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VACUUM FURNACE BRAZING OPEN CELL RETICULATED FOAM TO STAINLESS STEEL TUBING

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DISCLAIMER

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ABSTRACT

A heat exchanging device for separating hydrogen isotopes was designed using open cell reticulated copper foam that was brazed to stainless steel tubing. It is anticipated that the copper foam in the annular space of a tube-in-tube (TnT) style heat exchanger would improve the thermal efficiency; it is further anticipated that brazing the foam to the inner tube that is alternately filled with heating and cooling fluid, would further improve the thermal efficiency of the process.

The development included alloy and process development. Two series of alloys were developed using electro-brush plating to apply the braze materials. The processing temperatures were either high, approximately 980°C, or low temperature, approximately 550°C. High temperature brazes were comprised of copper-gold alloys and low temperature alloys of gold-indium. The heating rate and furnace environments were examined to ensure acceptable braze conditions. Additional development activities included foam internal diameter sizing, foam and tube assembly, and foam and brazement mechanical property characterization.

This paper describes the intended application and development effort required to braze the copper foam to the stainless steel tubing. Challenges, such as differences in thermal expansion, loss of high temperature strength, and excess braze material will be discussed.

INTRODUCTION

A new heat exchanger that will be used to separate hydrogen isotopes was developed by the Savannah River Technology Center (SRTC). The application is for a thermal cycling absorption process (TCAP) unit. The TCAP uses differences in absorption properties in palladium to separate low mass isotopes from higher mass isotopes. Figure 1 schematically shows the physical arrangement for the TCAP, the effective points at which product (high mass isotopes) and raffinate (low mass isotopes) are derived, and the presence of a plug flow reverser (PFR). All of which make it possible to purify hydrogen isotopes to the tens of ppm range using the TCAP technology. Although the process has been used successfully for a number of years, there is room for significant improvement in cycle time and thermal efficiency by changing the heating and cooling medium from gaseous nitrogen to a thermal fluid. This change in thermal media requires significant changes in design.

The TCAP cycles between –25 and 125°C. Decreasing the duration of the cycle will increase the throughput of impure gas and increase the productivity of the system. The desire for a rapid change in temperature of the system and an improvement in overall heat transfer may be

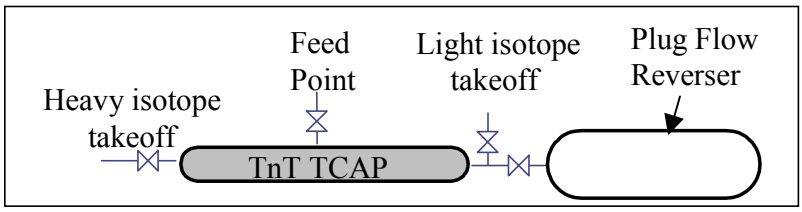


Fig. 1. Typical TCAP design layout.

achieved by adding high thermal conductivity metal to the tube in tube (TnT) TCAP annular space and will improve the efficiency, however, it is also desirable to keep the overall thermal mass as low as possible to maximize the heating and cooling of the product gases, rather than the process hardware. If one considers the addition of a copper foam, it is apparent that the material could be friction fit onto the inner tube or metallurgically bonded. Since the foam is in the annular space, one could also conceive bonding to both inner and outer tubes. This concept was eliminated early in the development due to perceived thermal fatigue problems from expansion and contraction in which the foam would likely fracture in the center of the annular space. Finally, there are a myriad of choices with respect to materials, process, fabrication, and operation. This paper will discuss the braze composition and processing selected for fabricating the TnT TCAP.

BACKGROUND

Material

The TnT TCAP is made from two concentric tubes of type 316L stainless steel. The outer tube was 1.5 inches in diameter with a wall thickness of 0.035 inch while the inner tube was 0.75 inch in diameter, also with a 0.035 inch wall. One improvement that was suggested to improve the heat transfer was to incorporate copper foam for the annular space. Copper was selected because of its high thermal conductivity while foam was selected since it can act to support the Pd particles that allow the separation to occur. Fig. 2 shows the cross-section of the TnT TCAP. Another feature that affects the processing is the presence of an aluminide permeation barrier. The barrier coating is on the internal surface of the internal tube and the external surface of the outside tube, Fig. 2. The coating will minimize contamination of the thermal fluid and the space surrounding the TnT. It is desirable to braze at a temperature different than the coating temperature so neither the braze nor the coating is adversely affected by the subsequent processing.

