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Evaluation of Braze Joints for Hydrogen Purification Diffuser

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Abstract

Hydrogen isotope purification technology uses a thin wall palladium – silver tube that is typically brazed into a manifold. The typical commercial hydrogen purifier uses relative short tubes and significant number of them to produce high purity hydrogen with little regard for the residual hydrogen in the raffinate. Our diffuser design requires both the product and raffinate streams to be as pure as possible, to extract as much hydrogen as possible with very low residual hydrogen in the raffinate. In the past, the diffuser vendor was responsible for both alloy selection and process development, that has left a knowledge gap. In order to fill this gap, this project was initiated to develop alloy process knowledge to compare alloys, to understand the processes, to better facilitate production of diffusers, and to own the technical requirements to produce diffusers that meet design goals and requirements. The diffuser operates between 350 and 430°C. The goal is to have a braze that 1) has with a melting temperature where the operating temperature is between 0.4 and 0.6 Th(abs), 2) is compatible with hydrogen, 3) can be vacuum furnace brazed, and 4) does not require flux.

Introduction

Hydrogen isotopes are routinely separated from inert gas species using palladium-based membranes. Palladium 25% silver (Pd-25Ag), by weight, membranes are used at the Savannah River Site for this purification step. The membrane is heated to approximately 350°C and the hydrogen isotopes diffuse through the membrane while the raffinate is exhausted to a secondary plenum. These components can be arranged in a variety of configurations and several different vendors and designs have been used at the SRS (1).

For the systems to safely operate, they are comprised of several different materials and alloys. These components may be pressure boundaries and are ASME listed materials, such as the 300 series austenitic stainless steel. These materials are commonly selected because of their weldability and fabricability (2,3). In addition, the austenitic stainless steels are largely resistant to hydrogen embrittlement (4-9).

The joining of the structural materials of stainless steel to the processing materials of palladium tubing requires a transition from stainless steel. In order to make this change, brazing is employed since a metallurgical bond is needed for leak tightness and mechanical attachments are not suitable.

Brazing was selected since it can join materials with different materials in a manner that doesn't adversely affect the properties and chemistry of either material (10). In order for the alloys to be properly bonded several criteria must be satisfied. These include flowability, material compatibility, wettability, and temperature limits.

Braze flowability is often limited by the melting range of selected alloy. To ensure good flowability, a narrow melting range is often recommended (10). The flowability is important since the assemblies require brazes that are configured for vertical up and vertical down flow (11).

Material compatibility is an important aspect of the braze selection also. The braze must be compatible with hydrogen, stainless steel or other intermediate materials, and Pd-25Ag. The primary concern for the Pd-25Ag is that there is minimal erosion since the tubing wall thickness is between 75 and 125 µm.

Wettability is also important to successfully join materials. The wetting is described by the balance of three surface energies terms: γ_{SV}, the interfacial energy between the solid and the vapor, γ_{SL}, the interfacial energy between the solid and liquid, and γ_{LV}, the interfacial energy between the liquid and vapor:

$$\gamma_{SL} = \gamma_{SV} - \gamma_{LV} \cos \theta \quad (1)$$

in which θ is the angle between the solid and the liquid, with wetting corresponding to $0 < \theta < 90°$ and non-wetting $\theta > 90°$ (10, 12, 13). The wetting angle can be measured using the sessile drop test (14).

The final requirement is that the braze not melt during operation, to ensure stable materials properties and to minimize diffusion interactions, the solidus temperature was selected to be nominally twice the operating temperature (15). As indicated above, the nominal operating temperature of the diffuser is 350°C (623 K) providing a target solidus point of 973°C.

Thermal expansion mismatch can induce high stresses and may cause failures. One way to control these thermal strains is to add interlayers. The CTE of Type 304L stainless steel is 17.2 ppm/K (16) while that of Pd-25Ag is approximately 12.8-14.3 ppm/K (17), This difference can cause thermal fatigue for the tubing, recall it is about 100 microns thick. The consequence of failure of a diffuser is significant since they are used to process tritium in a glovebox, and they cannot be repaired if they fail and must be disposed of as radioactive waste. Consequently, employing methods that minimize residual stresses is important. SRS uses a nickel insert that has a CTE of 13.3 ppm/K (18) to decrease the thermal strain component and provide a higher strength material for the interface.

