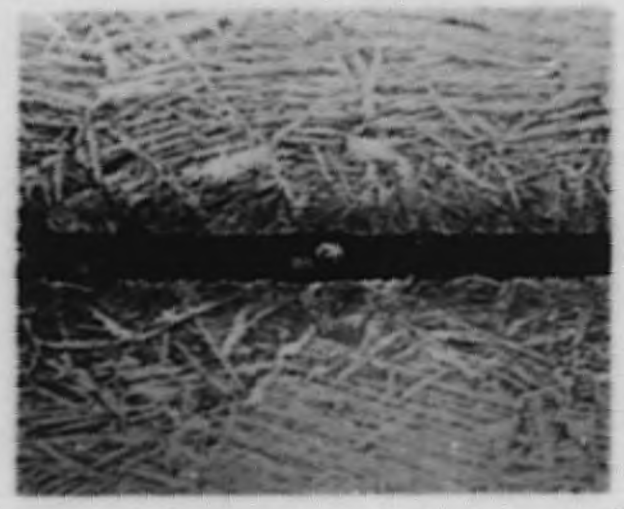
Neg. No. 13457 Mag. X 1 2/3

Figure 40 - Appearance of 3-Mil Spaced Joints with Ni-20% Pd-10% Si Filler Metal After 1355 Hours in 680°F Autoclave.



Neg. No. 13456 Mag. X 4

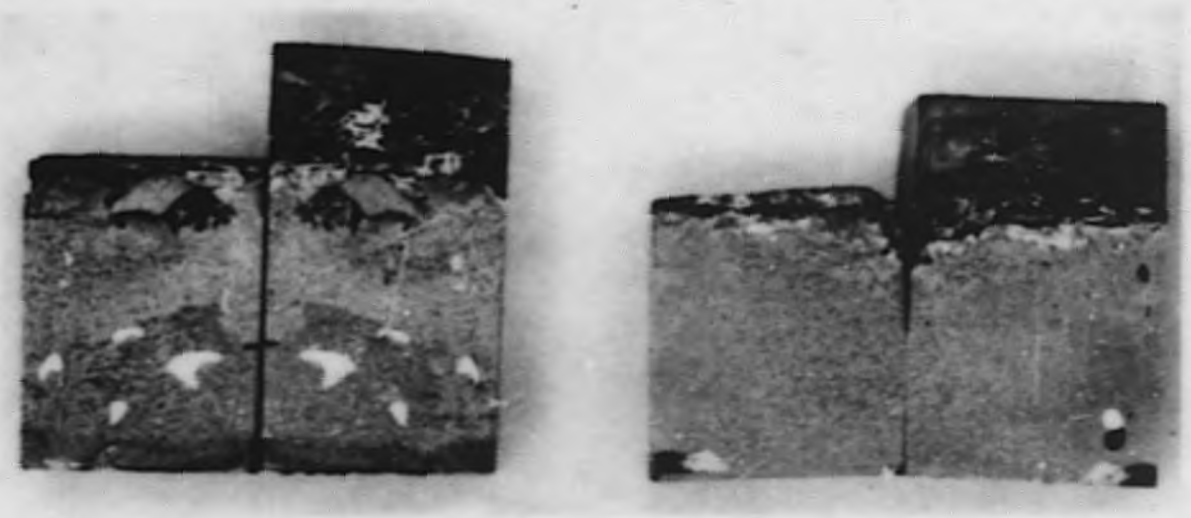
Figure 41 - Appearance of One Joint From Figure 40 Showing Network of Unattacked Filler Metal Surrounding Attacked Regions.



Neg. No. 14047 Mag. X 150

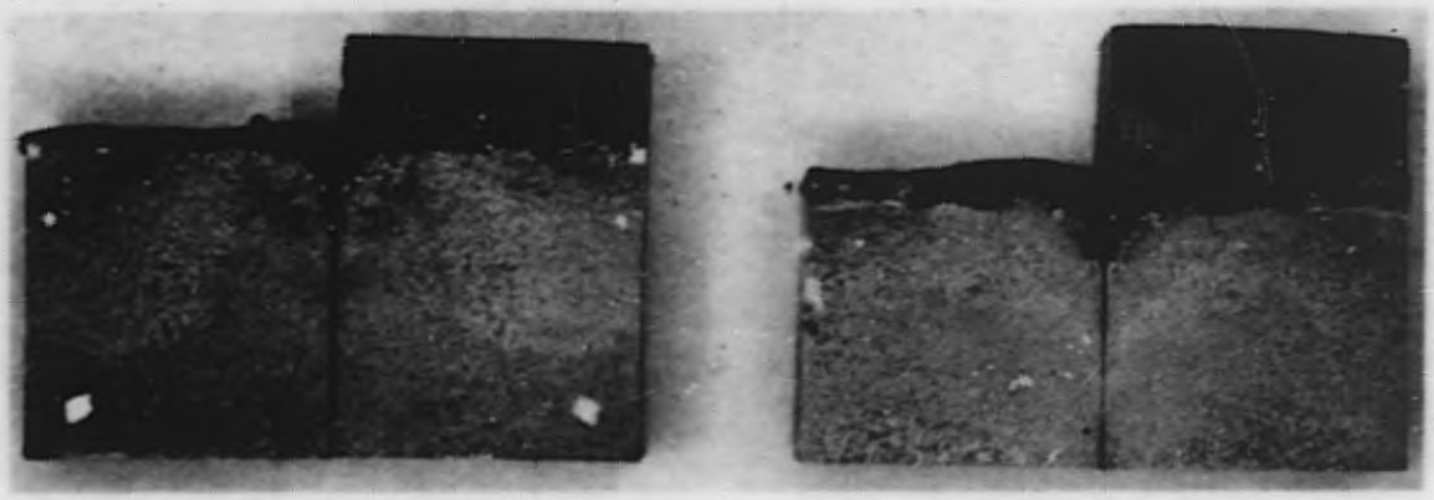
Micro No. 06500

Figure 42 - Microstructure of 1-Mil Spaced Brazement Using Ni-20% Pd-10% Si Filler Metal.



