

# A Barrier Layer Approach to Limit Ti Scavenging in FeNiCo/Ag-Cu-Ti/Al<sub>2</sub>O<sub>3</sub> Active Braze Joints

*Molybdenum-coated spacers produced strong, hermetic joints when assembled with a brazing temperature of 850°C*

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**ABSTRACT.** Poor hermeticity was observed with Al<sub>2</sub>O<sub>3</sub>/Fe-29Ni-17Co spacer/Al<sub>2</sub>O<sub>3</sub> joints braze with the active Ag-Cu-Ti filler metal. A Ti<sub>x</sub>O<sub>y</sub> reaction layer did not form at the Ag-Cu-Ti/Al<sub>2</sub>O<sub>3</sub> interface because titanium was scavenged from the filler metal via the formation of an (Fe, Ni, Co)-Ti phase. Altering the brazing parameters did not curtail the scavenging mechanism. A molybdenum barrier layer was sputter-deposited on the Fe-29Ni-17Co spacer with thicknesses of 100, 250, 1000, 2500, or 5000 Å. The 250-Å molybdenum-coated spacers produced hermetic joints having excellent strength when assembled with an 850°C (1562°F) brazing temperature (3 or 5 min brazing times). Molybdenum thicknesses from 250 to 5000 Å resulted in hermetic joints with excellent strength when the brazing temperature was increased to 875°C (1607°F). It was determined that a minimum Ti<sub>x</sub>O<sub>y</sub> thickness of approximately 0.75 to 1.0 μm was required for hermeticity. A Ti<sub>x</sub>O<sub>y</sub> reaction layer thickness in the range of 0.75 to 2.0 μm provided consistently good pull strength performance.

## Introduction

Ceramic materials are suited for a range of engineering applications, including fuel cells, the hot section of internal combustion engine systems, and advanced electronic components (Refs. 1, 2). In most of these structures, ceramics are attached to metal alloys in order for the assembly to provide the required functionality. Filler metal joining and, specifically, brazing have been used successfully to join metal alloys to ceramics (Refs. 3, 4). Filler metal wetting and spreading on ceramics is achieved with either a metallization layer or through the use of active filler metals. The active filler metal, 63.3Ag-35.1Cu-1.6Ti (Cusil ABA™), has been

used in a number of metal-ceramic joining applications (Ref. 5). It is based upon the eutectic Ag-Cu composition, 72Ag-28Cu, having solidus and liquidus temperature equal to 780°C (1436°F) (Ref. 6). The Cusil ABA™ Alloy also contains titanium as the “active” element that promotes wetting on both oxide and nitride ceramics.

An application was identified in which two pieces of alumina (Al<sub>2</sub>O<sub>3</sub>) were to be joined together with an Fe-29Ni-17Co (Kovar™) alloy interlayer, or spacer, between them (Refs. 7, 8). The joint was required to be hermetic and have adequate mechanical strength. The Ag-Cu-Ti active filler metal met process temperature requirements and eliminated the need to metallize the ceramic surfaces. When prototype joints were assembled using the ASTM F-19 “tensile button” configuration, they had adequate pull strength, but the joints were not consistently hermetic.

An analysis was made of the failed braze joints. There was no evidence of gross cracking in the ceramic body, in the filler metal, nor at the filler metal/Al<sub>2</sub>O<sub>3</sub> interfaces. However, as illustrated by the low magnification optical micrograph in Fig. 1, a “lacework” phase was observed in the filler metal field near the latter’s interface with the Fe-29Ni-17Co spacer. No Ti-based reaction layer, designated as Ti<sub>x</sub>O<sub>y</sub>, formed at the filler metal/Al<sub>2</sub>O<sub>3</sub> interface. By comparison, an Al<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> braze joint assembled without the Fe-29Ni-17Co spacer did not develop a lace-

work phase; it exhibited a significant Ti<sub>x</sub>O<sub>y</sub> reaction layer at the Ag-Cu-Ti/Al<sub>2</sub>O<sub>3</sub> interface, and the braze joint was hermetic. Therefore, the following two points became evident: 1) The Fe-29Ni-17Co spacer was clearly a factor in the degradation of braze joint performance; 2) a Ti<sub>x</sub>O<sub>y</sub> reaction layer is required at the Ag-Cu-Ti/Al<sub>2</sub>O<sub>3</sub> interface to ensure hermeticity of the braze joint. (Determining a minimum thickness of the Ti<sub>x</sub>O<sub>y</sub> reaction layer that would provide joint hermetic was an ancillary result of this study.)

