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Sodium Compatibility of Refractory Metal Alloy-Type 304L Stainless Steel Joints

Excellent results are obtained with AWS BNi-3 and modified BNi-5 filler metals in the form of metallic glass foils during the induction brazing (under vacuum) of Mo, Re, Ta and W alloys to Type 304L stainless steel

BY F. M. HOSKING

ABSTRACT. The induction brazing in a vacuum of Mo, Re, Ta, and W alloys to Type 304L stainless steel with AWS BNi filler metals was investigated. Metal powder (BNi-5 and BNi-7) and metallic glass (BNi-3 and modified BNi-5) brazing filler metal alloys were evaluated. Excellent brazed joints were obtained with the BNi-3 and modified BNi-5 metallic glass foils. Cracks and porosity were observed in the metal powder BNi-5 and BNi-7 brazes. The as-brazed, refractory metal—Type 304L stainless steel samples—were also qualified in a sodium environment of 1073 K (1472°F) for 130 hours (h) with 2 and 100 ppm oxygen concentration.

There was no significant chemical corrosive attack observed on any of the sodium samples and weight changes were generally negligible. Braze separation along the refractory metal interface and crack growth in the filler metal, however, were observed in the metal powder brazes after the sodium exposures. As a result, the metal powder filler metals were not recommended.

A band of discontinuous voids in the metallic glass brazes near the refractory metal interface was also detected. Metallographic, thermal and microprobe analyses revealed that these voids were caused by a diffusion mechanism called Kirkendall porosity. Since the voids were not connected and would not provide a leak path, the metallic glass filler metals were recommended for brazing refractory metal alloys to Type 304L stainless steel and for subsequent sodium exposures.

Introduction

Refractory metal alloys are routinely used as vessels to contain high temperature reactions. Unfortunately, the fabrication of these materials is not an easy task. Joining is especially a problem. This is because most joining methods, such as fusion and solid state welding, exceed the recrystallization temperature of the alloy. As a result, the ductile-to-brittle transition temperature (DBTT) is raised well above room temperature, and the heat affected zone (HAZ) becomes prone to brittle failure.

High temperature brazing is, however, a viable joining alternative which avoids the DBTT problem. Brazing temperatures are generally lower than the recrystallization temperature. Nickel alloys (AWS BNi classification) are the most common filler metals used. The only critical requirement is that the maximum service temperature of the joint must not exceed the recommended service temperature of the filler metal.

The Advanced Reactor Research Department at Sandia National Laboratories, Albuquerque, has an on-going program to study reactor post-accident heat removal. An in-pile reactor debris bed experiment has been proposed to evaluate the heat transfer characteristics between UO_2 and Na. The crucible material for the experiment must survive a high temperature liquid-vapor sodium environment.

Several refractory metal alloys (Mo, W, Re, and Ta alloys) were selected as prob-

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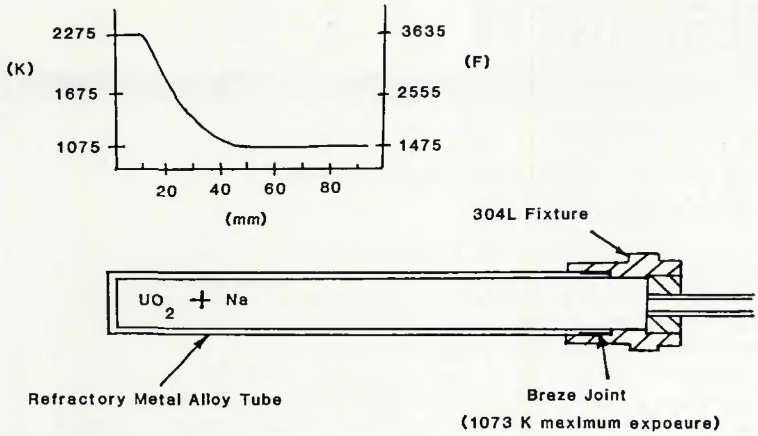

Fig. 1—Diagram of a UO_2/Na high temperature test tube

able crucible candidates. A program (Ref. 1) was developed to determine the commercial availability and sodium compatibility (corrosion and mechanical) of these alloys. The investigation included a high temperature test to evaluate the survivability of refractory metal tubes containing a UO_2/Na mixture. Maximum tube temperatures were 2273 K (3632°F) at the bottom and 1073 K (1472°F) at the top.* The temperature gradient away from the hot zone at the bottom of the tube was −55 K/mm (−2515 F/in.). Figure 1 shows a schematic of the temperature requirements.

The fixturing design required a hermetic joint between the Type 304L stainless steel collar and the tube top. The steel collar was then used to make a closure weld over the refractory metal tube opening. Since the service temperature of the refractory metal-Type 304L stainless joint was not to exceed 1073 K (1472°F), high temperature brazing was considered. Qualification of the filler and base metals in a 1073 K (1472°F) sodium environment was a prerequisite before proceeding with the high temperature tube tests. The purpose of this study was to qualify the refractory metal alloy, filler metal, and Type 304L stainless steel braze combinations.

Refractory Metal Alloy Brazing

Refractory metal alloys should be brazed at temperatures below their recrystallization temperature when maximum joint strength is a requirement. If the brazing temperature must exceed the recrystallization temperature, time at temperature should be kept to a minimum. Brazing is done in a vacuum or inert atmosphere to avoid harmful oxidation of the refractory metal.

Induction brazing in a vacuum (Refs. 2,3) is especially attractive. Heating takes place very quickly, due to the induced current concentration, so that there is minimal grain growth. The brazing temperature is rapidly achieved, resulting in a minimal interaction between the filler and base metals. The vacuum atmosphere also minimizes oxidation, eliminates the need for a flux, and yields a relatively clean, nonporous braze joint. The only requirement in a vacuum is that the vapor pressures of the filler metal constituents must be below that of the working vacuum pressure.

A variety of brazing alloys can be used to join similar or dissimilar refractory filler metal alloys (Refs. 4,5). Silver and copper filler metals are selected for lower service temperatures near 900 K (1160°F). Nickel alloys are used for intermediate temperatures up to 1255 K (1800°F). Refractory metals can even be brazed with lower melting point refractory metal alloys for higher service temperature requirements. Dissimilar joints of refractory metals and stainless steel are routinely joined with nickel alloys (AWS-BNi). There are also experimental alloys which have been developed, although these are not commercially available.

Sodium corrosion resistance is a key requirement for most nuclear reactor hardware. Soenen (Ref. 6) and Slaughter *et al.* (Ref. 7) have examined the effect of sodium on several commercial and experimental nickel brazing alloys. Soenen evaluated the sodium resistance of stainless steel clad, Chromel-Alumel thermocouples which were brazed to nickel-chrome heating wire. AWS BNi-1, BNi-2, BNi-5, BNi-7 and modified BNi-8 filler metals were used. Dynamic sodium testing was done from 700 K (800°F) to 975 K (1296°F) for exposure times up to 7000 h. Soenen found that the BNi-1 and BNi-2 (Ni-Cr-Si-Fe-B), BNi-5 (Ni-Cr-Si) and modified BNi-8 (Ni-Si-Mn) alloys gave satisfactory corrosion resistance. The BNi-7 (Ni-Cr-P) alloy showed signs of sodium corrosion.