Neg. No. 14274 Mag. X 2 1/2

Figure 43 - Appearance of 1-Mil Spaced Joints Brazed with Ni-20% Pd-10% Si Filler Metal After Corrosion Testing in 600°F Water for 1279 Hours.



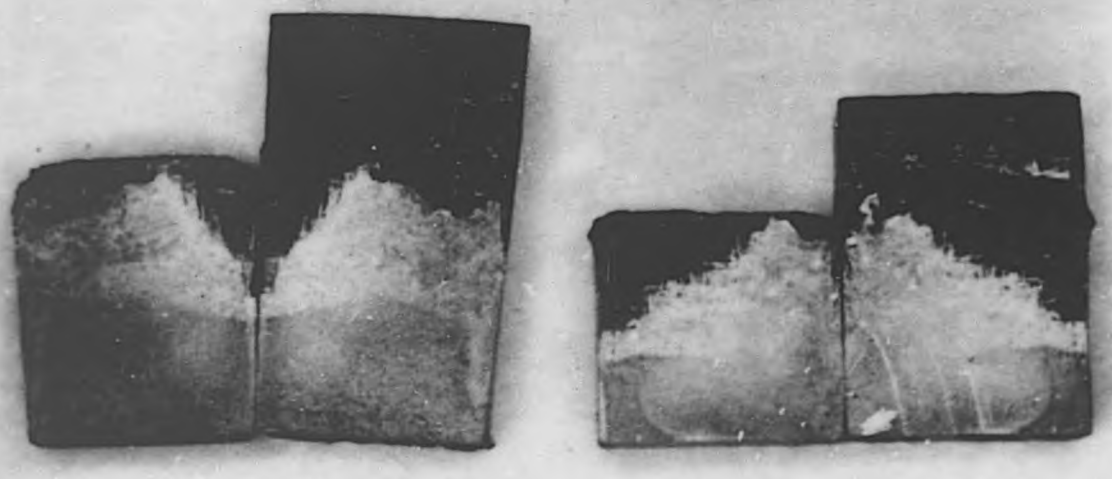
Neg. No. 14229 Mag. X 3

Figure 44 - Appearance of 1-Mil Spaced Brazements Made with Ni-20% Pd-10% Si Filler Metal After 1349 Hours of Corrosion Exposure in 680°F Water.

Neg. No. 14042 Mag. X 150

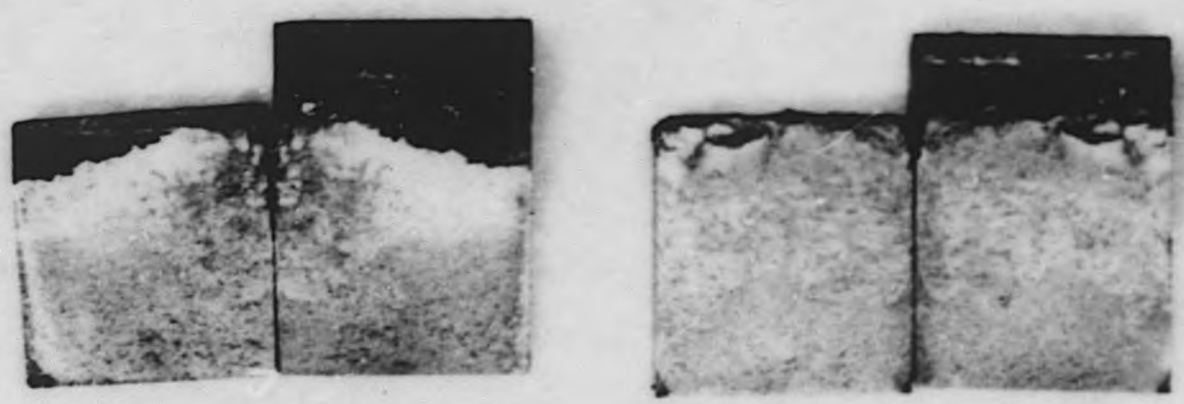
Micro No. 06560

Figure 45 - Microstructure of 3-Mil Spaced Joint Brazed with Ni-20% Pd-10% Si Filler Metal. Base metal is Zircaloy 3A.



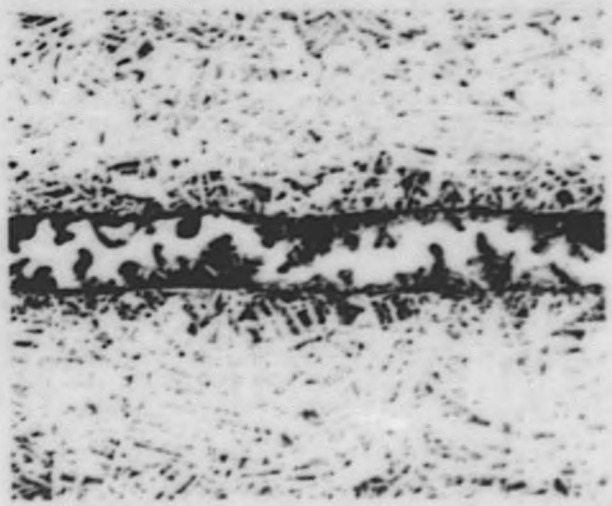
Neg. No. 14277 Mag. X 2 1/2

Figure 46 - Appearance of 1-Mil Spaced Brazements Brazed with Ni-20% Pd-10% Si Filler Metal After 1255 Hours of Exposure to 680°F Water. Zircaloy 3A used as base metal.



