Microstructural and Mechanical Characterization of Actively Brazed Alumina Specimens

Alumina wetting and tensile specimens are brazed with Au-Ni-Mo-V active brazing alloys.


ABSTRACT. Alumina (94 and 99.8% grade compositions) was brazed directly to itself with gold-based active brazing alloys (ABA’s) containing vanadium additions of 1, 2 and 3 weight percent. The effects of brazing conditions on the joint properties were investigated. Wetting behavior, interfacial reactions, microstructure, hermeticity and tensile strength were determined. Wetting was fair to good for the ABA and base material combinations. Microanalysis identified a discontinuous Al-V-O spinel reaction product at the alumina-braze interface. Tensile strength results for 94% alumina were uniformly good and generally not sensitive to the vanadium concentration, with tensile values of 85-105 MPa. There was more variability in the 99.8% alumina strength results, with values ranging from 25-95 MPa. The highest vanadium concentration (3 wt. %) yielded the highest joint strength for the brazed 99.8% alumina. Failures in the 99.8% alumina samples occurred at the braze-alumina interface, while the 94% alumina specimens exhibited fracture of the ceramic substrate.

* Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.
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Introduction

The development of active brazing as a reliable joining technology for engineered ceramics (ceramic-to-ceramic and metal-to-ceramic joints) requires a fundamental understanding of the interfacial and bulk microstructural features of the brazement. In general, the mechanical behavior of any brazed assembly is intrinsically dependent on these features, as well as the residual stress state in the joint. However, when joints involve a ceramic substrate with high modulus and limited ductility (compared to metals), interfacial structures are particularly important in determining mechanical behavior of the bonded assembly. By correlating the joint structure with mechanical strength, a relationship can be developed that provides the basis for engineering critical braze joints with properties that satisfy explicit processing and service requirements.

Active braze alloys (ABA’s) have been developed as a means to directly wet a ceramic, without the need for pre-metallization of its surface. Because the ABA’s ability to work depends on the chemical reaction(s) that occurs between the active element(s) in the braze and the ceramic, a fundamental understanding of how the brazing parameters affect the interfacial reaction kinetics is an important step toward controlling and optimizing the ABA process. Once this is achieved and the braze chemistry, microstructures and properties are quantified, structural responses can be predicted.

Early active alloy systems primarily utilized titanium as the active component. The resulting filler metals were limited to processing in either vacuum or inert atmospheres, since titanium forms hydrides in reactive hydrogen atmospheres. Recently, a new family of alloys was developed that is more compatible with hydrogen, employing vanadium as the active constituent. These second-generation ABA’s expand the application of active brazing technology to areas where the preferred, or required, furnace atmosphere is dry hydrogen. Because these V-
containing alloys are relatively new, interfacial and microstructural data for prototype ceramic joints are limited. Such braze joints have yielded generally acceptable hermeticity and tensile strength, but the reaction product(s) responsible for adhesion, a necessary condition for realizing the required joint properties, is not well understood.

The present work examined the materials and processing requirements associated with actively brazing 94 and 99.8 (wt. %) alumina with a V-containing ABA. The braze composition is based on a modified AWS BAu-4 chemistry (82Au-18Ni, wt. %), with 0.75% Mo and three different V concentrations (1 to 3 wt. %). Wetting behavior, interfacial reactions, microstructure, and tensile button strength were determined.

**Experimental Conditions and Metrics**

**Materials and Test Specimens**

The base materials consisted of two grades of alumina ceramic, 94 and 99.8 weight percent (92 and 99.8 volume percent) procured from Wesgo Ceramics, Belmont, CA and Coors Ceramics, Golden, CO respectively. The 94% composition contains a glassy phase consisting primarily of silicon, aluminum, magnesium and calcium oxides that is deliberately added to the Al₂O₃ as a sintering aid. Both ceramics were air fired at 1575°C (2867°F) for 2 hours prior to brazing in accordance with a manufacturer’s recommendations (Ref.1).

