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FURNACE BRAZING OF ZIRCALOY

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FURNACE BRAZING OF ZIRCALOY

E. R. Slaughter

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An experimental investigation was initiated to develop furnace brazing of Zircaloy or Zircaloy-clad nuclear reactor components. The strength and corrosion resistance of brazements were determined and techniques were developed for preplacing the brazing alloy to prevent contamination and to maintain dimensional stability during brazing. Brazements of high strength and adequate dimensional accuracy were produced, but the brazing cycles impaired the corrosion resistance of Zircaloy in high-temperature steam and water.

FURNACE BRAZING OF ZIRCALOY

E. R. Slaughter

SUMMARY

This investigation was initiated to develop a process for the furnace brazing of Zircaloy-clad nuclear core fuel assemblies. The principal advantage of furnace brazing over a fusion welding process is the elimination of distortion caused by steep thermal gradients inherent in welding.

This investigation showed that furnace brazing could consistently produce high-strength brazements with adequate dimensional tolerances for fuel assemblies. Zircaloy which was subjected to a brazing cycle followed by slow cooling was, however, less corrosion resistant than untreated Zircaloy.

Zircaloy slow cooled from the brazing temperature had weight gains 45% greater than those of untreated Zircaloy in 140-day, 680°F water-phase corrosion tests and much larger weight gains in 110-day, 750°F steam corrosion tests. Post-brazing thermal treatments failed to improve the corrosion resistance.

Since slow cooling through the alpha plus beta range caused the poor corrosion resistance of brazed Zircaloy, the problem of corrosion resistance could be avoided by lowering the brazing temperature. The addition of 10 to 13% iron to a Zircaloy-beryllium brazing alloy lowered the liquidus temperature from 1830°F to approximately 1535°F and offered a possible solution to the problem of poor corrosion resistance.

Strength of simulated fuel plate to side plate joints was a function of the joint clearance and thermal history. Tensile specimens, which had small joint clearances and had been subjected to a diffusion-promoting brazing cycle, fractured away from the brazed joints in a ductile manner. Lower strengths and brittle fractures occurred in tensile specimens which had a nearly continuous beryllium-rich phase in the joints. Larger joint clearances increased the amounts of the beryllium-rich phase retained in the joints.

Atmospheric contamination during brazing impaired the flow characteristics of the brazing alloy. The vacuum ordinarily obtained in a production vacuum annealing furnace was inadequate to protect the brazing alloy, but adequate protection from contamination was obtained consistently by simple procedures for improving the vacuum.

A method of preplacing the brittle brazing alloy was based upon the exceptional capillarity of the brazing alloy. Brazements were designed to have one or more continuous networks of capillary joints to be brazed. These brazements were brazed by the capillary flow from one or more relatively large pieces of the brazing alloy. The brazing alloy flowed upward against the force of gravity as much as 30 in. by capillary action. The reliability of this method for small brazements was demonstrated by the brazing of 6 brazements with 8 vertical joints, each with no unbrazed joints.

A method for using small, reusable graphite spacers to maintain coolant channel thickness during brazing showed promise of controlling this dimension within acceptable limits.

INTRODUCTION

Furnace brazing of Zircaloy or Zircaloy-clad components possesses certain advantages over fusion welding in the assembly of nuclear core assemblies. Furnace brazing and fusion welding are compared as follows:

Furnace Brazing	Fusion Welding
1) Furnace brazing causes no significant thermal gradients.	1) Steep thermal gradients cause shrinkage and distortion during fusion welding.
2) Inaccessible joints are readily brazed.	2) Joints must be accessible for welding.
3) There are no limitations on thickness of sections joined.	3) The practical upper limit on the thickness of sections which can be fusion welded is approximately 0.2 inches.
4) Many joints may be brazed simultaneously.	4) Fusion welding is a progressive operation.

A previous study was made to develop corrosion resistant brazing alloys for Zircaloy (Ref 1). Several corrosion resistant brazing alloys were developed, but alloys containing 4 to 6% beryllium and 94 to 96% Zircaloy were determined to have the best combination of corrosion resistance, melting point, strength, flow characteristics, and absence of erosive action on the base material. A nominal composition of 5% beryllium-95% Zircaloy-2 was chosen as the brazing alloy for this investigation. Although beryllium and certain of its compounds are extremely toxic (Ref 2), the proper precautions should allow the handling of beryllium alloys safely.

Although an apparently satisfactory brazing alloy had been developed for Zircaloy, it was anticipated that major problems would be encountered if this alloy were used to furnace-braze nuclear core assemblies. The major anticipated problems were: (1) maintaining the corrosion resistance of Zircaloy cladding after brazing, (2) obtaining adequate mechanical properties of brazed joints, (3) preplacing the brittle brazing alloy, and (4) maintaining critical dimensions.

EXPERIMENTAL WORK AND DISCUSSION

Corrosion Resistance of Zircaloy Brazements

The thermal history of Zircaloy-2 affects its corrosion resistance in high-temperature water and steam. Since the major application for brazing of nuclear core components would be assemblies whose geometry and size would prevent their being cooled rapidly by convection and radiation from their exterior surfaces, slow cooling of at least the central regions of these assemblies must be expected.

The effect of slow cooling from high temperatures upon the corrosion resistance of Zircaloy-2 has been investigated. Early work (Ref 3) showed that the weight gain of Zircaloy-2 in long-term steam and water corrosion tests increased with increasing annealing temperatures in the range from 1475° to 1850°F, but these data indicated no important effect of cooling rate upon corrosion resistance. However, the data of a recent investigation (Ref 4) showed a cooling-rate dependence of the corrosion resistance, but little dependence on the annealing temperature in the range from 1450° to 1850°F for rapidly-cooled specimens. Weight gains of specimens slowly cooled from 1850°F were increased by a factor of roughly three over specimens annealed at 1450°F. It was shown that a minimum cooling rate of 90°F/min through the range from 1850° to 1472°F is sufficient to obtain acceptable weight gains.

Poor corrosion resistance of Zircaloy brazements resulting from slow cooling from brazing temperature was anticipated. Four possible solutions were considered: (1) thermal treatments after brazing, (2) use of a lower-melting-range brazing alloy, (3) induction brazing to localize high temperatures and permit rapid cooling, and (4) inert gas quenching from brazing temperature.

Induction brazing and inert gas quenching were rejected as possible solutions. Induction brazing would introduce steep thermal gradients and require accessibility to the joints, thereby losing the principal advantages of furnace brazing. Quenching by forced convection of an inert gas through the coolant passages of brazed nuclear components would require excessive amounts of equipment and development effort. An adequate mass flow of an inert gas through a typical nuclear component could be attained at reasonable gas velocities only by pressurizing the furnace to a relatively high pressure (several hundred pounds per square inch). Gas quenching would also introduce thermal gradients and possible distortion.

The possibility of improving the corrosion resistance by thermal treatment was based upon the hypothesis that the poor corrosion resistance of slow-cooled Zircaloy-2 is caused by partitioning effects during cooling through the alpha plus beta range (approximately 1850° to 1475°F). Alloying elements and impurity atoms have different solubilities in alpha and beta zirconium. The partitioning of such elements between co-existing alpha and beta would depend upon the relative amounts of the phases, solubilities of such elements in both phases, and time. Hence, the cooling rate through the two-phase region would affect the composition of regions. The regions which transformed last would be depleted in alpha-soluble elements and enriched in beta-soluble elements. If such an alloy were subsequently maintained for prolonged periods at a high temperature within the alpha range, homogenization would occur, and, hence, the corrosion resistance might be restored.

Three thermal treatments were used in the study of the effect of thermal treatments on the corrosion resistance of slow-cooled Zircaloy-2 brazements. The treatments will be hereafter termed: (1) slow-cooled treatment, (2) alpha-annealed treatment, and (3) two-phase annealed. Comparison of the corrosion resistance of slow-cooled and alpha-annealed brazements was expected to establish whether homogenization treatments in the alpha range would improve the corrosion resistance of slow-cooled Zircaloy-2. The two-phase annealed brazement, which was homogenized in the high beta and alpha field (1750°F), was included in the corrosion study since it was known that dispersion of beryllium from joints by diffusion improved mechanical properties.

The corrosion specimens were prepared from an ingot of atmosphere-melted, reactor-grade Zircaloy-2 (FU120). The design of the brazement and corrosion coupons is shown in Fig. 1. The surfaces of the dummy fuel plates were in the cold-rolled and pickled condition, but the side plates were fabricated by machining 0.025 in. or more from the surfaces of hot-rolled bar.

Prior to brazing, the components of the brazements were scrubbed with a detergent (Alconox), rinsed in hot tap water, immediately wiped with cloth saturated in acetone, and finally wiped with cloth saturated with absolute ethyl alcohol.

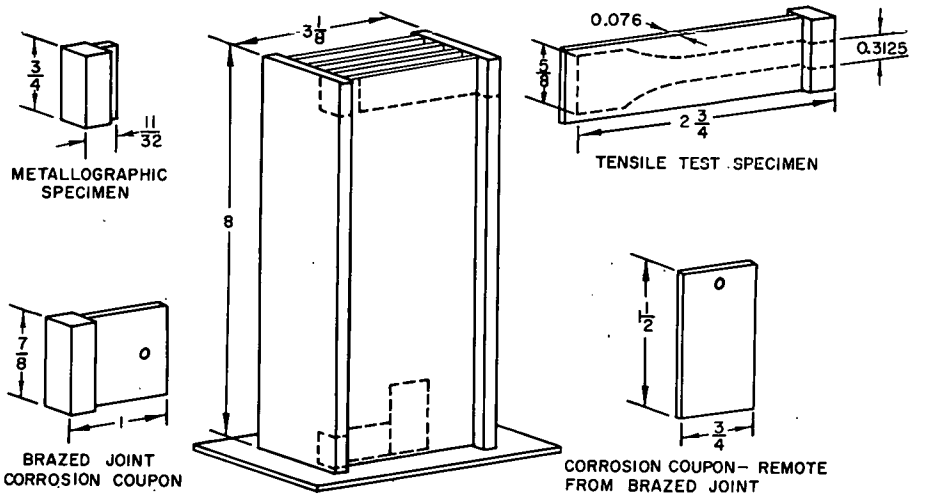


Fig. 1 Brazement and Specimens for Corrosion and Tensile Tests; All Dimensions in Inches

The components were assembled, as shown in Fig. 1, and secured by strips of Zircaloy (not shown) tack welded between the side plates. A single piece of brazing alloy weighing approximately 7 grams was placed at the bottom of the center channel. The brazing alloy used was prepared by the Zircaloy-crucible melting procedure which will be discussed in a later section. The precautions taken to secure a protective atmosphere (high vacuum) will also be discussed in a later section.

