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DEVELOPMENT OF A BRAZING PROCESS FOR SEALING
INSTRUMENTATION LEADS USING A LITHIUM BEARING BRAZE ALLOY

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DEVELOPMENT OF A BRAZING PROCESS FOR SEALING
INSTRUMENTATION LEADS USING A LITHIUM BEARING BRAZE ALLOY

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INTRODUCTION

The instrumentation leads in NRX-A reactors are sealed against hydrogen leakage by brazing them into cylindrical plugs (seal blocks) which are then mechanically sealed into openings in the pressure vessel. For NRX-A1 and NRX-A2, this sealing operation was performed with an ASTM B Cu P-5 braze alloy. To make this joint, the lead surfaces had to be plated (gold was most effective) and the seal block was inlaid with a copper disc using a supplementary brazing operation. Thus the reliability of the process depended upon the proper performance of two brazing operations and one plating operation.

This report describes the development qualification and application of a brazing process that eliminates the gold plating operation and the supplementary inlay brazing operation without effecting any of the several constraints that the application places on any seal brazing process developed for it:

1. Process temperatures must not exceed 1375°F (this temperature is too low to permit the use of a reducing atmosphere such as hydrogen).
2. Corrosive fluxes were to be avoided if possible; since (a) their complete removal could not be assured, (b) observations made on flux-brazed joints for this application indicated a trend toward higher levels of porosity and inclusions than were observed when the system did not use flux.
3. The seal block was finish machined to close tolerance and had to be protected during brazing.
4. The sealing operation had to be accomplished on the reactor itself so that conventional brazing furnaces could not be used.

The process covered by this report accomplished its objectives through the application of a lithium-bearing, low-temperature, silver solder that is capable of brazing stainless steel without

a flux. The development of the process controls required to cause this highly fluid material to wet the joint surfaces rather than the adjacent surfaces and form a sound joint without the use of a flux are covered in the following sections.

MATERIALS

The assembly consists of a 304 stainless steel seal block through which a number of 348 stainless steel leads are passed. It is between the surface of the leads and of the holes that the joint must be made. The joint extends approximately 1/4 inch through the seal block membrane. Some trial seal blocks were composite structures with a copper (inlaid) surface through which the stainless steel leads passed.

The brazing alloy is basically an ASTM-B-260 B Ag-1 alloy* with .5% lithium added by the manufacturer. The composition is as follows:

Silver	44 - 46%
Copper	14 - 16%
Zinc	14 - 18%
Cadmium	23 - 25%
Lithium	.5% maximum
Solidus	1125°F
Liquidus	1145°F

The above temperatures represent the unmodified B Ag-1 composition. Lithium effects the working temperatures because it forms a high temperature oxide during the heating cycle. In addition, the fluxing action involves LiOH having an optimum temperature of reaction with the metal oxides between 840°-1660°F. Therefore exact brazing temperature depends upon the

*For example Easy Flo 45 produced by Handy and Harman Company, New York, New York

amount of oxide encountered in a particular joint.

The brazing material is available only as 1/32" wire, which was used throughout this program, but can be produced in other forms on special order at an increase of 600% or more in cost.

EQUIPMENT

Two brazing facilities were applied to the development of this process. Each facility consisted of an induction heating power supply and a quartz chamber to provide an inert gas envelope for the work piece.

450 KC Brazing Facility: This facility involves a 10 KW R.F. oscillator. Power input was controlled manually by observing the melting point and flow behavior of the braze alloy. A three inch quartz tube with a fixed inlet and outlet extending through solid covers on either end provided the brazing atmosphere. This high frequency facility characteristically produced a sharp gradient between the O.D. and center of the seal block. This gradient provided a test of the temperature equalizing capability of the copper inlay. This facility was used in determining the need for the copper inlay and in studying the flow of the lithium-modified brazing alloy on copper.

10 KC Brazing Facility: This facility was used for all development and qualification testing except for the evaluation of the role of the copper inlay. The 10 KC equipment was installed for the brazing of NRX-A2 and is described in TME-1044. The low (10 KC) frequency provides for more uniform heating through the work piece and also permits the use of thermocouples on the work piece to control brazing temperatures. The environmental chamber used on the 450 KC facility was transferred for the initial tests and evolved to the configuration shown in Figure 1 (from tool drawing 710J416) for the actual qualification and production brazing.