Slaughter *et al.* brazed nickel and stainless steel T-joints with a wide variety of commercial and experimental filler metals. The joints were exposed to static and dynamic sodium environments. They found that the BNi-3 (Ni-Cr-B), BNi-5 (Ni-Cr-Si) and modified BNi-5(Ni-Cr-Si-B) filler metals were compatible in 1089 K (1500°F) sodium for 100 h. Brazes made with nickel filler metals, containing tin and phosphorous, but no silicon or chromium, were severely attacked.

Based on Soenen and Slaughter's work, it appears feasible to expose refractory metal-Type 304L stainless steel joints that are brazed with selected nickel alloys in a sodium environment. The service conditions will dictate the filler and base metal selection.

Joint design also becomes very critical when brazing dissimilar metals. For example, refractory metals have a lower thermal expansion coefficient (approximately 60% lower) than stainless steel. The refractory metal should be surrounded by the higher thermal expansion material to avoid creating tensile stresses in the joint after brazing. This also necessitates starting with a tight joint clearance, since the clearance will be larger at the brazing temperature.

Refractory Metal Alloy and Filler Metal Candidates

Low temperature, 1073 K (1472°F), sodium compatibility tests were used to screen a wide variety of refractory metal alloys before proceeding with the high temperature tube experiments. The response of the alloys, both chemical and mechanical, to a sodium environment of 573–1073 K (572–1472°F), 10–130 h exposure, and 2–100 ppm oxygen concentration in the sodium, were critical in selecting the tube material, and eventual crucible material. The test matrix for the brazing study was not as extensive as for the refractory metal evaluation. The most extreme environmental conditions were selected to qualify the filler metals; these conditions were 1073 K (1472°F)/130 h/2 and 100 ppm oxygen.

Ta-10W, T-111, Mo, W, Mo-13Re, Mo-26Re, Mo-41Re, W-26Re, Re (CVD and wrought), Re-5W(CVD), and TZM alloys were evaluated. Table 1 lists the recrystallization temperatures and times for these alloys. Except for the tantalum alloys and Mo, the brazing temperatures of AWS BNi filler metals were well below the refractory metal recrystallization temperatures. For the tantalum alloys and Mo, the BNi temperatures were of the same order as the recrystallization temperatures.

AWS BNi alloys have excellent oxidation and corrosion resistant properties. They are compatible with vacuum brazing due to the low vapor pressures of

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273 K (Kelvin) = 0°C (Celsius).

Table 1—Refractory Metal Alloy Candidates for the In-Pile Reactor Debris Crucible Material

Alloy, wt-%	Recrystallization Temperature, K (F°)	Time, hours
Ta-10W	1450 (2150)	1.0
T-111 (7-9 W, 2-2.8 Hf, bal. Ta)	1450 (2150)	1.0
Mo	1375 (2015)	0.5
W	2275 (3635)	0.5
Mo-13Re	1875 (2915)	0.5
Mo-26Re	1875 (2915)	0.5
Mo-41Re	1805 (2790)	1.0
W-26Re	2175 (3455)	0.5
Re(CVD)	1810 (2800)	0.5
Re(Wrought)	1675 (2555)	0.5
Re-5W(CVD)	1810 (2800)	0.5
TZM (0.5 Ti, 0.08 Zr, bal. Mo)	1805 (2790)	0.5

their alloying constituents. The maximum, recommended operating temperature 1255K (1800°F) of the BNi alloys is well above the 1073 K (1472°F) service temperature to which the braze joint would be exposed. For these reasons, AWS BNi filler metals were selected for the study. BNi-3, BNi-5, modified BNi-5, and BNi-7 filler metals were evaluated. Soenen and Slaughter found that the BNi-7 alloy was susceptible to sodium corrosion. However, the BNi-7 alloy would provide a corrosion benchmark for the other filler metal selections. Chemical compositions and brazing temperatures are listed in Table 2. The refractory metal alloy and filler metal combinations are listed in Table 3.

Nickel filler metals are not very ductile and are difficult to fabricate into preforms. As a result, the alloys are generally purchased in only rod and powder form. The powder is applied with either an organic binder or adhesive transfer tape. The binder is vaporized during the heating cycle.

A relatively new technology (Ref. 8) has been developed to fabricate thin, ductile AWS BNi foils. The alloys are rapidly quenched to form an amorphous ribbon. The glassy structure, referred to as a metallic glass, is easily preformed for complex joint designs. The ribbons are also 100% dense; this significantly reduces joint shrinkage and porosity as compared to the less dense powder alloy mixtures. Braze contamination is also minimized since no organic binders are needed.

The test filler metals were purchased in several forms. The BNi-5 alloy came as a metal powder on an adhesive transfer tape. A powder-binder mixture was used for the BNi-7 alloy. The BNi-3 and modified BNi-5 alloys were 0.05 mm (0.002 in.) thick metallic glass foils.

Sample Preparation, Brazing Apparatus and Procedure

Refractory metal sheet specimens, with a thickness of 1.5 to 2.0 mm (0.06 – 0.08 in.) and a joining surface of 100 mm^2 (0.16 in.^{2}), were used for the brazing evaluation. Sample preparation involved abrading the bond surface with a 280 grit abrasive paper, followed by a 400 grit pass. The surfaces were then cleaned with acetone and blown dry. The Type 304L stainless steel substrates were prepared in a similar manner.

Preparation of the metallic glass filler metals (BNi-3 and modified BNi-5) was relatively simple. The foils were cut into square preforms, each 16× 16 mm (0.63 × 0.63 in.). The size guaranteed complete coverage of the bond surface. The foils were also cleaned in acetone before stacking the braze assembly.

The powder-plastic binder filler material (BNi-7) was mixed to a volumetric ratio of three parts binder to two parts metal powder. The volatile nature of the organic binder required the use of the mixture within a relatively short time after its preparation. The paste was applied to the Type 304L stainless steel surface, and the refractory metal was placed on top of the filler metal.

The adhesive transfer tape (BNi-5) was prepared similar to the foil alloys. A 16 × 16 mm (0.63 × 0.63 in.) preform was cut from the adhesive roll. The preform was then pressed onto the Type 304L stainless steel surface, and the protective layer on the preform was removed before brazing.

