The fabrication of switches and other high-voltage components often requires joining metal contacts to nonmetallic insulator materials such as ceramics. Brazing is the logical, and sometimes only, joining method available to the manufacturer due to high production volumes, material property differences, and joint performance requirements. While other high-temperature joining methods such as diffusion bonding, transient liquid phase bonding, or variants thereof have been used successfully to braze metals to nonmetals, furnace brazing processes have become the industry standard for large- and small-scale production processes. Prior to the brazing process, in many cases the nonmetal component is metalized using a molybdenum-manganese/nickel plating process (Refs. 1, 2) to promote proper wetting by the brazing filler metal. The subsequent brazing operation is performed in a manner similar to a standard metal-metal braze process. Alternative ceramic metallization methods have been proven to perform similarly (Ref. 3).

In the more recent past, however, brazing processes have been developed that allow a metal to be joined to a nonmetal without prior metalization. These brazing processes have progressed from the use of metal-hydride powders applied directly to the nonmetal faying surfaces and clad metallic strips with an “active” element layer, such as titanium, to alloys with active elements available in powder, paste, or sheet form (Refs. 4, 5). Another method for joining metals to nonmetals, known simply as direct brazing, can be made using conventional filler materials. Although useful in limited cases, the direct brazing process takes advantage of a substrate metal’s limited solubility in liquid braze filler metal and oxide stability to react with the nonmetal substrate, without the need for metalization or expensive active braze filler metals (Ref. 6).

**Background.** In specific applications, niobium metal is joined to single crystal alumina (sapphire) or polycrystalline alumina ceramic. Because niobium metal has limited solubility in many high-temperature braze filler materials, such as copper, gold, nickel, etc., and forms relatively stable oxides, it is well suited for use in direct brazing operations. The very similar coefficients of thermal expansion (CTE) of sapphire and niobium result in minimized residual stress in brazed components. Additionally, hermetically sealed, long-life components can be made reliably without the use of more expensive active braze filler metals. These traits, as well as the lack of formation of brittle intermetallic phases with alumina ceramic or sapphire, make niobium an attractive candidate for direct brazing.

**Direct Brazing.** Direct brazing of niobium to alumina ceramic and sapphire has been successfully demonstrated as a manufacturing process for high-reliability components such as high-voltage switches and hermetically sealed packages (Ref. 7). The choice of metal-ceramic brazing method, brazing filler metal, atmosphere, temperature, etc., can result in a broad range of observed strengths for tensile test samples. ASTM-F19 tensile samples (Ref. 8) made from 94% alumina and brazed to Fe-29Ni-10Co interlayers showed strengths ranging from 76 to 147 MPa (11–21.3 ksi) (Ref. 9). While some of these
differences can be explained by variations in the physical and mechanical properties of the braze filler metals or atmospheres used in the joining environment, the tensile strength of direct-brazed metal-nonmetal samples is consistently lower than other brazing methods when using commonly used temperature profiles. For the same brazing filler metals, Stephens et al. (Ref. 7) reported strengths 50% lower for tensile samples that were direct-brazed compared to those that had been metalized using the moly-manganese/nickel plating process, even though no notable differences in joint hermeticity were observed.

A literature search on niobium-ceramic or niobium-sapphire brazing reveals that while not exhaustively studied, the joining of ceramic or sapphire to itself using niobium alone or in combination with other filler metals by brazing, diffusion bonding, and other liquid and partially liquid processes is well documented (Refs. 10, 11). Marks et al. reported alumina four-point bend specimen strengths exceeding 240 MPa when specific sample preparation and processing conditions were followed (Ref. 10). This literature also reveals that the research laboratory joining methods, fixturing means, vacuum levels, temperature cycles, and equipment necessary to achieve the high strengths are not always practical or obtainable when the manufacturer is limited to industrial furnace equipment and standard brazing processes. Recognizing this, an effort has been made to incorporate some of the more readily achieved differences in processing with the goal of increasing the tensile strengths of direct-brazed niobium-sapphire assemblies, without affecting the joint hermeticity.

**Experimental Procedure**

Due to the inability to easily fabricate sapphire tensile buttons, niobium-sapphire assemblies were fabricated using niobium tensile buttons machined to ASTM-F19 ceramic tensile button dimensions. After an initial comparison of sapphire interlayer thicknesses of 0.25 and 0.41 mm (0.010 and 0.016 in.) and finding no statistical differences in strength or hermeticity, the thicker material was chosen for the remaining brazed samples (0.016 in. thick). The sapphire washers were cut 30 deg off the C-axis in what is known as the random orientation, a less-expensive crystal orientation that typically yields the most products from a sapphire boule or ingot.