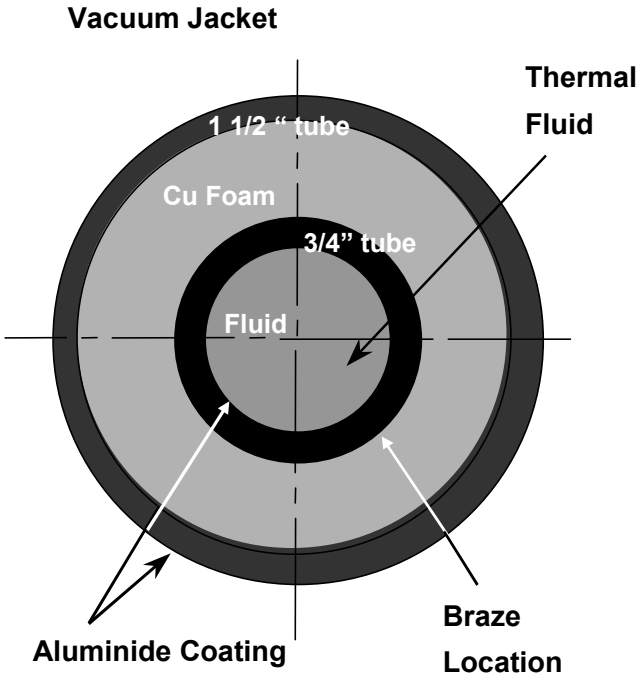


Fig. 2. Schematic cross-section of TnT TCAP.

The copper foam is comprised of an

open cell reticulated structure of open, duodecahedronal-(Twelve sided three-dimensional) shaped cells connected by continuous, solid metal ligaments. The relative density of the foam versus solid copper is about 6.5-9.5%. This presents a challenge to braze alloy application since typical braze placement techniques would result in approximately 10 times more braze material than needed. Fig. 3 shows one of the copper foams considered for this application. The open structure void space was designed to accommodate typically Pd coated particles for maximum efficiency.

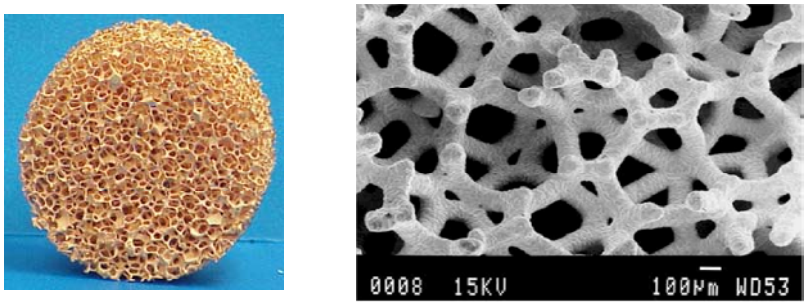


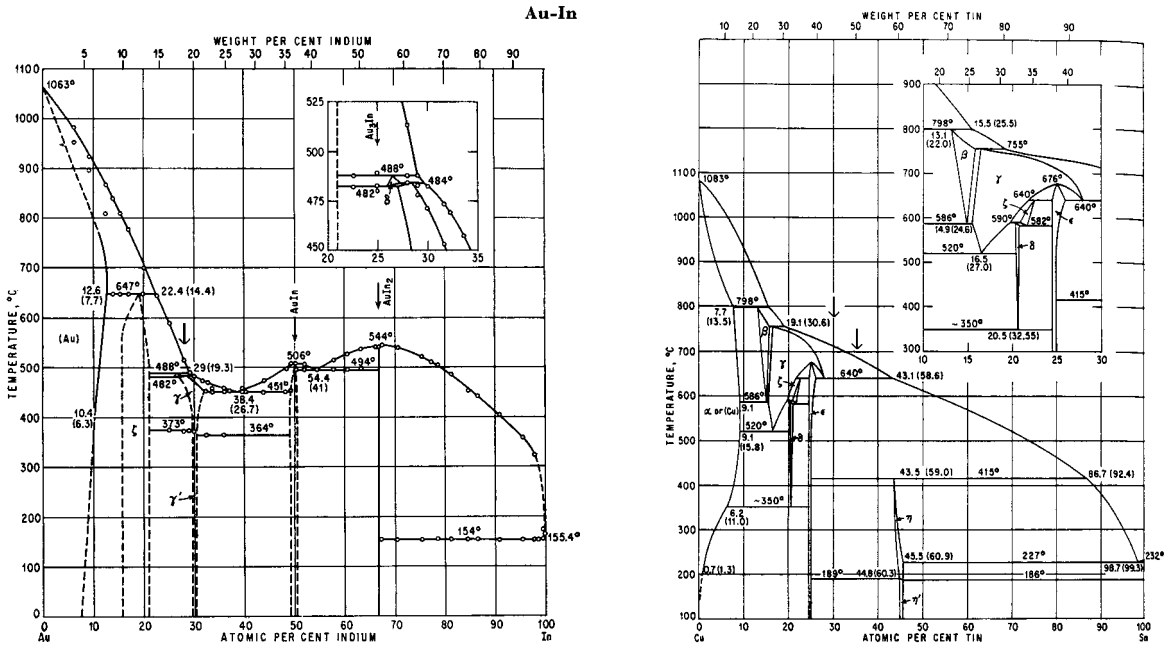
Fig. 3. Low (0.83X) and high magnification images of the copper foam used for the brazing study. Actual pieces had holes drilled in the center to accommodate the inner tube.

