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Brazing Refractory Metals Used in High-Temperature Nuclear Instrumentation

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***Abstract*—As part of the U. S. Department of Energy (DOE)-sponsored Next Generation Nuclear Project (NGNP) currently ongoing at Idaho National Laboratory (INL), the irradiation performance of candidate high-temperature gas reactor fuels and materials is being evaluated at INL's Advanced Test Reactor (ATR). The design of the first Advanced Gas Reactor (AGR-1) TRISO fuel experiment, currently being irradiated in the ATR, required development of special techniques for brazing niobium and molybdenum. Brazing is one technique used to join refractory metals to each other and to stainless steel alloys. Although brazing processes are well established, it is difficult to braze niobium, molybdenum, and most other refractory metals because they quickly develop adherent oxides when exposed to room-temperature air. Specialized techniques and methods were developed by INL to overcome these obstacles. This paper describes the techniques developed for removing these oxides, as well as the ASME Section IX-qualified braze procedures that were developed as part of the AGR-1 project. All brazes were made using an induction coil with an inert or reducing atmosphere at low pressure. Other parameters, such as filler metals, fluxes used, and general setup procedures, are also discussed.**

***Index Terms*—high-temperature irradiation, induction brazing, refractory metal brazing, stainless steel alloys.**

I. Introduction

As part of the U. S. Department of Energy (DOE)-sponsored Next Generation Nuclear Project (NGNP), Idaho National Laboratory (INL) is currently conducting an experiment series designated the Advanced Gas Reactor (AGR) TRISO fuel experiments to qualify the TRISO fuel irradiation performance for Very High Temperature Reactor (VHTR) applications. The first experiment, AGR-1, began irradiation in the INL Advanced Test Reactor (ATR) in December 2006 [1] and is scheduled for removal in the fourth quarter of 2009. This experiment was designed to test TRISO-coated particle fuel at nominal NGNP operating temperatures of 1200–1250°C.

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The fuel particles were coated with a thermosetting resin and pressed into cylindrical fuel compacts, which were, in turn, placed into graphite holders. Metal sheathed thermocouples and gas lines were inserted into small holes drilled in the graphite holders.

The materials originally proposed for the thermocouple sheaths and gas lines were austenitic stainless steels (SST) or nickel alloys (Inconel alloys). However, it was determined that at high temperatures, transition metals such as iron, chromium, or nickel could form carbides with the potential of attacking the silicon carbide (SiC) layer in the TRISO-coated particles. Thus, the decision was made to use only refractory metals, such as niobium and molybdenum, because they do not produce the same types of deleterious interactions with the SiC fuel coating in the high-temperature regions of the capsule. Niobium tubing was used for the gas lines and molybdenum was used for the support structures. Also, the INL-developed High-Temperature Irradiation-Resistant ThermoCouples (HTIR-TCs) sheathed with a niobium alloy were used in the highest temperature regions of the AGR-1 experiment [2], [3]. The joining and sealing of these materials was critical to the success of the AGR-1 experiment.

As is typical for most ATR instrumented experiments, several pressure bulkheads are part of the AGR-1 design. These bulkheads are penetrated by the thermocouple sheaths and temperature control gas lines, as well as structural elements, and a seal must be effected between the bulkhead and the leads/structural elements passing through. In the AGR-1 experiment, these bulkheads were 35 mm in diameter, 7–8 mm thick, and composed of 316 grade stainless steel. The leads and structural elements were 1.5 mm and 6.4 mm in diameter, respectively.

Because of the dissimilarity of the metals, brazing appeared to be the only practical method of creating a seal between the bulkheads and the leads/structural elements. Typically, brazes within ATR experiments are qualified to a national standard. Therefore, ASME Section IX [4] was selected as the standard to be used for the AGR-1 experiment. Section IX has two criteria: (1) strength of the brazed joint must be at least equal to the minimum published strength of the base metal (as demonstrated by pull testing), and (2) the procedure must produce a joint with 80% fill. The procedures developed for the AGR-1 experiment met both of these criteria.

II. Discussion

A. Filler Metal and Braze Temperature

Nearly all recent ATR experiments requiring brazing utilize the gold-nickel eutectic consisting of 82% gold and 18% nickel, and designated BAu-4 by the American Welding Society (AWS). The gold-nickel eutectic is not mentioned prominently by standard brazing handbooks as a filler metal for refractory metals, probably because most applications involving the refractory metals are for high-temperature applications and require high-temperature strength. The bulkheads in typical ATR experiments are not normally subject to temperatures above 500°C; AWS BAu-4 retains a great deal of strength at this temperature and worked well for this experiment.