The ASTM-F19 94% alumina ceramic tensile specimens were brazed using standard 0.25-mm- (0.010-in.-) thick niobium interlayers in the typical configuration. The brazing atmosphere used for all samples was ultrahigh vacuum, approximately 1.0E-07 torr at peak brazing temperature. The sample preparation, testing, and metallography techniques used for brazing with BAu-3 braze filler metal were followed for the active filler metal brazed samples, with the exception of the processing temperatures, which were adjusted for the differences in liquidus and solidus temperatures. The thermal cycle used was a typical ramp of 15°C/min to 25°C below the solidus temperature of the braze filler metal, allowed to equilibrate for 15 min, then proceed at 10°C/min to a...
temperature 30°C above the liquidus temperature of the braze filler metal and soaked for 2 min before cooling. The cooling profile was 25°C/min to a temperature 25°C below the braze filler metal solidus temperature, at which time the ramp was changed to 10°C/min for the remainder of the cycle. The solidus and liquidus temperatures of the brazing filler metals used are displayed in Table 1.

Completed tensile button assemblies were leak checked using a Pfeiffer Qualytest™ HT 265 helium mass spectrometer leak detector. A representative whole and fractured 94% alumina tensile button is shown in Fig. 1. Assemblies with leak rates lower than 1.0 E–10 atm-cc/s were determined to have no detectable leak. Once leak checked, the tensile buttons were tensile tested using a 22 kip MTS Servohydraulic test frame at a crosshead speed of 8.3E–06 m/s (3.3E–04 in./s). The tensile strength was determined using the cross-sectional area of the tensile button-niobium interlayer brazement area, 1.11E–04 m² (1.80E–01 in.²). The brazing thermal cycle, helium leak test, and tensile test procedures followed were the same as used for the alumina ceramic tensile button assemblies. Additional niobium-sapphire samples for metallographic analysis were made by brazing 0.41-mm-(0.016-in.-) thick sapphire washers to 0.25-mm-(0.010-in.-) thick niobium interlayer washers using 0.051- and 0.076-mm-(0.002- and 0.003-in.-) thick BAu-3 braze filler metal preforms. Following the brazing operation, the niobium-sapphire samples were cross sectioned and analyzed. An image showing the center portion of a niobium tensile button assembly is shown in Fig. 2. Undamaged portions of the brazed niobium-alumina tensile button assemblies were utilized for further analysis using the SEM. All of the SEM samples were encapsulated prior to cross sectioning and polishing.

Results and Analysis

Displayed in Table 2 are the series of eight experimental furnace cycles performed on sapphire and 94% alumina tensile buttons and one, number 9, from a previous effort in 2005. Following the fabrication, testing, and evaluation of the first three series of samples (niobium tensile buttons with sapphire interlayers), it was determined to perform a series of runs using 94% alumina tensile buttons to determine if the process space had shifted from work performed previously. This concern was primarily due to the low average tensile strengths obtained using the conventional braze filler metal, BAu-3 (34.7 MPa), and two active filler metals, 35Au-62Cu-2Ti-1Ni (21.5 MPa) and 97Ag-1Cu-2Zr (37.9 MPa). The alumina tensile button samples in Series 4 and 5 were joined using Cusil-ABA® and BAu-3 brazing filler metal, respectively. Cusil-ABA, a low-temperature filler metal of interest, yielded the highest tensile strengths in this study, 105 MPa on average. BAu-3 is the braze filler metal currently used in a direct-brazing application by a component supplier. Series 5 closely duplicates previous direct-brazing work performed in 2005 (Series number 9 in Table 2), which is the baseline for the work presently being evaluated. The thermal cycle used for Series number 9 was the same as that used by the component manufacturer in 2005 and is comparable to Series number 5, the thermal cycle used currently by the same component manufacturer. Although different compositions of 94% alumina ce-
ramic were used, the average tensile strengths obtained in Series 5 (55.1 MPa) are very similar to those obtained previously (61 MPa), as reported by Stephens (Ref. 6), and would appear to indicate that the results obtained by the first three series were not anomalies. The most noteworthy difference observed is that all of the samples were hermetic in the Series 5 run while only half were hermetic in 2005.