Braze alloy evaluation and characterization were imitated on five alloys that met these criteria, the alloys were selected from prior experience, vendor discussions, and review of the Brazing Handbook. This article describes the testing and results that resulted in the down selection of BAu-4 as the alloy of choice for fabrication of hydrogen purification test articles.

Experimental

As indicated, five braze alloys, 0.020" diameter wire, were selected for testing and subsequent down selecting. These alloys are listed with nominal compositions in Table 1. In addition, type 304L (Fe 18% Cr 8% Ni) and Ni 200 (99% Ni) were used. The nominal compositions are:

Table 1. Nominal composition of the braze alloys investigated.

Name	Pd	Au	Ni	Ag	Cu	In
Palniro7	8	70	22			
BAu-4		82	18			
Incusil				63	27	10
Palsil-10	10			90		
Palcusil25	25			54	21	

Brazing was conducted in a Centorr Vacuum Industries furnace with a 12" x 12" x 18" hot zone. The samples were placed on blocks to keep them from the floor of the furnace and the furnace was evacuated to at least $8x10^{-4}$ Torr and then heated at 10°C / min to 25°C below the solidus temperature and held for ten minutes to equilibrate the temperature and then heated at 20°C/min to the brazing temperature and held for 10 minutes. This thermal cycle was used to help ensure that all the parts were at temperature. While the sub-solidus soak is not required for the few samples that were brazed in the initial trials it may become important when the furnace load increased.

Sessile drop samples were prepared by alcohol cleaning the stainless steel, nickel, and Pd-25Ag coupons. Stainless steel and nickel coupons were cut from sheet stock while the Pd-25Ag coupons were prepared by cutting a 6 mm diameter tube into approximately 20 mm long pieces and splitting them axially and rolling them flat. This preparation was chosen since the Pd-25Ag tubing was available and sheet stock was expensive. Braze pieces 12 mm long were cut from the roll and placed on the various substrates. The furnace cycle was run at the brazing temperatures listed in Table 2 and the samples were evaluated.

Table 2. Solidus, liquidus, and brazing temperatures (°C) used for the alloys selected.

Braze	T_s	T_L	(T_L+25)	(T_L+50)	(T_L+75)
Palniro7	1005	1045	1070	1095	1120
BAu-4	950	950	975	1000	1025
Incusil	605	725	750	775	800
Palsil-10	970	1070	1095	1120	1145
Palcusil25	900	950	975	1000	1025

The sessile drop samples were examined using a Keyence VR3000 digital macroscope to measure the wetting angle. The complementary angle to the wetting angle was measured and the wetting angle was calculated by difference. The maximum height of the braze droplet was also determined.

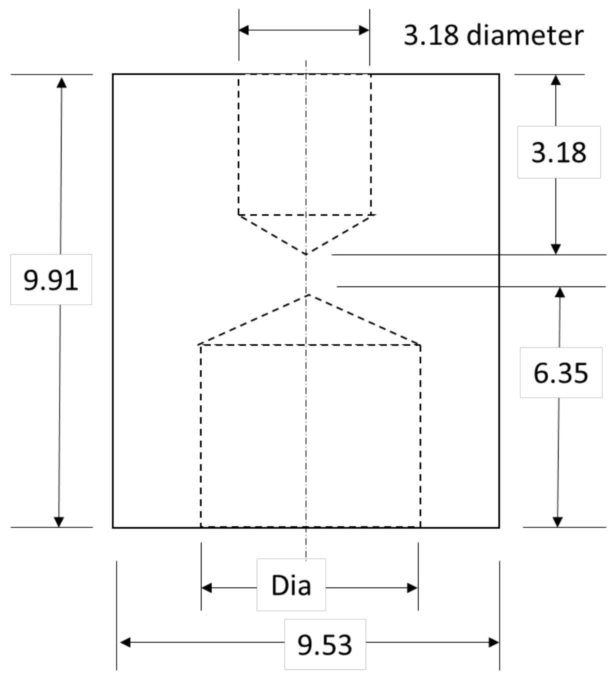


Figure 1. Sketch of Ni-200 socket braze fitting used to assess the flowability of the brazes, all dimensions in inches.