Due to its eutectic properties, the AWS BAu-4 filler alloy exhibits distinct flow characteristics when the melt point is reached (949°C). All brazes were performed visually and without temperature instrumentation. Power to the induction coil was cutoff within 15 seconds of when visible flow of the gold alloy occurred.

B. Oxide Removal

Initial brazing tests between SST and niobium produced mixed results with limited wetting between niobium and the AWS BAu-4 filler metal. Pull-through to the under side of the bulkhead was non-existent. It was hypothesized that the oxide film was preventing good wetting, although this is not mentioned as an impediment by standard handbooks [5], [6]. A pickling solution consisting of 35% HNO_3, 5% HF, and 60% H_2O has been found useful for removing oxides prior to brazing titanium [7], and this solution was used to clean the niobium leads prior to brazing as well.

This solution produced a marked improvement in wetting, and pull-through to the back side of the bulkhead was visible (see Fig. 1 and Fig. 2). However, results were still not reliably reproducible. Very good wetting is required to simultaneously produce multiple fillets across a bulkhead approximately 35 mm in diameter. Also, since hydrofluoric acid poses serious health hazards, special handling methods and precautions were required, making this method of cleaning the surface difficult to use in practice.

The best practical method for removing the oxide layer just before brazing was by electrolytic dissolution (see Fig. 3). This was done by covering a carbon electrode with a piece of knit cotton fabric soaked in a solution of 7.5% H_2SO_4, 15.5% $(NH_4)_2SO_4$, and 77% H_2O (percent by weight). This solution is sold as LDC Activator No. 1 by Liquid Development Company, of Cleveland, OH. A voltage of 6–15 volts was then applied. The tool was connected to the positive lead, while the item being cleaned was connected to the negative lead.

The cleaned surface needed to be brazed as soon as possible after cleaning, preferably within 1 hour, to avoid re-oxidation.

C. Atmosphere During Brazing

Brazing was conducted in a tempered glass tube heated by a high-frequency induction coil (see Fig. 4) using different inert gas environments.. Several test brazes were made using a reducing environment (Argon + 2% H_2), and brazes of good appearance were achieved. However, because niobium is known to embrittle in a hydrogen atmosphere, this variation was not pursued further. The best results were achieved with an atmosphere consisting of ultra-high purity argon gas (99.999%, <1 ppm H_2O, <1 ppm O_2).

D. Flux

Although brazing without flux in an inert environment is theoretically possible, the addition of flux was found to be helpful in achieving good wetting and filler metal flow. Several high-temperature fluxes were used, but a proprietary formulation called "*Handy Flux Hi-Temp Boron Modified*," from Lucas Milhaupt, of Cudahy, WI, was found to be superior for this application.

E. Joint Clearance

Typical to most brazing applications, a snug joint clearance was found to promote filler metal pull-through. Joint clearances of 0.025 to 0.075 mm were used on all of the AGR-1 bulkheads.

III. Conclusion

The design of the first Advanced Gas Reactor (AGR-1) fuel experiment, currently being irradiated in the ATR, required the development of special techniques for brazing refractory metals to stainless steel alloys (see Fig. 5). The key impediment to joining these metals is surface-adherent refractory oxides that must be removed before brazing. The most practical method of accomplishing this was by electrolytic dissolution using an ammonium sulfate and sulfuric acid solution with an applied voltage of 6-15 volts. After the oxide layer was removed, it was necessary to perform the brazing step quickly in a very high purity argon gas environment to prevent the cleaned surfaces from reoxidizing.