The brazements were subjected to three thermal cycles:

1) Slow cooled–This cycle consisted of brazing at 1832°F for 1 hr and slow cooling (75°F/hr) to 1300°F. The cooling rate below 1300°F was believed to be unimportant. Therefore, when the temperature reached 1300°F, the brazements were moved to the cold zone in all three cycles.

2) Alpha annealed–This cycle consisted of brazing at 1832°F for 1 hr, slow cooling (75°F/hr) to 1427°F, holding at that temperature for 16 hr, and slow cooling from 1427° to 1300°F.

3) Two-phase annealed–This cycle consisted of brazing at 1832°F for 1 hr, slow cooling (75°F/hr) to 1750°F, holding at that temperature for 8 hr, slow cooling (75°F/hr) to 1410°F, holding at that temperature for 8 hr, and slow cooling from 1410° to 1300°F.

Corrosion coupons were machined from three brazements for a factorial corrosion experiment to include four factors at the levels indicated:

1) Coupons including brazed joints and coupons remote from brazed joints,

2) The three thermal treatments–slow cooled, alpha annealed, and two-phase annealed,

3) 750°F, 1500 psi steam corrosion tests and 680°F water-phase corrosion tests, and

4) Specimens pickled after brazing and specimens not pickled after brazing.

Triplicate specimens were used for each condition. Control specimens of the untreated Zircaloy (FU120) were also included.

The results of these corrosion tests are shown in Table I and Figs. 2 and 3. Photographs of the specimens are shown in Figs. 4 through 7.

Weight gains of unpickled specimens were all substantially greater (100 to 600 mg/dm^2) than the corresponding pickled corrosion coupons after the first cycle of 14 days in steam or 28 days in

TABLE I

WEIGHT GAIN (mg/dm^2) OF BRAZED ZIRCALOY-2 IN STEAM AND WATER CORROSION TESTS

Condition	Steam Corrosion Tests - 750°F 1500 psi						Water Corrosion Tests - 680°F Saturation Pressure				
	14 days	28 days	56 days	84 days	112 days	140 days	28 days	56 days	84 days	112 days	140 days
Slow-cooled											
Braze joint	175	212	253	316	*	--	26	33	64	72	85
Remote from joint	172	199	312	347	*	--	25	31	54	65	75
Alpha-annealed											
Braze joint	184	230	270	318	*	--	29	37	71	80	95
Remote from joint	177	222	286	337	*	--	25	31	58	67	82
Two-phase annealed											
Braze joint	353	423	*	--	--	--	41	128	177	191	208
Remote from joint	266	311	356	*	--	--	26	41	93	107	123
Hot-rolled Zircaloy											
(not brazed)	31	36	68	96	120	143	22	29	35	42	56

* Corrosion products spalling

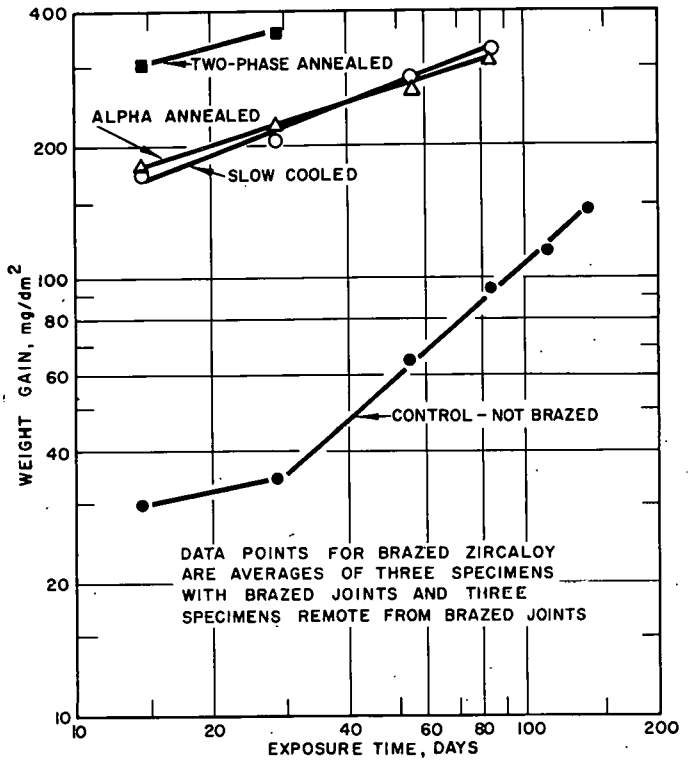


Fig. 2 Weight Gain of Brazed Zircaloy in 750°F Steam

water. Weight gains of the unpickled specimens were not included in Table I, as they were believed to be inaccurate due to spalling of corrosion products during the first corrosion test cycle. It was noted that those surfaces of the unpickled coupons which were machined after brazing appeared to have more nearly normal corrosion films than the surfaces exposed to the furnace atmosphere (Figs. 4 and 5). Thus, the corrosion resistance was apparently lowered by contamination of the surfaces during brazing. Such contamination could have been caused by the furnace atmosphere or by residues remaining on the surfaces when cleaned. This contamination must have been at least partially removed when 0.001 to 0.002 in. was removed from each surface by pickling, since the pickled coupons exhibited better corrosion resistance.

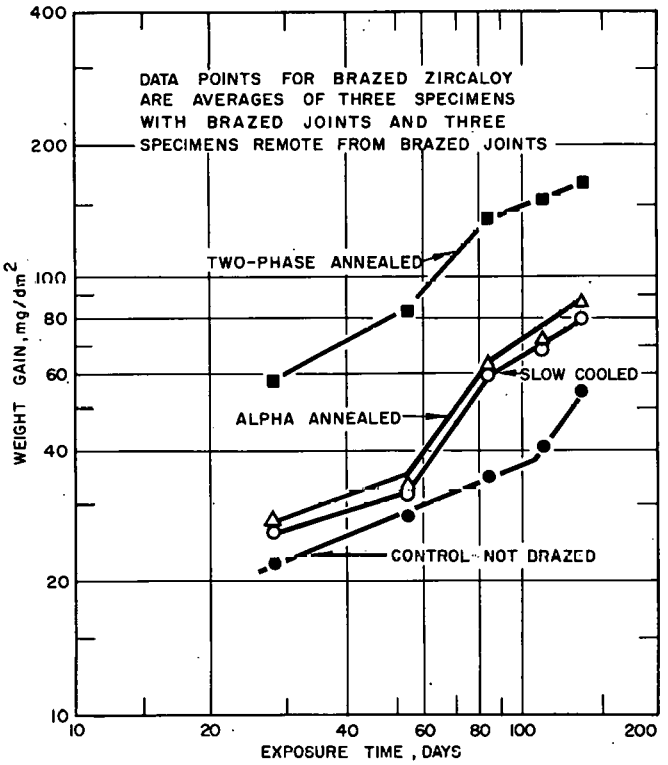


Fig. 3 Weight Gain of Brazed Zircaloy in 680°F Water

The corrosion films were thicker at the brazed joints than in areas remote from brazed joints, as indicated by their appearance and by larger weight gains. After 28 days in 680°F water, for example, the brazed joints of pickled coupons exhibited a yellowish-brown adherent corrosion product, while surfaces remote from the brazed joints had a lustrous black film (Fig. 4). The two-phase annealing treatment accentuated the effect of the brazed joints on the corrosion resistance (Fig. 5). Since the area of the brazing alloy exposed was only a small fraction of the total area, the effects of the brazed joints on the weight gains were largely obscured. Therefore, the significantly higher weight gains observed for the brazed joint specimens indicated that brazed joints had a pronounced effect on the corrosion resistance. While the corrosion resistance of the brazed joints was inferior to that of Zircaloy remote from brazed joints, there was no penetration of corrosive attack into brazed joints after 140 days in 680°F water.

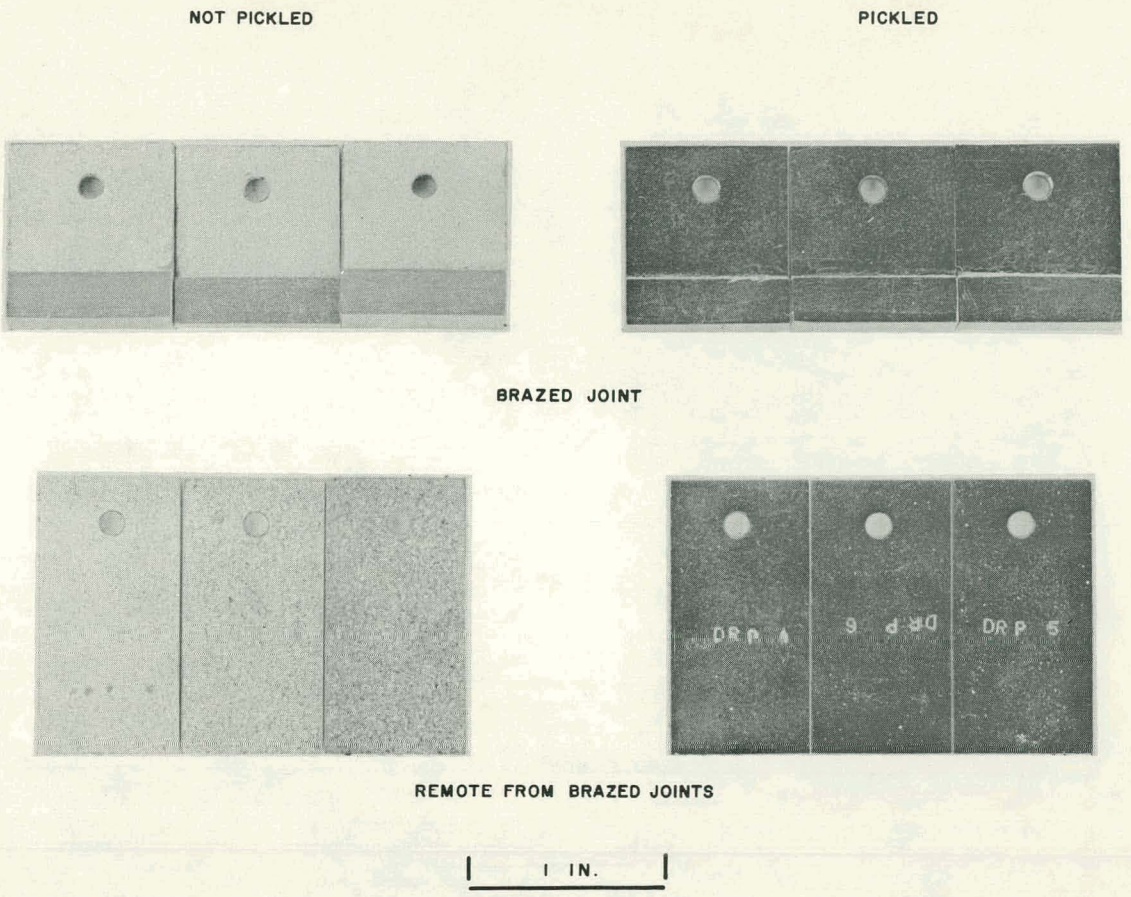


Fig. 4 Slow-Cooled Corrosion Coupons Tested 28 Days in 680°F Water

All brazing cycles used caused large increases in the weight gains of Zircaloy-2 in 750°F steam corrosion tests (Fig. 2). The weight gain of Zircaloy which was subjected to a brazing cycle was, in general, 3 to 10 times as large as that of the untreated Zircaloy. In the steam corrosion tests, the alpha-annealed and the slow-cooled treatments produced essentially identical behavior, while the two-phase annealed treatment had the largest weight gains.