Socket braze fitting samples were machined from Ni 200 with the shape shown in Fig. 1. The diametral gaps varied from 0.10 to 0.25 mm. The required amount of braze was estimated from the gap and area. The minimum length of braze to fill the gap was 3 cm. The braze was placed in several different positions as shown in Figure 2. Nickel (CTE: 13 ppm/K) is used as an interlayer to help accommodate the difference in coefficients of thermal expansion of the Pd-25Ag (14 ppm/K) and the stainless steel (17 ppm/K). This interlayer was intended to reduce strain by about 50%, for pure Pd.

Metallographic examination of the sessile drop samples and socket braze samples were sectioned, mounted in epoxy, ground and polished using standard metallographic sample preparation and examined in the as polished condition on a

Keyence VHX-5000. The wetting angle and potential surface erosion were determined. Samples were examined at magnifications up to 1000X.

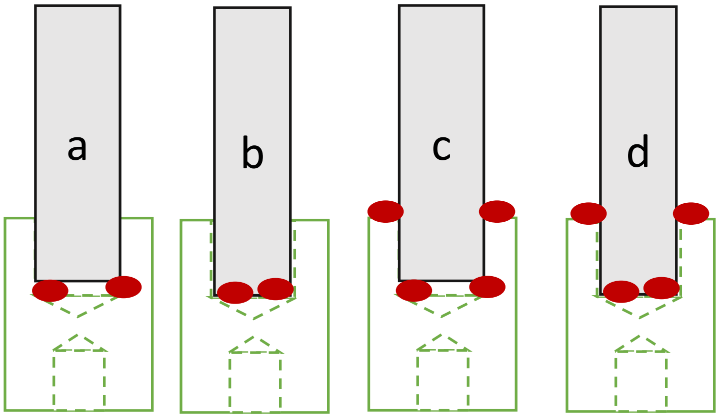


Figure 2. Braze placement / configuration (a) internal in contact with sidewall tube not fully seated (b) internal in contact with sidewall tube not fully seated with external rings and (c) internal with tube fully seated and (d) internal with tube fully seated and external rings.

Nondestructive testing was conducted on the braze tube samples. Digital radiography (DR) was conducted using a 220 kV source at 18W. A CsI imager with a 100 µm pixel size was used. The sample was configured such that the geometric magnification provided 10 µm resolution.

Ultrasonic testing was also conducted using an immersion technique. Two different scan resolutions were used to assess the sensitivity. The details for the two scans are shown in Table 3. Parameters for a lower resolution scan, set 1, and a higher resolution scan, set 2 are shown.

Table 3. Ultrasonic test scan parameters for low (set 1) and high (set 2) resolution scans.

Parameter	**Set 1**	**Set 2**	Units
Motion Control			
Index Range	0.200	0.200	Inches
Step Count	10	25	
Resolution	0.020	0.008	Inches
Surface Angle	90	90	Deg
Scan Axis	Z	Z	
Scan Direction	Up	Up	
Ultrasound			
Energy	115	115	mV
Gain	38	38	dB
Frequency	20 MHz	15 MHz	MHz
Probe	263409	313777	
Probe Distance	36	45	µs

Results

The sessile drop samples were placed in the furnace as shown in Figure 3. As can be seen, the samples were placed on spacers to keep them off the floor of furnace. They were placed near the center of the furnace both side to side and front to back. After evacuation, the samples were heated to the braze temperatures indicated in Table 2. Sessile drop testing of the five brazes, three substrates, and three braze temperatures revealed that four of the brazes adequately wet all three substrate materials, while the fifth braze did not. A typical photograph of the sessile drop coupons is shown in Fig. 4, for the BAu-4 braze on all three substrates and three temperatures. As can be seen specifically for this braze the wire spread on the stainless steel and Pd-25Ag alloy while still retaining some of its shape, while it wet on the nickel in a more substantial manner. The wetting angles for all the samples are presented in Table 4. It is apparent, that all these material combinations would be acceptable for further development, except Incusil on 304L SS. This rather surprising result shows a complete lack of wetting and absolutely no interaction between these materials, such that the braze melted and created a small ball that rolled off the surface. Additional tests were conducted with more aggressive cleaning to verify the lack of wetting, and these samples also balled up.