Alloy Selection

Several brazing alloy producers were contacted to determine the efficacy of using different alloy compositions. The requirements for selection included 1) minimizing total braze thickness to supply the small quantity required for the open foam structure, 2) ensuring well bonded braze pre-placement, 3) minimizing braze erosion and filament undercutting, 4) maximizing final foam contact to inner and outer tube wall which leads ultimately to 5) minimizing brazing temperature.

Initial braze selections included commercially available gold and nickel alloys, BAu-4 and BNi-2. These were pre-wet onto the ¾ inch tube and then brazed. These samples contained excessive quantities of braze and the samples exhibited unacceptable erosion, even the thinnest commercial braze sheet, 0.001", contained excessive braze. The pre-wet cycle did not always produce a smooth interface. Since the braze quality depends on the contact points, it was expected that the discontinuities from the pre-wet cycle would inhibit good bonding. Also during these experiments, a decision to change the processing sequence from brazing prior to coating to coating prior to brazing resulted in abandoning the high temperature braze alloys. This decision was based on technical difficulties with the pre-wetting and damage that was caused to the foam during the thermal cycle. Based on these preliminary results and the program decision to proceed with a lower temperature braze at around 550°C alternative methods of braze placement were pursued.

Table 1. Nominal composition of alloys used (wt%)				
Type 316L:	68 Fe 17 Cr 12 Ni 1 Si 2 Mn .03 C		0.035" wall	
BAu-4:	82Au 18 Ni		0.001"	
BNi-2:	82.5 Ni 7 Cr 3 B 4.5 Si 3 Fe		0.002"	
Au-Cu:	45 Au 55 Cu		0.00036"	
Au-In:	82 Au 18 In		0.000158"	
Sn-Cu:	45 Sn 55Cu;	50 Sn 50 Cu	0.001"	0.001"
Ag:	100 Ag		0.001"	



(a) (b)

Fig. 4. (a) Gold-indium and (b) copper-tin phase diagrams. The alloys evaluated are indicated by the arrows.

In order to control the small amount (thin layer) of braze alloy, electroplating, specifically brush electroplating, was investigated. The braze amount is tightly controlled by the process, i.e., Faraday's equation. ($w = I * t * M / (n * F)$, where w is the weight plated (g/s), I is the current (A), M is the atomic mass of the metal, n is the valence of the metal ion, t is the time (s) and F is Faraday's constant, 96,500 C). Very thin layers can be applied by controlling the time and current to minimize the amount of excess braze. The alloy composition can be modified by changing the thickness of the layers and alloys can be developed by plating controlled thicknesses of appropriate elements.

During electroplated braze alloy selection, three concepts and multiple braze alloys were considered. The simplest approach was to use a silver diffusion bond, the second approach used a "high temperature" Au-Cu braze, 55%-45% Cu by weight , and the third used low temperature brazes, either Au-In, 82% Au-18% In, or Cu-Sn, 45%Sn-55% Cu, brazes. The alloys were selected based on having a low melting point eutectic at a desirable brazing temperature. Phase diagrams for the two alloys selected for further development are shown in Fig. 4. To enhance the fabricability, the stainless steel tubes were plated with a very thin (0.00005") nickel strike. Since the nickel was not expected to melt and alloy with the braze material at the braze temperature chosen, the alloying effect of this deposit was not included in the alloy development.