The ABA compositions were based on the Au-Ni-Mo-V quaternary system; their chemistries are listed in Table 1. The nominal V concentration was 1, 2, or 3 weight percent. Braze preforms were fabricated from 0.076 mm (0.003 in) thick foil stock obtained from Wesgo Inc. The general liquidus temperature range for these three alloys, reported by the manufacturer, was 955-970°C (1751-1778°F).
Braze properties were determined using two different test geometries. The first utilized a flat ceramic surface and a 6 mm (0.25 in) diameter braze alloy disk to quantify wetting behavior. The test was based on the area-of-spread or sessile drop approach (Refs. 2,3). The second test geometry was based on the ASTM F19-64 (Ref. 4) tensile button specimen for evaluating the tensile strength of brazed ceramics, shown schematically in Fig. 1. Seven F19 replicates were processed per brazing condition.

**Brazing Conditions**

Wetting and mechanical test specimens were heated to 1000 or 1020°C (1832 or 1868°F) with 0.003” (.076 mm) thick braze preforms in a slightly positive dry hydrogen atmosphere having a dewpoint of approximately –60°C. Tensile specimens were brazed in a fixture designed to maintain axial alignment. A small weight was placed on top of the ceramic/braze foil assembly to produce a total bonding pressure of 1.0 psi (7 kPa).

Two furnace profiles were investigated; the only difference in the profiles was the peak temperature. The thermal ramps and times were constant. The nominal profile was as follows:

- Heat from ambient to 925°C at 10°C/min.
- Soak at 925°C for 10 min.
- Heat from 925°C to the peak temperature (1000 or 1020°C) at 5°C/min.
- Soak at peak temperature for 5 min.
- Furnace cool from peak temperature to 800°C at approximately 15°C/min.
- Continue furnace cool from 800°C to 400°C at 10°C/min.
- Complete remaining cool to ambient at 5°C/min.

The furnace temperature was controlled with thermocouples located next to the wetting substrates or on the fixtured tensile specimens. Orientation in the furnace (top vs. bottom) was maintained for each tensile sample.
Analyses and Measured Responses

The brazed samples were evaluated for braze wettability, hermeticity, and tensile strength. The ASTM F19 tensile specimens were helium leak checked, dimensionally inspected for axial alignment, and tested in tension. The leak tests were performed with an Alcatel ASM-10 Helium Leak Detector. The machine was calibrated with a standard calibrated helium leak. Tests were conducted with technical grade helium. The annular region of the test specimen was evacuated and helium was introduced around the outer fillet. If no leaks were detected, the test scale was changed to increasing helium sensitivity levels until the machine limit was reached. If a leak was detected, the leak range was quantified. The percentage of no detectable leaks (NDL) per data set was then calculated. Specimen alignment measurements were conducted with an optical profilometer. Axial and radial positioning, including tilt and bore concentricity were measured.

Room temperature tensile tests were performed with a hydraulic load frame in displacement control mode at a test rate of 0.0076 mm/s (0.0003 in/s). Collated fixturing was used to align the test specimens in the grips during tension testing. The tophalf of each specimen, as determined by its orientation in the brazing furnace, was loaded in the upper grip of the test machine. Tensile results were compared to baseline values obtained from a control set of metallized and nickel plated (Mo-Mn-Ni process) 94% alumina tensile button specimens that were brazed with conventional 82Au-18Ni filler metal at 1000°C.

Finally, one brazed tensile button specimen from each processing group was selected for microstructural analyses. The sample was cross-sectioned, mounted, and metallographically polished for examination using both optical and scanning electron microscopy. Additionally, thin foils were prepared for transmission electron microscopy.

Experimental Results
Wetting Results

The wetting trials indicated that the braze preform retracted from its original disc shape to form an irregular sessile drop, with braze remnants over the initial preform perimeter (Fig. 2). Contact angles of the main droplet generally varied between 30 to 45 degrees, with wetting consistent for each braze composition on both alumina materials.

Contact angle, which represents the tangent at the intersection between the alumina substrate and the edge of the braze droplet, is an excellent indicator of braze wettability. A value of 45 degrees or less usually corresponds to acceptable wetting. Best wetting occurs as the angle decreases and approaches zero (ideal wetting).

Based on the limited wetting tests that were conducted, there did not appear to be significant differences in general wetting between the three braze alloys. The 1V composition did yield a larger contact angle range, with some values as high as 60 degrees. The 2 and 3V-containing alloys gave more consistent wetting results, but did not produce substantially lower angles. The average wetting angle was similar for each alloy. There also appeared to be more braze material on the dewetted 94% alumina surfaces as the vanadium concentration was increased.

