Microstructural and Mechanical Characterization of Actively Brazed Alumina Tensile 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 (ABAs) containing nominally 1, 2 or 3 wt-% vanadium. The effects of brazing conditions on the joint properties were investigated. Wetting behavior, interfacial reactions, microstructure, hermeticity and tensile strength were determined. Wetting was generally fair to good for the ABA and base-material combinations. Microanalysis identified a discontinuous reaction product at the alumina-braze interface as an Al-V-O spinel-type phase. Tensile strength of the 94% alumina specimens was generally not sensitive to the vanadium concentration and consistent within an 85–105 MPa range. The tensile data for the 99.8% alumina specimens, however, had significantly greater variability, with values ranging from 25 to 95 MPa. The highest value was obtained for the samples brazed with the filler metal containing 3 wt-% vanadium. Fractures occurred either along the braze-alumina interface for the 99.8% alumina specimens or through the alumina piece with the 94% alumina samples.

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 (ABAs) have been developed as a means to directly wet a ceramic, without the need for metallization of its surface (Refs. 1–11). Since 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 ABAs expand the application of “active brazing technology” to areas where the preferred, or required, furnace atmosphere is dry hydrogen, such as in the fabrication of high-voltage tube assemblies. Since these vanadium-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 vanadium-containing ABA. The braze composition is based on a modified AWS BAu-4 chemistry (82Au-18Ni, wt-%), with 0.75% Mo and three different vanadium concentrations (1 to 3 wt-%). Wetting behavior, interfacial reactions, microstructure and tensile strength were determined. The results are reported and discussed below.

Experimental Conditions and Test Criteria

Materials and Test Specimens

The base materials consisted of two grades of alumina ceramic, 94 and 99.8 wt-% (92 and 99.8 vol-%), procured from WESGO Ceramics, Belmont, Calif., and Coors Ceramics, Golden, Colo., re-
**Brazing Conditions**

Wetting and mechanical test specimens were heated to 1000 or 1020°C (1832 or 1868°F) with 0.076-mm (0.003-in.) thick braze preforms in a slightly positive-pressure, dry-hydrogen atmosphere having a dew point 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/ceramic assembly to produce a consistent bonding pressure of 7 kPa (1.0 lb/in.²).

Two temperature/time brazing regimes were investigated. The only difference between the two cycles was the peak temperature. Otherwise, the thermal ramp times were the same. The nominal profile was as follows:

- Heating from ambient to 925°C at 10°C/min.
- Soaking at 925°C for 10 min.
- Heating from 925°C to peak temperature (1000 or 1020°C) at 5°C/min.
- Soaking at peak temperature for 5 min.
- Furnace cooling from peak temperature to 800°C at 15°C/min.
- Continued furnace cooling from 800 to 400°C at 10°C/min.
- Final cooling to ambient temperature at 5°C/min.

The furnace temperature was controlled with thermocouples located next to the wetting substrates or on the fixture to ensure consistent bonding. A small weight was placed on top of the ceramic/braze foil/ceramic assembly. A small weight was placed on top of the ceramic/braze foil/ceramic assembly to produce a consistent bonding pressure of 7 kPa (1.0 lb/in.²).

### 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 part axial alignment and tested in tension mode. The leak tests were performed with an Alcatel ASM-10 helium leak detector. The machine’s leak rate was calibrated with a standard 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 (0.003 in./s). Universal collared fixturing was used to align the test specimens in the grips during tension testing. The top half 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 (AWS BAu-4) at 1000°C.

Finally, one brazed tensile specimen from each processing group was selected for microstructural analyses. A 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.

### Table 1 — Active Brazing Alloy Composition (wt-%)

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

Wetting Behavior

The wetting trials indicated 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 and 45 deg. Higher values were also observed, although they were not as common. The general experimental observation was that the wetting behavior on both alumina materials was relatively consistent from one braze composition to the next.