An electron microprobe analysis (EMPA) determined the lacework phase to be composed of iron, cobalt, nickel, copper, and titanium segregated into two sublayer compositions (Ref. 8). An iron-rich sublayer developed when the lacework phase was located near the Fe-29Ni-17Co spacer; a nickel-rich sublayer formed when the lacework phase was situated farther into the filler metal. The iron-rich phase had a composition of (Fe<sub>1.0</sub>Ni<sub>0.23</sub>Co<sub>0.27</sub>Cu<sub>0.03</sub>)<sub>2.3</sub>Ti when the elemental concentrations were normalized to an iron content equal to one. The nickel-rich sublayer composition was computed to be (Fe<sub>0.14</sub>Ni<sub>1.0</sub>Co<sub>0.17</sub>Cu<sub>0.25</sub>)<sub>3</sub>Ti when the elemental concentrations were normalized to a unity nickel content. This analysis provided conclusive evidence that the lacework phase had scavenged titanium from the molten filler metal, thereby preventing the development of a sufficiently thick Ti<sub>x</sub>O<sub>y</sub> reaction layer at the Ag-Cu-Ti/Al<sub>2</sub>O<sub>3</sub> interface that would provide the required hermeticity.

A study by Hahn, Kim, and Kang examined the strength of Al<sub>2</sub>O<sub>3</sub>/Fe-38.2Ni-13.0Co-4.7Nb-1.5Ti-0.03Al (Inconel 909™) braze joints made with the same Ag-Cu-Ti filler metal (Refs. 9, 10). They observed a relatively thick reaction layer along the Ag-Cu-Ti/Fe-Ni-Co interface that contained iron, nickel, cobalt, and titanium. No quantitative composition was determined by the authors.

Wielage, Podlesak, and Klose observed the formation of a reaction layer similar to

## KEY WORDS

- Brazing
- Ceramics
- Hermeticity
- Ag-Cu-Ti Filler Metal
- Molybdenum-Coated Spacers
- Joint Pull Strength
- Barrier Layer
- Titanium Scavenging

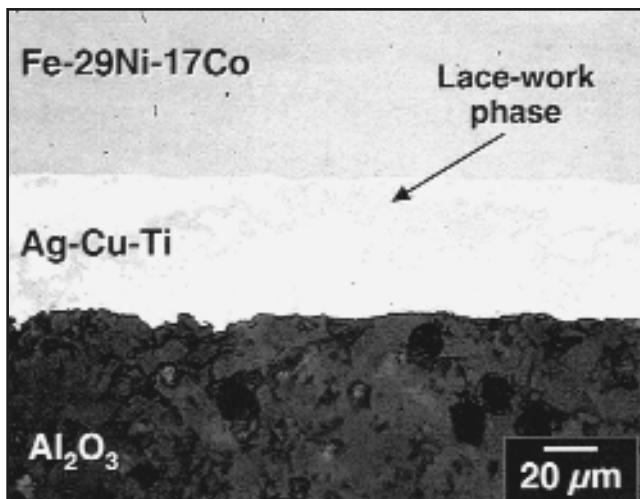


Fig. 1 — Optical micrograph of an  $\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3$  joint made with a Fe-29Ni-17Co interlayer between it and using the Ag-Cu-Ti filler metal. The brazing conditions were 850°C and 5 min.