For the higher temperature application, in order to achieve the appropriate compositions, the braze alloys were deposited by applying the nickel strike to a thickness of 1.3μm (0.00005"), followed by 2.54 μm (0.0001") of gold, and topped with 6.6 μm (0.00026")of copper. The order of the gold and copper was selected to minimize the likelihood of erosion during brazing. This alloy has a melting point of 960-990°C and the nominal brazing temperature was 980°C.

For the lower temperature application, i.e., 440-640°C, the order of braze element application was varied for both the Au-In and Cu-Sn systems. In one case the mixture was applied using the lower melting constituent on the surface while in the other, the higher melting constituent was on the surface. The brazing temperatures for both alloy systems ranged from 440 to 640°C. The Au-18 In alloy is formed by electroplating the nickel strike to a thickness of 1.3 μm (0.00005"), indium to a thickness of 1.47 μm (0.000058"), and gold to a thickness of 2.54 μm (0.0001") and the Cu-45 Sn alloy was established by plating thicknesses of 1.3 μm (0.00005") Ni, 25.3 μm (0.000996") Cu, and 25.4 μm (0.0010") Sn.

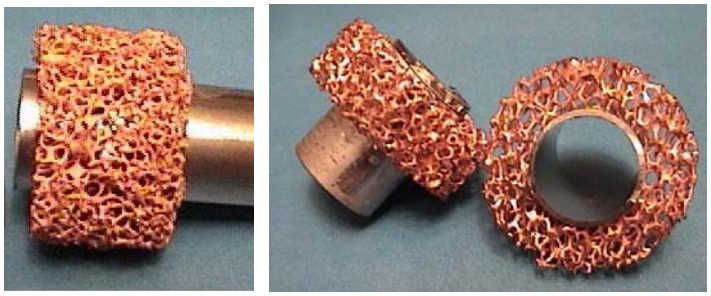
Processing

All brazing was conducted in a vacuum furnace. The maximum pressure used was 10^{-5} torr. The heating and cooling rates were carefully controlled to optimize the brazing conditions. The sample cleanliness was ensured by cleaning in absolute alcohol. The commercial grade of alcohol has sufficient water, up to 5%, to actively corrode the copper foam and cause discoloration. Samples were heated at prescribed heating rates. The rings were interference fit on the ¾ inch tubes.

RESULTS AND DISCUSSION

Fig. 5. Copper foam piece brazed to type 316L SS using Au-Cu at 980°C

The high temperature brazing was successful in bonding the copper foam to the stainless steel. A typical sample that was brazed simply by placing the copper foam ring over the tube and supporting the ends of the tube in the furnace is shown in Fig. 5. This sample exhibits a significant deviation from surface contact on the lower portion of the tube in addition to apparent melting on the upper surface. The deformation of the copper foam was attributed to high temperature creep. Fixturing mandrels were used to minimize the deformation of the copper foam. For later tests, the inner tube was supported using a stainless steel ring while the outer edge of the foam was supported using the larger diameter outer tube of the TnT TCAP. This fixture was successfully used to prevent excessive foam creep, but the contact points on the outer diameter were decreased due to thermal expansion mismatch between stainless steel and copper, 15 x 10^{-3} in/in/°C for 316 SS vs 21 x 10^{-3} in/in/°C for Cu[3]. In addition to the thermal expansion mismatch and creep issues, the effect of impurities and copper vaporization in the furnace created difficulties. The high temperature braze alloy development was successful for bonding the foam to the tube, but other problems were encountered that eliminated its use. The final issue that prevented it from being used was a change in the fabrication



(a) (b)

Fig. 6. Samples of 45 Sn 55 Cu brazed at 425°C. (a) Cu on external surface, 0.001" (b) Sn on external surface, 0.0005".

sequence. The aluminide coating was applied prior the brazing operation. This change necessitated the change from high temperature to a lower temperature brazing (below 700°C).

Silver diffusion bonding was attempted using a 25 μm thick silver layer on the external surface of the tube. The samples were heated to 650°C for hold times ranging from 15 to 60 minutes. In all cases, the extent of the creep damage was significantly less and some bonding between the foam and tube was achieved. However, the strength of the bond was deemed inadequate and during tear testing, failure occurred between the foam and the braze.