Surface analysis on dewetted 94% alumina surfaces was conducted with scanning electron microscopy. The analytical results revealed braze material concentrated along the exposed glassy phase in the alumina grain boundaries. Bridging occurred occasionally between the smaller braze islands, forming longer braze segments (Fig. 3). In these dewetted areas, while the braze material was occasionally found situated on the surface of alumina grains, there was a definite preference for the metal to be retained at grain boundary areas.

Thermodynamic calculations were performed to determine probable reaction products between the ceramic and braze materials. Gibbs free energy values were calculated for simple alumina and silica reactions with V and Mo at 1020°C. In all cases, the resulting redox reaction yielded an energetically unfavorable (positive free energy value -Table 2). For example, the
Gibbs energies for the alumina and V reactions were 260 kJ/mol or greater. The closest to a negative free energy was obtained with silica and V, with a 9 kJ/mol value. The lower silica/V free energy corresponds to the observed wetting behavior of the glassy phase in the 94% alumina binder. The computations suggest that a more complex reaction occurs between the active braze constituent and the surface oxide, particularly on the 99.8% alumina specimens.

Hermeticity and Tensile Test Results

The brazed ASTM F19 tensile specimens were used to evaluate joint hermeticity and tensile strength; the results are summarized in Table 3.

Approximately 80% of the brazed 94% alumina tensile specimens were hermetic; the metric for hermeticity was defined as a leak rate less than 1.0 x 10^{-9} \text{ cm}^3/\text{s} (\text{std. helium atmosphere}). The test specimens that “failed” had a leak rate of 10^{-7} to 10^{-4} \text{ cm}^3/\text{s} (\text{std. helium atm.}). These leaks were attributed to microcracks in the alumina near the braze interface or insufficient braze material through the annular joint, where misalignment of the top piece in some of the specimens produced a tapered joint. Similar leak results were obtained with the 99.8% alumina tensile specimens. In general, the 1V-ABA/99.8% alumina samples had the highest leak rates.

The formation of braze balls at the joint’s free surface also affected joint hermeticity. These point defects were observed only on the 99.8% alumina tensile specimens, usually one specimen per data set. The leak distribution for these specimens was generally mixed, with both leakers and non-leakers. As with the braze droplets on the wetting samples, the braze balls concentrate high residual stresses in the ceramic that can initiate fine cracks (Fig. 4), which are then potential leak paths. Even with an hermetic joint, these stress-induced defects can affect the joint’s mechanical strength. Their presence can be minimized by controlling the braze volume, joint clearance, applied load, processing conditions, and interfacial reactions.
Tensile tests results were dependent on the type of alumina, braze composition, and the brazing temperature (Table 3). The most consistent results were obtained with the 94% alumina specimens. Their tensile strengths were nominally 95-100 MPa (13.8-14.5 ksi), compared to the metallized, baseline strength of 93 MPa (13.5 ksi). The only data set that fell below this range was for the samples brazed with the 3V-ABA at 1000°C. These samples failed at 85 MPa (12.3 ksi), suggesting a possible brazing temperature effect on strength for the higher V-containing composition. Failure locations varied for the 94% alumina specimens, but most showed a mixture of substrate (ceramic) and braze metal failure. There was a slight preference (~60%) for failure to be associated with the bottom braze interface or ceramic.

The 99.8% alumina tensile strengths spanned a larger stress range, which was clearly influenced by the brazing temperature and ABA composition. The strengths were generally lower than those obtained with the 94% alumina material. The 1V-ABA samples yielded intermediate tensile values, with an average strength of 58 MPa (8.4 ksi). At both brazing temperatures, the standard deviation of specimen strengths exceed 25 percent of the average.

Strengths of the specimens brazed using the 2V-ABA composition were significantly lower than their one percent vanadium counterparts. The tensile strengths of specimens brazed at 1020°C were in the range of 25 MPa (3.6 ksi), well below the baseline condition. The 1000°C strengths were slightly higher, with an average value of 35 MPa (5.1 ksi).

Finally, the 99.8% alumina and 3V-ABA specimens produced joint strengths closest to the 94% alumina test results. The 1000°C samples failed at 70 MPa (10.2 ksi), while the 1020°C specimens failed at 95 MPa (13.8 ksi).