A high frequency induction power supply was used to heat the samples. The

Table 3—Refractory Metal Alloy and Filler Metal Combinations

Refractory metal alloy	BNi-3 (metallic glass)	AWS BNi Filler Metals BNi-5 (metal powder)	AWS BNi Filler Metals Modified BNi-5 (metallic glass)	BNi-7 (metal powder)
Ta-10W	X		X	X
T-111			X	X
Mo	X	X	X	
W	X	X	X	
Mo-13Re		X	X	
Mo-26Re		X	X	
Mo-41Re	X	X	X	
W-26Re		X	X	
Re(CVD)	X	X	X	
Re(Wrought)		X	X	
Re-5W(CVD)		X	X	
TZM	X	X	X	

Table 2—Commercial AWS BNi (Nickel) Filler Metals for Sodium Compatibility Evaluation

AWS classification	Alloy form	Nominal chemical composition, %	Brazing temperature, K (°F)
BNi-3	Metallic glass (0.05 mm foil)	4.5 Si, 3.2 B, bal. Ni	1340 (1950)
Modified BNi-5	Metallic glass (0.05 mm foil)	19 Cr, 7.3 Si, 1.5 B, bal. Ni	1450 (2150)
BNi-5	Metal powder (adhesive transfer tape)	19 Cr, 10 Si, bal. Ni	1355-1410 (1980-2075)
BNi-7	Metal powder (powder/binder)	14 Cr, 10 P bal. Ni	1255-1340 (1800-1950)

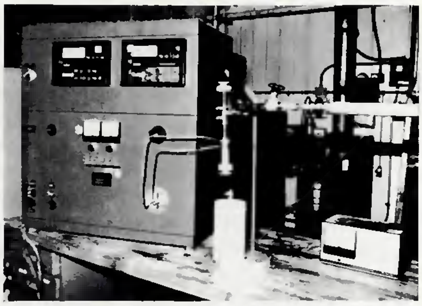

Fig. 2 – Apparatus for induction brazing under vacuum

brazing station is shown in Fig. 2. The vacuum chamber consisted of an open-ended, quartz tube with brass O-ring caps for sealing. The tube had a working vacuum of 1.33×10^{-3} Pa (10^{-5} torr) and was pumped down with a turbomolecular pump backed by a roughing pump. Its leak rate was less than 0.67 Pa/h (5 μm/h) when isolated from the pumping system.

Each brazing sample was placed on an alumina stage and positioned in the center of the quartz tube. The sample was heated with a four turn, 51 mm (2 in.) diameter, copper induction coil. Power supply settings of 250 dc milliamperes (grid) and 0.6 dc amperes (A) (plate) were used for each braze. Obtaining a uniform brazing temperature across the refractory metal-Type 304L stainless steel interface and observing flow of the liquid filler metal were mainly used to determine brazing times. The induction power was turned off approximately 10 seconds (s) after the above temperature and flow conditions were reached. The short brazing times prevented the formation of brittle intermetallics along the braze interface. Brazing temperatures were also near the recrystallization temperature of the Ta-10W, T-111, and Mo samples; consequently, time-at-temperature was kept to a minimum.

Temperatures were measured with an optical pyrometer and were generally 1350 K ± 25 K (1970°F ± 45°F) at the brazing temperature. Fogging of the quartz tube during the bake-out of the organic products of the powder-binder and powder-adhesive tape alloys made temperature monitoring especially difficult. As a result, the temperature readings were used only as a brazing estimate.

Uniform temperature profile across the base metals and flow of the filler metal, which were determined visually, were the key prerequisites for a satisfactory brazing cycle. Total brazing times, including heat up, varied from 75 to 90 s. Helium gas was back-filled into the chamber shortly after the power was turned off to facilitate cooling of the brazed sample. Each filler metal and refractory metal alloy combination was replicated twice.

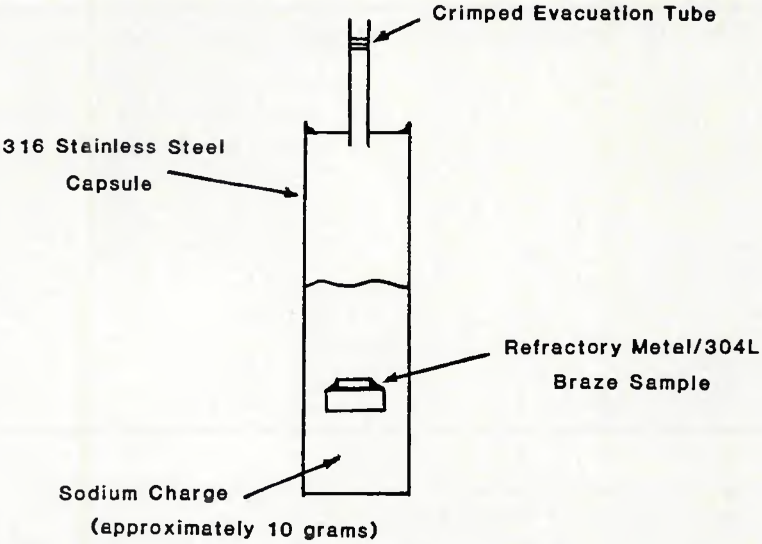

Fig. 3 – Low temperature, sodium corrosion test capsule

As-Brazed and Sodium Compatibility Analysis of the Braze Joints

The as-brazed samples were sectioned into three parts prior to evaluating their structure and sodium compatibility. One piece was used to metallographically evaluate the as-brazed sample. The other two pieces were available for subsequent sodium exposure. Knoop microhardness profiles (0.2 kilogram load, 15 s) were taken across the as-brazed joints and were compared to similar profiles taken after the liquid sodium tests.

Each low temperature, sodium exposed sample was preweighed on a Gram-atic balance before loading it into its sodium test capsule. The capsules were fabricated from 25.4 mm (1.0 in.) diameter × 1.7 mm (0.067 in.) wall, Type 316 stainless steel tubing – Fig. 3. Approximately 10 grams (g) of liquid sodium were poured into each capsule. After the sodium solidified, a brazed sample was dropped into the capsule. A Type 316 stainless steel cap was then fitted over the open end of the capsule and gas tungsten arc (GTA) welded hermetically around its edge. The loaded capsule was evacuated through a 3.2 mm (0.125 in.) diameter stainless steel tube that was part of the cap assembly. The capsule was then sealed with a pinch-and-resistance weld. The loading and welding procedures were done in a glove box under an argon atmosphere.

The loaded test capsules were placed into oxidation resistant heat treating envelopes. The envelopes were crimped, loaded on a tray, and placed in an air furnace. A static, sodium test of 1073 K (1472°F) for 130 h with 2 ppm or 100 ppm oxygen concentration was then done. After completing the sodium test, the samples were recovered and thoroughly cleaned with isopropyl alcohol. They were weighed and compared to the pretest weights to determine if there were any significant weight changes.

The samples were also metallographically examined for corrosive attack. Microhardness profiles were taken across the braze to note hardness changes due to sodium or temperature exposure. The results of these tests were used to determine the filler metals and braze joints for the high temperature, sodium compatibility test.

Results and Materials Evaluation

Table 4 lists the as-brazed microhardnesses and metallographic results for the various refractory metal alloy-filler metal-Type 304L stainless steel brazing combinations. The static sodium results are given in Table 5 for the 1073 K (1472°F)-130 h-2 ppm oxygen concentration exposure, and in Table 6 for the 1073 K (1472°F)-130 h-100 ppm oxygen concentration exposure. There were no significant differences observed for the 2 and 100 ppm oxygen levels.