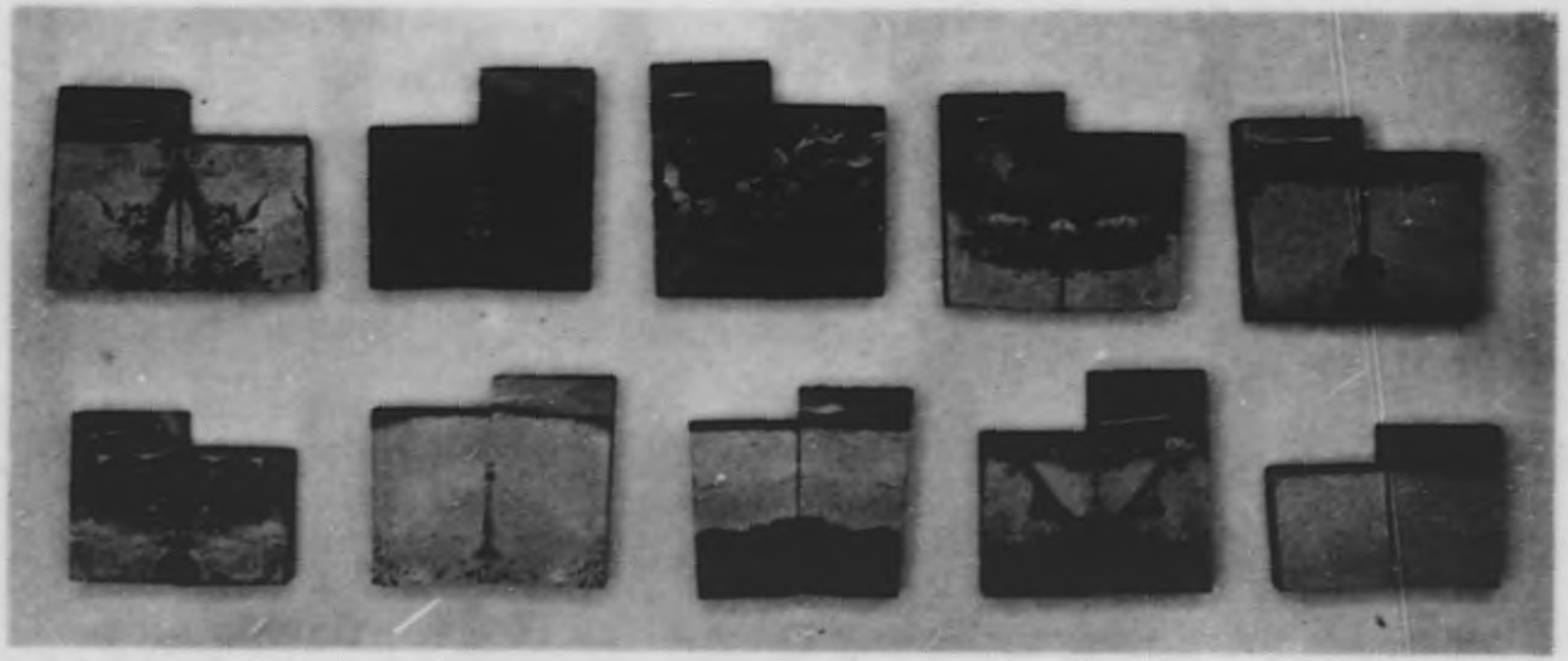
Neg. No. 14277 Mag. X 2 1/2

Figure 47 - Appearance of 3-Mil Spaced Brazements using Ni-20% Pd-10% Si Filler Metal After 1255 Hours of Exposure to 680°F Water. Base metal is Zircaloy 3A.



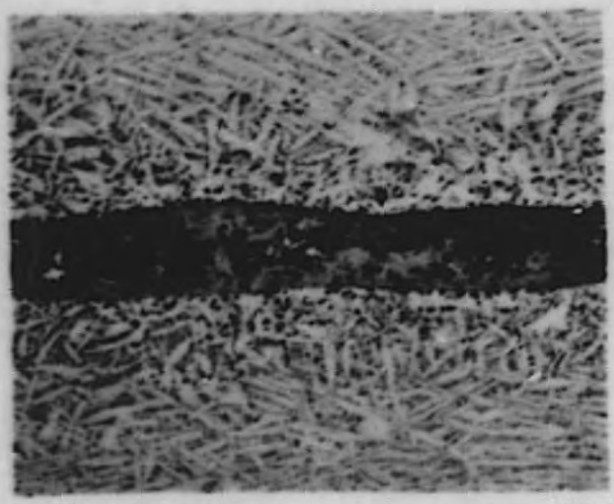
Neg. No. 13239 Mag. X 150
Micro No. 13995

Figure 48 - Microstructure of Brazement with Kanigen Deposited Filler Metal.



Neg. No. 13698 Mag. X 1 1/3

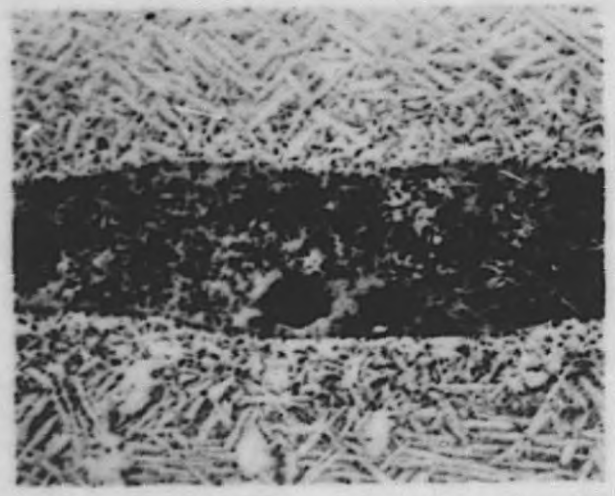
Figure 49 - Appearance of Brazements with Deposited Kanigen Filler Metal After 1200 Hours in 650°F Autoclave.