PROCESS DEVELOPMENT

The development effort was carried out on the 10 KC brazing unit on which the final brazes would be made (except for evaluation of the need for the copper insert where 450 KC equipment was used to generate a steep thermal gradient). This development effort was concentrated in the following areas:

1. Joint Design
2. Control of Alloy Flow
3. Control of Brazing Chamber Atmosphere
4. Control of the Brazing Time-Temperature Cycle
5. Optimizing a Time-Temperature Cycle
6. Prebrazing Cleaning of the Work Piece

1. Joint Design

The primary consideration in designing a brazed joint of this type is to assure that the clearance between the outer surfaces of the leads and the inner surface of the hole are such that the braze alloy can flow the .250-inch length of the joint. Clearances between leads and the individual holes they pass through must be considered to be random and they may vary along the length of the joint. From observations of micro sections on specimens produced for NRX-A1 and NRX-A2, the following relationships appear to hold.

Zero Clearance: When the lead firmly touches the hole wall for any length greater than about $1/32$ ", micro examination indicates that non-reactive braze alloys such as B Ag-1 will not flow into the tightly closed region.

.000-.005" Clearance: Flow and freedom from internal voids can be expected up to .005" if the time-temperature cycle and pre-braze cleaning are controlled.

.005-.007" Clearance: Breaks in the alloy flow may occur in this region. Small variations in temperature, time, and cleanliness probably are responsible for the scatter of data.

.007" and Greater Clearance: Alloy run through these clearances leaving a break in the continuity of the joint.

Selection of brazing clearances for a joint wherein many leads must be assembled through a single block represents a compromise between a suitably large clearance for the sake of assembly and small clearances to assure reliable flow. In the following chart (based upon drawing tolerances) it will be noted that most joints have at least .0025" clearance and the upper limit is near .007".

TABLE I
ESTABLISHED CLEARANCE DIMENSIONS
(in inches)

Lead Diameter			Hole Diameter		Diametrical Clearance	
Nominal	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum
.025	.024	.026	.0285	.0295	.0025	.0055
.045	.040	.045	.0455	.0465	.0005 ⁽¹⁾	.0065
.062	.062	.065	.0685	.0695	.0035	.0075
.090	.088	.090	.0935	.0945	.0035	.0065

(1) A check of twenty-five leads indicated that this condition would not be encountered. The largest lead measured was .043 which would result in a .0025" clearance. The hole could be reworked if necessary for an interfering lead.

Minimizing the possibility of an excessive clearance does not eliminate the problems associated with those portions of almost every joint where the lead is pressed firmly against the

wall of the hole. To overcome this situation, the lead bundle is subjected to vibration (120 cycle) at the first evidence of melting. The effect is believed to be confined to the upper portion of the joint and assures a seal in this region as a minimum. The major effect is to make sure that each lead is moved away from the wall (simultaneously reducing clearances on the opposite side of the joint, which promotes flow) thus permitting the liquid braze alloy to flow into all parts of the joint. Mechanical stirring as this operation is repeated removes entrapped oxides and gas. In addition the vibration eliminates the possibility of braze ring "hang up".

As part of the joint design effort, a series of tests was run to make sure that the copper inlay was not required for other than metallurgical reasons since observations on NRX-A1 indicated that this inlay tended to equalize temperatures across the face of this inductively heated work piece.

Because the 10 KC unit used for brazing NRX-A1 and NRX-A2 was temporarily unavailable, testing of the lithium modified alloy on the copper inlayed block was initiated on the 450 KC induction equipment in the WANL Materials Department. Further this high frequency equipment tended to emphasize the need for temperature equalization from the outside of the work piece to the center.

When specimens brazed with the lithium modified B Ag-1 alloy were sectioned, it was observed that the cadmium and zinc of the B Ag-1 basis alloy had penetrated the copper even when the brazing cycle was only one-thirteenth as long as the cycle considered for production (i.e., about 45 seconds instead of 540 seconds). When the B Ag-1 was depleted of cadmium and zinc, a skull (layer of higher melting alloy) formed on the surface of the joint. (Figure 2). In several joints the skull could be removed manually.

In an effort to retain the advantages of the copper, a nickel plate* was placed on the surface of the inlay as a diffusion barrier. Erosion resulting from penetration of the copper was

*Both Watts nickel and reduction plated nickel were applied. Neither appeared to have any advantage over the other except that the reduction plating process coated the I.D. of the holes.

observed (Figure 3) but no skull formed as evidenced by the sound, bright fillets.

As a result of these trials it appeared that the metallurgical disadvantages of the copper out-weighed any thermal conductivity advantages and the copper disc was removed from further test specimens.

Finally, tests were run to determine the problems associated with joining stainless steel directly to stainless steel without copper to reduce the thermal gradient (but using the 450 KC unit which produced a somewhat more severe gradient than would be encountered at 10 KC). The results are shown in Figure 4. All joints in the test piece exhibited continuous fillets and the joints, when sectioned, were void free. However, the test piece represents a simple arrangement of leads and considerable development effort had to be expended in developing a heating cycle that would braze more complex arrangement of leads.