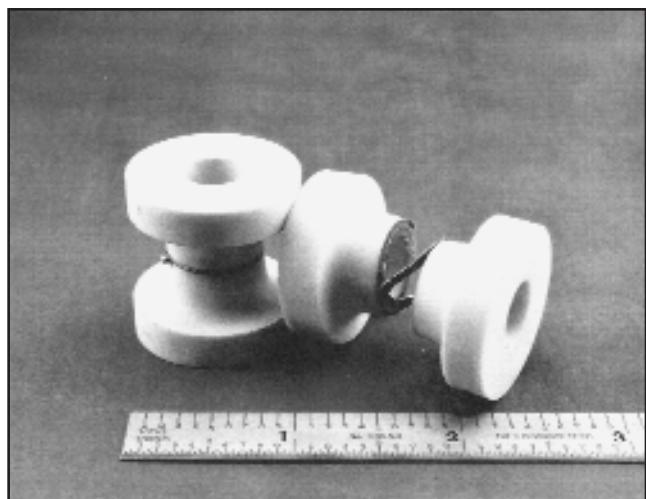


Fig. 2 — Geometry of the ASTM-F19 tensile button specimen. The location of the spacer and brazed joints are shown in the tested sample on the right-hand side of the photograph.

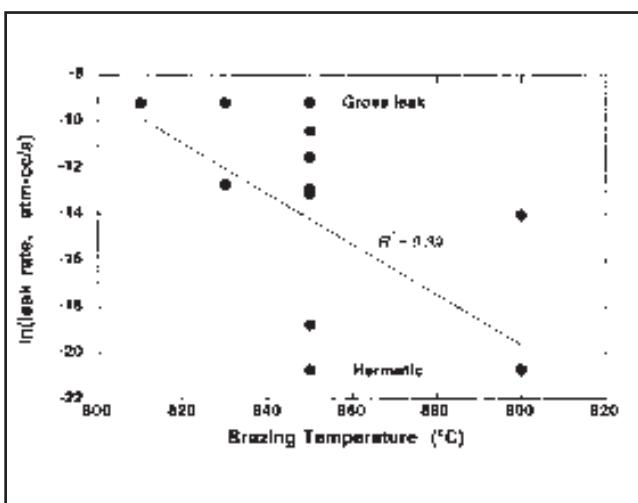


Fig. 3 — Logarithm (natural) of the leak rate as a function of brazing temperature for a brazing time of 5 min.

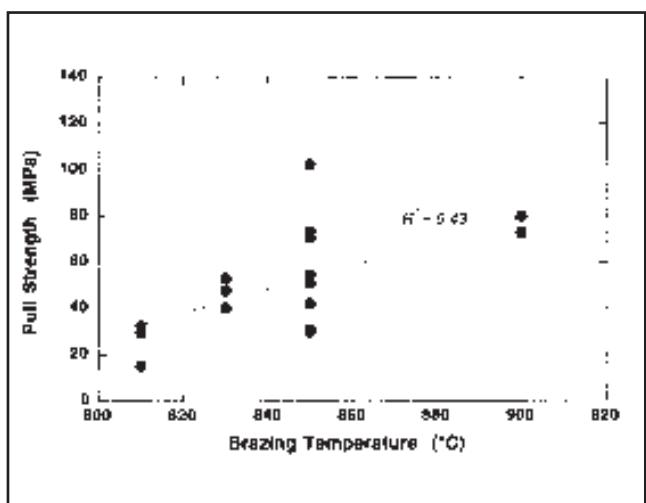


Fig. 4 — Joint pull strength as a function of brazing temperature for a brazing time of 5 min.

the aforementioned lacework phase between a Ag-27Cu-3Ti filler metal and an Fe-Ni-Co alloy (Ref. 11). They determined that the reaction layer had two sublayer compositions. The sublayer closest to the Fe-Ni-Co base alloy had the  $\text{Fe}_{13}\text{Ni}_{47}\text{Co}_{10}\text{Cu}_8\text{Ti}_{22}$  composition and was approximately 1  $\mu\text{m}$  thick. The second sublayer next to the filler metal had a  $(\text{Fe}, \text{Ni}, \text{Co})_3\text{Ti}$  composition and was approximately 2  $\mu\text{m}$  thick. Both sublayer compositions were very similar to those of the lacework phase noted above.