Neg. No. 14167 Mag. X 150

Micro No. 14008

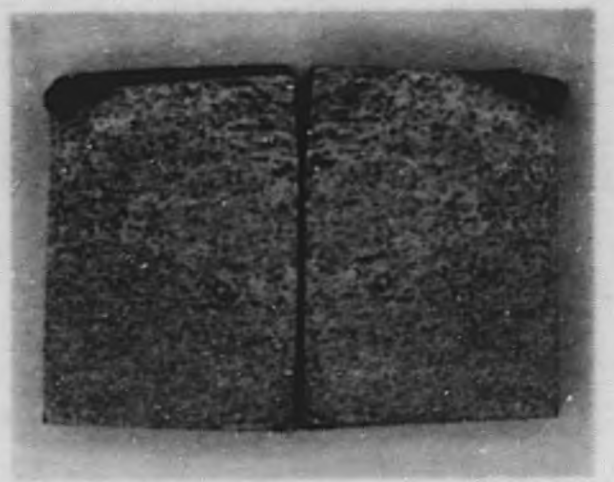
Figure 50 - Microstructure of Brazement with Deposited Kanigen Filler That was Diffused into Base Metal.



Neg. No. 14168 Mag. X 150

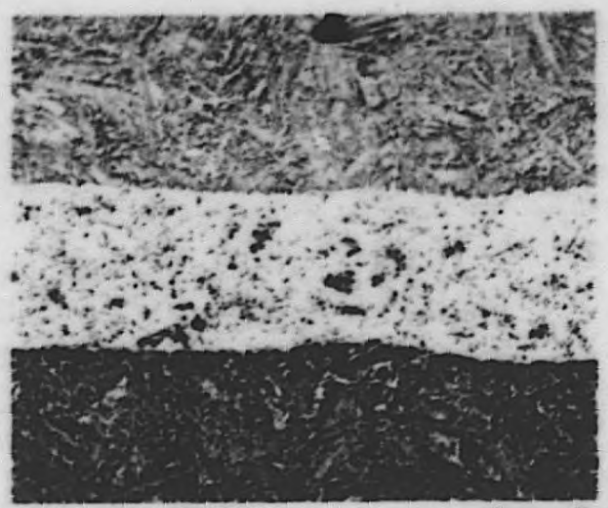
Micro No. 14008

Figure 51 - Same Brazement as Above Showing Totally Enclosed Voids.



Neg. No. 14355 Mag. X 3

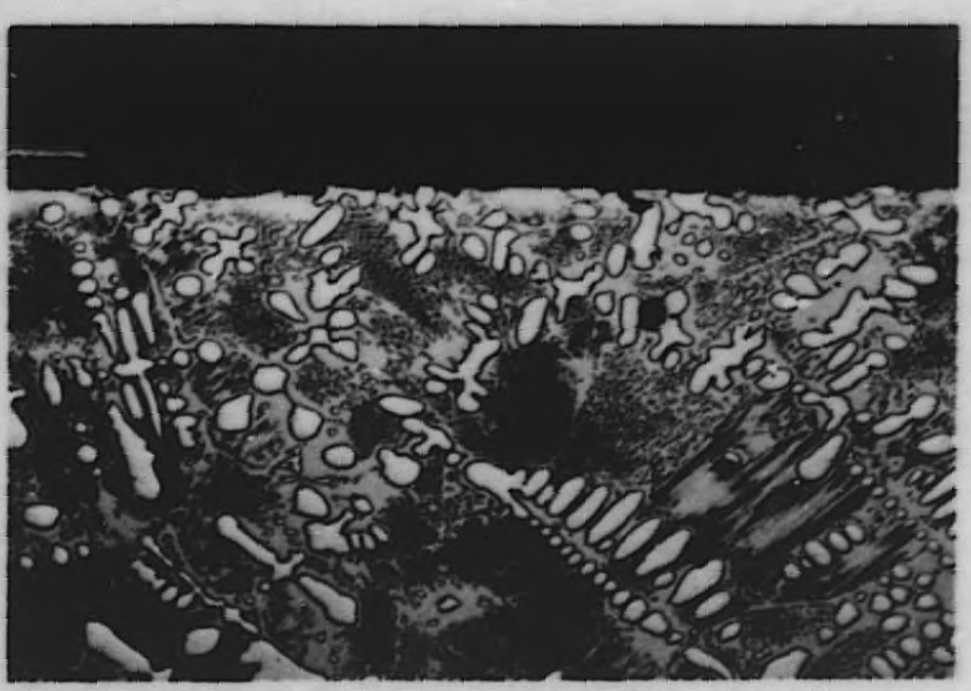
Figure 52 - Appearance of Above Brazement (Figs. 50-51) After 1321 Hours of Exposure in 680°F Water.



Neg. No. 14216 Mag. X 150

Micro No. 06939

Figure 53 - Microstructure of Joint With Kanigen Deposited and Diffused Filler Metal. Base Metal is Zircaloy 3A.