The 99.8% alumina specimens failed primarily at the bottom metal-ceramic interface, with occasional fracture occurring in the bottom ceramic piece. Nearly 70 percent of the failures were along this lower braze interface.
Microstructural Analysis

Cross-sections of the 94% alumina brazed tensile specimens revealed structures similar to those shown in Figure 5. Joints were typically 60-80 microns (.002-.003 in) wide, porosity-free, with several phases distributed throughout the microstructure. The braze filler metal maintained intimate contact with the alumina substrate along the entire bond interface. The 99.8% alumina specimens contained identical microstructural features, although there were localized regions along the braze interfaces where slight separations were found between the metal and alumina (Figure 6). Large globular features (dark particles in Figure 5) were observed in the upper half of each joint; the remainder of the microstructure consisted of large, two phase grains separated by finer particles.

The chemical composition of the various constituents in one specimen, obtained by wavelength dispersive spectroscopy (WDS), is shown in Figure 7. The large globular particles (Point 1) were found to be nickel-rich and contained the majority of the molybdenum in the joint. Their composition suggests that these particles have a lower density than the remainder of the joint, which is consistent with their preferential distribution towards the top interface. The smaller dark particles (Point 3), distributed at boundaries between gold-rich grains, also contained a high nickel content, but only small amounts of molybdenum.

The nickel-rich particles exhibited a surprising distribution throughout the various joints. Some of the tensile specimens, due to load imbalance during brazing, produced joints with non-uniform braze thickness. Examination of these joints revealed a nearly uniform volume of the globular phase (as opposed to volume fraction) in both thin and wide areas. Since the initial distribution of the braze alloy (foil) is uniform, these results suggest that the globular particles form quickly as the filler metal melts, but are not mobile when the ceramic substrates shift and molten braze is redistributed.
Examination at higher magnification reveals that the nickel-rich particles are not a single phase, but rather a textured structure with non-uniform composition (Figure 8). Average composition of these particles (Table 4) varied with both filler metal composition and brazing temperature, but was independent of ceramic substrate.

Examination of the 94% alumina fracture surfaces revealed large areas of transgranular ceramic failure (Figure 9a). However, in many cases the fracture path traversed across the braze joint several times, resulting in substrate failures on both sides of the joint. The transition regions typically revealed localized intergranular ceramic failure, as shown in Figure 10. At these locations, the braze metal remained well bonded to the ceramic, with ductile failure of the gold-rich phase and limited deformation of the darker, nickel-rich areas.

Conversely, the 99.8% alumina fractures were dominated by failures at the metal-ceramic interface, with the fracture path almost exclusively proceeding along a single ceramic interface. The limited areas of ceramic substrate failure exhibited substantial intergranular failure of the alumina (Figure 9b). Far more common was the fracture appearance shown in Figure 11, where the solidified braze filler appears to have separated cleanly from the ceramic. The resulting metallic surfaces show almost no deformation, and the individual constituents of the braze joint are clearly visible.

No interfacial reaction layer was observed using optical or scanning electron microscopy (SEM). However, transmission electron microscopy (TEM) revealed a very thin layer of material at the metal-ceramic interface. This layer, which appears scalloped in Figure 12, was found at several but not all locations examined on both 94 and 99.8% alumina specimens. These features, situated between the alumina grains and the braze metal (both gold-rich and nickel-rich phases) typically measured about 20-30 nm (0.8-1.2μm) at the widest point.

Higher magnification views of the interface region between the metal and ceramic are shown in Figure 13. A narrow (approximately 20 nm) thick reaction layer is identified at the interface. From electron diffraction and Fourier analysis of the observed lattice fringes, the
orientation of the alumina grain was determined to be along a <1101> zone. Using the alumina lattice fringes as an internal calibration, the spacing of the horizontal lattice fringes observed in the interfacial layer were measured to be 4.8 angstroms. This spacing is consistent with the 4.84 angstrom spacing measured from a selected area electron diffraction pattern also taken from the interfacial region.

EDS analysis of the interfacial region (Figure 14) indicated that only oxygen, vanadium and aluminum were present; no gold, nickel or molybdenum (or silicon in the 94% alumina samples) was detected. To identify the phase of the interfacial layer, the interplanar angles and spacings measured from a selected area diffraction pattern obtained from the interfacial layer were compared against diffraction data listed in the Powder Diffraction File (PDF) database for compounds of vanadium-oxygen, vanadium-oxygen-aluminum, vanadium-aluminum, and elemental vanadium.