Figure 3. BAu-4 sessile drop test coupons on stainless steel, nickel, and Pd-25Ag coupons as placed in the vacuum furnace.

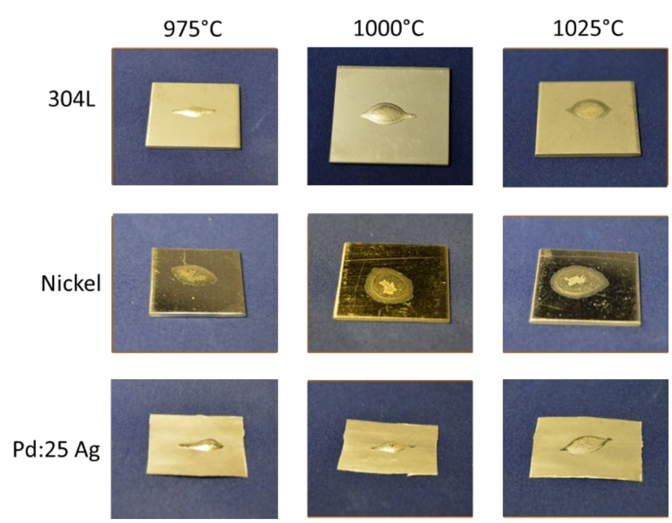


Figure 4. BAu-4 sessile drop test coupons after brazing at the temperatures indicated in Table 2. The wetting angles were measured using the Keyence VR3000 and are presented in Table 4.

Due to the difference in CTE, stainless steel was dropped from the socket braze fitting testing. Further, the samples were shown to adequately wet the nickel and Pd-25Ag at braze temperatures of T_L + 25, as shown in Fig. 5, it was decided to braze socket samples. Also, due to the lack of wetting exhibited by the Incusil on stainless steel, this alloy was dropped from further consideration; a potential approach to assembly is to braze the Pd-25Ag to the nickel socket fitting and to braze the nickel socket fitting to the stainless steel, which can then be welded into a stainless steel plenum.

Table 4. Wetting angles for the brazes at the three braze temperatures.

		Braze Temperature		
Braze	Substrate	Tl + 25	Tl + 50	Tl + 75
Palniro-7	Ni	2.37	2.507	2.30
Palniro-7	Pd-Ag	17.31	12.061	15.38
Palniro-7	SS	9.99	6.332	5.76
BAu-4	Ni	5.44	2.670	2.37
BAu-4	Pd-Ag	23.83	21.563	7.89
BAu-4	SS	23.36	13.920	6.20
Incusil	Ni	1.35	1.792	1.59
Incusil	Pd-Ag	29.58	34.253	25.49
Incusil	SS	180.00	180.000	180.00
Palsil-10	Ni	0.00	0.000	0.00
Palsil-10	Pd-Ag	26.23	25.979	29.94
Palsil-10	SS	1.83	2.163	1.76
PalCuSil	Ni	2.53	2.468	0.00
PalCuSil	Pd-Ag	38.12	31.352	22.59
PalCuSil	SS	0.76	0.000	0.00

The fitting samples that had different gaps, different quantities of braze, different braze locations were brazed using the thermal profile that was used for the sessile drop testing. The tube segments were not weighted and there was some deviation from normal. The diametral gaps were C=0.05mm, A=0.23 mm, and B=0.28 mm. Photographs of the four braze alloy samples are shown in Fig. 6.

All the samples exhibit braze fillets, although the Palsil-10 appears to be excessively fluid and may have spread more than desired, if this situation becomes an issue, the braze stop-off could be considered. The other samples are shiny and appear to have bonded well.