After the first 14-day cycle in the steam corrosion test, the corrosion coupons of brazed Zircaloy exhibited flecks of a yellowish-brown corrosion product (Fig. 6). As the corrosion tests continued, this corrosion product increased to form a nearly continuous layer and began to spall after 28 to 84 days of corrosion testing.

In 680°F water corrosion tests, as in the steam corrosion tests, the brazing cycles caused increases in the weight gains of Zircaloy. The two-phase annealed treatment caused the largest increases in weight gains while the alpha-annealed treatment consistently produced slightly larger weight gains than did the slow-cooled treatment.

After 28 days in 680°F water, flecks of the yellowish-brown corrosion product were not visible on the slow-cooled and alpha-annealed coupons (Fig. 4). After 140 days in 680°F water, the slow-cooled and alpha-annealed coupons were flecked with this corrosion product (Fig. 7), while the two-phase annealed coupons were coated almost continuously.

Low Melting Range Brazing Alloys

The most desirable solution to the corrosion problem would be the development of a corrosion resistant brazing alloy with a melting range below the transition temperature of Zircaloy, but the

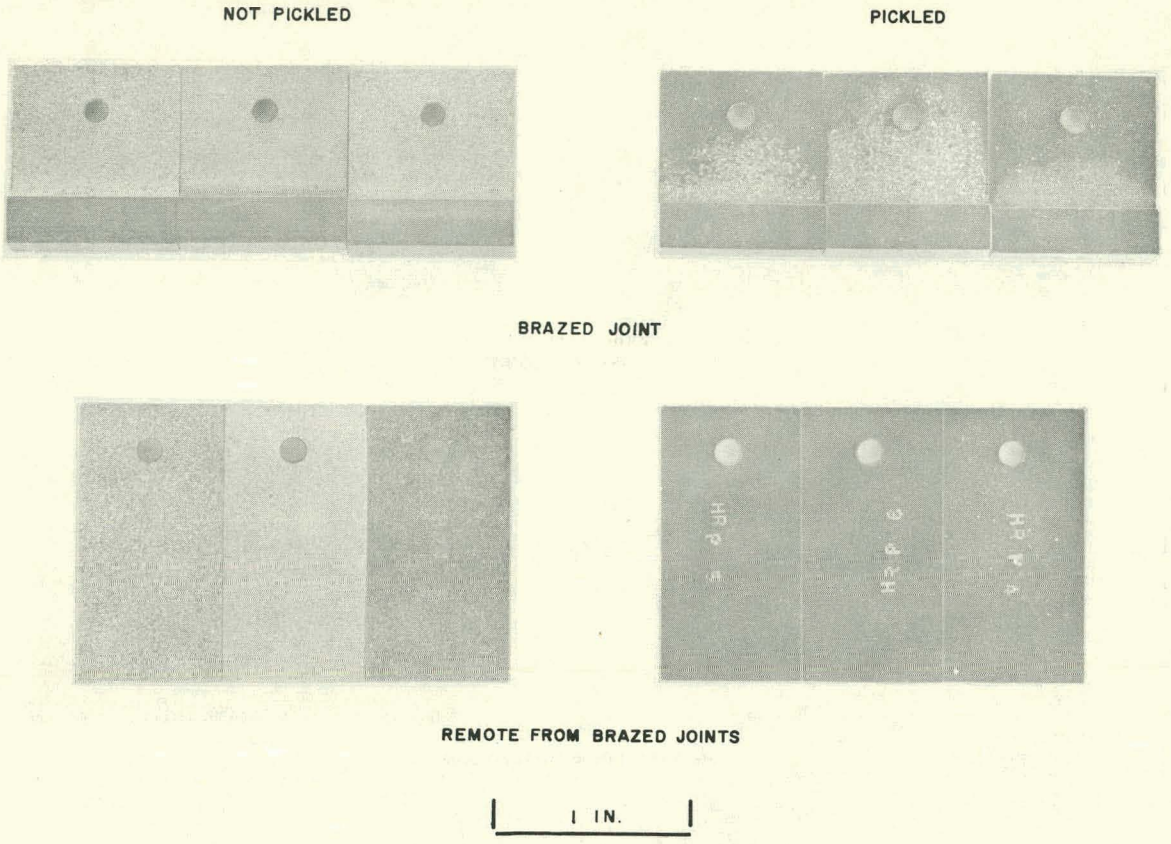


Fig. 5 Two-Phase Annealed Corrosion Coupons Tested 28 Days in 680°F Water

development of a corrosion resistant brazing alloy melting in the lower portion of alpha plus beta range of Zircaloy might be more likely. Slow cooling from the lower portions of the alpha plus beta range is reported (Ref 4) to cause small increases in weight gains of Zircaloy-2 in 750°F steam corrosion tests when compared to the untreated material, while much larger increases in weight gains are caused by slow cooling from 1650°F and higher temperatures. Thus, a brazing alloy with a melting range in the lower portion of the alpha plus beta range of Zircaloy may be acceptable.

During the development of the zirconium-beryllium brazing alloys (Ref 1), many brazing alloys were screened for corrosion resistance in a 1200-hr test in 680°F water. Some zirconium-based brazing alloys containing iron showed promising corrosion resistance. An assembly brazed with an 80% Zr - 10% Fe - 10% Cr alloy was unattacked in 1235 hr in 680°F water, and assemblies brazed with an 80% Zr - 10% Sn - 10% Fe and a 70% Zr - 15% Fe - 15% Mn alloy showed only moderate attack in 1200 hr.

Since the binary eutectic of iron with zirconium has a lower melting point than that of beryllium with zirconium, the addition of iron to beryllium-zirconium alloys might be expected to lower their melting range and perhaps retain adequate corrosion resistance.

A series of zirconium-base alloys were prepared by nonconsumably arc melting 50 buttons in an inert gas atmosphere. The nominal compositions of these alloys and a crude approximation of the amounts of liquid phase formed at several temperatures are presented in Table II.

From these data, it appeared that the alloys containing 4% beryllium, 10% or 13% iron, and balance Zircaloy-2 have narrow melting ranges which are low enough to be of interest for brazing alloys. These and other similar alloys are being evaluated by Bettis Plant.

TABLE II

NOMINAL COMPOSITIONS AND APPROXIMATE MELTING RANGES OF EXPERIMENTAL BRAZING ALLOYS

Identification	Nominal Composition, %					Approximate Amount of Liquid Phase, %							
	Be	Fe	Cu	Cr	Zircaloy-2	1472°F	1490°F	1515°F	1535°F	1560°F	1610°F	1650°F	1695°F
B554	5	5	--	--	90	0	0	10	--	10	--	25	25
B555	5	10	--	--	85	0	0	10	--	75	100	100	100
B556	7	5	--	--	88	0	0	10	--	10	10	10	10
B557	7	10	--	--	83	0	0	10	--	10	--	25	100
B558	7	5	5	--	83	0	10	10	--	10	10	50	75
B559	5	3	3	--	89	0	10	10	--	10	10	25	75
B569	4	7	--	--	89	--	--	--	10	10	--	--	--
B570	4	10	--	--	86	--	--	--	100	100	--	--	--
B571	4	13	--	--	83	--	--	--	100	100	--	--	--
B572	4	5	--	5	91	--	--	--	10	75	--	--	--
B573	6	7	--	--	87	--	--	--	10	10	--	--	--
B574	6	10	--	--	84	--	--	--	10	10	--	--	--
B575	6	13	--	--	81	--	--	--	25	25	--	--	--
B576	6	5	--	5	84	--	--	--	10	10	--	--	--

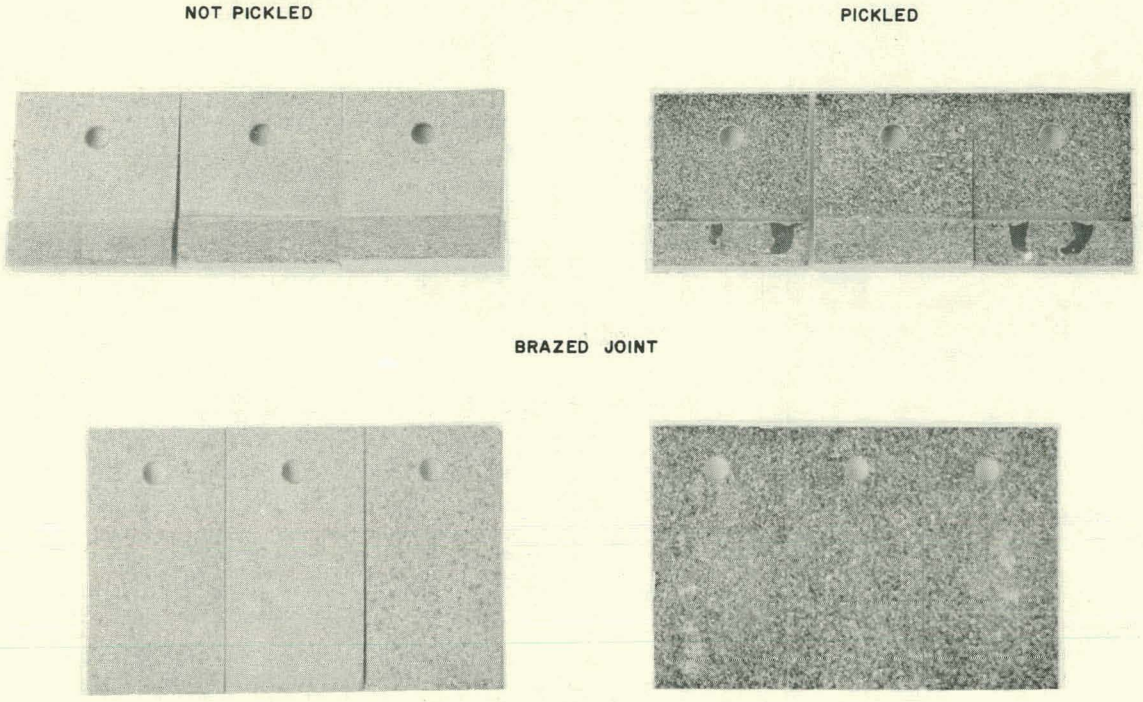


Fig. 6 Slow-Cooled Corrosion Coupons Tested 14 Days in 750°F Steam

The structures of "thick" and "thin" portions of a joint brazed 1 hr at 1560°F with 5% Be - 10% Fe - 85% Zircaloy brazing alloy are shown in Figs. 8a and 8b.