The analysis eliminated the majority of the compounds from further consideration on the basis of inconsistent d-spacings and/or interplanar angles. Only for vanadium-oxygen-aluminum compounds were matches obtained with the observed diffraction pattern. Specifically, three compounds (Table 5) including a cubic phase of AlVO₃ and cubic and tetragonal phases of AlV₂O₄ have reported structures that are consistent with the experimental diffraction pattern. Each of these phases matches the observed diffraction pattern quite well; the calculated and measured interplanar angles are within 1 degree and the measured d-spacings are all consistent to within about 3%.

All three phases are closely related structurally. The powder diffraction file describes both cubic phases as spinel structures; typically, a spinel has a formula type of AlB₂O₄. The PDF also describes AlVO₃ as a metal-deficient spinel. With the present diffraction data, it is not possible to further distinguish between these three structures.
Discussion

Microscopic Considerations

The binary Au-18Ni (BAu-4) composition will not wet alumina substrates. Generally, this lack of wettability can be attributed to the nature of atomic bonding (either ionic or covalent) in ceramics that lack the delocalized bonding electrons found in metals (Ref. 5). Alumina is comprised of atoms of high electronegativity, leading to its strongly ionic character compared to other ceramics of engineering interest, particularly non-oxides such as Si$_3$N$_4$ and SiC. Consequently, a braze alloy must have a high oxidation potential in order to generate the chemical reaction(s) necessary to wet alumina. Small additions of titanium to several face centered cubic elements (Cu, Ni, Au) have been shown to facilitate wetting on alumina through the formation of a titanium-oxide reaction layer (Refs. 6-8). Vanadium is a less potent oxidizing agent than titanium, thus reduction of alumina by V-bearing braze alloys is more difficult, as evidenced by the unfavorable free energy values for simple oxide reactions. Thermodynamic data for more complex systems, such as the spinel-type compounds indicated by the diffraction results are not readily available. However, electron microscopy results suggest that the reaction layer is either non-existent or extremely thin (undetectable) in many areas.

Since the braze alloy was preplaced, no flow or wetting was required to ‘fill’ the joint. Previous investigators (Refs. 9,10) have suggested mechanisms for time dependent formation of a reaction product, where the reaction layer forms at multiple, isolated locations at the braze-ceramic interface. These islands can, over time, grow laterally as the reaction progresses, eventually leading to complete convergence. In the areas between the islands of reaction product, the braze alloy appears to be at least weakly bonded directly to the alumina substrate.
Previous researchers (Refs. 11,12) have found that both gold and nickel can adhere to Al₂O₃, although bond strengths are below the strength of the ceramic. Bogicevic and Jennison (Ref. 13) suggest that partial monolayer of metal atoms can bind strongly to alumina through ionic bonding. However, at thicknesses greater than one monolayer, the nature of the alumina-metal bond changes from ionic to electrostatic, with a drastic decrease in bond strength. It seems likely that the metal-ceramic interface in tensile specimens fabricated in the current study possess a mixture of well bonded metal (facilitated by the AlV₂O₄ or AlVO₃ reaction product) and areas of weak bonding. The tensile results suggest that the 94% alumina specimens contain a larger percentage of strongly bonded regions than the high purity specimens.

Both the nucleation and growth rate of the reaction layer may be affected by crystallographic orientation of the individual Al₂O₃ grains. Previous studies have found a large variation in calculated surface energy as a function of orientation for ionic crystals (Refs. 14,15), in contrast with metallic crystals where surface energies are much more isotropic.

In the current study, brazing time was held constant. While the reaction layer appeared to be discontinuous in both 94 and 99.8% alumina specimens, the strength of the 94% specimens was clearly superior. Assuming that the individual grains of alumina have essentially the same composition and a random orientation in both ceramic substrates, then the primary difference in bond strength appears to be related to the presence of the glass grain boundary phase present in the 94% specimens. As previously noted, SiO₂ has marginal thermodynamic stability in the presence of vanadium at the brazing temperature. Furthermore, at 1000°C, SiO₂ is reduced in a hydrogen atmosphere having a dewpoint of approximately -80°C, only slightly drier than the environment used for these experiments. Small quantities of silicon were detected in the braze joints of the 94% specimens (Figure 7), evidence of some reduction of SiO₂ during brazing.