2. Control of Alloy Flow

At brazing temperature the alloy was observed to be extremely fluid and flowed unrestrained over the clean surface of the seal block. Three methods were tried to correct this flow problem:

1. Counterbored Hole: It was reasoned that a counterbore in the hole would serve as a dam for the molten alloy. A 1/16" deep counterbore was drilled at each hole to receive the braze rings. However the alloy climbed the walls of the counterbore and flowed in a random manner as before.

2. Pre-oxidation: The top surface of the seal block was oxidized lightly prior to machining the lead holes. The oxide layer around the holes served as an effective "stop-off" to the alloy flow resulting in a satisfactory braze of each lead.

3. Prolonged Process Heating Time: With this method the seal block temperature was held at 1100°F (25° below solidus) for 4 minutes. The temperature was immediately raised to

1200°F (55° over liquidus) and held for 2 minutes. The total heating time was 11-1/2 minutes. The resulting brazes were excellent with fillets formed at the top and bottom of the web. Long heating times had been considered detrimental to good braze practice because oxidation resulting from an increased amount of impurities within the chamber and loss of the low melting constituents (zinc and cadmium) of the alloy. The above trials disproved theories relating to the desirability of short brazing times. Apparently the leads and surfaces of the holes are protected by the clean, fresh argon gas entering at the bottom (Figure 1). In every test sample the underside of the seal block surface was free of discoloration.

3. Control of Brazing Chamber Atmosphere

Figure 1 shows the construction of the chamber. The correct position of the argon gas inlet ring was arrived at after considerable experimentation. A 1/4" change in vertical location of the inlet will noticeably upset the behavior of the brazing because its position controls important process factors such as gas preheat temperature (as the gas passes through the joint to the braze rings) and the equalization of gas flow through the lower and upper purge exits.

The composition of the gas in the chamber must be recognized as an important variable in achieving fluxing action when a lithium modified brazing alloy is used. Moisture* in the chamber atmosphere is believed** to form LiOH on the surface of the lithium modified brazing alloy. This hydroxide will dissolve almost every known metal oxide. Further this hydroxide is molten in the practical brazing range (840-1660°F). Thus the chamber must function in such a manner that it provides enough moisture to form LiOH without providing free oxygen that would severely oxidize the work piece surfaces and react with the brazing alloy to form refractory (2700°F melting point) Li₂O. The chamber shown in Figure 1 provides the proper balance without the deliberate addition of moisture.

* Argon gas dewpoints were maintained between -60°F and -70°F.

** Bredz, N. and Schwartzbart, H. "Recent Progress in Development of Self Fluxing Air Proof Brazing Alloys" Welding Journal Research Supplement, March 1961.

4. Control of the Brazing Time-Temperature Cycle

The brazing temperature is controlled by a thermocouple placed in the outer rim of the seal block (Figure 5). The Thermo-Electronic potentiometer on-off controller relay is connected in the D.C. field circuit of the Westinghouse 30 KW - 10 KC motor generator.

Tests were run to determine the actual temperature in the center of the seal block relative to the temperature measured at the control thermocouple location. The center temperature was measured on a separate thermocouple connected to a De-Var recorder at various levels of power input. The minimum temperature difference when the outer thermocouple was at the 1250°F brazing temperature was 90°F. This condition was achieved when heating at a power level of 4.5 KW.

The recorder readings also verified the ability of the control system to maintain brazing temperature within 8°F.

5. Optimizing a Time-Temperature Cycle

To establish a reliable temperature and time cycle for the process it was necessary to recognize the affect of the following:

1. Thermal conductivity through the stainless steel web of the seal block without the copper inlay.
2. Random thermal conductivity paths across the molten braze alloy. Detailed in TME-1044.
3. Activity of the lithium at brazing temperature.
4. Change in liquidus temperature from the stated value as a result of loss of low melting constituents.

The effect of the first three items above was offset by establishing a "soaking" period at the various temperature levels so that all members of the assembly reached brazing temperature at the same time. The stepped temperature profile was applied manually for NRX-A3 however an

automatic programmed cycle will be tried in subsequent brazing.

The fourth item, it would appear, might best be controlled by establishing a minimum brazing temperature. However, experience suggested that the brazing temperature must be 105° above the manufacturer's specified liquidus of the braze alloy. The elevated temperature was necessary to (1) increase the fluxing action of the LiOH formed by the lithium contained in the alloy and (2) to overcome the higher solidus temperature due to unavoidable loss of zinc and cadmium. The loss of these two alloy constituents was evidenced by the appearance of minor "dusting" of the instrumentation leads at the finish of the braze cycle.