The socket samples were radiographed using the conditions described above. The radiographs were examined, and defects were detected and are described in detail in Table 5.

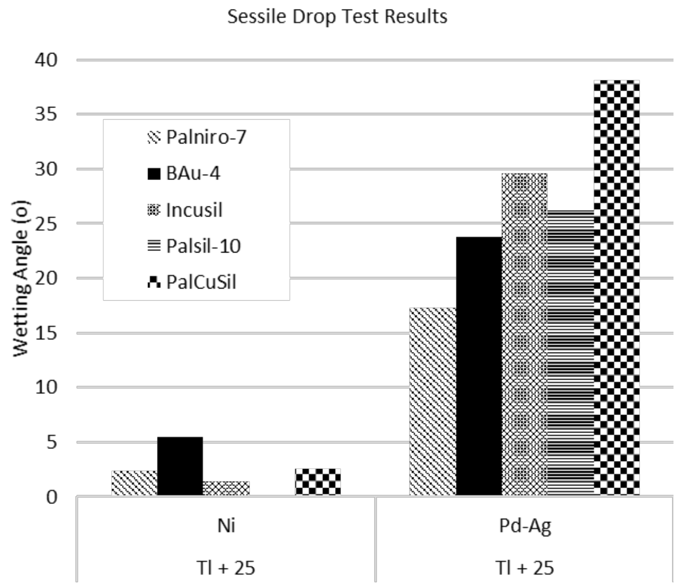


Figure 5. Graphical representation of the wetting angle for Ni and Pd-25Ag at a braze temperature of T_L + 25°C.

Figure 6. Macrophotographs of the brazed socket fitting samples.

Table 5. Observations from radiography.

ID	Ni ID	Braze	ID rings	OD rings	Comments
C2	6.40	Palniro-7	3	0	small void, linear blemish at top
A2	6.55	Palniro-7	3	2	2 small voids
B2	6.63	Palniro-7	3	3	medium void above shoulder
C1	6.40	BAu-4	3	0	2 small voids
A1	6.58	BAu-4	3	2	small void, linear void at top
B1	6.63	BAu-4	3	3	multiple small voids, medium-large voids above shoulder
C4	6.43	Palsil-10	3	0	large, medium and small voids, linear void in shoulder
A6	6.73	Palsil-10	3	2	large no-fill areas top and bottom, multiple medium voids
B4	6.63	Palsil-10	3	3	large no-fill areas at bottom, large void at top with blemishes
C3	6.40	Palcusil	3	0	multiple medium voids, medium linear void
A3	6.53	Palcusil	3	2	multiple medium voids, multiple blemishes
B3	6.63	Palcusil	3	3	multiple medium-large voids, linear void
B5	6.63	Palsil-10	3	3	large no-fill areas at bottom, large void at top with blemishes
A5	6.55	BAu-4	2	1	3 medium, 1 small void, linear indication spanning 2 voids – **intentionally starved**
C6	6.40	BAu-4	3	0	**No defects**

Note: C6 was processed by fully inserting the tube into the fitting and then placing the braze filler down the center of the tube. Other tube fittings were assembled by placing the filler metal into the fitting and pushing the tube down as far as it would go. This approach left gaps at the bottom of the tube.

The radiographs of the Pd-25Ag tube brazed into the nickel socket fitting using Palcusil and brazing at T_L + 25°C (975°C) are shown in Fig. 7. This sample exhibits the defects described in Table 5. The defects are highlighted by the arrows and occur for several possible reasons, including excessive gaps at the bottom of the tube and fitting, excessive gaps from fit up, etc.

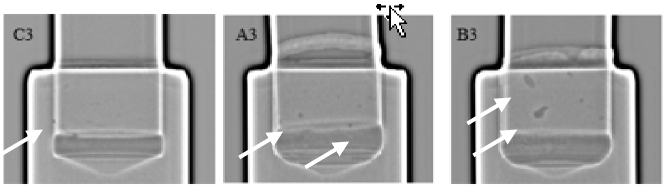


Figure 7. Radiographs from Pd-25Ag tubing brazed into Ni-200 fittings with Palcusil at 975°C, sample descriptions match Table 5.