The metallic glass alloys (BNi-3 and modified BNi-5) gave the best as-brazed structures. Excellent wetting and flow of the filler metal with minimal porosity in the braze were observed – Figs. 4A-4B. The TZM-modified BNi-5-Type 304L stainless steel braze was the exception. Cracks and braze separation along the modified BNi-5/TZM interface were severe – Fig. 4C. The difficulty in brazing TZM was not unexpected since the titanium and zirconium additives in the alloy would readily form oxides on the TZM surface. The BNi-3 alloy did not have a cracking problem, but some porosity was found in the TZM-BNi-3-Type 304L stainless steel braze.

The powder-binder mixtures (BNi-5

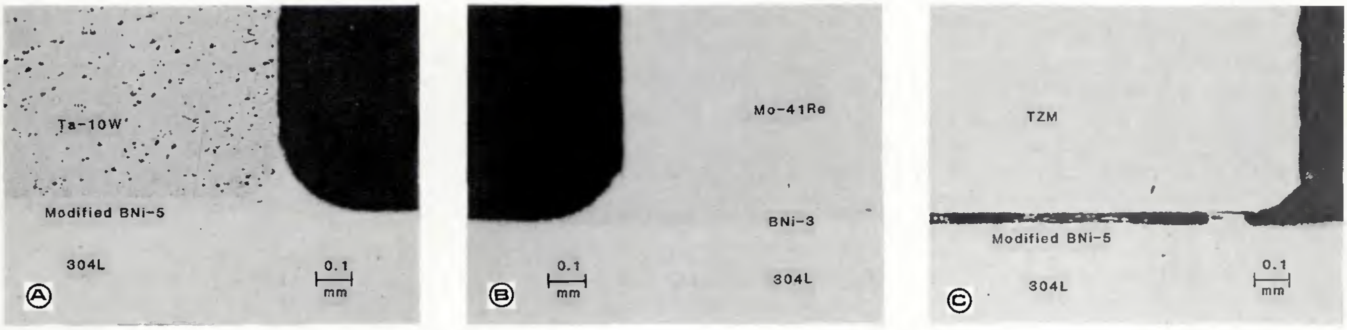

Fig. 4—As-brazed microstructures of the metallic glass, filler metals: A—Ta-10W-modified BNi-5-Type 304L stainless steel; B—Mo-41Re-BNi-3-Type 304L stainless steel; C—TZM/modified BNi-5-Type 304L stainless steel

and BNi-7) did not provide particularly good braze joints. Significant porosity and cracks were observed in the filler metal portion of the braze. Representative structures are shown in Fig. 5. It was not surprising to find porosity, since the filler metal was not 100% dense. After the binder was vaporized, the remaining metal powder layer was approximately 50–60% dense. As a result, porosity and large voids were formed in the braze and could not be completely removed before the filler metal solidified.

The as-brazed microhardness values

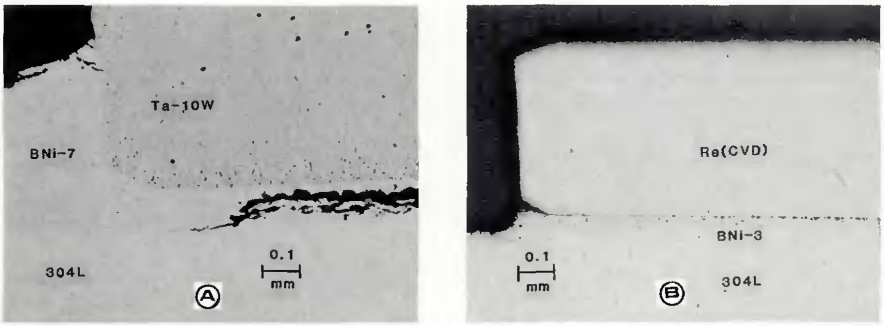

Fig. 5—As-brazed microstructures of the metal powder filler metals: A—Ta-10W-BNi-7-Type 304L stainless steel; B—Re-5W(CVD)-BNi-5-Type 304L stainless steel

Table 4—Knoop Microhardness[a] and Metallographic Observations for the As-Brazed Refractory Metal-Type 304L Stainless Steel Braze Samples

		Microhardness			
Refractory metal	Filler metal	Refractory metal	Filler metal	304L	Metallographic remarks
Ta-10W	BNi-3	266 ± 12	690 ± 27	199 ± 7	Flow and wetting by filler metal.
Ta-10W	Modified BNi-5	276 ± 18	704 ± 30	207 ± 2	Flow and wetting by filler metal.
Ta-10W	BNi-7	264 ± 16	605 ± 20	194 ± 6	Cracks and porosity in the braze.
T-111	Modified BNi-5	264 ± 10	613 ± 9	197 ± 17	Flow and wetting by filler metal.
T-111	BNi-7	254 ± 8	586 ± 4	187 ± 8	Porosity in the braze.
Mo	BNi-3	278 ± 9	645 ± 31	195 ± 7	Flow and wetting by filler metal.
Mo	Modified BNi-5	263 ± 10	643 ± 25	193 ± 7	Flow and wetting by filler metal.
Mo	BNi-5	263 ± 17	594 ± 16	190 ± 11	Porosity in the braze.
W	BNi-3	544 ± 19	634 ± 23	209 ± 9	Flow and wetting by filler metal; cracks in W.
W	Modified BNi-5	568 ± 20	636 ± 30	204 ± 6	Flow and wetting by filler metal; cracks in W.
W	BNi-5		Braze failure		Separation of braze at W interface.
Mo-13Re	Modified BNi-5	298 ± 17	587 ± 50	197 ± 14	Flow and wetting by filler metal.
Mo-13Re	BNi-5	314 ± 30	610 ± 50	199 ± 8	Porosity in the braze.
Mo-26Re	Modified BNi-5	320 ± 45	645 ± 49	201 ± 11	Some porosity; flow and wetting of filler metal.
Mo-26Re	BNi-5	312 ± 40	576 ± 59	194 ± 14	Porosity in the braze.
Mo-41Re	BNi-3	375 ± 33	632 ± 37	188 ± 6	Flow and wetting of filler metal.
Mo-41Re	Modified BNi-5	358 ± 45	631 ± 12	196 ± 7	Flow and wetting of filler metal.
Mo-41Re	BNi-5	401 ± 42	539 ± 47	190 ± 5	Porosity and cracks in the braze.
W-26Re	Modified BNi-5	652 ± 35	646 ± 11	198 ± 4	Flow and wetting of filler metal.
W-26Re	BNi-5	687 ± 8	514 ± 28	191 ± 5	Porosity, cracks and filler separation at the W-26Re interface.
Re(CVD)	BNi-3	260 ± 15	751 ± 40	176 ± 10	Flow and wetting of filler metal.
Re(CVD)	Modified BNi-5	229 ± 25	643 ± 8	172 ± 4	Flow and wetting of filler metal.
Re(CVD)	BNi-5	251 ± 34	598 ± 55	176 ± 8	Porosity in the braze.
Re(Wrought)	Modified BNi-5	289 ± 20	685 ± 25	188 ± 10	Flow and wetting of filler metal; corner of Re cracked.
Re(Wrought)	BNi-5	335 ± 35	622 ± 50	193 ± 10	Porosity and cracks at Re interface.
Re-5W(CVD)	Modified BNi-5	273 ± 21	652 ± 15	185 ± 4	Flow and wetting of filler metal.
Re-5W(CVD)	BNi-5	258 ± 18	592 ± 48	178 ± 19	Porosity in braze.
TZM	BNi-3	352 ± 30	658 ± 37	205 ± 8	Some porosity; flow and wetting of filler metal.
TZM	Modified BNi-5	298 ± 51	582 ± 60	189 ± 18	Separation at filler metal-TZM interface.
TZM	BNi-5	317 ± 52	550 ± 40	202 ± 6	Porosity in braze.