Therefore, a study was performed, the objective of which was to determine a means by which to minimize or eliminate the titanium scavenging mechanism in  $\text{Al}_2\text{O}_3/\text{Fe}-29\text{Ni}-17\text{Co}/\text{Al}_2\text{O}_3$  assemblies brazed with the Ag-Cu-Ti filler metal. The

first of two approaches examined the effect of brazing parameters on the scavenging process. The second approach investigated the use of a molybdenum barrier coating on the Fe-29Ni-17Co spacer to prevent formation of the lacework phase and its scavenging of titanium. Hermeticity and tensile strength, as well as the joint microstructures, were evaluated in this effort.

## Experimental Procedures

### Specimen Configuration

The  $\text{Al}_2\text{O}_3$  base material was Wesgo<sup>TM</sup> AL500 obtained in the ASTM F19 "tensile button" geometry and shown in Fig. 2 (Ref. 12). In some instances, a second as-

sembly geometry was used in which two "straight-walled" hollow cylinders were brazed with the Fe-29Ni-17Co spacer. The faying surfaces had the same dimensions as the small-diameter annulus of the ASTM F19 samples. Both the tensile buttons and the straight-walled cylinders were air fired at 1575°C (2867°F) for 2 hours prior to brazing.

The braze joint was constructed by placing a 0.25-mm (0.010-in.) -thick Fe-29Ni-17Co alloy washer (spacer) between the two  $\text{Al}_2\text{O}_3$  tensile buttons. A 51- $\mu\text{m}$  (0.002-in.) -thick washer of the 63.3Ag-35.1Cu-1.6Ti (Cusil ABA<sup>TM</sup>) filler metal was located between the Fe-29Ni-17Co spacer and respective  $\text{Al}_2\text{O}_3$  button.