Ultrasonic testing was also used to assess the quality of the braze joints, although one or the other techniques would have been adequate. The two scan strategies both revealed the defects although the slower scan provides better resolution of the defects. Scans from samples C4 and C6, that showed large defects and no defects, respectively, are shown in Fig. 8.

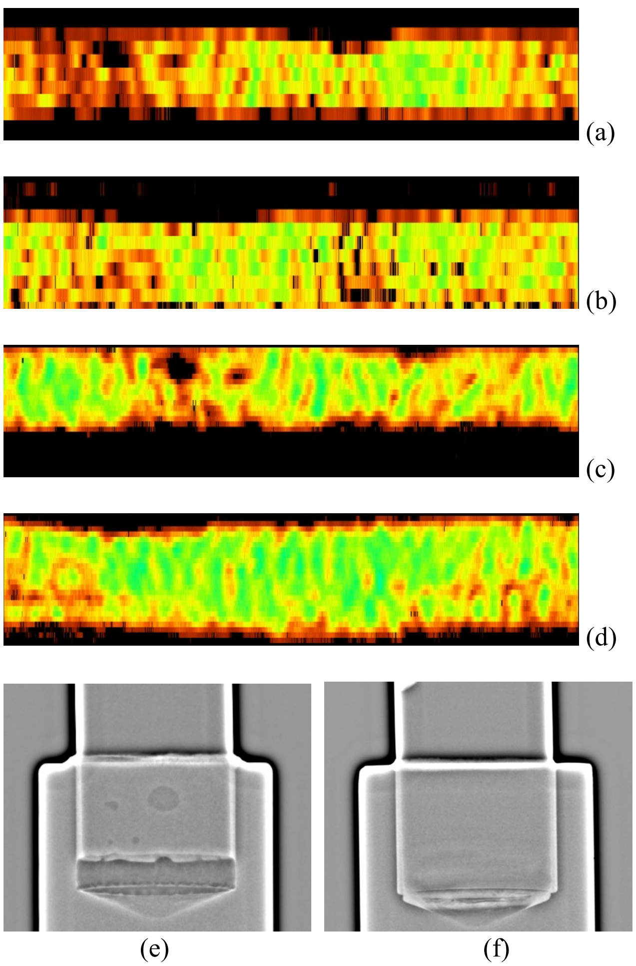


Figure 8. UT and RT results for sample C4 and C6. (a) C4 low resolution UT, (b) C6 low resolution UT, (c) C4 High resolution UT, (d) C6 high resolution UT, (e) C4 RT and (f) C6 RT.

The radiographs are shown to demonstrate that both techniques work well to detect braze defects in this material combination. Also note that the sample assembly was modified for sample C6 where the Pd-25Ag tube was placed fully in the bottom of the fitting and braze rings were placed in the center of the tube. This joint relied exclusively on capillary action to draw the braze into the joint. As can be seen by the lack of defects, the 50 µm gap and an all capillary action was effective at forming an acceptable joint.

Samples were metallographically examined to evaluate the quality of the joint. All the samples were sectioned and examined in the as polished condition. The defects observed by nondestructive evaluation (NDE) techniques were verified, as expected. The presence of the large gaps in the Palsil-10 brazed socket fitting samples, i.e., A6 and B4, was readily apparent from the metallography. Based on the amount of braze applied, these samples should have had excess material present. Cross sections of fitting sample C1, a BAu-4 50 µm gap sample and A6, a Palsil-10 180 µm gap sample are shown in Figure 9.