Preparation of Beryllium-Zirconium Brazing Alloy

During the development of Zircaloy-beryllium brazing alloys (Ref 1), the preparation of alloys by nonconsumably arc melting small buttons presented no problems. However, the preparation of larger amounts of Zircaloy-beryllium alloys presented problems in obtaining homogeneous alloys with the nominal melting range.

Preparation of the 5% Be - 95% Zircaloy-2 brazing alloy by induction melting in a beryllia-washed graphite crucible produced an alloy with a substantially higher melting range than that reported for arc-melted buttons of the identical nominal composition (melting range approximately 1780° to 1813°F). During brazing experiments the induction-melted alloy was only partially melted at the maximum operating temperature (1900°F) of the available heat treating furnace. This high melting range was judged to be a serious disadvantage; therefore, other melting practices were used to obtain a low melting range alloy.

Combinations of nonconsumable arc melting and consumable electrode melting left significant amounts of unmelted Zircaloy feed particles in a matrix of Be-enriched alloy. Spectrographic analysis indicated that the Be-enriched portion contained from 5.9 to 6.6% Be. The failure of these melting operations to dissolve all of the Zircaloy probably resulted from a combination of two factors. The density of the liquid phase was less than the density of Zircaloy, thereby allowing the Zircaloy particles to settle to the cool, lower portions of the molten pool. Also, there was a large difference between the melting ranges of Zircaloy and the Be-Zircaloy alloy.

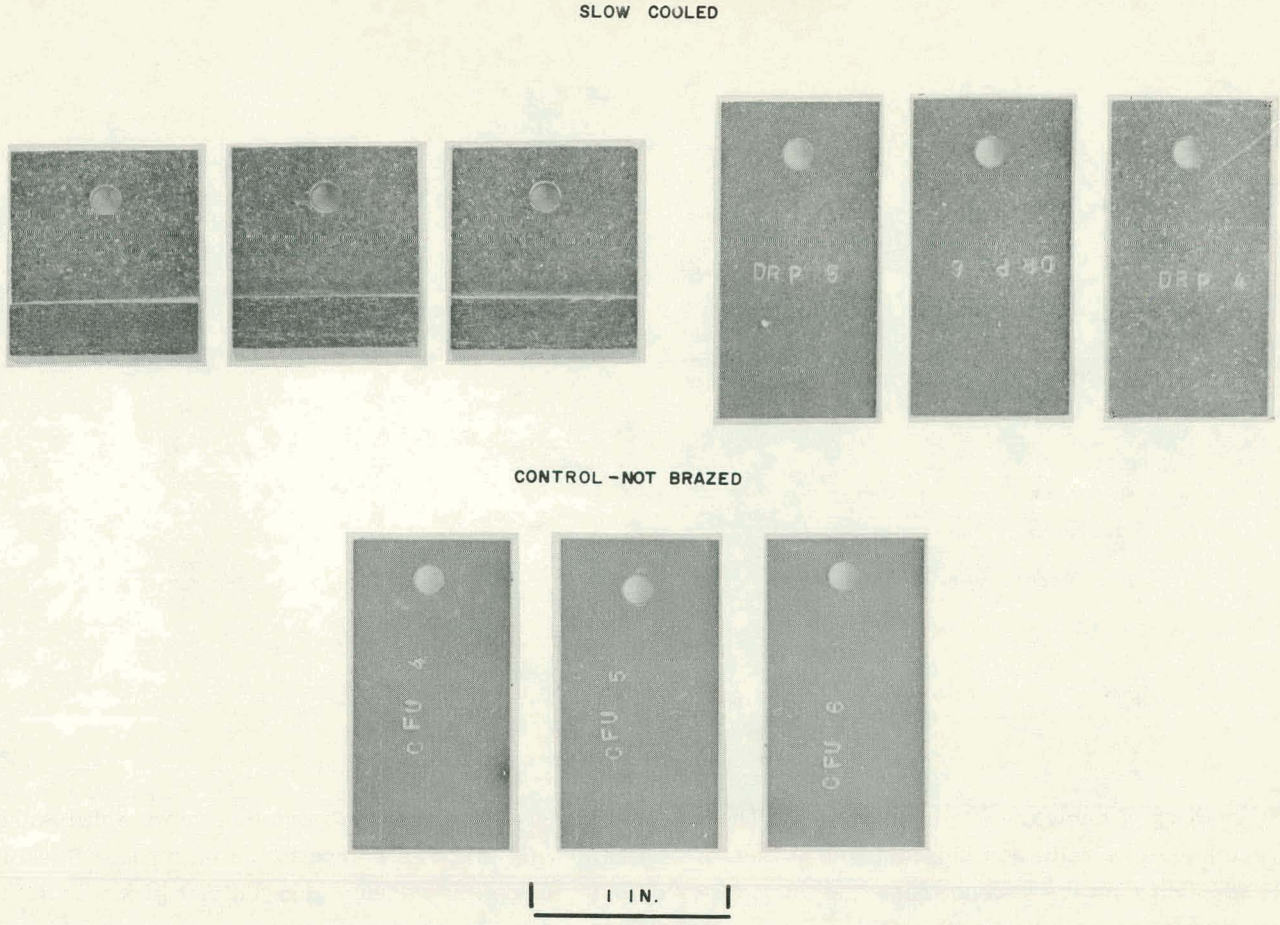


Fig. 7 Slow-Cooled Corrosion Coupons Tested 140 Days in 680°F Water

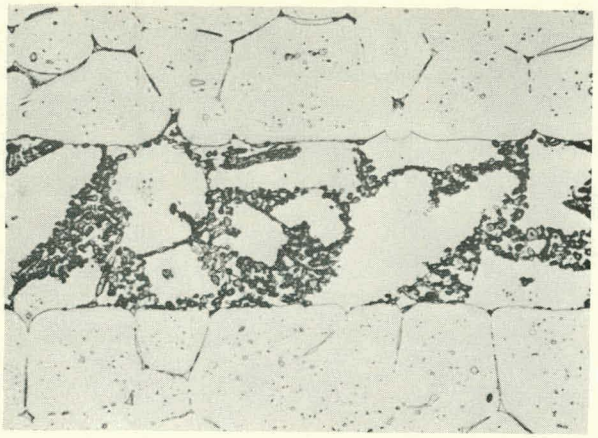
A homogeneous brazing alloy of approximately eutectic composition was obtained by remelting an ingot produced by nonconsumable-electrode arc melting to dissolve or settle the undissolved Zircaloy particles. The remelting was accomplished in a Zircaloy crucible in a vacuum furnace at 1832°F for 2 hr. The brazing alloy was allowed to solidify in the crucible and then was removed by sectioning the mass. The liquidus temperature of this alloy was approximately 1832°F and spectrographic analysis indicated a beryllium content of 4.3%. However, this material was porous near the center of the mass because of solidification shrinkage.

An improved method of preparing Zircaloy-Be alloys was developed by Bettis Plant. A laminated electrode for consumable melting was prepared by tack welding a rod of beryllium to Zircaloy strips so that a cross section contained the correct proportions of Zircaloy and beryllium. A sound ingot, weighing two pounds, was produced by arc melting this electrode consumably in a water-cooled copper crucible. The macro etching of a longitudinal section revealed no evidence of segregation. The Zircaloy - 5% Be brazing alloy used during the final phases of this investigation was prepared in this manner.

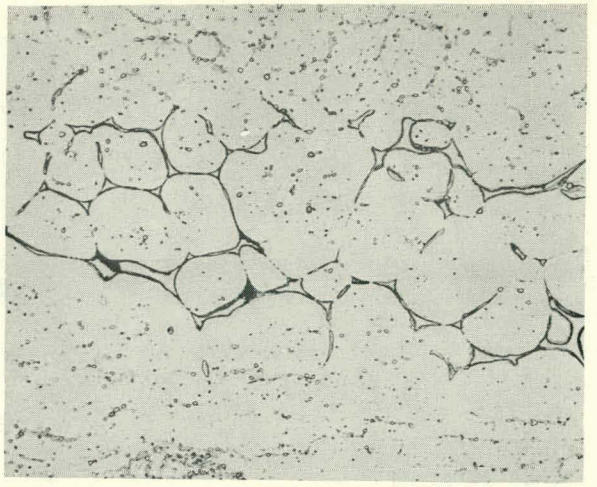
Effects of Furnace Atmosphere

The reactivity of Zircaloy with common gases at elevated temperatures dictated the use of either a noble gas or a high vacuum during brazing. The use of vacuum throughout this investigation was based upon the possibility that an inert gas could be trapped in joints and prevent the entry of brazing alloy.

The greater portion of the brazing reported in this investigation was accomplished in a relatively large (18-in. diam by 7-ft long hot zone) vertical annealing furnace used for production



a Thick Joint Structure



b. Thin Joint Structure

Fig. 8 Structures of Joints Brazed with a 5% Beryllium, 10% Iron, and 85% Zircaloy Brazing Alloy; Both Structures 250X

annealing of nuclear core components. The vacuum gages on this furnace were close to the diffusion pump and the radiation shields, and piping offered relatively high resistance to the molecular flow of gases between the vacuum gage and the furnace retort. Thus, the vacuum gage did not give a reliable indication of pressure within the furnace retort. The observed pressure readings varied little for various furnace charges, although varying contamination of the Zircaloy indicated considerable differences in the degree of vacuum. The observed pressures were typically less than 0.03 microns prior to heating and during cooling, but rose to approximately 0.1 to 0.2 microns as the brazing temperature was attained. The effects of the furnace atmosphere can be discussed most rationally in terms of the appearance of the Zircaloy and brazing alloy as affected by various procedures.