The molybdenum barrier layers were sputter deposited on the Fe-29Ni-17Co

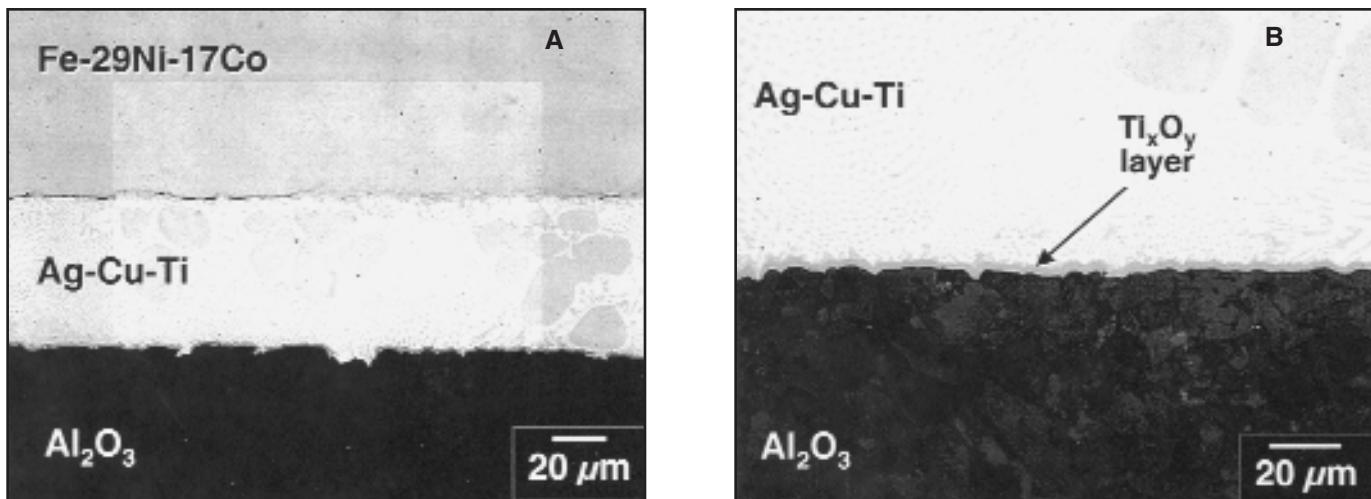


Fig. 5—Optical micrographs of the following: A—the entire braze joint; B—the filler metal/ $\text{Al}_2\text{O}_3$  interface from the test specimen having a 5000-Å Mo layer on the Fe-29Ni-17Co spacer. The process conditions were 850°C and 5 min.

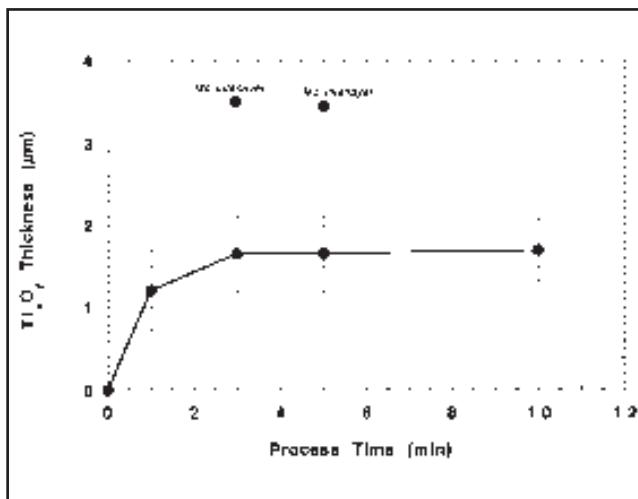


Fig. 6—The  $\text{Ti}_x\text{O}_y$  reaction layer thickness as a function of brazing time for Fe-29Ni-17Co spacers coated with 5000 Å of molybdenum. The brazing temperature was 850°C. Corresponding data for the 100% molybdenum spacer have been included.

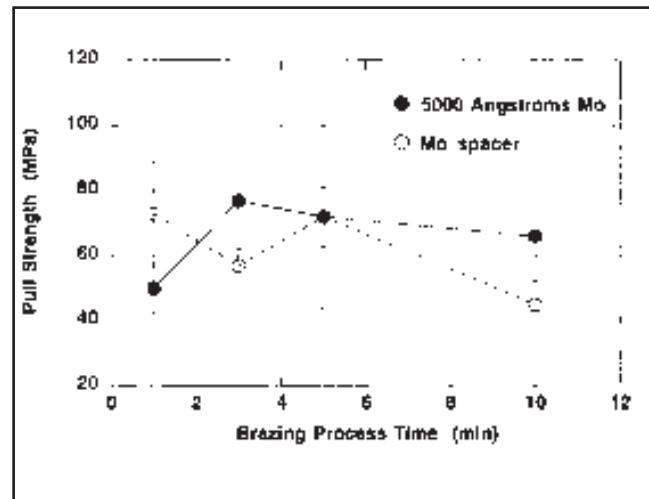


Fig. 7—Pull strength as a function of brazing time for a 850°C brazing temperature. Specimens were assembled with a 5000-Å Mo-coated, Fe-29Ni-17Co spacer or with the 100% molybdenum spacer.

spacer surfaces. The Mo coating thicknesses included 5000, 2500, 1000, 250, and 100 Å. In addition to the Mo-coated Fe-29Ni-17Co spacers, braze joints were also constructed with 100% molybdenum spacers having the same dimensions as the Fe-29Ni-17Co washers.

#### Process Parameters

The braze joints were fabricated according to the following general furnace schedule where  $T_p$  and  $t_p$  are the peak (or brazing) temperature and time:

25–730°C (77–1346°F); 10°C/min (18°F/min) ramp

730°C (1346°F), 15 min hold

730°C– $T_p$ ; 5°C/min (9°F/min) ramp

$T_p$ ,  $t_p$  hold

$T_p$ –730°C, 10°C/min (18°F/min) ramp

730–25°C (77°F), furnace cooling ramp.