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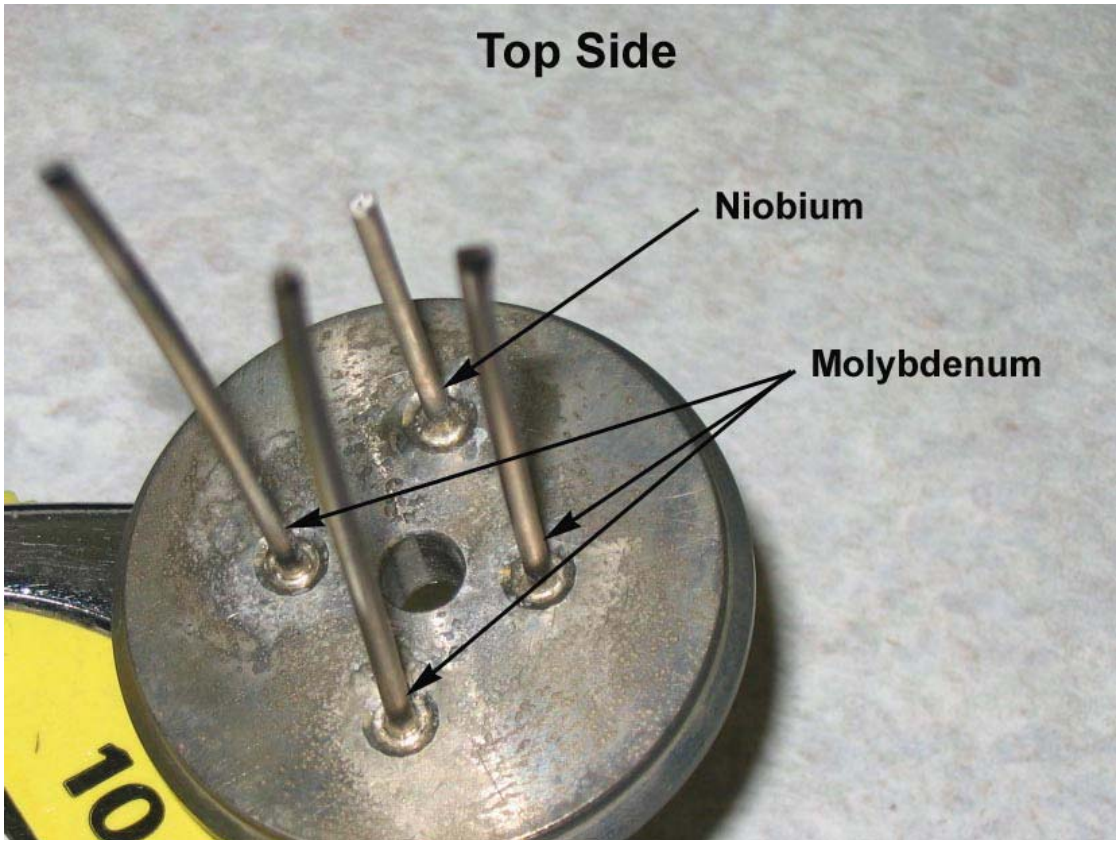

Fig. 1. Initial braze test (top side) using nitric-hydrofluoric acid to remove oxides. Refractory leads were pickled for 90 seconds in acid, followed by a demineralized water rinse, and air dried.