Two alloys from the Cu-Sn family were tested. The alloys were 50:50 and 45:55 Sn:Cu. These alloys were applied with either the Sn as the inner or Sn as the outer layer. The rationale for the two combinations was to determine which alloy sequence would cause more erosion of the foam, an undesirable consequence. The control on the amount of braze alloy deposited was not as good as was expected. In many cases, there was excessive braze alloy which promoted "pooling" and erosion. The typical appearance of samples with the Sn on the external surface and Cu on the external surface is shown in Fig. 6. It is evident from these images that the order of the braze constituents is important. Having the low melting point constituent in contact with the foam resulted in more braze erosion than was deemed acceptable. Brazing at 425°C did not result in complete fusion of the braze constituents. In light of this, the minimum target braze temperature was raised to 540°C. Additional testing did not demonstrate a suitably controlled system. There were inconsistencies in the products of the brazed Cu-Sn samples.

Fig. 7. Macrophotograph of foam brazed using Au/In and bond strength tested.

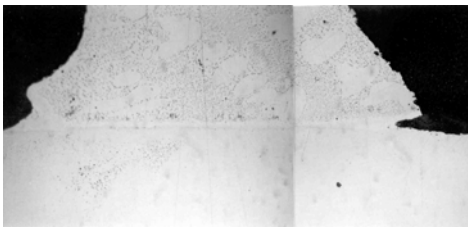


Fig. 8. Optical micrograph of Au-In brazed copper foam (200X).

The development of the Au-18 In braze process was coincident with that of the Cu-Sn. Many of the same approaches were tried with either the higher or lower melting constituent on the surface near the copper. The brazing temperature ranged from 500 to 650°C. The heating cycle was well controlled. The programmed rate was comprised of three steps as follows for a brazing temperature of 550°C: Heat from RT to 150°C at 20°C/minute, hold 30 minutes, 150 - 530°C, at 20°C/min, no hold, 530-550°C at 3°C/min hold 15 minutes, 550 to 100°C, cool at 20°C/min or slower. This type of thermal schedule was successfully used to braze both samples and ultimately the TnT TCAP components. Samples with the In in contact with the Cu suffered from braze pooling and other issues, while samples with the Au in contact with the Cu did not exhibit these detrimental effects. Thus, the decision was made to use a gold-indium alloy in which the layers were applied as Ni strike, In, and Au.

The gold surface was also more resistant to wear that occurred as the copper foam was being loaded from one end of the tube. More detailed characterization was conducted on this alloy-sample configuration. Samples were examined using metallography, scanning electron

microscopy (SEM), and bond strength testing. A typical optical micrograph of a bonded section is shown in Fig. 8. This image shows a fillet radius in the braze and some structure in the foam. It is apparent that the copper foam is cast and comprised of dendritic structure. SEM analysis of the dark spots shown revealed only copper. The braze exhibits good wetting on both the copper foam and the stainless steel, as evidenced by the low contact angle. This can be more clearly observed from the SEM micrographs in Fig. 9. These images show low and high magnification micrographs of the same areas. The spots indicated in Fig. 9 were used for microchemistry analysis using semi-quantitative x-ray energy dispersion analysis (XEDA). The microchemistry results are shown in Fig. 10. The composition of the copper foam is nearly 100 Cu, while there is intermixing in the braze region which resulted in a maximum Indium content of about 13%. The amount of alloy dilution is not unexpected.

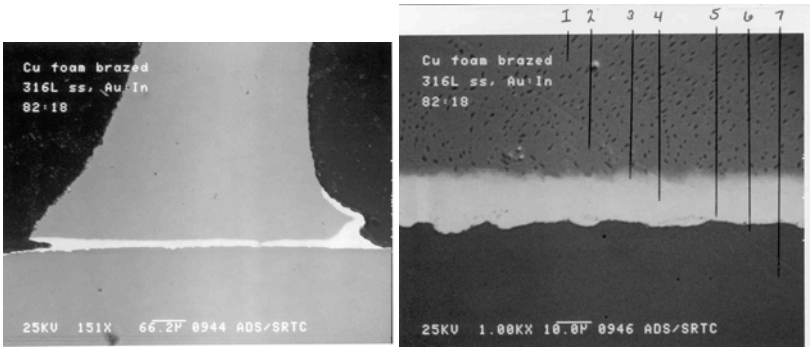


Fig. 9. SEM micrographs of brazed copper foam.