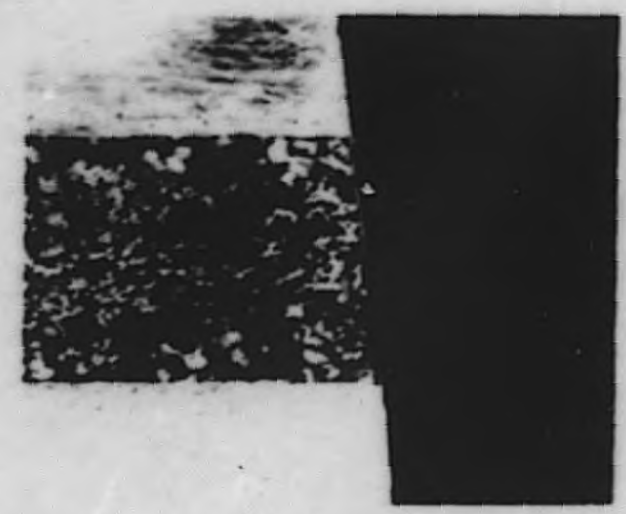
Neg. No. 13823 Mag. X 150

Micro No. 11,004

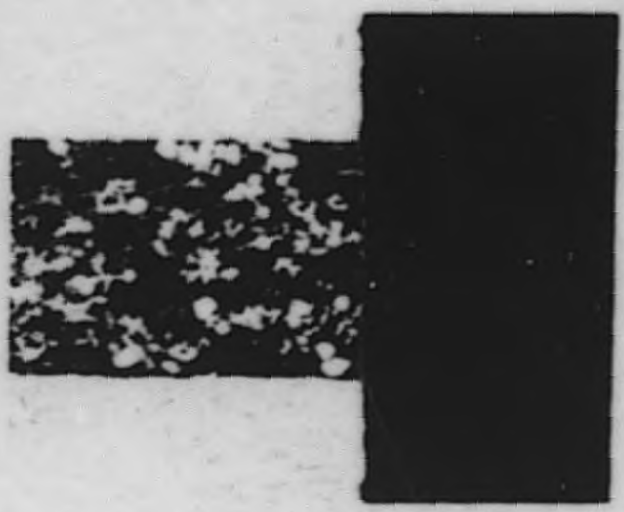
Figure 54 - Cross Section of Kanigen Block After 3379 Hours of Exposure in 680°F Water.

Neg. No. 13175 Mag. X 2

Figure 55 - Appearance of 3-Mil Spaced Brazement with Zr-5% Be Filler Metal After 1374 Hours of Exposure in 680°F Autoclave.



Neg. No. 13236 Mag. X 150
Micro No. 13990

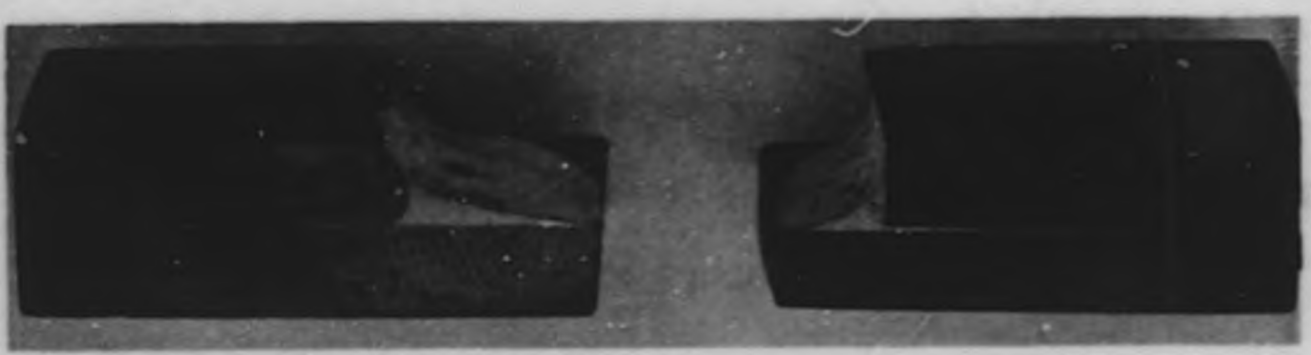


Neg. No. 13237 Mag. X 150
Micro No. 13991

Neg. No. 13238 Mag. X 150
Micro No. 13993

Figures 56, 57 and 58 - Microstructure of Brazements Brazed with Zr-5% Be Filler Metal After 1374 Hours of Exposure to 680°F Water.

Note thin corrosion line at edge of specimens.

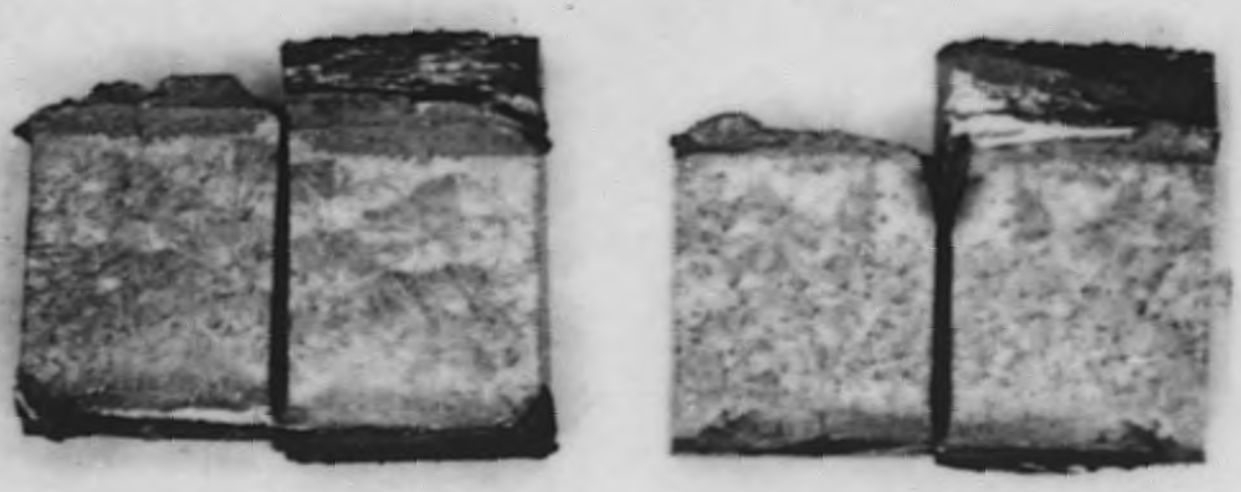


Neg. No. 13130 Mag. X 3

Figure 59 - Appearance of Unbroken 3-Mil Brasements with Zr-5% Be Filler Metal After 137½ Hours of Exposure to 680°F Water.