The furnace atmosphere, rather than residues on the surface of the Zircaloy from the cleaning operation, was the principal source of contamination. This fact was established by observing the effect of the geometry of the specimen upon the films formed on the Zircaloy.

At elevated temperatures, gaseous corrosion films dissolve in Zircaloy and, if the rate of solution exceeds the rate of formation, a metallic luster is maintained throughout a heating cycle. If the rate of formation is increased to exceed the rate of solution, a corrosion film is formed during the heating cycle. Throughout this investigation, Zircaloy surfaces, which formed the interior surfaces of nearly enclosed cavities in Zircaloy, exhibited a more metallic luster than did the exterior surfaces of Zircaloy specimens which were exposed directly in the furnace retort without the protection of any gettering action. If the source of the contamination were residues upon the surface of the Zircaloy, recesses would have surfaces contaminated at least as badly as exposed surfaces. Since this was not true, the furnace atmosphere must have been the source of contaminants.

Graphite fixtures were employed to prevent eutectic formation between Zircaloy and ferrous furnace hardware. Zircaloy surfaces in contact with outgassed graphite maintained lustrous metallic surfaces.

There were four general types of procedures used to prevent contamination during brazing. These are listed in order of increasing effectiveness:

1) A large furnace retort with a small charge of Zircaloy was evacuated and immediately heated to brazing temperature.

2) A large furnace retort with a small charge of Zircaloy was evacuated for extended periods (as much as 16 hr) and heated for brazing.

3) A small charge of Zircaloy was placed within a small graphite retort with Zircaloy gettering strips, and the graphite retort was placed in the large furnace retort. Then, the furnace was evacuated for 16 hr prior to heating.

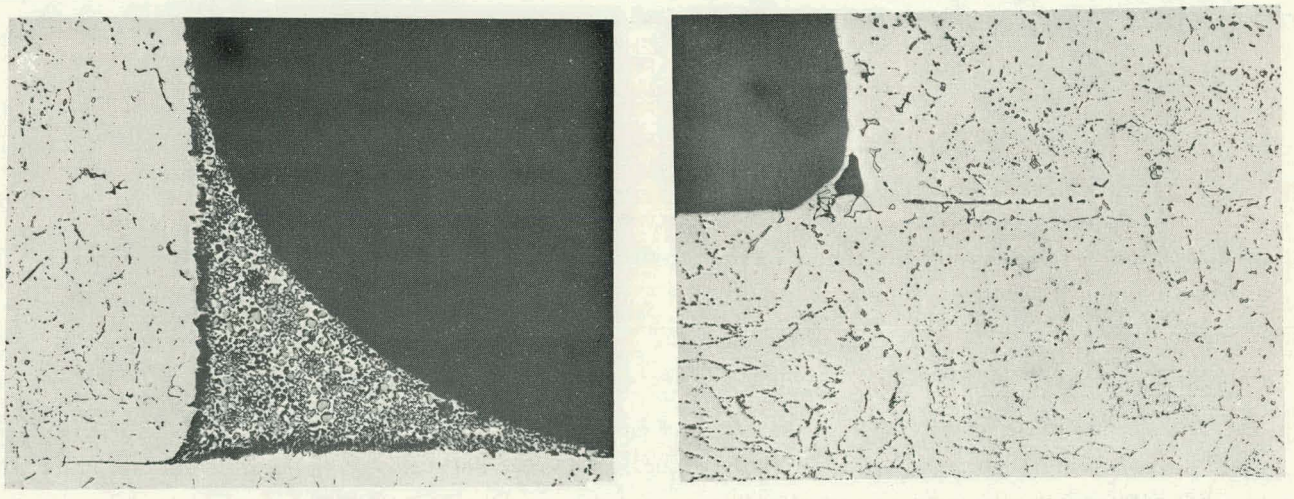
4) This procedure differed from the third procedure in that evacuating the furnace to approximately 5 microns pressure, backfilling with an inert gas to approximately atmospheric pressure, and evacuating briefly was substituted for the extended evacuation cycle.

The third and fourth procedures produced approximately equivalent results.

The flow of the brazing alloy was affected by the purity of the atmosphere. Although there was a continuous gradation of effects from the highest purity atmosphere observed (highest vacuum) to the lowest purity atmosphere (poorest vacuum), it is convenient to discuss these effects for three arbitrarily selected conditions. For convenience these will be termed "best," "good," and "poor" atmospheres; although, no quantitative measure of pressure can be ascribed to them.

Under the influence of the best atmosphere, the brazing alloy wet the Zircaloy at a very small angle and showed a pronounced tendency to seek capillary joints. The capillarity of the brazing alloy under the best conditions was measured and will be discussed in a later section. Figure 9a shows a fillet of brazing alloy which exhibited a very small angle of contact.

Under the influence of a good atmosphere, the brazing alloy wet the Zircaloy at a greater contact angle than under the best conditions (Fig. 9b). The brazing alloy showed a strong tendency to seek capillary joints.



a. Effect of Best Atmosphere

b. Effect of Good Atmosphere

Fig. 9 Effect of the Atmosphere upon the Angle of Contact between the Brazing Alloy and Zircaloy; Both Structures 40X

Under the influence of a poor atmosphere, the brazing alloy crept across plane surfaces either horizontally or vertically, as well as flowing into capillary joints. A solid film formed on the surface of the liquid brazing alloy, and gas, which was apparently a product of a reaction between the brazing alloy and the atmosphere, collected in bubbles under this film, as shown in Fig. 10. Figure 11 shows another view of the same specimen in which the brazing alloy showed the influence of a good atmosphere. The better atmosphere was accomplished by a graphite crucible and Zircaloy

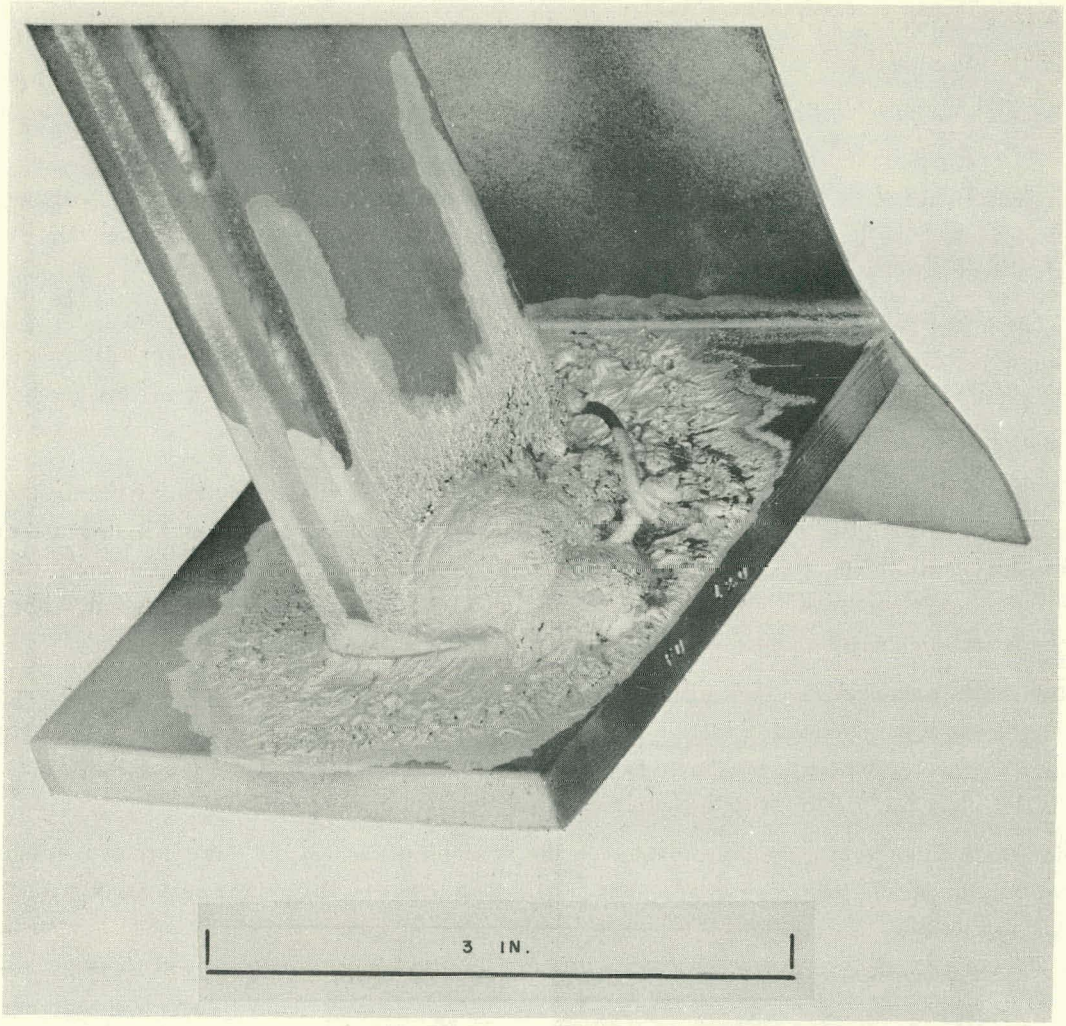


Fig. 10 Effect of a Poor Atmosphere on the Brazing Alloy

gettering strips which shielded the region better. In the pressure ranges obtained during this investigation, gas flow is of the molecular type, and line of sight shielding by a gettering material affords protection from gaseous contamination. Thus, the purity of the atmosphere can vary locally to a significant degree.

Preplacing Brazing Alloy

The Zircaloy-Be brazing alloy is brittle and has not been fabricated into foil or wire for convenient preplacing at brazed joints. Further, nuclear component dimensional requirements place strict limitations on the amount and distribution of the brazing alloy. The process must yield a high degree of confidence that all of the joints have been brazed, yet there cannot be excess brazing alloys which might restrict coolant passages or cover fuel alloy. Thus, a method of preplacing the brazing alloy was required which closely controlled the amount of brazing alloy and insured complete brazing.