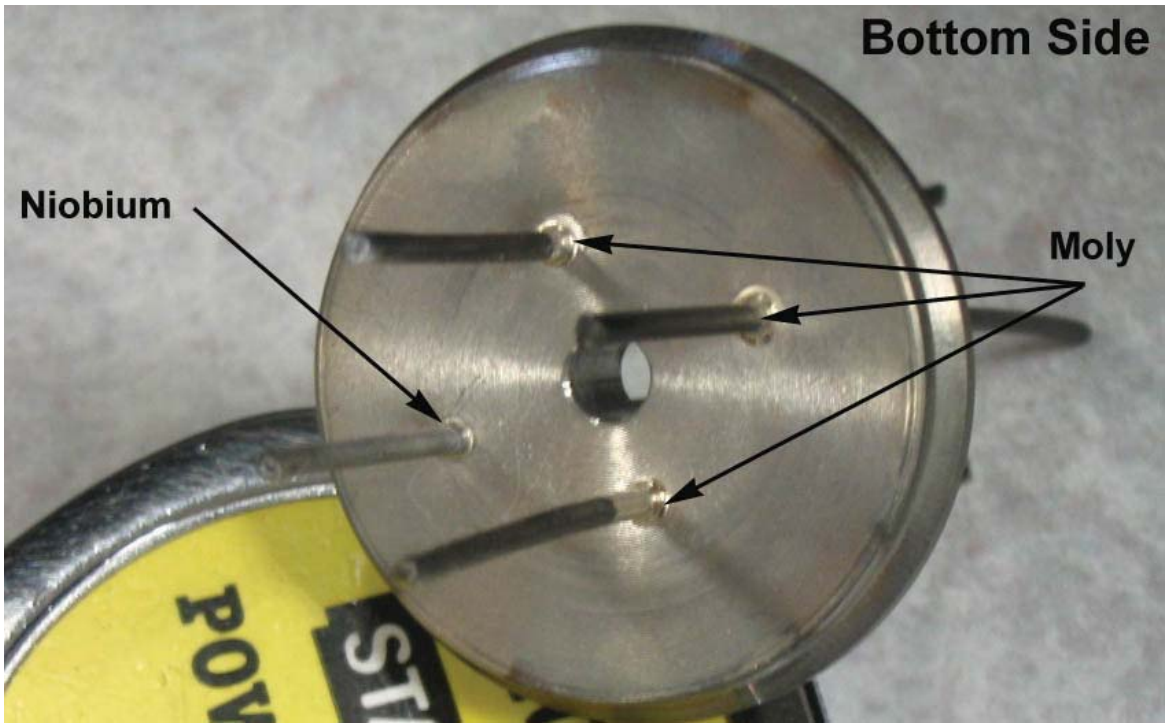

Fig. 2. Initial braze test (bottom side) using nitric-hydrofluoric acid.

Fig. 3. Cleaning of surface of refractory lead to be brazed. Tool on the right consists of a graphite-tipped electrode covered with a cotton sock that had been soaked in sulfuric acid/ammonium sulfate solution. The refractory metal surface was scrubbed until the sock wiped clean.

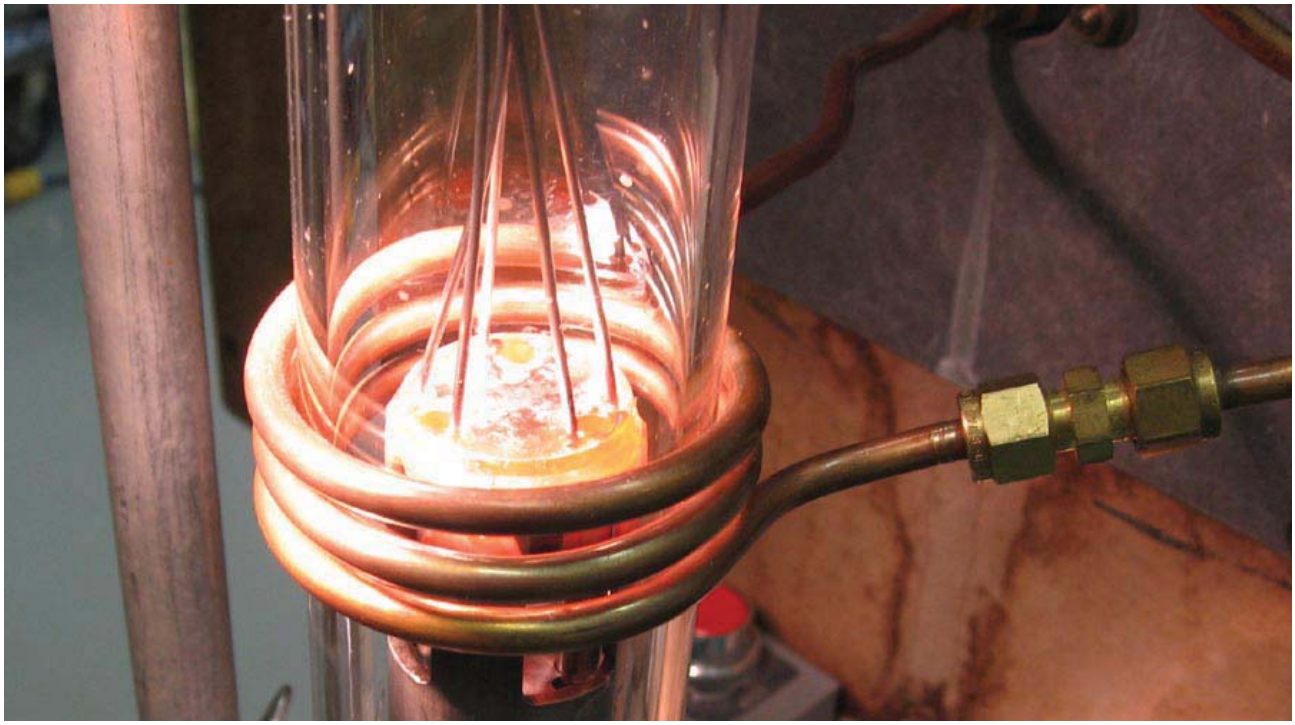

Figure 4. Typical AGR-1 bulkhead being induction brazed inside glass chamber filled with argon. Niobium leads can be seen coming out of the top. Molybdenum structural elements are hidden below.