Surprisingly, the niobium-sapphire tensile button strengths were much lower than the niobium-alumina ceramic tensile buttons. The average strength of the alumina ceramic tensile buttons brazed using BAu-3 was 55-61 MPa (Series 5 and 9) vs. only 35 MPa (Series 1) for the niobium-sapphire assemblies. While sapphire is known as a relatively strong material in the flaw-free state, with tensile strengths typically more than twice those of 94% alumina ceramic, it has a fracture toughness of approximately half that of alumina ceramic, depending on the fracture plane (Ref. 12). Notably, the tensile strengths of the niobium-sapphire tensile buttons were independent of the sapphire washer thicknesses used. A cross-section SEM image and energy-dispersive spectroscopy (EDS) map of a niobium-sapphire assembly brazed with BAu-3 can be seen in Fig. 3. As shown by the EDS map in Fig. 3B, the niobium substrate diffusion to the sapphire interface is minimal. No concentration of the niobium metal at the sapphire interface is seen. Figure 4 is a composite image showing the same SEM image displayed in Fig. 3, and EDS maps showing the distribution of the filler metal elements gold, copper, and nickel. As can be seen in Fig. 4B, the majority of the nickel has migrated to the niobium substrate surface. A comparison of the niobium EDS map (Fig. 3B) with the nickel EDS map (Fig. 4B) does show a reaction between these elements; however, that compound was not identified.

Figure 5 is an image of a niobium and sapphire sample brazed with active filler metal 35Au-62Cu-2Ti-1Ni. The addition of titanium to the braze filler metal results in a clearly visible reaction layer between the sapphire and filler metal. Even with this reaction layer, however, the average tensile strength of the samples was only two thirds that of the samples brazed with BAu-3, as shown in Table 2 when comparing Series 1 to Series 2. In addition to lower strength, half of the Series 2 samples failed the helium leak test. The reasons for the failures and lowered tensile strength are unknown at this time. The EDS maps in Fig. 6 portray the relative elemental compositions of the brazed cross section previously seen in Fig. 5. The reaction between the titanium in the brazing filler metal with the sapphire interface is clearly seen. Also evidenced are reactions between the niobium substrate with the nickel, gold, and titanium filler metal material, but not with the copper.

As can be seen in Table 2, a zirconium-containing braze filler metal was also evaluated (Series 3). Tensile strengths of nearly 150 MPa have been achieved using this brazing filler metal with 94% alumina tensile buttons and Fe-29Ni-17Co interlayers (Ref. 13). Because of this, it was anticipated that similarly high tensile strengths could be achieved with the sapphire and niobium components. It is believed that no attempts to braze niobium substrates to sapphire interlayers have been made using this particular braze filler metal previous to this experiment. While all of the niobium-sapphire samples made using this brazing filler metal passed the helium leak test, as can be seen in Table 2, the average tensile strengths were much less than expected for the niobium tensile buttons with the sapphire in-

Fig. 7 — SEM image of niobium-sapphire sample brazed with 97Ag-1Cu-2Zr.

Fig. 8 — SEM image and EDS maps of niobium-sapphire sample brazed with 97Ag-1Cu-2Zr.
Modified Thermal Cycle Series

Previously mentioned, and seen in Figs. 5 and 6, is the high concentration of titanium at the sapphire interface, clearly defining the reaction layer between the braze filler metal and sapphire substrate. Similarly, Figs. 7 and 8 show a reaction interlayer between the zirconium in the braze filler metal and sapphire. These results, the lack of a clear reaction layer between the niobium and sapphire when using BAu-3, and results from previously referred to studies (Ref. 10), led to the decision to make additional samples with BAu-3 and modified thermal cycles. Using studies mentioned by Marks et al. for guidance, it was determined that two approaches would be used: 1) increasing only the peak soak time, and 2) increasing both the peak soak time and peak soak temperature. The peak soak time would be increased from 5 to 120 or 240 min while the peak soak temperature would be increased by 200°C. It should be noted that Marks adjusted a third parameter, joint preload. For this particular case, however, it was determined that the recommended preloads would be difficult to achieve in a production brazing process. ASTM-F19 94% alumina ceramic tensile buttons with a niobium interlayer 0.25 mm thick and niobium tensile buttons with a 0.41-mm-thick sapphire interlayer were prepared and brazed with BAu-3 braze filler metal.

As was expected, the extended soak times resulted in noticeable evaporation of the braze filler metal, evidenced by condensed filler metal on the metal shielding and other cooler regions in the nearby proximity of the furnace hot zone. This evaporation was rather extreme for the samples processed at the elevated peak brazing temperature of 1260°C. While recognizing that the pressure (vacuum) levels of production equipment could be one to two orders of magnitude greater than the equipment used for these experiments, there would still be excessive braze filler metal evaporation occurring. For this reason, the higher brazing temperature was deemed to be unsuitable for production processes, and the second planned high-temperature thermal cycle was canceled.

The details for these trials, designated as Series 6–8, are shown in Table 2. Lengthening the peak soak time to 240 min while keeping the joint preload and the peak soak temperature constant had the desired effect for the niobium-ceramic samples, but resulted in a greatly reduced average tensile strength decrease for the niobium-sapphire samples. The average strength of the niobium-alumina ceramic tensile samples (Series 6) was increased by 73%, while the average niobium-sapphire sample strength (Series 7) was reduced to 6 MPa, a decrease of 83%. Even with this large disparity in strengths, no differences in the joint hermeticity between the two types of samples were measured.