The capillary flow of the brazing alloy throughout a network of numerous capillary joints from a few relatively large pieces of brazing alloy was the method of preplacing the brazing alloy employed in this investigation.

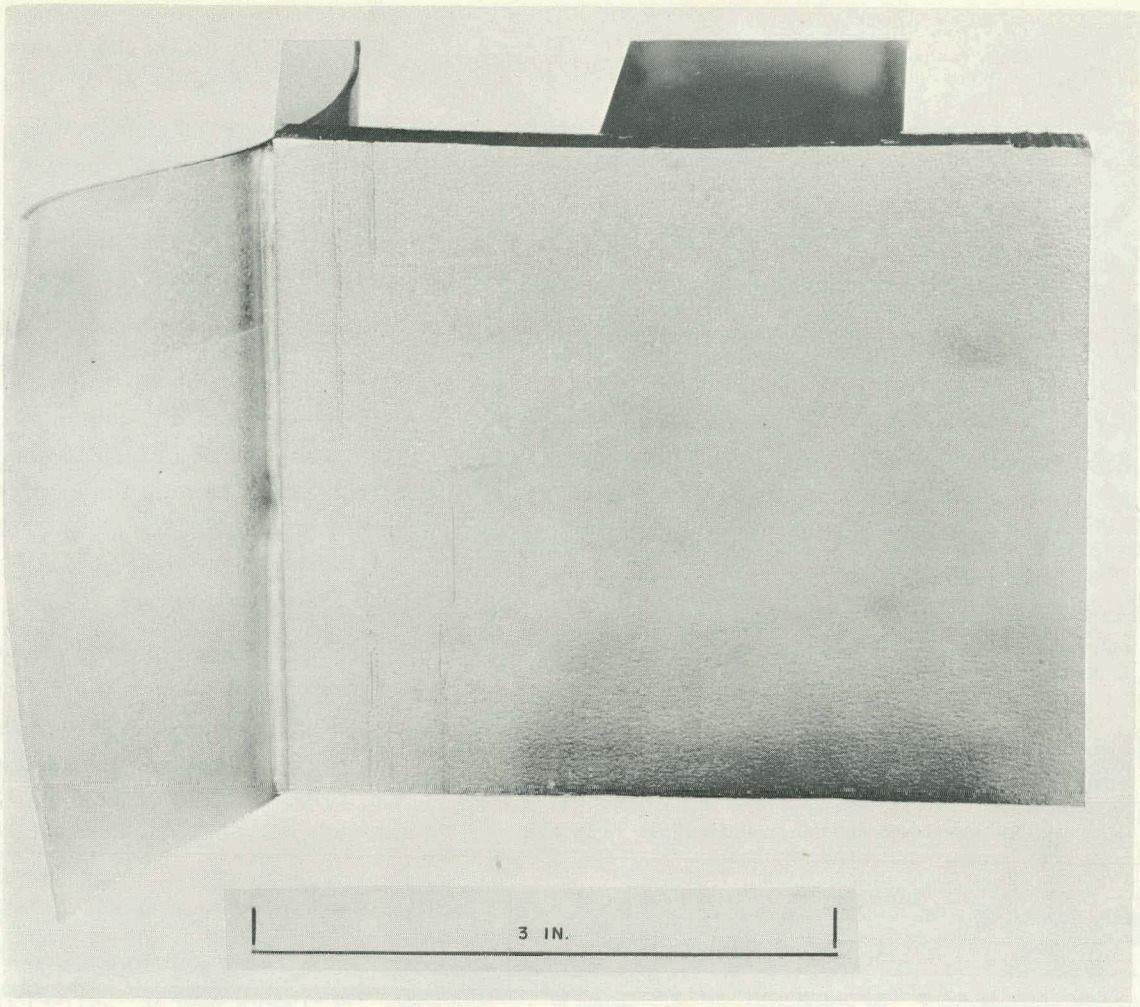


Fig. 11 Effect of a Good Atmosphere on the Brazing Alloy

A measure of the capillarity of the brazing alloy was obtained by using specimens having V joints with 1/2° included angle. Two bars 1-1/2 x 9/32 x 48 in. were in contact along one side, while the other edges of the bars were separated by shims as shown in Fig. 12. The edges in contact were subjected to a clamping force because of the shrinkage when Zircaloy strips were welded to the edges of the bars. These specimens were suspended vertically in the brazing furnace. An excess of brazing alloy was provided at the bottom and the specimens were brazed.

After brazing, these specimens were sectioned at frequent intervals and examined metallographically to determine the maximum thickness of the joint which had filled with brazing alloy as a function of height above the source of the brazing alloy. The results are shown in Fig. 12.

The capillarity of the brazing alloy caused it to flow 21 in. or more against the force of gravity in the thin portions of 1/2° included angle V joints. With thicker joints, the brazing alloy rose to lesser heights. Considerable differences were noted between two duplicate specimens which were, however, brazed at different times with brazing alloys of the same nominal composition but from different lots. Both lots of brazing alloys were prepared by the Zircaloy-crucible melting procedure described in a previous section. The cause of the difference in behavior between the two specimens is not known.

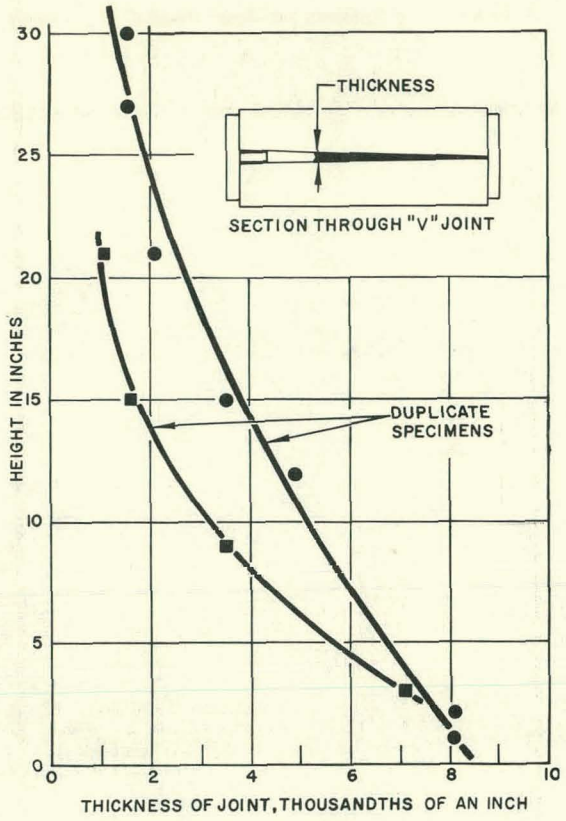


Fig. 12 Capillarity of the Brazing Alloy

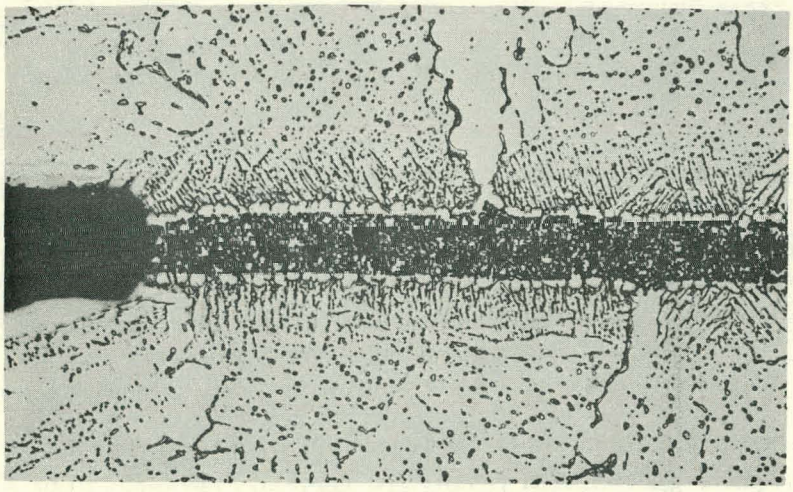


Fig. 13 Growth of Primary Zirconium-Rich Phase into Brazing Alloy; 250X

Evidence of the growth of a primary zirconium-rich phase into the liquid brazing alloy during brazing was noted during the metallographic examination of the V-joint specimens. A possible mechanism for this phenomenon is that beryllium diffuses into the base material and depletes the brazing alloy of beryllium, thereby raising the liquidus temperature and causing the precipitation of a zirconium-rich phase. Figure 13 shows the primary zirconium-rich phase in a specimen which had been brazed 1 hr at 1830°F and rapidly cooled.

The precipitation of the primary zirconium-rich phase during brazing might restrict the flow of the brazing alloy through thin joints. Therefore, a series of experiments was conducted to determine the minimum joint clearance needed for flow of brazing alloy.

Three specimens were prepared by fusion welding pairs of 1/2-in. wide strips along their edges so that smooth machined surfaces were forced together by the welding shrinkage. These specimens were brazed with brazing alloy at the ends of the strips in contact with the tight joint.

The brazing alloy did not flow into these joints more than approximately 0.020 in. This distance was approximately the depth to which changes in the microstructure were observed due to diffusion of beryllium into solid Zircaloy during the brazing cycle.

The brazing alloy did not penetrate into joints tightly clamped by welding shrinkage, but this effect was almost entirely absent in the less tightly-clamped joints of the corrosion-tensile-specimen brazements. In these brazements there were joints 0.087-in. wide, with a nominal zero clearance lightly clamped during brazing which adjoined thicker capillary joints. Approximately 85 metallographic sections from these brazements were examined, and only one

exhibited a small portion of a joint with unbrazed areas. This area appeared to be due to failure of the brazing alloy to penetrate a tight joint.

The reliability of capillary flow as a method of preplacing the brazing alloy was demonstrated with six specimens of the type shown in Fig. 1. These specimens contained a total of 48 vertical joints, each 8 in. long. All of these joints were brazed along their entire length as evidenced by fillets of brazing alloy.

An upward capillary flow of the brazing alloy may not be sufficient to braze long assemblies. Therefore, the possibility of assisting the force of capillary action with the force of gravity was investigated by placing the brazing alloy at the top of an assembly. The assembly consisted of 15 dummy fuel plates inserted in two grooved side plates 22 in. long. The details of the upper portion of the assembly were designed to provide horizontal capillary joints approximately 0.010-in. thick along each grooved side plate. The horizontal capillary joints intersected all of the vertical joints between the dummy fuel plates and the grooved side plates. It was intended that the horizontal joints act as distributors which would feed brazing alloy to all of the vertical joints simultaneously from two pieces of brazing alloy.