The presence of the glassy grain boundary phase could contribute to the improved strength of the 94% specimens by several mechanisms. Since the glass phase represents approximately 8
volume percent of the specimen, the surface area of alumina exposed to the molten braze alloy is reduced accordingly.

Secondly, following the air-firing step, a thin (angstroms) layer of silicon-rich material (Ref. 16) covers or partially covers the newly exposed (machined) surfaces. This coverage, in addition to the original 8% surface component, may facilitate wetting and possibly reduce the time necessary for nucleation of the reaction layer.

Finally, the reduction of SiO$_2$ by vanadium, or by hydrogen, would lead to the presence of either free Si or O in the molten braze filler. These compositional changes may influence the thermodynamic activity of vanadium in the braze alloy, thus changing the growth kinetics of the interface reaction product. Similarly, Si or O in the molten filler may also act as a catalyst for the reaction, although no Si was detected in the reaction layer at the metal-ceramic interface.

Macroscopic Considerations

Solidification of binary Au-Ni alloys occurs as a single phase solid solution. However, at lower temperatures (below 700-800°C) this structure becomes unstable, and, if the cooling rate is sufficiently slow, a phase separation will occur resulting in nickel-rich and gold-rich phases (Ref. 17). The presence of a small amount of Mo in these braze alloys is thought (Ref. 18) to stabilize an additional phase (which facilitates mechanical working of the alloys in production). As previously noted, the compositions of the braze alloys examined in this study appear to have extended phase instability at temperatures close to their liquidus temperatures. These results are consistent with those of Kang and Kim (Ref. 19) who detected two discrete melting events in experimental two-phase Au-Ni compositions containing Mo, Fe and Cr additions. Stephens and Hamann, in studies of bulk samples of the commercial Au-15Ni-0.7Mo-2.1V alloy (Ref. 20), identified chemical compositions of two phases from samples annealed at 910°C and then water quenched. The composition of the Ni-rich phase in their bulk alloy is included, for comparison
to brazed specimens, in Table A. Note that the volume fraction of the equilibrium Ni-rich (V containing) phase is high compared to that found in the braze joint microstructures of this study, primarily due to the presence of small amounts of both vanadium and molybdenum found in gold-rich areas and the eutectic constituent of the braze joint (Figure 7).

The propensity for tensile specimen failures to be associated with the lower metal-ceramic interface may be explained by several factors. The nickel (and vanadium)-rich globular phases are preferentially distributed towards the top of the joint (Fig. 5). Since vanadium is fundamentally involved in the reaction with the ceramic substrate, a higher vanadium concentration towards the top of the joint (found in a lower density liquid phase) could result in a more developed reaction product (higher percentage) along this upper interface. Additionally, the globular phases contain the majority of the Mo and V content of the filler material; these elements possess a lower coefficient of thermal expansion than either gold or nickel. Thus the presence of the globular phase may locally reduce the thermal expansion coefficient of the braze alloy near the metal-ceramic interface, thereby diminishing the residual stresses near that interface.

Finally, thermocouple data for instrumented tensile specimens indicated that during cooling, the temperature gradient was oriented down, i.e. heat was preferentially extracted from the braze joint from the top. Consequently, solidification proceeded from the top ceramic interface (either from a reaction layer or from the alumina substrate) towards the bottom. The solidifying metallic phases, either Ni-rich or Au-rich would have nucleated on the ceramic structure at the upper solid-liquid interface, with some preferred crystallographic orientation.

Conclusions

The brazing studies conducted on polycrystalline alumina specimens in the current investigation have led to an understanding of some of the factors that determine mechanical and
microstructural behavior when using Au-Ni-Mo-V filler metals. The following conclusions are drawn from the results of this work:

1) Au-15.5Ni-0.7Mo filler metals containing 1, 2 or 3 percent vanadium exhibit limited wetting on either 94 or 99.8 percent alumina substrates at temperatures of 1000° and 1020°C for 5 minutes in a dry hydrogen atmosphere. All of the filler metals showed a preferential tendency to wet the glassy phase found in the 94% alumina specimens.

2) Specimens brazed using 94 percent alumina showed consistently high strengths and good hermiticity at both brazing temperatures using all three filler compositions. Tensile fractures consistently occurred in the ceramic substrate.