6. Prebrazing Cleaning of the Work Piece

During the process development trials inconsistencies in braze flow were observed on test pieces cleaned only in solvents. On the other hand, the external appearance and macro sections of salvaged test blocks from which the copper insert was removed by pickling showed continuous braze flow on every hole. This flow characteristically extended through the joint forming fillets on the underside of the joint as well as on top of the joint. Acid passivation was adopted as a cleaning method for all blocks as a result of the above observation. The following process was employed.

1. Degrease in ultrasonic cleaner
2. Rinse in alcohol
3. Immerse in following solution at 120-140°F
 - 10-20% HNO₃
 - 1- 2% HF
 - Water
4. Rinse in demineralized water (150-180°F)
5. Dry with N₂ (from which oil, grease and moisture have been removed)
6. Seal in bags until used

During process development the leads were cleaned by:

1. Abrading with 220 grit silicon carbide mesh
2. Wipe with alcohol

This process had been developed for cleaning the inlayed-copper and gold plated surfaces for the NRX-A1 and NRX-A2 applications. However, during the production brazing of the seal for the NRX-A3 shield, gaps were observed in several fillets. A resin-like material was observed in the worst of the gaps. A review of the prebrazing condition of the parts indicated that the leads were covered with a varnish-like material resulting from failure to remove drawing compounds and shop dirt during several baking-out cycles prior to delivery to WANL. This material had been removed visually (in ordinary light) but it is possible that a considerable amount remained since such compounds are not readily attacked by solvents and they are fairly transparent to ordinary light. The situation on NRX-A3 (shield) was probably aggravated by the tendency of this residue to collect in the joint as the long leads were threaded through. Thus it appeared that the gold plating operation used on NRX-A1 and NRX-A2 not only provided a readily wetted surface but also provided for the effective removal of this varnish. Accordingly several steps were taken to assure varnish free surfaces on future leads. Before step 2 above the leads were wiped with a phosphoric acid-alcohol mixture that had proved effective in removing small amounts of partly polymerized organic contaminants. In addition to the above internal correction vendors were advised to clean in-process material with the HNO_3 -HF solution used on the seal plugs. Finally, all future heating operations at the vendors are to be accomplished only after careful removal of all dirt from the surface of the work piece.

RESULTS

The process was qualified using the heating profile described on pages 7-8. The first two samples brazed were tested at 1000 lbs helium and at LN_2 with no indications. All subsequent leak testing was done at 1000 lbs helium. A series of 23 seal blocks were brazed in succession (without adjusting the process settings). No leaks were detected. The operator qualification consisted of two brazes per configuration or a total of eighteen. There were no leaks in the operator qualification brazes. Process Specification 294543-13 was issued covering the new process. Three seal blocks have been brazed for NRX-A3. One of these three, specifically, the HO-10 configuration for the simulated shield was brazed unsuccessfully on the first run (see Prebrazing Cleaning for a discussion of the cause of the defect). However the assembly was repaired successfully.

CONCLUSIONS

1. A fluxless brazing process has been developed and qualified using a lithium bearing alloy (B-260-BAg-1+5 Li) and meets the requirements of the application.
2. The new process has eliminated the gold plating of instrumentation leads and the seal block inlay operation.
3. The process has provided a continuous braze around the leads from top to bottom of the seal block web capable of withstanding 1000 psi pressure of LN_2 temperatures.
4. The process has been applied to 41 successive pre qualification and qualification test assemblies without any indication of leaks.
5. The process has been applied to three production assemblies for NRX-A3. Two were entirely successful. The third required a single, successful repair and also pointed up the need

for special precautions to prevent and/or remove varnish-like deposits resulting from dirt that had been baked onto the leads during their manufacture.

6. Process Specification 294543-13 covering the brazing procedure has been issued.
7. Procedures for successfully cleaning the leads and for protecting them during heating operations during their manufacture have been developed and documented in the appropriate equipment specifications E-675495 and E-675502.

FIGURE 1 - BRAZING FIXTURE

FIGURE 3 - NICKEL-PLATED SEAL BLOCK BRAZE

FIGURE 4

348 STAINLESS STEEL LEAD TO 304 STAINLESS STEEL USING
ASTM B-260BAg-1 + .5 Li BRAZING ALLOY 45X

FIGURE 5

BRAZED SEAL BLOCK ASSEMBLY
WITH HEAT CONTROL THERMOCOUPLE