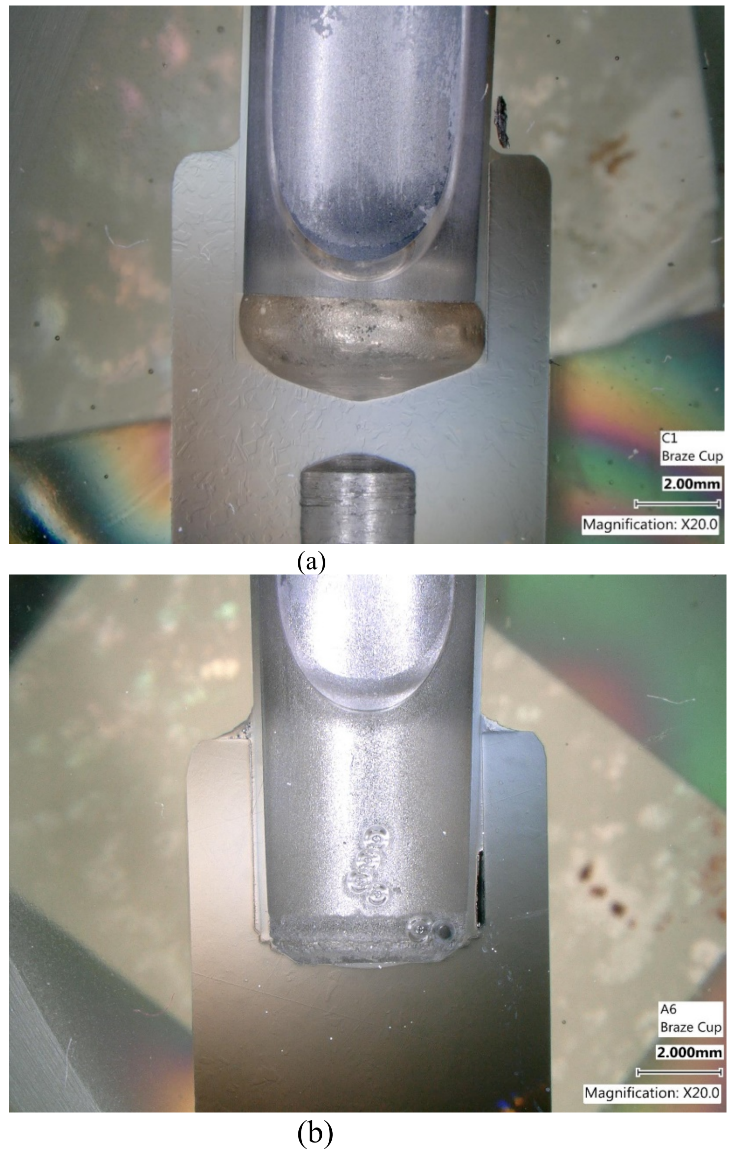


Figure 9. Low magnification micrographs showing the (a) sample C1 -- BAu-4 with a 50 µm gap and (b) sample A6 - Palsil-10 with a 180 µm gap, both brazed at T_L + 25C.

The average gap of the samples is reported, it is apparent that the tube in sample C1 had shifted during processing and was nearly in contact on the left side of the joint, despite being so narrow, this region was filled with braze.

Further development of the braze fittings was undertaken to develop a joint that could be more easily assembled and would be more likely to assure that the braze placement was consistent. The fittings were modified to include a braze ring support at the bottom of the fitting. The purpose of this braze ring placement is two-fold. The first is to ensure that the braze is protected from radiant heat and does not melt prior to the bulk of the component being at the brazing temperature, and the second is to provide a visual quality check that shows that the braze formed a fillet via capillary action. A sketch of the fitting is shown in Fig. 10.