(a) 0.2 kilogram load, 15 seconds (s).

for the filler metal generally ranged from 600 to 650 Knoop. These values were somewhat higher than the 450-500 Knoop hardness readings that are normally obtained for a furnace braze at longer brazing times. The difference was attributed to the shorter brazing times which were used and which would limit diffusion of the filler metal constituents into the base metals.

There were no significant weight changes measured after the 1073 K (1472°F)-130 h static sodium tests (2 ppm and 100 ppm oxygen concentration in the sodium). The 2 ppm oxygen in sodium tests resulted in weight losses of 0—0.05% for the Ta-10W-Type 304L stainless steel brazes and 0.15% for the T-111-Type 304L stainless steel brazes. Negligible changes were recorded for the remainder of the refractory metal alloy-Type 304L stainless steel samples. For sodium containing 100 ppm oxygen, minor weight gains of approximately 0.10% were observed for the majority of the braze combinations. The T-111 samples exhibited the smallest weight gains.

Metallographic analysis of the sodium exposed, metal powder brazes showed crack growth in the BNi-5 and BNi-7 filler metal portion of the brazes. Braze separation along the refractory metal alloy/braze interface was also observed—Fig. 6. Fillet braze metal attack by the sodium (2 and 100 ppm oxygen content) was negligible. An average change of 20-40 Knoop in the filler metal hardness was detected after the sodium tests. These minor changes in hardness were attributed to limited diffusion of the braze elements into the refractory metal due to the break at its interface. Based on the poor structural appearance of the metal powder fillers, before and after sodium exposure, the powder-binder BNi-5 and BNi-7 filler metals were not recommended for the high temperature sodium compatibility test fixtures.

The metallic glass brazing foils presented a more interesting analysis. Minor fillet braze metal attack by the sodium, 25 to

Table 5—Knoop Microhardness[(a)], Weight Change %, and Metallographic Observations for the 1073 K (1472°F)-130 Hour-2 ppm Oxygen Sodium Tests

Refractory metal	Filler metal	Microhardness Refractory metal	Filler metal	Type 304L	Weight change Grams	%	Metallographic remarks
Ta-10W	Modified BNi-5	245 ± 2	563 ± 17	221 ± 1	0	0	25 micron fillet attack; some voids in braze.
Ta-10W	BNi-7	251 ± 8	634 ± 50	208 ± 8	−0.0025	−0.05	50 micron fillet attack; some cracks in braze.
T-111	Modified BNi-5	268 ± 2	510 ± 8	207 ± 2	−0.0072	−0.15	25 micron fillet attack; some voids in braze.
T-111	BNi-7	270 ± 3	554 ± 11	218 ± 2	−0.0073	−0.15	Fillet attack and braze separation along the T-111 interface.
Mo	Modified BNi-5	270 ± 12	439 ± 39	193 ± 6	+0.0002	+0.01	Small voids near Mo interface.
Mo	BNi-5	246 ± 45	533 ± 40	186 ± 23	+0.0014	+0.03	Braze separation at Mo interface.
W	Modified BNi-5	536 ± 19	513 ± 26	208 ± 25	+0.0004	−0.01	Some fillet attack; voids in the filler metal; long crack in the tungsten.
W	BNi-5						As-brazed samples failed along the braze on cooling, no sodium evaluation.
Mo-13Re	Modified BNi-5	280 ± 5	479 ± 43	212 ± 5	−0.0005	−0.01	30 micron fillet attack; heavy band of voids along braze and Mo-13Re interface.
Mo-13Re	BNi-5	292 ± 4	604 ± 55	199 ± 5	+0.0019	+0.05	Cracks and braze separation at the Mo-13Re interface.
Mo-26Re	Modified BNi-5	314 ± 36	468 ± 33	221 ± 3	+0.0010	+0.02	Minor fillet attack and voids in the fillet.
Mo-26Re	BNi-5	307 ± 6	545 ± 21	201 ± 4	+0.0009	+0.02	Severe cracking and braze separation at Mo-26Re interface.
Mo-41Re	Modified BNi-5	373 ± 2	480 ± 45	221 ± 11	+0.0003	+0.01	Voids in braze near Mo-41Re.
Mo-41Re	BNi-5	414 ± 30	546 ± 60	185 ± 2	+0.0002	+0.01	Cracks and braze separation near Mo-41Re.
W-26Re	Modified BNi-5	593 ± 8	505 ± 49	221 ± 2	+0.0010	+0.02	25 micron fillet attack; voids in filler metal near W-26Re.
W-26Re	BNi-5	606 ± 2	496 ± 11	175 ± 1	0	0	Cracks and braze separation at W-26Re interface.
Re(CVD)	Modified BNi-5	245 ± 16	485 ± 22	189 ± 10	+0.0019	+0.05	Minor fillet attack; void band in braze.
Re(CVD)	BNi-5	257 ± 26	624 ± 40	182 ± 2	0	0	Cracks and voids in braze.
Re(Wrought)	Modified BNi-5	295 ± 60	554 ± 30	212 ± 18	0	0	30 micron fillet attack; voids in braze near Re.
Re(Wrought)	BNi-5	296 ± 58	582 ± 24	188 ± 2	+0.0004	+0.01	Cracks and separation of braze at Re.
Re-5W (CVD)	Modified BNi-5	254 ± 4	541 ± 34	188 ± 4	0	0	Voids in braze along Re-5W-BNi-5 interface.
Re-5W(CVD)	BNi-5	255 ± 5	636 ± 49	195 ± 11	+0.0011	+0.03	Cracks along Re-5W and BNi-5 interface.
TZM	Modified BNi-5	308 ± 60	470 ± 55	174 ± 27	+0.0004	+0.01	Fillet attack; separation at TZM-braze interface.
TZM	BNi-5	294 ± 42	577 ± 57	194 ± 9	0	0	Cracks and voids in braze; cracks in TZM.

(a) 0.2 kilogram load, 15s.