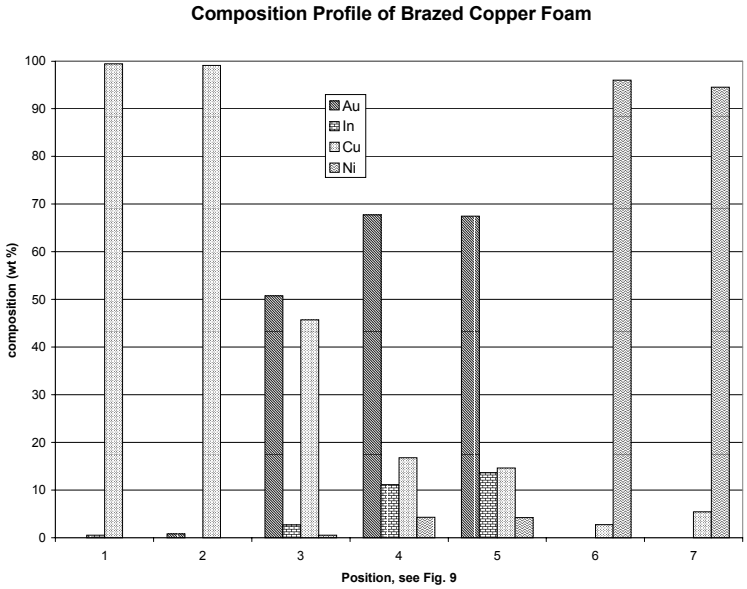


Fig. 10. Composition profile of brazed copper foam.

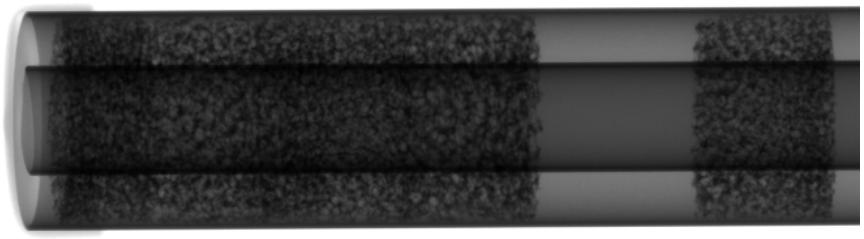


Fig. 11. X-ray radiograph showing the brazed assembly and tight packing of the foam disks on the left and a spaced disk on the right

The braze strength of the joint was determined using a "push out" test. The brazed samples were placed on a mandrel, a plunger with a larger diameter than the inner tube was then use to try to push the foam off of the ¾ inch tube. The load at failure was determined. Previous testing indicated that the nominal crushing load for the copper foam was between 120 and 200 pounds, depending on the density. It is established that strength is proportional to density squared. The load required to break the

foam free was consistent with the strength of the foam. In most cases, the foam failed prior to brazement failure, as shown in Fig. 7 where the foam ligaments are attached to the tube on the tested sample.

Based on successfully demonstrating brazing using Au-In, the TnT TCAP was assembled. The braze cycle used was as indicated above. Samples were included in the production heat treatment to demonstrate successful brazing. Fig. 11 shows a radiograph of one of the trial pieces. This piece clearly shows the inner tube and the copper foam. The gap between the block of foam pieces on the left and the piece on the right is intentional.

SUMMARY

A braze alloy and process were developed to metallurgically bond copper foam to stainless steel. This heat exchanger like application should exhibit superior heat transfer to the process gas due to the minimization of interfacial resistances. Testing of the system will be pursued to validate the brazing approach.

CONCLUSIONS

High temperature brazing resulted in extensive creep damage to the copper foam. The high temperature brazing also changed the interference fit between the outer tube and the inner tube due to differential thermal expansion.

Copper-tin braze alloys caused excessive braze erosion and were largely uncontrollable for the brazing process.

Silver solid state diffusion bonding does not provide suitable strength for the application.

A Au-18 In alloy will metallurgically bond copper to stainless steel at a moderate temperature. This braze temperature minimizes the damage due to creep and thermal expansion. The braze alloy wets both copper and stainless steel but does not appear to cause excessive braze erosion.

ACKNOWLEDGEMENTS

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