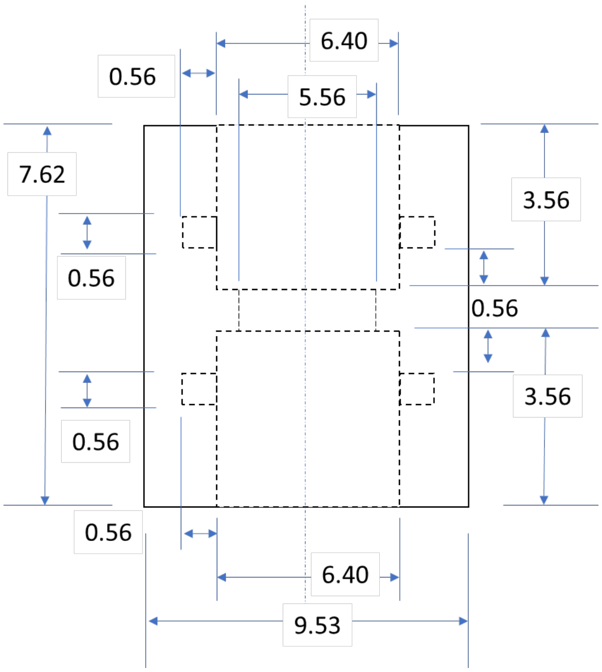
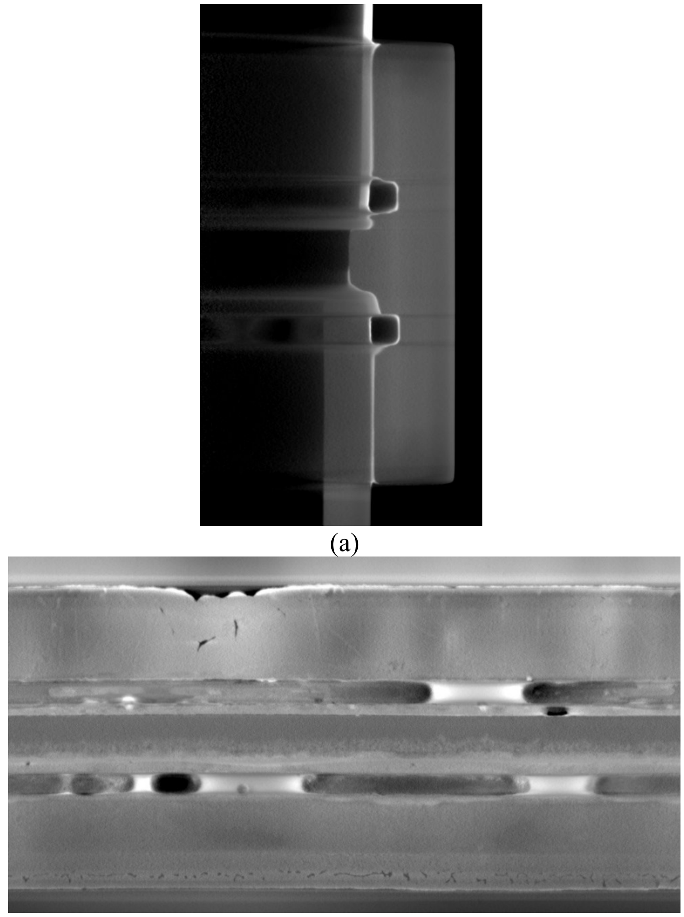


Figure 10. Modified union fitting for the 50 µm and a braze ring reservoir.

To develop the process further, the union type sample shown in Figure 10 was tested using BAu-4, a Pd-25Ag tube on one end and a stainless-steel tube on the other. The intent of using these materials was to facilitate welding of the tubing into a stainless-steel plenum. Other approaches at welding the Ni-200 fitting to stainless steel were successful but required additional technique development. Using a single braze step to bond both the Pd-25Ag and the stainless steel reduces the overall complexity for the design. The radiographic results of this sample are shown in Figure 11.



(a)

(b)

Figure 11. Radiograph of the modified braze joint between type 304L SS and the Ni fitting and the Pd-25Ag and the nickel fitting. a) is a through radiograph and b) is the entire CT scans layed flat. There is a small defect in the filler and a few small voids. The braze placement groove acted as a reservoir for the joints.

Conclusions

All the brazes selected wet the Ni-200 and Pd-25Ag tubes. Four of the five wet the Type 304L SS as well. The Incusil did not wet the SS.

BAu-4 and Palniro-7 exhibited superior wetting on the Ni-200 and Pd-25Ag.

Maintaining the lowest possible braze temperature and maximizing the wetting is important for the process. A braze temperature of 975°C was selected for BAu-4.

Modifying the union fitting improved the joint quality and braze placement.

Acknowledgments

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