Series 8, the only set of alumina ceramic tensile button samples brazed with the increased peak soak time (120 min) and peak soak temperature (1260°C), had a noticeably different visual appearance from the other samples. The braze fillets were more rough and granular, had a gray color, and appeared to have a lesser fillet volume, although no measurements were made. All of these samples leaked substantially, and had an average tensile strength of 39.4 MPa, which was a decrease of about 28.5% from the baseline condition, Series 5.

Conclusions

The ability to make strong sapphire-sapphire joints using niobium and liquid-metal in well-controlled laboratory conditions has been previously demonstrated by various researchers. Attempts to understand and describe the bonding mechanisms and requisite substrate requirements have been made; however, more efforts are necessary to understand the relationship between joint strength and surface roughness for brazed niobium-

<table>
<thead>
<tr>
<th>Series</th>
<th>Material</th>
<th>Interlayer Thickness</th>
<th>Filler Metal Type</th>
<th>Peak Soak Temperature (°C)</th>
<th>Time (Min)</th>
<th>Leak Check</th>
<th>Average Tensile Strength (MPa)</th>
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<tbody>
<tr>
<td>1</td>
<td>Nb</td>
<td>0.41 mm</td>
<td>BAu-3</td>
<td>1060</td>
<td>2</td>
<td>6/6</td>
<td>34.7</td>
</tr>
<tr>
<td>2</td>
<td>Nb</td>
<td>0.41 mm</td>
<td>BAu-3</td>
<td>1060</td>
<td>2</td>
<td>2/4</td>
<td>21.5</td>
</tr>
<tr>
<td>3</td>
<td>Nb</td>
<td>0.41 mm</td>
<td>97Ag-1Cu-2Zr</td>
<td>985</td>
<td>5</td>
<td>4/4</td>
<td>37.9</td>
</tr>
<tr>
<td>4</td>
<td>94ND10</td>
<td>0.25 mm</td>
<td>Cusil-ABA</td>
<td>855</td>
<td>5</td>
<td>5/5</td>
<td>102.0</td>
</tr>
<tr>
<td>5</td>
<td>94ND10</td>
<td>0.25 mm</td>
<td>BAu-3</td>
<td>1060</td>
<td>2</td>
<td>5/5</td>
<td>55.1</td>
</tr>
<tr>
<td>6</td>
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<td>0.25 mm</td>
<td>BAu-3</td>
<td>1060</td>
<td>240</td>
<td>5/5</td>
<td>95.5</td>
</tr>
<tr>
<td>7</td>
<td>94ND10</td>
<td>0.25 mm</td>
<td>BAu-3</td>
<td>1260</td>
<td>120</td>
<td>0/5</td>
<td>39.4</td>
</tr>
<tr>
<td>8</td>
<td>Nb</td>
<td>0.25 mm</td>
<td>BAu-3</td>
<td>1060</td>
<td>240</td>
<td>5/5</td>
<td>5.9</td>
</tr>
<tr>
<td>9①</td>
<td>Al-500</td>
<td>0.25 mm</td>
<td>BAu-3</td>
<td>1058</td>
<td>5</td>
<td>2/4</td>
<td>61.0</td>
</tr>
</tbody>
</table>

①Series Number 9, performed in 2005, is shown for reference.
sapphire structures. Less understood are the mechanisms by which niobium diffuses through liquid braze filler metal to react with sapphire in typical brazing assembly processes that use rapid thermal cycles with minimal joint loading.

Modifying a standard brazing profile by increasing the peak soak time from 5 to 240 min did result in increased tensile strength for niobium-94% alumina ceramic samples. When joining niobium to sapphire, the same modification in a thermal cycle resulted in an average strength decrease, compared to the baseline samples. No differences in sample hermeticity from the baseline samples were measured when only the peak soak time was increased.

Increasing the peak temperature by 200°C and peak soak time from 5 to 120 min resulted in a slight strength increase. Unfortunately, all of the samples processed at these conditions failed the helium leak test.

Previous research regarding the direct-brazing of niobium to alumina revealed in TEM images bonding of niobium-containing compounds to the glassy phases between the alumina grains (Ref. 14). Similarly, Hosking et al. reported for active braze filler metals that because the majority of the oxide bonds are made with the high-temperature glass materials used to join the alumina grains in the ceramic material, lower-purity alumina grades often outperform high-purity ceramics with regard to brazed joint strength and hermeticity (Ref. 15). It still remains to be determined if the niobium reaction region increased with the extended soak time.

Acknowledgments

The authors express their warm thanks to the following persons who made this work possible: Tom Crenshaw, Alice Kilgo, and Bonnie McKenzie.

References


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