Contact angle along the outer edge of the braze droplet on the alumina substrate is an excellent indicator of braze wettability. If its value is 45 deg or less, wettability is usually considered acceptable. Wetting behavior improves as the angle decreases. Ideal wetting occurs when the contact angle approaches zero.

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

Surface analysis on de-wetted 94% alumina surfaces was conducted using 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 de-wetted areas, 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 vanadium and molybdenum at 1020°C. In all cases, the resulting oxide reduction and interfacial reaction yield an energetically unfavorable (positive) free-energy value (Table 2). For example, the Gibbs free-energy change for the reaction between alumina and vanadium free energy is 260 kJ/mol or greater. The closest to a negative free-energy change is for the reaction between silica and vanadium, a 9 kJ/mol value. The smaller free-energy change also corresponds to the experimentally observed wetting by each alloy to the 94% alumina glassy phase, which contains a significant amount of silica. The computations suggest more complex reactions occur between the active braze constituent and the surface oxide, particularly for the 99.8% alumina specimens.

<table>
<thead>
<tr>
<th>Chemical Reaction</th>
<th>G (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Al}_2\text{O}_3 + 2\text{V} \rightarrow \text{V}_2\text{O}_3 + 2\text{Al}$</td>
<td>331</td>
</tr>
<tr>
<td>$\text{Al}_2\text{O}<em>3 + 3\text{V} \rightarrow \text{V}</em>{2/3}\text{Si} + 2\text{Al}$</td>
<td>262</td>
</tr>
<tr>
<td>$\text{SiO}_2 + 2\text{V} \rightarrow \text{Si} + 2\text{VO}$</td>
<td>49</td>
</tr>
<tr>
<td>$\text{SiO}_2 + \text{Mo} \rightarrow \text{MoO}_2 + \text{Si}$</td>
<td>287</td>
</tr>
</tbody>
</table>

where $G = \Delta H_{298} + \int \Delta C_p dT - T \Delta S_{298} - T \int \Delta C_p/T dT$, integrated from 298 to 1293 K.
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 criteria for hermeticity was defined as a leak rate less than 1.0 $\times$ 10$^{-9}$ cm$^3$/s (standard helium atmosphere). The test specimens that “failed” had a leak rate of $10^{-7}$ to $10^{-4}$ cm$^3$/s (standard helium atmosphere). 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 for the 99.8% alumina tensile specimens. The 99.8% alumina samples that were brazed with the 1% vanadium alloy had the greatest dropout due to leaks.

The formation of braze balls at the joint’s free surface (Fig. 4) also affected joint hermeticity. These discrete, local features 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 concentrated high residual stresses in the ceramic that can initiate fine cracks (Fig. 4), which are then potential leak paths. Even with a 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 test results were dependent on the type of alumina, brazing filler metal composition and the brazing temperature (Table 3). The most consistent results were obtained with the 94% alumina specimens. Their tensile strength was nominally in the 95–100 MPa (13.8–14.5 ksi) range, compared with that of the metallized, “baseline” samples, 93 MPa (13.5 ksi). The only data set that fell below this range was for the samples brazed with the 3% vanadium composition at 1000°C. These samples failed at 85 MPa (12.3 ksi), suggesting a possible brazing temperature effect on strength for the higher vanadium-containing filler metal. Failure locations varied for the 94% alumina specimens, but most showed a mixture of substrate (ceramic) and braze failure. There was a slight preference (~60%) for failure to be associated with the bottom braze interface or ceramic.

The tensile strength of the 99.8% alumina specimens had a larger stress range, which was clearly influenced by the brazing temperature and ABA composition. The strength was generally lower than that obtained with the 94%-alumina material. The samples brazed with the 1% vanadium ABA yielded intermediate tensile values, with a nominal average strength of 58 MPa (8.4 ksi). At both brazing temperatures, the standard deviation of specimen strengths exceeded 25% of the average.