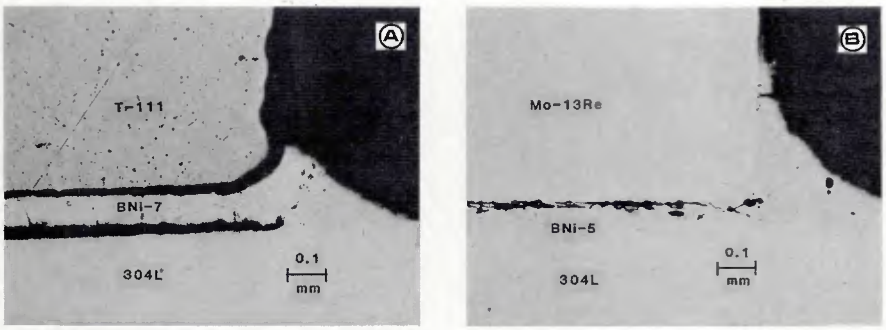

Fig. 6—Sodium exposed (1073 K (1472°F)-130 h-2 ppm oxygen content) microstructures of the metal powder brazes: A—T-111-BNi-7-Type 304L stainless steel; B—Mo-13Re-BNi-5-Type 304L stainless steel

30 microns (approximately 0.001 in.) deep, was observed for the majority of the modified BNi-5 filler metals and was not considered a serious problem for the high temperature tests. However, a band of discontinuous voids was also detected in the braze near the refractory metal alloy interface. The voids were especially pronounced for the Mo and W alloys that were brazed with the modified BNi-5 alloy. Figure 7 shows a representative range of the void concentrations.

Sodium corrosion was not suspected as a cause of the voids, since the weight changes were relatively small compared to the number of voids observed. Transverse cuts were made through a sodium-exposed sample, and the same void pattern was observed in the braze even though it had not come in contact with the sodium. Filler microhardness readings fell by 100–150 Knoop from the as-brazed measurements of 600–700 Knoop. Voids were also found in a Mo-41Re-modified Bni-5-Type 304L stainless

Table 6—Knoop Microhardness[a], Weight Change %, and Metallographic Observations for the 1073 K (1472°F)-130 Hour-100 ppm Oxygen Sodium Tests

Refractory metal	Filler metal	Microhardness: Refractory metal	Microhardness: Filler metal	Microhardness: Type 304L	Weight change: Grams	Weight change: %	Metallographic remarks
Ta-10W	BNi-3	257 ± 3	475 ± 60	217 ± 4	+0.0027	+0.06	Irregular 25 micron fillet attack; some voids at 304L interface.
Ta-10W	Modified BNi-5	255 ± 6	528 ± 43	210 ± 3	+0.0045	+0.09	Small concentration of voids in the braze.
Ta-10W	BNi-7	276 ± 2	577 ± 38	194 ± 5	−0.0003	−0.01	25 micron fillet attack; cracks and braze separation at Ta-10W.
T-111	Modified BNi-5	264 ± 8	498 ± 15	211 ± 2	0	0	Minor fillet attack and void concentration.
T-111	BNi-7	254 ± 11	544 ± 20	209 ± 6	+0.0016	+0.03	Cracks and braze separation.
Mo	Modified BNi-5	284 ± 37	488 ± 32	231 ± 21	+0.0050	+0.09	Minor void concentration in the braze.
Mo	BNi-5	255 ± 23	587 ± 31	204 ± 7	+0.0049	+0.09	Cracks and braze separation.
W	BNi-3	518 ± 17	489 ± 27	233 ± 6	+0.0047	+0.09	Cracks in the W; small voids in filler metal; minor fillet attack.
W	Modified BNi-5	472 ± 44	486 ± 33	282 ± 27	+0.0039	+0.07	Voids in the braze, crack in the W.
W	BNi-5						As-brazed samples failed along the braze on cooling, no sodium evaluation.
Mo-13Re	Modified BNi-5	286 ± 18	465 ± 46	209 ± 3	+0.0047	+0.09	30 micron fillet attack; heavy band of voids in braze.
Mo-13Re	BNi-5	300 ± 4	577 ± 33	225 ± 17	+0.0043	+0.09	Braze cracks and separation; crack in Mo-13Re.
Mo-26Re	Modified BNi-5	295 ± 37	494 ± 42	223 ± 11	+0.0047	+0.09	25 micron fillet attack, voids in braze.
Mo-26Re	BNi-5	330 ± 23	537 ± 39	196 ± 16	+0.0042	+0.08	Fillet cracks and braze separation.
Mo-41Re	BNi-3	351 ± 21	463 ± 31	203 ± 13	+0.0037	+0.08	Voids in braze.
Mo-41Re	Modified BNi-5	331 ± 17	487 ± 44	237 ± 21	+0.0045	+0.09	Voids in braze.
Mo-41Re	BNi-5	395 ± 41	559 ± 18	193 ± 7	+0.0059	+0.10	Braze separation.
W-26Re	Modified BNi-5	575 ± 55	487 ± 40	253 ± 15	−0.0025	−0.05	25 micron fillet attack, braze voids.
W-26Re	BNi-5	632 ± 17	539 ± 45	188 ± 3	+0.0056	+0.10	Braze separation.
Re(CVD)	BNi-3	239 ± 22	476 ± 36	197 ± 5	+0.0035	+0.07	Voids in braze.
Re(CVD)	Modified BNi-5	255 ± 29	536 ± 25	211 ± 15	+0.0050	+0.10	25 micron fillet attack; voids in braze.
Re(CVD)	BNi-5	246 ± 34	590 ± 10	187 ± 20	+0.0048	+0.10	Braze cracks and separation.
Re(Wrought)	Modified BNi-5	299 ± 15	569 ± 31	215 ± 9	+0.0040	+0.07	30 micron fillet attack; some voids.
Re(Wrought)	BNi-5	298 ± 9	591 ± 28	193 ± 7	+0.0056	+0.11	Fillet cracks and braze separation at Re.
Re-5W(CVD)	Modified BNi-5	322 ± 18	525 ± 15	210 ± 15	+0.0059	+0.12	Voids in braze.
Re-5W(CVD)	BNi-5	317 ± 22	631 ± 51	218 ± 7	+0.0048	+0.10	Some braze separation at Re-5W.
TZM	BNi-3	354 ± 17	467 ± 39	210 ± 6	+0.0037	+0.08	Cracks in fillet and TZM; some voids.
TZM	Modified BNi-5	299 ± 33	475 ± 5	203 ± 2	+0.0050	+0.09	Fillet attack and voids in braze; TZM cracks.
TZM	BNi-5	312 ± 30	547 ± 37	200 ± 8	+0.0056	+0.11	Cracks in braze and TZM; braze separation.

[a] 0.2 kilogram load, 15 s.

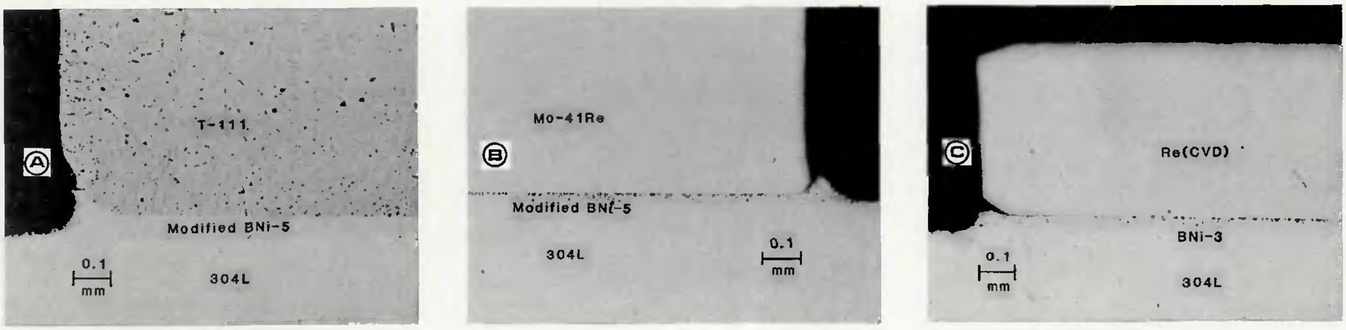

Fig. 7—Sodium exposed (1073 K (1472°F)-130 h-2 and 100 ppm oxygen content) microstructures of the metallic glass brazes: A—T-111-modified BNi-5-Type 304L stainless steel (2 ppm O); B—Mo-41Re-modified BNi-5-Type 304L stainless steel (2 ppm O); C—Re(CVD)-BNi-3-Type 304L stainless steel (100 ppm O)

steel control sample after a 1073 K (1472°F)-130 h-vacuum treatment. These observations were more indicative of a diffusion process.