Neg. No. 14048 Mag. X 150
Micro No. 06502

Figure 60 - 1-Mil Spaced Brasement with Zr-4% Be Filler Metal.

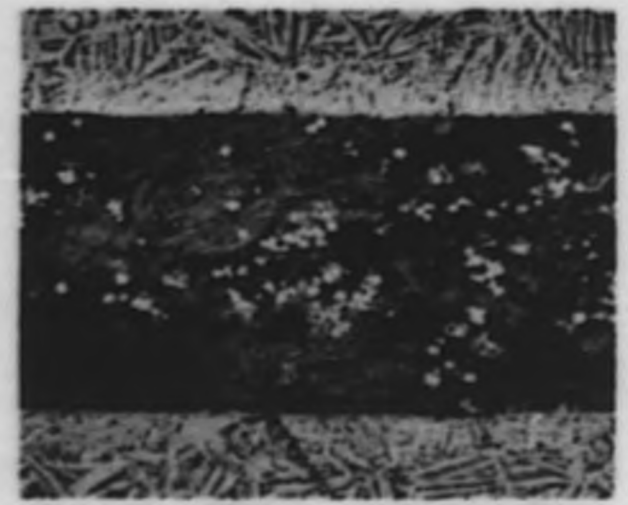


Neg. No. 14276 Mag. X 2 1/2

Figure 61 - Appearance of 1-Mil Spaced Joints Brazed with Zr-4% Be Filler Metal After 1279 Hours at 600°F.

Neg. No. 14226 Mag. X 3

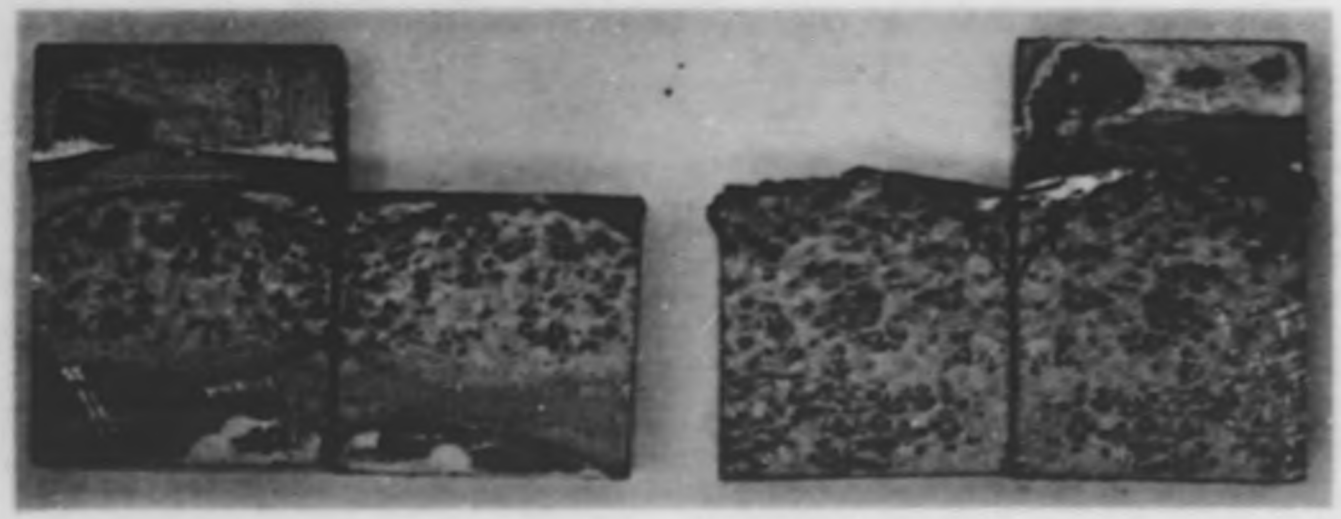
Figure 62 - Appearance of 1-Mil Spaced Joints with Zr-4% Be Filler Metal After Exposure in 680°F Water for 1349 Hours.



Neg. No. 13822 Mag. X 150

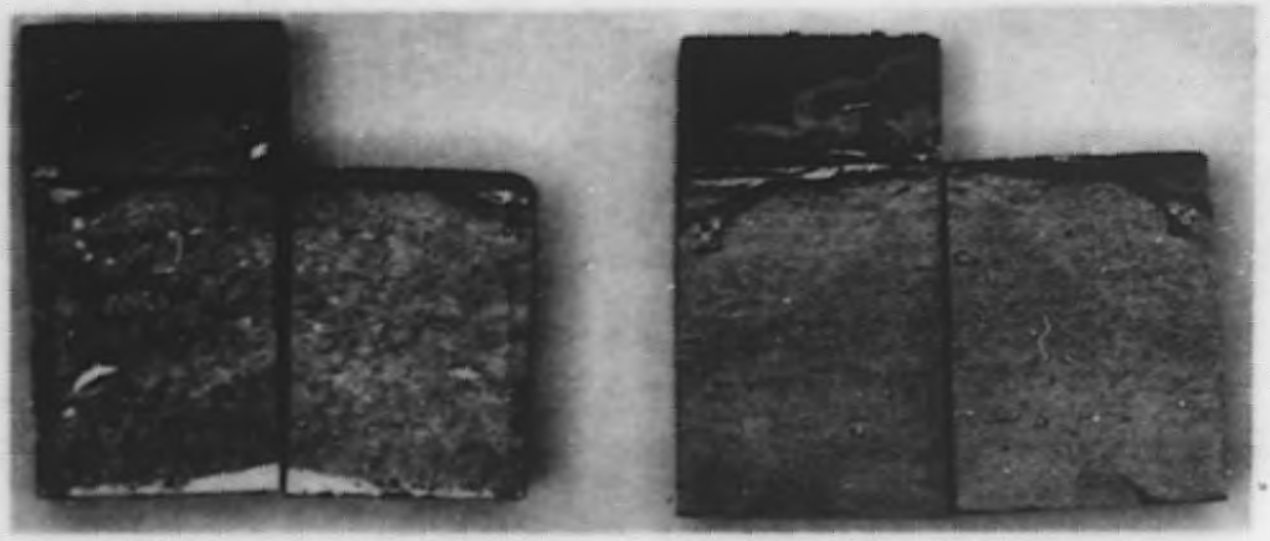
Micro No. 14001

Figure 63 - Microstructure of 3-Mil Spaced Brazement Using Zr-4% Be Filler Metal. Base metal is Zircaloy 3A.