Strength of the 99.8% alumina samples brazed with the 2% vanadium ABA was significantly lower than those that were brazed with the 1 and 3% vanadium-containing filler metals. The average tensile strength of the 1% specimens brazed at 1020°C was 25 MPa (3.6 ksi), well below the typical baseline strength for similar metallized alumina specimens. The 1000°C strength was slightly higher, with an average value of 35 MPa (5.1 ksi).

Finally, the 99.8% alumina specimens, brazed with the 3% vanadium ABA, produced a joint strength closest to the 94% alumina tensile values. 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% 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 Fig. 5. Joints were typically 60–80 microns (0.002–0.003 in.) wide and porosity-free, with several phases distributed throughout the microstructure. The braze maintained continuous, uninterrupted contact with the alumina substrate along the entire braze 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 — Fig. 6. Large globular features (dark particles in Fig. 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 Fig. 7. The large globular particles (Point 1) were found to be nickel-rich, and they contained the majority of the molybdenum in the joint. Their composition suggests these particles have a lower density than the remainder of the joint, which is consistent with their preferential distribution toward 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.

Examination at higher magnification reveals the nickel-rich particles are not a single phase but rather a textured structure with nonuniform composition —

**Table 4 — Composition and Volume Fraction of Ni-Rich Particles in 99.8% Al₂O₃ Braze Joints**

<table>
<thead>
<tr>
<th>Braze Joint (% V)</th>
<th>Braze Temp. (°C)</th>
<th>Composition (wt-%)</th>
<th>Volume Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (1.0 V)</td>
<td>1000</td>
<td>36.1</td>
<td>7.3</td>
</tr>
<tr>
<td></td>
<td>1020</td>
<td>34.9</td>
<td>8.3</td>
</tr>
<tr>
<td>2 (1.8 V)</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 (2.9 V)</td>
<td>1000</td>
<td>26.5</td>
<td>12.0</td>
</tr>
<tr>
<td></td>
<td>1020</td>
<td>25.8</td>
<td>13.7</td>
</tr>
<tr>
<td>(2.1 V&lt;sup&gt;a&lt;/sup&gt;)</td>
<td>n/a</td>
<td>10.9</td>
<td>7.2</td>
</tr>
</tbody>
</table>

<sup>a</sup> Analysis of bulk Au-Ni-Mo-V braze alloy from Stephens and Hamann, Ref. 30.

The nickel-rich particles exhibited an interesting distribution throughout the various joints. Some of the tensile specimens, due to load imbalance or misalignment during brazing, produced joints with variable braze thickness. Examination of these tapered joints revealed a nearly uniform spatial distribution of the globular phase (as opposed to the local compositional volume fraction) across the thin (25 µm) and thick (125 µm) areas of the joint — Fig. 8. Since the initial thickness of the braze alloy (foil) was uniform, these results suggest the lower-density, nickel-rich particles formed during melting and solidification of the filler metal and segregate to the upper region of the higher-density, gold-rich phase in the wider braze gaps.

Examination at higher magnification reveals the nickel-rich particles are not a single phase but rather a textured structure with nonuniform composition —
Fig. 9. Average composition of these particles (Table 4) varied with both filler metal composition and brazing temperature but was independent of the ceramic substrate. The compositional data suggest a (Au, Mo, V)Ni₂ or 3 compound.

Examination of the 94% alumina fracture surfaces revealed large areas of transgranular ceramic failure — Fig. 10A. 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 Fig. 11. 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 — Fig. 10B. Far more common was the fracture appearance shown in Fig. 12, where the braze appears to be 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 rippled in Fig. 13, 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 (0.8–1.2 µm) at the widest point.

EDS analysis of the interfacial region

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

Table 5 — Al-V-O Structures Identified as Possible Reaction Layer Compounds Based upon X-Ray Diffraction Data

Fig. 11 — Regions of braze metal failure in the 94% Al₂O₃ tensile specimens that indicate a ductile fracture mode in the gold-rich areas and limited deformation of the nickel-rich particles (arrows).