Elemental profiles for Ni, Cr, Si and B were made for the as-brazed and sodium exposed Mo-41Re-modified BNi-5 foil-Type 304L stainless steel samples. The analyses are shown in Figs. 8 and 9, respectively. The concentrations are only relative intensities, but they do show the general trend of compositional diffusion of Cr and B into the Mo-41Re base metal. The boron was especially mobile. The location of the voids corresponded to this diffusion zone. The diffusion phenomenon is commonly referred to as Kirkendall porosity (Refs. 9, 10).

Kirkendall porosity was not seen as a serious problem for the high temperature sodium compatibility fixtures, since the band of voids did not provide a connected network that would leak. The metallic glass BNi-3 and modified BNi-5 filler metals were, therefore, recommended. The TZM-Type 304L stainless steel joint was the exception. Cracks and braze separation were found in the as-brazed, modified BNi-5 and sodium-exposed BNi-3 brazes.

Prototypic Hardware Brazing

The AWS BNi metallic glass foils that were qualified in the 1073 K (1472°F)-130 h sodium environment were used to fabricate full scale, high temperature UO_2/Na compatibility test fixtures. Collars of Type 304L stainless steel were brazed to 19 mm (0.75 in.) diameter × 1.25 mm (0.05 in.) thick wall refractory metal alloy tubes. Closure welds on the collars were used to seal the tubes after loading them with UO_2 and Na. The loaded tubes were evacuated and back filled with helium before testing.

T-111, Ta-10W, Mo-41Re, Re (CVD), and Re-5W(CVD) were the tube materials chosen for the high temperature tests. The alloys were selected from a concurrent materials study (Ref. 11) that evaluated the influence of temperature, time, and oxygen concentration in the sodium on the mechanical and corrosion integrity of the various refractory metal alloys. Induction brazing under vacuum was used to join Type 304L stainless steel collars to the T-111, Ta-10W and Mo-41Re tubes.

The Re and Re-5W tubes were electron beam (EB) brazed. The technique involved defocusing the beam along the edge of the Type 304L stainless steel collar and melting it (beam focused up, 45 kV, 10 mA, 8 mm/s). The liquid steel then flowed and wetted the refractory metal surface. Induction brazing could also be used on the Re and Re-5W tubes, but the high temperature test schedule necessitated EB brazing before the BNi filler metal brazes were properly qualified in sodium.

A tight joint clearance of 0.025 mm (0.001 in.) was designed for the prebrazed collar-tube assembly. Otherwise, the clearance would become too large at the brazing temperature for effective capillary flow due to the thermal expansion difference between the stainless steel and refractory metal alloy. A two step surface was machined into the collars to accommodate the tight clearance and also provide a reservoir to preplace the brazing foil. Figure 10 shows a schematic of the joint design. Approximately three windings of the 0.05 mm (0.002 in.) thick foil were used.

The collar-tubes were inductively brazed in a 1.33×10^{-3} Pa (10^{-5} torr) vacuum. A high frequency induction power supply set at 0.5 A (dc) grid and

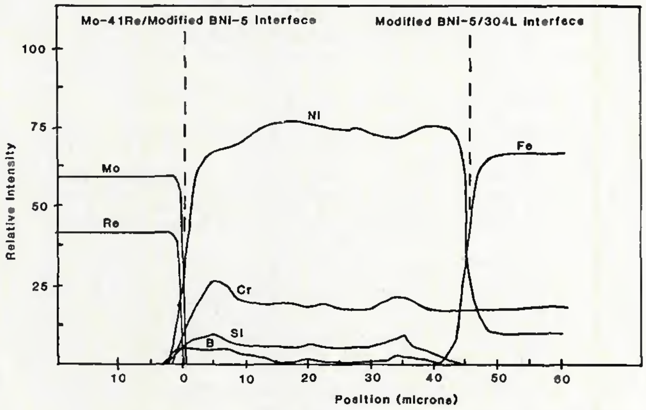

Fig. 8—Compositional profile of an as-brazed, Mo-41Re-modified BNi-5-Type 304L stainless steel sample

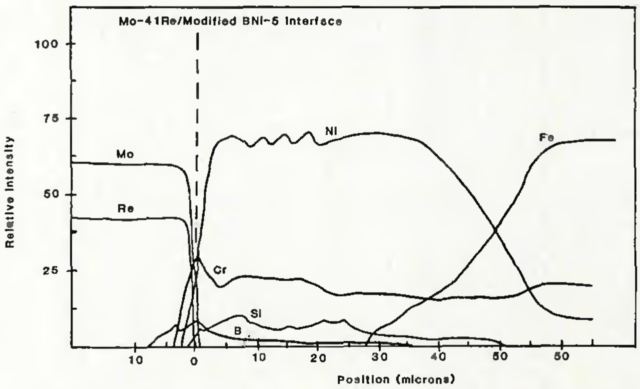

Fig. 9—Compositional profile of a sodium exposed (1073 K (1472°F)-130 h-2 ppm oxygen) Mo-41Re-modified BNi-5-Type 304L stainless steel braze sample