Neg. No. 14277 Mag. X 3

Figure 64 - Appearance of 3-Mil Brazements with Zr-4% Be Filler Metal After 1361 Hours at 680°F. Base metal is Zircaloy 3A.



Neg. No. 13601 Mag. X 3

Figure 65 - Appearance of 3-Mil Spaced Joints Using Zr-2.5% Be Filler Metal After 1212 Hours in 680°F Water.

Neg. No. 11488 Mag. X 1

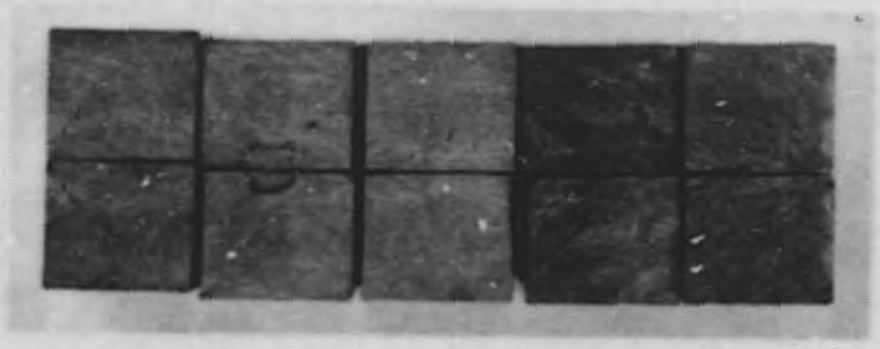
Figure 66 - Furnace Brazed T-Joint Brazed with Zr-4% Be Filler Metal.

Neg. No. 14987 Mag. X 2

Figure 67 - Charpy Impact Bars Brazed with Ni-20% Pd-10% Si Filler Metal. Left specimen broken at R.T.; Right specimen broken at 550°F.

Neg. No. 14988 Mag. X 2

Figure 68 - Charpy Impact Bars Brazed with Flowed Kanigen Filler Metal. Left two specimens broken at R.T.; Right specimen broken at 550°F.



Neg. No. 14989 Mag. X 2

Figure 69 - Charpy Impact Bars Brazed with Zr-4% Be Filler Metal. Left three specimens broken at R.T.; Right two specimens broken at 550°F.

Neg. No. 14990 Mag. X 2

Figure 70 - Unbrazed V-notch Zircaloy 2 Charpy Bars. Left three specimens broken at R.T.; Right three specimens broken at 550°F.

APPENDIX A

ALLOY PREPARATION AND MELTING TEMPERATURES OF THE MORE PROMISING ALLOYS

I. ALLOY PREPARATION:

(All of the alloys which were arc melted were inverted between each striking of the arc)

A. Preparation of Alloy No. 3, Kanigen Plating of Zircaloy (Ni-6.8 P)

1. Electroclean

Composition of bath:
22 gm of Orthosil per liter of distilled water
Heat bath to about 160°F. Make specimen cathodic by applying a direct current. The anode can be the steel container itself.
Time: 2 to 3 minutes.

2. Rinse in water

3. Pickle

Composition of pickling bath:
20-25% HNO_3
5% HF
70-75% H_2O

Immerse specimen in bath for 1 to 3 minutes or until surface is completely etched.

4. Rinse in water

5. Plate

Composition of bath:

Nickel Chloride ($NiCl_2 \cdot 6H_2O$)	30 g/l
Sodium Hypophosphite ($NaH_2PO_2 \cdot H_2O$)	10 g/l
Sodium Citrate ($Na_3C_6H_5O_7 \cdot 5\text{-}1/2H_2O$)	100 g/l
Ammonium Chloride (NH_4Cl)	

Neutralize with NH_4OH to a pH of 8 to 10.

Temperature -- boiling or 90°-100°C.
Rate of deposition about .0003 in. per hour.

When the bath begins to boil, immerse the pretreated Zircaloy specimens in Kanigen solution. Hold iron (wire) in contact with the surface of the specimen until the surface of the specimen

begins to bubble. Remove the iron from the solution at this point. Add hot water when needed to maintain the proper concentration, remembering to keep the solution boiling at all times.

Remove the specimens when desired thickness is reached, rinse in water, and allow to dry.

B. Preparation of Alloy No. 7, 70 Ni-20 Pd-10 Si

Two 50-gm melts of this alloy have been made by arc melting using a 1/2 in. diameter tungsten electrode. Both melts used 35 gm Ni, 10 gm Pd and 5 gm Si.

One melt was melted in a copper block with tungsten striking stud. Furnace was pumped to 50 microns three times and purged with He (all He used is grade A). Furnace was then pumped to 30 microns and He introduced. Melting was as follows:

Time	Amps	Volts
10 sec	250	40
10 sec	250	40
10 sec	250	40

The other melt of alloy No. 7 was done in a copper crucible. Furnace was purged as above. Melting was as follows:

Time	Amps	Volts
1 min	600	30
1 min	700	30
1 min	600	30

C. Preparation of Alloy No. 14, 57 Ni-30 Ge-13 Cr

This alloy was obtained from the General Electric Company in the form of a fine powder.