Higher magnification views of the interface region between the metal and ceramic are shown in Fig. 14. A narrow (approximately 20 nm thick) reaction layer was 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> type zone. Using the alumina lattice fringes as an internal calibration, the spacing of the horizontal lattice fringes observed in the interfacial layer was 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
Fig. 13 — TEM image of the braze metal-alumina interface; the reaction layer has a rippled appearance.

Fig. 14 — HRTEM image of the braze metal-alumina interface that was used to obtain lattice parameters of the brazing reaction product.

Fig. 15 — X-ray spectrum of the braze metal-alumina reaction layer shows the presence of oxygen, aluminum and vanadium.

(Fig. 15) indicated 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 AlVO$_3$ and cubic and tetragonal phases of AlV$_2$O$_4$ 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 deg 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 AlB$_2$O$_4$. The PDF also describes AlVO$_3$ 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 does 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. 15). Alumina atomic bonds have strong ionic characteristics compared with other ceramics of engineering interest, particularly nonoxides such as Si$_3$N$_4$ and SiC. Consequently, a braze alloy must have a high oxidation potential 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. 16–18). Vanadium is a less-potent oxidizing agent than titanium. Thus reduction of alumina by vanadium-containing 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 the reaction layer is either nonexistent 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. 19, 20) 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. 21, 22) have found both gold and nickel can adhere to
Al₂O₃, although bond strengths are below the strength of the ceramic. Bog-
ivicevic and Jennison (Ref. 23) suggest a pa-
rial monolayer of metal atoms can
bind strongly to alumina through ionic
bonding. However, at a thickness 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 the met-
ceramic interface in tensile specimens
fabricated in the current study possess a
mixture of well bonded metal (facilitated
by the Al₂V₃O₇ or Al₂V₃O₆ reaction pro-
duct) and areas of weak bonding. The ten-
sile results suggest 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 in-
dividual Al₂O₃ grains. Previous studies
found a large variation in calculated sur-
face energy as a function of orientation
for ionic crystals (Refs. 24, 25), in con-
trast 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 the individual
grains of alumina have essentially the
same composition and a random orienta-
ton in both ceramic substrates, then the
primary difference in bond strength ap-
ppears to be related to the presence of
the glass-grain boundary phase present in the
94% specimens. As previously noted,
SiO₂ has marginal thermodynamic stabil-
ity in the presence of vanadium at the
brazing temperature. Furthermore, at
1000°C, SiO₂ is reduced in a hydrogen at-
mosphere having a dew point of approx-
imately –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
(Fig. 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 vol-%
of the specimen, the surface area of alu-
mina exposed to the molten braze alloy
is reduced accordingly.

Secondly, following the air-firing step, a
very thin layer of silicon-rich material,
approximately 10 angstroms or less thick
(Ref. 26), covers or partially covers the
newly exposed (machined) surfaces. This
coverage, in addition to the original 8% surface component, may facilitate wet-
ting and possibly reduce the time neces-
sary for nucleation of the reaction layer.

Finally, the reduction of SiO₂ by va-
nadium, or by hydrogen, would lead to the
presence of either free silicon or oxygen in
the molten braze filler. These compo-
sitional changes may influence the ther-
modynamic activity of vanadium in the
brazing process, thus changing the kinetic
netics of the interface reaction product.
Similarly, silicon or oxygen in the molten
filler may also act as a catalyst for the re-
action, although no silicon was detected
in the reaction layer at the metal-ceramic
interface. Traces of silicon were found in
the joint.