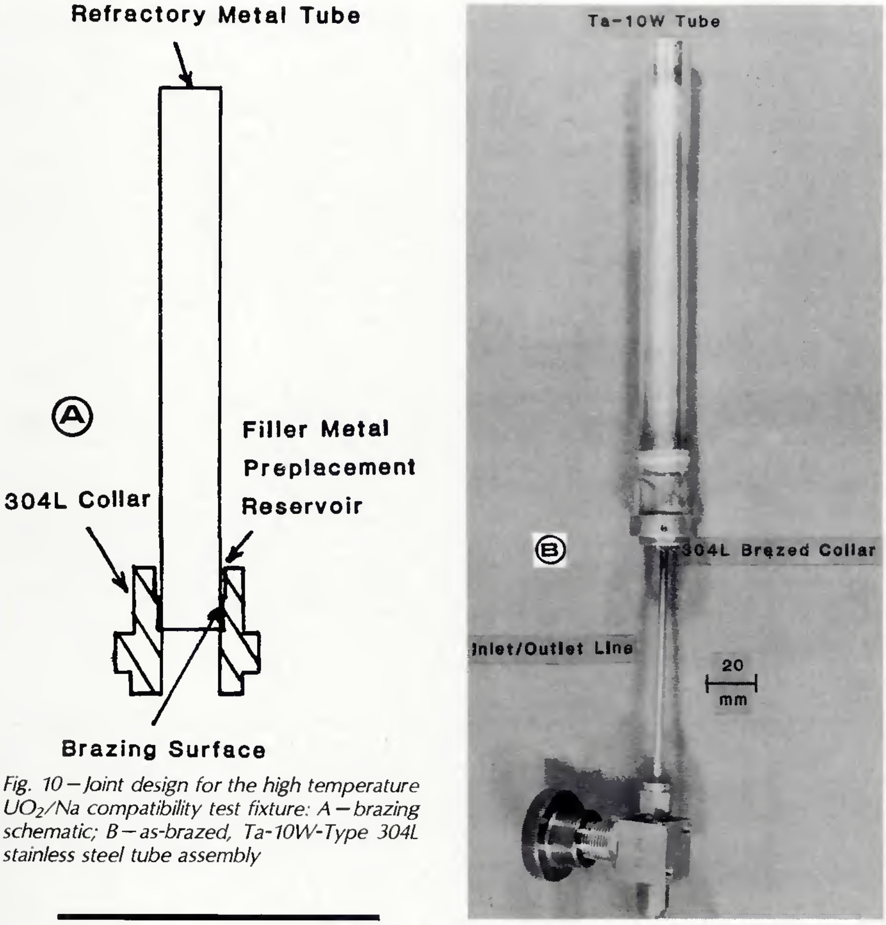

Fig. 10 — Joint design for the high temperature UO_2/Na compatibility test fixture: A — brazing schematic; B — as-brazed, Ta-10W-Type 304L stainless steel tube assembly

1.25 A (dc) plate current was used to heat the assembly. Brazing times, including heat up, were approximately 180 s in duration. The times were primarily based on the condition of liquid filler metal flow and equilibrating the brazing temperature across the refractory metal alloy interface. The brazed assembly was cooled by backfilling the vacuum chamber with helium gas. The T-111 and Ta-10W tubes were brazed with the metallic glass, modified BNi-5 alloy. BNi-3 was used on the Mo-41Re tube.

Two different high temperature UO_2/Na test cycles were run. The first involved loading 40% of the tube with UO_2 debris and 10 g of sodium. The bottom end of the tube was 17.5 mm (0.7 in.) long; it was inductively heated up to 2273 K (3632°F), held there for 1 h; cooled to 1073 K (1472°F) and held there for 2 h; heated to 2273 K (3632°F) and held there for 1 h, etc. Five cycles at the 2273 K (3632°F) plateau were required. The temperature along the 17.5 mm (0.7 in.) zone was isothermal. The remaining length of the tube saw a maximum temperature of 1073 K (1472°F) at its top with a temperature gradient of roughly −55K/mm (−2515°F/in.) from the isothermal zone.

All tube fixtures, except the Mo-41Re tube, survived the 2273 K (3636°F), five cycle test. The braze in the Mo-41Re fixture developed a leak after the entire tube went isothermal during a 2273 K (3632°F) cycle. The braze was not qualified for the higher temperature exposure, and remelting of the braze would be expected under these conditions. Another Mo-41Re/BNi-3 foil/304L fixture was fabricated and UO_2/Na tested without a problem. The test debris was removed from the tubes, and the tubes were sectioned for metallographic analysis. Figures 11 and 12 show representative microstructures.

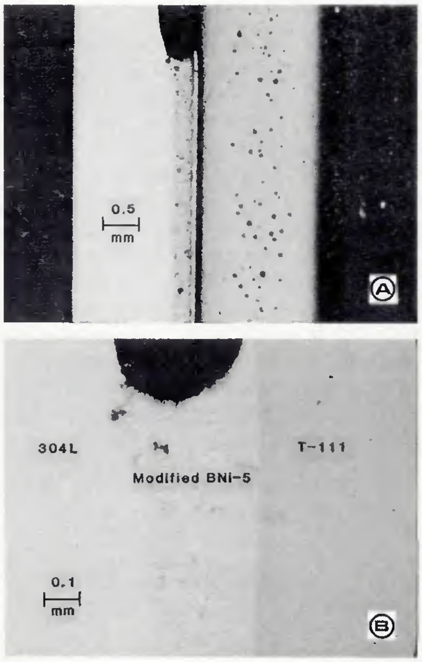

Fig. 11 — Post-test microstructure of a high temperature UO_2-Na compatibility tube joint: (A) and (B) T-111-modified BNi-5-Type 304L stainless steel

A second test was conducted for only the Ta-10W and Mo-41Re alloys. New tubes were loaded with 85 g of UO_2 and 12 g of Na. The test required an 18 h exposure of the tube end to a temperature of 1273 K (1832°F) and 6 h within a temperature range of 1073 K (1472°F) to 1773 K (2732°F). Both tubes survived the second high temperature UO_2/Na tests.

Conclusion

1. AWS powder/binder filler metals BNi-5 and BNi-7 are not recommended for induction brazing refractory metal alloys to Type 304L stainless steel for subsequent exposure to a 1073 K (1472°F)-130 h sodium environment. During testing, cracks and porosity were observed in the as-brazed samples. Crack growth and braze separation at the refractory metal alloy interface were also

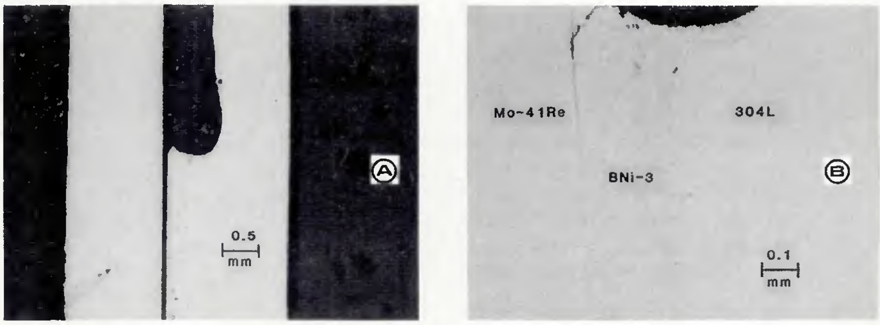

Fig. 12 — Post-test microstructure of a high temperature UO_2/Na compatibility tube joint: (A) and (B) Mo-41Re-BNi-3-Type 304L stainless steel

observed after sodium exposure.

2. AWS metallic glass filler metals BNi-3 and modified BNi-5 are recommended for brazing Mo, Re, Ta and W alloys to Type 304L stainless steel. In general, excellent joints were obtained during tests with the metallic glass fillers. After a 1073 K (1472°F)/130 h sodium exposure, a band of discontinuous voids was formed in the brazes near the refractory metal interface. The void concentration was especially pronounced for the Mo and W alloys that were brazed with the modified BNi-5 filler metal. Voids were attributed to Kirkendall porosity and not sodium corrosion. High temperature UO_2/Na compatibility test fixtures were successfully brazed with these alloys.

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