D. Preparation of Alloy No. 31, 77 Cu-20 Pd-3 In

This alloy has been prepared by both induction and arc melting methods.

One 10-gm melt contained 7.7 gm Cu, 2 gm Pd and 0.3 gm In. This alloy was arc melted in a copper block with a stud, using a 1/2 in. diameter tungsten electrode. The furnace was pumped down to 50 microns and purged three times with He. Furnace was then pumped down to 40 microns and He introduced. Melting was as follows:

Time	Amps	Volts
4 sec	200	60
4 sec	200	60
3 sec	200	60
3 sec	200	60
5 sec	200	60

Two 30-gm melts (23.1 gm Cu-6.0 gm Pd-0.9 gm In) were induction melted. Melting was done in high purity alundum crucibles. The melting chamber in each case was pumped down to 1 micron and purged with He that had been passed through a cold trap and a Ti sponge furnace to increase its purity. The bell jar was then pumped below 1 micron, He introduced and melting accomplished in about four minutes. One of the melts was remelted by arc in a Cu crucible as follows:

The furnace was pumped to 50 microns and purged three times with He. Furnace was then pumped to 30 microns and He was introduced.

Time	Amps	Volts
10 sec	400	30
8 sec	400	30

E. Preparation of Alloy No. 34, Zr-2.5 to 6 Be

This alloy has been made with nominal compositions ranging from 2.5 to 6% Be. The Zr used in all of the melts was Zircaloy. The Be used for early melts was in the form of pellets with a purity of 95%. Later melts were made using electrolytic flake beryllium with a purity of 99.5%.

All of the melts were arc melted using a 1/2 in. diameter tungsten electrode.

Two 5% Be melts have been made - one of 10 gm and the other of 25 gm. The 10-gm melt contained 9.5 gm of Zr and 0.5 gm Be. Melting was done in a copper crucible. Furnace was pumped to 50 microns and purged three times with He. Furnace was then pumped to 40 microns and He was introduced. Melting was as follows:

Time	Amps	Volts
8 sec	200	40
8 sec	200	40
8 sec	200	40
8 sec	200	40

The 25 gm melt contained 23.75 gm of Zr and 1.25 gm of Be. Melting was done in a Cu block with stud. Furnace was pumped to 50 microns and purged three times with He. Furnace was then pumped to 30 microns and He introduced. Melting was as follows:

Time	Amps	Volts
7 sec	200-300	35
7 sec	200	35
8 sec	200	40
8 sec	200	40

Two 5.25 Be melts of 30 gm each have been made. The charge was 28.425 gm Zr and 1.575 gm Be. One melt was done in a Cu block with stud. The furnace was pumped to 50 microns three times and purged three times with He. Furnace was then pumped to 25 microns and He introduced. Melting was as follows:

Time	Amps	Volts
10 sec	400	30
10 sec	400	30
10 sec	400	30
10 sec	600	20

The second melt was done in a Cu crucible. Furnace was pumped to 50 microns and purged three times with He. Furnace was then pumped to 30 microns and He was introduced. Melting was as follows:

Time	Amps	Volts
7 sec	500	30
7 sec	500	30
7 sec	500	30
7 sec	500	30

Two 5.50% Be melts of 30 gm each have been made. Content of each melt was 28.35 gm Zr and 1.65 gm Be. One melt was prepared in a Cu block with stud. The furnace was evacuated to 50 microns and flushed three times with He. The furnace was then pumped to 15 microns and He was introduced. Melting was as follows:

Time	Amps	Volts
16 sec	600	30
10 sec	600	30
10 sec	600	35
10 sec	600	35

The second melt was done in a Cu crucible. Furnace was pumped to 50 microns and purged three times with He. Furnace was then pumped to 30 microns and He was introduced. Melting was as follows:

Time	Amps	Volts
12 sec	700	30
10 sec	700	30
8 sec	700	30
8 sec	700	30

Two 30-gm melts of 5.75% Be alloy have been made. Content of melts consisted of 28.275 gm Zr and 1.725 gm Be. One melt was melted in a Cu block with stud. Furnace was pumped to 50 microns and purged three times. Furnace was then pumped to 35 microns, He introduced and arc struck as follows:

Time	Amps	Volts
20 sec	600	25
10 sec	200	30
10 sec	400	35
5 sec	200	30

The second melt was done in a Cu crucible. Furnace was pumped down to 30 microns after previously pumping to 50 microns and flushing with He three times. Helium was introduced and melting done as follows:

Time	Amps	Volts
7 sec	400	30
7 sec	400	30
8 sec	400	30
8 sec	400	30

Two 30-gm melts of Zr-Be alloy have been made with nominal Be contents of 6%. These melts contained 28.2 gm of Zr and 1.8 gm of Be. One melt was melted in a Cu block with stud. The furnace was pumped to 50 microns and purged three times with He. Furnace was then pumped to 35 microns and He added. Melting was as follows:

Time	Amps	Volts
9 sec	200	30
12 sec	200	30
12 sec	600	30
12 sec	600	35

The second melt was done in a Cu crucible. The furnace was pumped to 45 microns after being pumped to 50 microns and purged three times. He was introduced, and arc was struck as follows:

Time	Amps	Volts
6 sec	400	30
8 sec	400	30
8 sec	400	30
8 sec	400	30

The Zr-Be alloys that had nominal beryllium contents of 2.5 to 4.5% were all melted in a manner similar to the above Zr-Be alloys.

II. MELTING TEMPERATURES:

Alloy	Melting Range, °C
70 Ni-20 Pd-10 Si	1035 - 1050
57 Ni-30 Ge-13 Cr	1090 - 1120
77 Cu-20 Pd-3 In	975 - 1050
Zr-5 Be	970 - 985
Zr-5 to 6 Be	975 - 1005
Zr-2 to 4.5 Be	967 - 990

END