The assembly was brazed in a vertical position with the brazing alloy at the top. The brazing alloy flowed down certain of the vertical joints and collected at the bottom where it completely filled several spaces between the plates. Other vertical joints did not braze.

More uniform distribution of the brazing alloy occurred when the capillary force opposed the force of gravity rather than when the force of gravity acted in the same general direction as the capillary force.

Tensile Strength of Brazed Joints

The study of the mechanical properties of brazements was limited to the determination of the tensile strength of simulated fuel plate to grooved side plate joints. The tensile specimens were machined from brazements of the type prepared for corrosion testing (Fig. 1). Twenty or more tensile specimens could be prepared from each brazement. A metallographic specimen was available immediately adjacent to the brazed joint of each tensile specimen and, approximately, 85 metallographic specimens representing 5 brazements were examined. The joint design and tensile specimen used are shown in Fig. 14.

The first lot of components produced did not meet the requirements for the design of the groove (Fig. 14), since the included angle of the dummy plates was approximately 36-1/2° rather than 40°. Brazements were prepared from these components to study the effects of poor-fitting joints upon the tensile strength. A photomicrograph of a typical joint is shown in Fig. 15. The stresses in the brazed joints could not be computed from the load on the specimen. Therefore, the tensile strengths reported were the maximum stresses on the gage length.

All poorly fitted joints fractured in the brazed joint during tensile testing with strengths ranging from 23,600 to 52,500 psi. The average strength was 37,000 psi, which was approximately 55.7% of the average strength of specimens having closely fitting joints and a similar brazing cycle.

Components which satisfied the requirements for the groove and plate dimensions were used for the three corrosion test brazements and the tensile tests to be described.

Twenty tensile specimens were fabricated from the slow-cooled brazement. (See the previous section on Corrosion Resistance of Zircaloy Brazements for details of brazing cycle.) These specimens were chosen to represent all eight joints and various distances from the source of the brazing alloy, and had strengths ranging from 32,900 to 73,700 psi, with the mean being 67,500 psi. However, these specimens may be divided into two classes: (1) the twelve specimens which fractured

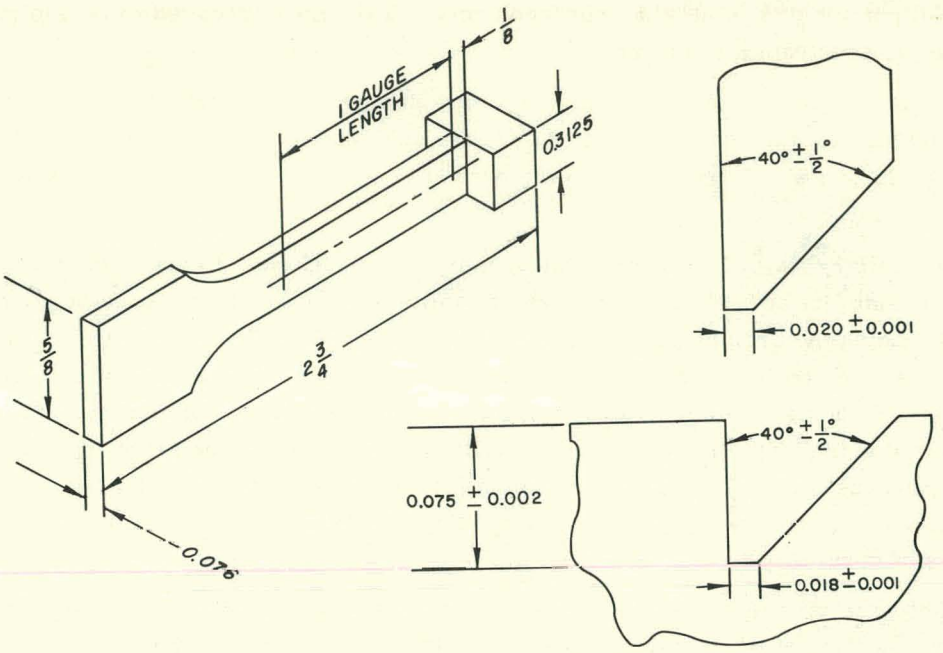


Fig. 14 Simulated Fuel Plate to Grooved Side Plate Joint and Tensile Specimen; All Dimensions in Inches

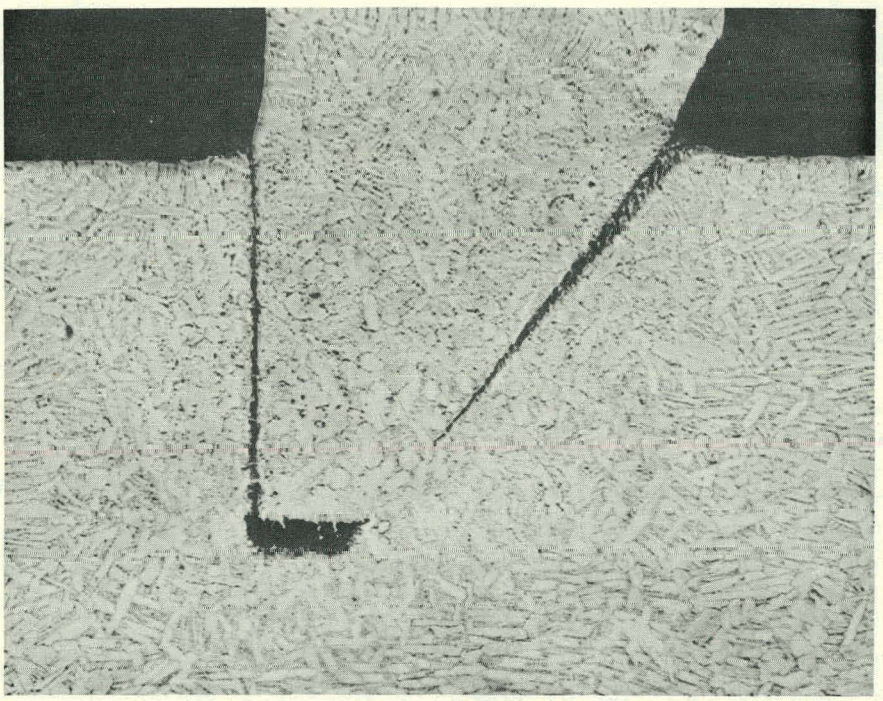


Fig. 15 Poorly Fitting Brazed Joint; 40X

through or adjacent to the brazed joints and (2) the eight specimens which fractured in a ductile manner in the gage length. The results of the tensile tests are presented in Table III.

TABLE III

TENSILE STRENGTHS OF BRAZED JOINTS

Condition	No. Specimens Fractured Away from Brazed Joint	No. Specimens Fractured through or near Brazed Joint	Max Tensile Strength, psi	Min Tensile Strength, psi	Ave Tensile Strength, psi	Ave Elongation in 1 In. Gage Length, %
Slow cooled	8	--	73,800	71,800	73,100	20
Slow cooled	--	12	72,500	32,900	61,900	2
Alpha annealed	9	--	82,000	80,600	81,300	20.4
Alpha annealed	--	5	81,600	36,800	67,400	8.8
Two-phase annealed	12	--	82,600	80,500	81,400	19.0
Two-phase annealed	--	2	82,700	79,900	81,300	6.0

Metallographic examination of sections adjacent to these tensile specimens revealed that strength of joint was related to the microstructure of the brazed joint. Dispersion of the beryllium from the joint by diffusion, as shown in Fig. 16, promoted the higher strengths. The presence of a continuous or nearly continuous beryllium-rich phase in the joint, as shown in Fig. 17a and 17b, reduced the strength.

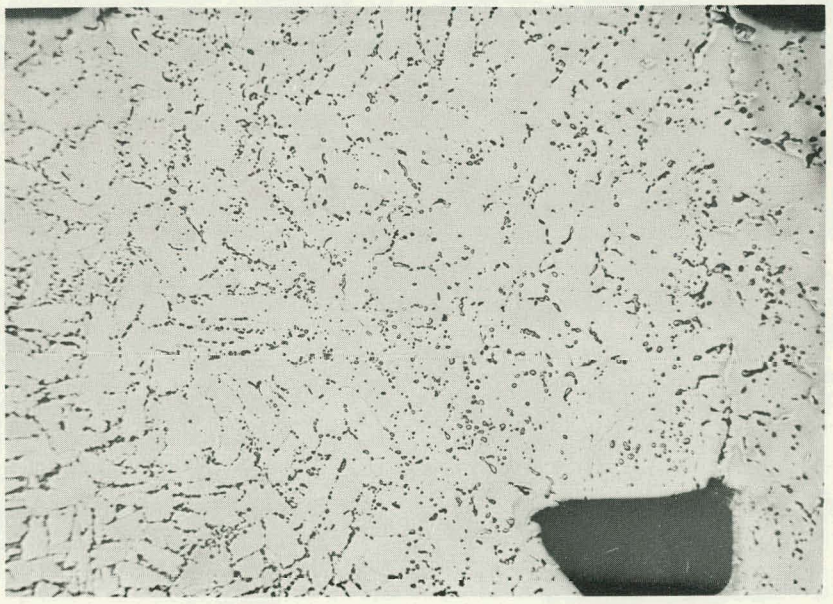
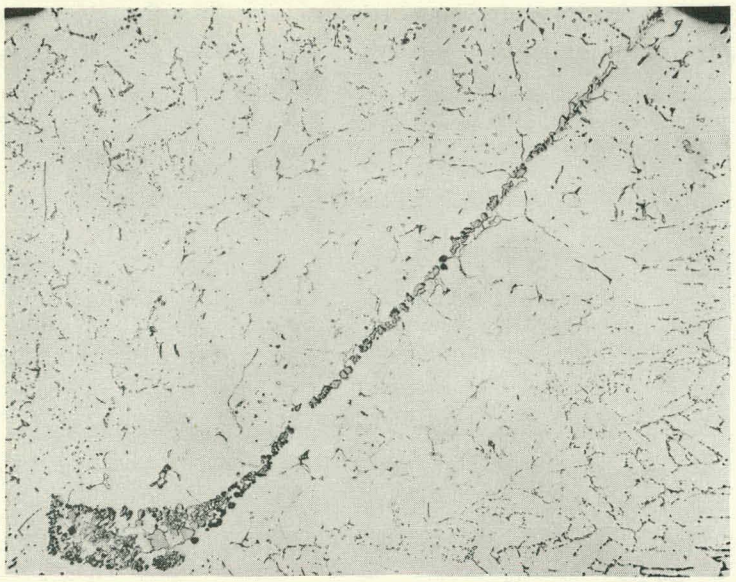
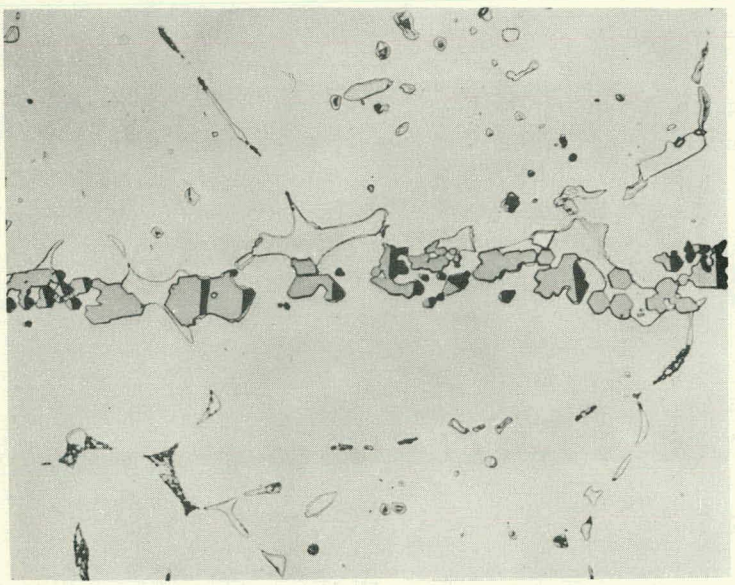