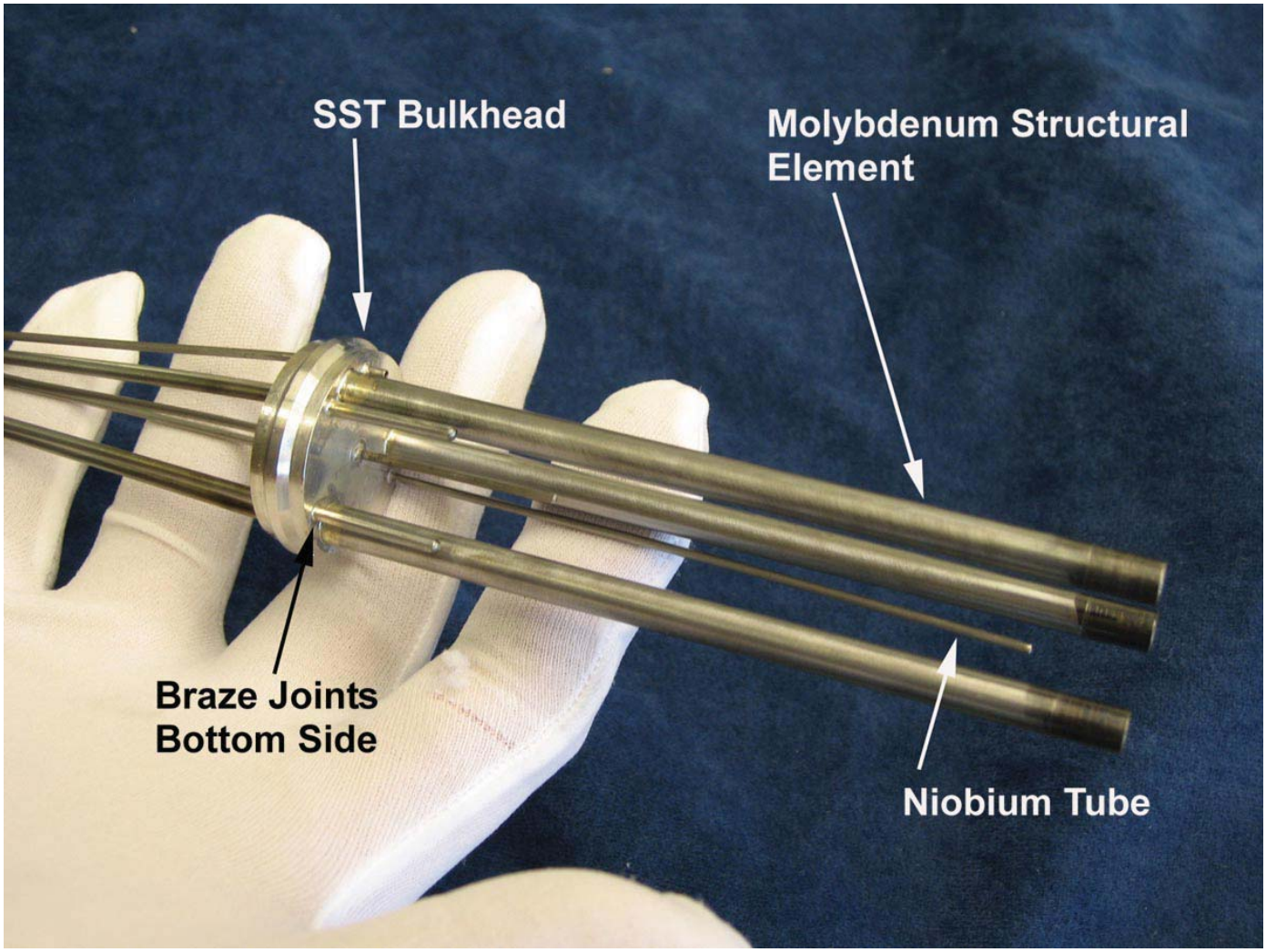

Figure 5. Completed bulkhead ready for incorporation into the AGR-1 experiment.