3) High purity alumina specimens produced hermetic joints when brazed with the 2 and 3 percent vanadium filler alloys, but joint strengths with all filler materials were generally low. Only the 3 percent vanadium composition produced joint strengths close to the levels obtained with the brazed 94 percent ceramic. The fracture paths in the 99.8 percent alumina specimens were at the metal-ceramic interface.

4) A reaction layer, which appears to be discontinuous, was observed at the metal-ceramic interface. This feature was identified as either a AlV₂O₄ or a AlVO₃ spinel-type structure.

5) Differences in joint strength between the two types of alumina can be attributed to the presence of a greater amount of glassy grain boundary binder phase present in the 94 percent alumina ceramic. Small amounts of Si were found in the braze microstructure of these specimens, indicating some dissolution or dissociation of SiO₂ during brazing. No evidence was found to identify conclusively the mechanism for the greater strength in the 94 percent alumina specimens.

6) Tensile failures were more likely to be associated with the lower metal-ceramic interface.
Acknowledgments

The authors would like to acknowledge the contributions of Ronnie Albers, Tom Crenshaw, Celeste Drewian, Tom Headley, Paul Hlava, Alice Kilgo, Doug Medlin, Nancy Yang, and Gary Zender to the project. The work was supported by the U. S. Department of Energy’s Defense Programs and Sandia’s Research Foundations.

References


Table 1 - Active Brazing Alloy Compositions (wt. %)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Au</th>
<th>Ni</th>
<th>Mo</th>
<th>V</th>
<th>Melting Point (°C)</th>
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<tbody>
<tr>
<td>Baseline</td>
<td>82.0</td>
<td>18.0</td>
<td>-</td>
<td>-</td>
<td>955</td>
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<tr>
<td>1</td>
<td>82.8</td>
<td>15.6</td>
<td>0.7</td>
<td>1.0</td>
<td>949–958</td>
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<td>2</td>
<td>81.8</td>
<td>15.7</td>
<td>0.7</td>
<td>1.8</td>
<td>940–960*</td>
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<tr>
<td>3</td>
<td>80.9</td>
<td>15.5</td>
<td>0.7</td>
<td>2.9</td>
<td>953-958</td>
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</table>

*solidus – liquidus temperature range

Table 2 - Free Energy Change for Possible Oxide Reduction Reactions at 1020°C

<table>
<thead>
<tr>
<th>Chemical Reaction</th>
<th>ΔG (kJ/mol)</th>
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<tbody>
<tr>
<td>Al₂O₃ + 2V → V₂O₃ + 2Al</td>
<td>331</td>
</tr>
<tr>
<td>Al₂O₃ + 3V → VO + 2Al</td>
<td>262</td>
</tr>
<tr>
<td>Al₂O₃ + 3/2Mo → 3/2MoO₂ + 2Al</td>
<td>726</td>
</tr>
<tr>
<td>SiO₂ + 2V → 2VO + Si</td>
<td>9</td>
</tr>
<tr>
<td>3/2 SiO₂ + 2V → V₂O₃ + 3/2 Si</td>
<td>49</td>
</tr>
<tr>
<td>SiO₂ + Mo → MoO₂ + Si</td>
<td>287</td>
</tr>
</tbody>
</table>

where \( ΔG = ΔH - TΔS = ΔH_{298} - TΔS + (ΔC_p dt) - T(ΔC_p/T dt) \), from 298°K to T(1293°K)
Table 3 - Tensile Strength of Brazed ASTM F19 Alumina Tensile Specimens

<table>
<thead>
<tr>
<th>Alumina Grade (%)</th>
<th>Braze Chemistry (wt. %)</th>
<th>Brazing Temperature (°C)</th>
<th>No Detectable Leaks, NDL, (%)</th>
<th>Tensile Strength (MPa)</th>
<th>Standard Deviation (MPa)</th>
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</thead>
<tbody>
<tr>
<td>94* Au-18Ni</td>
<td>1000</td>
<td>100</td>
<td>92.6</td>
<td>9.7</td>
<td></td>
</tr>
<tr>
<td>94 Au-Ni-Mo-1V</td>
<td>1000</td>
<td>71.4</td>
<td>95.8</td>
<td>15.7</td>
<td></td>
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<tr>
<td>94 Au-Ni-Mo-1V</td>
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<td>95.3</td>
<td>2.6</td>
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</table>