Fig. 16 High-Strength Brazed Joint; 40X

A statistical analysis of the data by grooves (there were eight grooves per brazement) and height (distance from source of brazing alloy) showed no significant difference in strength at 90% probability level. Thus, the observed differences in tensile strength were apparently the result of



a. 40X



b. 250X

Fig. 17 Low-Strength Brazed Joint

local, random differences in the joint strength rather than systematic differences between various grooves or the distance of flow of the brazing alloy.

The lower tensile strengths were, as previously mentioned, related to the presence of beryllium-rich phase in joint. The presence of the beryllium-rich phase was attributed to minor local variations in the joint clearance. Increases in joint thickness would increase the tendency to retain the beryllium-rich phase.

The alpha-annealed condition was intended to promote improved corrosion resistance; this cycle would also provide for somewhat greater diffusion of the beryllium. The tensile data in Table III show that a larger proportion of high strength joints occurred in the alpha-annealed specimens than in the slowly-cooled specimens.

The use of the two-phase annealing treatment was a further attempt to improve the tensile strength of the brazed joints by the dispersion of beryllium. The proportion of specimens which failed in a ductile manner away from the brazed joint was increased.

However, as noted in a previous section, the two-phase annealed treatment had a deleterious effect on corrosion resistance. This treatment would also be objectionable in that the increased opportunity for diffusion afforded by long time at high temperature might permit significant amounts of uranium to diffuse through the cladding.

Dimensional Stability during Brazing

Nuclear core design places strict requirements on certain dimensional tolerances. The maintenance of these tolerances during brazing was anticipated to be a major problem for several reasons. Zircaloy and Zircaloy-uranium fuel alloys have little strength at the brazing temperatures. Also, zirconium-based alloys undergo a phase transformation accompanied by a volume change upon heating to the brazing temperature. Further, there are no alloys suitable for use as fixtures which would closely match the thermal expansion of Zircaloy.

A preliminary experiment was conducted to determine the creep of a fuel element caused by a simulated brazing cycle. Strips were machined from rejected Zircaloy-clad, uranium-alloy fuel elements. These strips were supported horizontally as simple beams loaded only by their own weight during a simulated brazing cycle.

Strips supported on a 2-in. span sagged less than 0.001 in., but strips supported on a 4-in. span sagged 0.037 in. during the brazing cycle. Thus, thin Zircaloy members must have maximum unsupported spans of less than 4 in.

Two experiments were performed to study the effect of the brazing operation on the dimensional tolerances of specimens whose cross sections resembled those of a nuclear core component having flat-plate fuel elements. A fixture to support the exterior of the specimens and a system for internal support (spacers) were employed. The dimensional tolerance of simulated water channels was of particular interest.

The fixture was constructed of type 304 stainless steel lined with molybdenum to prevent contact between Zircaloy and stainless steel. Pneumatic bellows inflated with helium were incorporated in the fixture to compensate for the difference in thermal expansion between stainless steel and Zircaloy. These bellows applied force through a rigid member to two adjacent sides of the specimen, forcing the specimen against the opposite sides of the fixtures. The bellows were inflated and sealed at room temperature, so that gas pressure in the bellows at brazing temperature caused compressive stresses of approximately 20 psi in the dummy fuel elements during brazing.

Copper and steel spacers are used to support water channels of fuel assemblies during resistance and fusion welding operations. However, both of these materials form eutectics with Zircaloy at the brazing temperature and cannot be used as spacers during brazing.

Since graphite is not soluble in zirconium at the brazing temperature, it is suitable for use as a spacer material in contact with Zircaloy. However, the conventional form for spacers, a strip which has approximately the same dimensions as the channels, would be very fragile. Such a graphite spacer would be difficult or impossible to remove after brazing and could not be reused.

A method for the use of graphite spacers to support water channels is shown in Fig. 18. This method employed a multiplicity of small graphite spacers in each channel to effect spacing. The average thickness of the spacers was 0.0018 in. less than the average thickness of the water channels.

The width and length of the spacers, 7/16 x 1-1/4 in., were chosen as a compromise, since decreasing these dimensions would have made the spacers less fragile and more easily removed, and increasing these dimensions would have reduced the number of spacers required for a given degree of support.

The graphite spacers were inserted into the channels, positioned within the channels, and removed from the brazed assembly with the aid of a refractory metal retainer, whose thickness and width was intended to be sufficiently less than that of channel to allow insertion and removal without interference. The spacers fit in slots in the retainers. Strips of a molybdenum alloy (0.5% Ti-balance Mo) 0.015 x 2.25 in. were used in 0.060 x 2-1/2 in. channels. The maximum unsupported span was approximately 1-1/8 in.

The specimens had a 3 x 3 in. cross section and consisted of an assembly of twenty-one 7-in. long dummy fuel plates inserted into grooved side plates. A Zircaloy base was provided to support the brazing alloy and provide a capillary joint for the horizontal distribution of the brazing alloy to the base of each of the 42 grooves.

In the first experiment, brazing did not occur because of an error in furnace temperature. However, the temperature of the assembly reached approximately 1760°F, as indicated by incipient

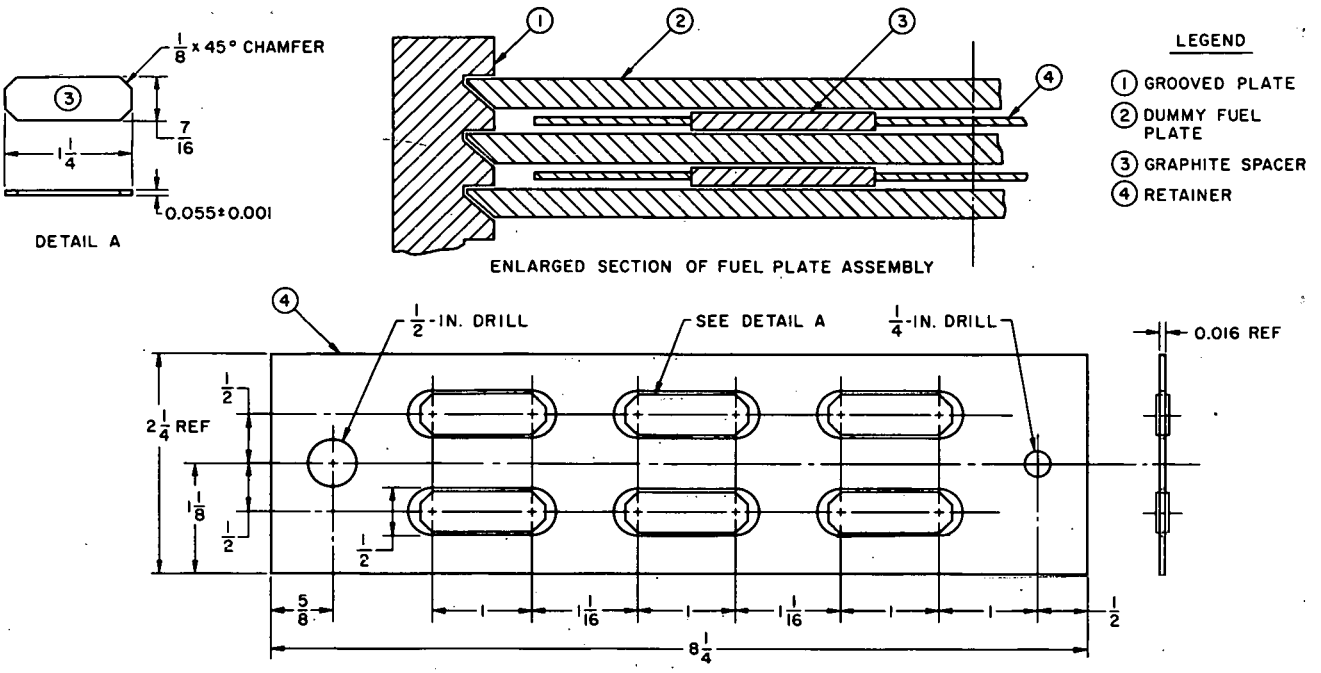


Fig. 18 Spacers for Coolant Channel Support during Brazing; All Dimensions in Inches

melting of the brazing alloy. With the side plates tightly clamped after the brazing cycle, the spacers were easily removed with only 2% breakage. There was no measurable reduction of average thickness of the spacers resulting from wear. Thus, the spacers were suitable for reuse.

The assembly had a standard deviation of channel thickness of 0.00137 in. after the brazing cycle. This variation in channel thickness was comparable to variations obtained in fusion welded assemblies, despite the excessive bowing (0.005 to 0.007 in. across the 2-1/2 in. width) of the plates prior to brazing. Thus, this method of support during brazing had eliminated much of the bowing of the dummy fuel plates.

During the second experiment, the vacuum furnace retort collapsed on the fixture under atmospheric pressure and caused gross distortion of the fixture and assembly. This prevented a study of the effectiveness of the spacer system. However, all 42 joints between side plates and dummy fuel plates were brazed throughout their length.

ACKNOWLEDGEMENTS

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