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 un-
bable, and, if the cooling rate is suffi-
ciently low, a phase separation will occur
resulting in nickel-rich and gold-rich phases (Ref. 27). The presence of a small
amount of Mo in these braze alloys is
thought (Ref. 28) to stabilize an addi-
tional phase (which facilitates mechan-
ical working of the alloys in production).
As previously noted, the compositions of
the braze filler metals examined in this
study appear to have extended phase in-
stability at temperatures close to their liq-
uidus temperatures. These results are
consistent with those of Kang and Kim
(Ref. 29), who detected two discrete
melting events in experimental two-
phase Au-Ni compositions containing
Mn, Fe and Cr additions. Stephens and
Hamann, in studies of bulk samples of
the commercial Au-15Ni-0.7Mo-2.1V
alloy (Ref. 30), identified chemical com-
positions of two phases from samples an-
nealed at 910°C and then water
quenched. The composition of the Ni-
rich phase in the bulk alloy is included
for comparison with the brazed speci-
mens (Table 4). Note the volume fraction
of the Ni-rich, vanadium-containing equilib-
rium phase in the bulk material
(Ref. 30) is relatively high compared to
that found in the actual braze joints.
The difference was attributed to the presence
of small amounts of vanadium and molybdenum in the gold-rich regions
and the eutectic constituent of the braze
joint — Fig. 7.

The propensity for tensile specimen
failures to be associated with the lower
metal-ceramic interface may be ex-
plained by several factors. The nickel
and vanadium) rich globular phases are
preferentially distributed toward the top
of the joint — Fig. 5. Since vanadium is
fundamentally involved in the reaction
with the ceramic substrate, a higher
vanadium concentration toward the top
of the joint (found in a lower-density liq-
uid phase) could result in a more devel-
oped reaction product (higher percent-
age) along this upper interface. Addi-
tionally, the globular phases contain
the majorities of molybdenum and
vanadium content of the filler material;
these elements possess a lower coeffi-
cient of thermal expansion than either
gold or nickel. Thus, the presence of
the globular phase may locally reduce
the thermal expansion coefficient of the
brazing alloy near the metal-ceramic in-
terface, thereby diminishing the residual
stresses near that interface.

Finally, the data on temperature dis-
tribution along tensile specimens indicated
heat was preferentially extracted from the
top piece of the braze specimen during
cooling. Consequently, the temperature
gradient imposed on the braze joint
could cause the liquid filler metal to so-
olidify from the top ceramic interface (ei-
ther from the reaction layer or from the
alumina substrate) toward the bottom in-
terface. The solidifying metallic phases,
either Ni- or Au-rich, would have nucle-
ated on the ceramic structure at the upper
solid-liquid interface, with some prefer-
ential crystallographic orientation.

Conclusions

The brazing studies conducted on
polycrystalline alumina specimens in the
current investigation have led to an un-
derstanding of some of the factors that
determine mechanical and microstruc-
tural 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-based filler met-
als containing 1, 2 or 3% vanadium ex-
hibit limited wetting on either 94 or
99.8% alumina substrates at tempera-
tures of 1000 and 1020°C for 5 min in a
dry hydrogen atmosphere. All filler met-
als showed a preferential tendency to wet
the glassy phase found in the 94% alu-
mina specimens.

2) Specimens made of 94% alumina
showed consistently high strength and
acceptable hermeticity after being
braze with the three ABA filler metals at
the two brazing temperatures. Tensile
fractures generally occurred in the ce-
ramic substrate.

3) High-purity 99.8% alumina speci-
mens yielded hermetic joints when
braze with the 2 and 3% vanadium filler
metals. However, their joint strength was
generally lower than comparable 94%
alumina braze specimens. The 1% van-
adium-containing alloy yielded good ten-
sile values, intermediate to the 1 and 3%
vanadium filler metals, but produced significantly more joint leaks. The 99.8% alumina specimens brazed with the 2% vanadium alloy yielded the poorest tensile properties. Only the 3% vanadium composition yielded joint strengths approaching the 94% alumina values. The fracture paths in the 99.8% alumina specimens occurred across the metal-ceramic interface.

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

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% 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% alumina specimens.

6) Tensile failures were more likely to be associated with the lower metal-ceramic interface, where joint solidification probably occurred last due to the thermal gradient imposed during cooling from the peak brazing temperature. The resulting reactions and structure favor a stronger top interface.

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