* Mo-Mn/Ni metallized surface finish (baseline condition)
Table 4 – Composition and Volume Fraction of Ni-rich Particles in 99.8% Al₂O₃ Braze Joints

<table>
<thead>
<tr>
<th>Braze</th>
<th>Temp. (°C)</th>
<th>Composition (w/o)</th>
<th>Volume Fraction</th>
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<tbody>
<tr>
<td></td>
<td>1000</td>
<td>Au</td>
<td>Mo</td>
</tr>
<tr>
<td>1 (1.0V)</td>
<td>1000</td>
<td>36.1</td>
<td>7.3</td>
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<td></td>
<td>1020</td>
<td>34.9</td>
<td>8.3</td>
</tr>
<tr>
<td>2 (1.8V)</td>
<td>1000</td>
<td>29.2</td>
<td>9.9</td>
</tr>
<tr>
<td></td>
<td>1020</td>
<td>27.7</td>
<td>10.2</td>
</tr>
<tr>
<td>3 (2.9V)</td>
<td>1000</td>
<td>26.5</td>
<td>12.0</td>
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<tr>
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<td>1020</td>
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<td>13.7</td>
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<tr>
<td>2.1V*</td>
<td>n/a</td>
<td>10.9</td>
<td>7.2</td>
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</table>

* From Stephens and Hamann, Ref.17

Table 5 – Al-V-O Structures Identified as Possible Reaction Layer

<table>
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<tr>
<th>Compound</th>
<th>PDF No.</th>
<th>Crystal Type</th>
<th>d-spacing (nm)</th>
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</thead>
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<tr>
<td>AlVO₃</td>
<td>25-0027</td>
<td>cubic</td>
<td>0.487</td>
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<tr>
<td>AlV₂O₄</td>
<td>25-0025</td>
<td>tetragonal</td>
<td>0.484</td>
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<tr>
<td>AlV₂O₄</td>
<td>25-0026</td>
<td>cubic</td>
<td>0.472</td>
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</table>
List of Figures

1. Cross-section schematic of a cylindrical ASTM F19 ceramic tensile button with braze fixturing.

2. Au-Ni-Mo-2V wetting samples for 94% (left) and 99.8% Al₂O₃ (right).

3. Surface (left) and cross-section (right) of 94% Al₂O₃ / Au-Ni-Mo-2V wetting sample.

4. Excess braze material expelled from the joint clearance can result in the formation of a "braze ball" shown here in cross-section. Note cracks in the ceramic substrate (arrow).

5. Cross-section of 94% Al₂O₃ sample brazed with Au-Ni-Mo-2V at 1000°C.

6. Cross-section of 99.8% Al₂O₃ sample brazed with Au-Ni-Mo-2V at 1000°C showing separation at the metal-ceramic interface.

7. Microstructure and EDS (weight percent) analysis of 94% Al₂O₃ sample brazed with Au-Ni-Mo-2V at 1000°C. Top of joint is at left.

8. Higher magnification back scattered electron image of the nickel-rich particles reveals a non-uniform structure.

9. Fractures of ceramic substrates were generally transgranular in the 99.8% Al₂O₃ (left) and intergranular in the 94% Al₂O₃ specimens (right).

10. Regions of braze metal failure in the 94% Al₂O₃ tensile specimens indicate ductile fracture of the gold-rich areas with more limited deformation of the nickel-rich particles (arrows).

11. Fracture of the Al₂O₃ specimens generally occurred by separation at the metal-ceramic interface; the resulting metallic surface shows almost no deformation.

12. A TEM image of the metal-ceramic interface reveals a scalloped-front reaction layer.
13. HRTEM was used to obtain a lattice parameter for a structure found between the braze and the Al$_2$O$_3$ substrate.

14. X-ray spectroscopy indicated the presence of only oxygen, aluminum and vanadium in the reaction layer at the Al$_2$O$_3$ surface.
Figure 7. Microstructure and EDS (weight percent) analysis of 94% Al₂O₃ brazed with Alloy 2 at 1000°C. Top of joint is at left.

<table>
<thead>
<tr>
<th>Point</th>
<th>Al</th>
<th>Si</th>
<th>Au</th>
<th>Ni</th>
<th>Mo</th>
<th>V</th>
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