Typical brazing parameters used with the Ag-Cu-Ti filler metal are peak temperatures of 850 to 875°C and peak times of 3 to 7 min. Although the analysis concentrated on specimens fabricated with similar parameters, a number of samples were also made using  $T_p$  and  $t_p$  values that were outside the traditional processing regime in order to determine the sensitivity of the Mo barrier approach to the process conditions. Those temperature and time limits were 810 to 900°C (1490 to 1652°F) and 1 to 30 min, respectively. All samples were fabricated under an Ar partial pressure of 1.0 to 1.5 torr.

#### Braze Joint Analyses

Each braze joint was evaluated for her-

micity. One end of the sample was plugged; the other end was attached to a calibrated He mass spectrometer. The center bore was placed under vacuum while the outer surfaces were flooded with He gas. A breach in the braze joint would lead to the inclusion of He into the bore and detection by the mass spectrometer. A joint was considered to have "no detectable leak" when the leak rate was less than the measurement error of the device—that is,  $1 \times 10^{-9}$  atm-cc(He)/s.

The mechanical strength of the braze joints was measured on a servo hydraulic load frame using a cross-head displacement rate of 10 mm/min (0.39 in./min). Three tensile button samples were tested per experimental condition. The maximum tensile load from each test was measured and then converted to a maximum

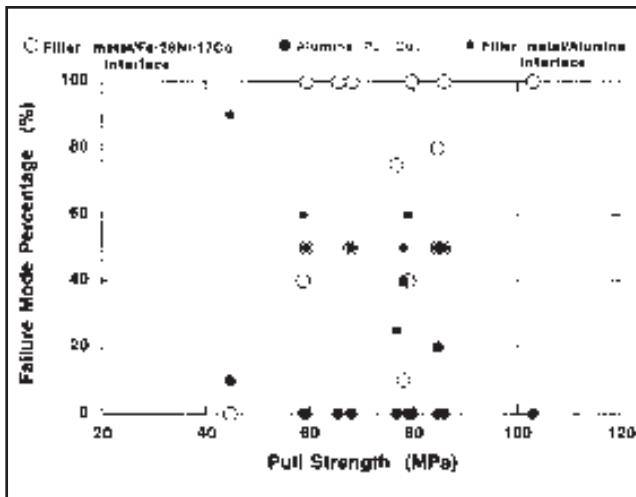


Fig. 8 — Failure mode as a function of pull strength for all samples having the 5000-Å molybdenum-coated Fe-29Ni-17Co spacer. Samples were brazed at 850 and 875°C.

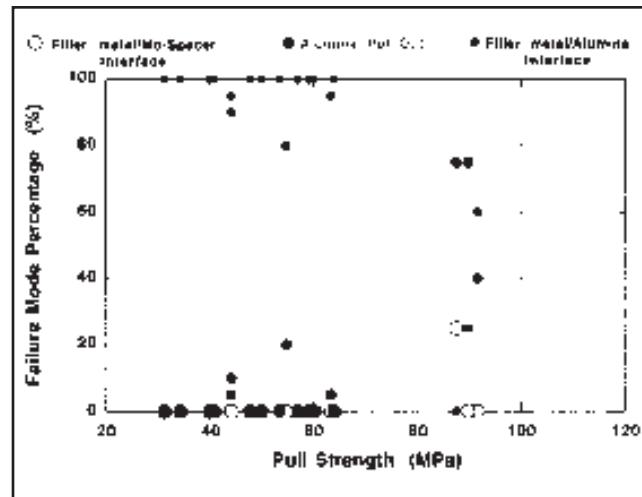


Fig. 9 — Failure mode as a function of pull strength for all samples having the 100% molybdenum spacer. Samples were brazed at 850 and 875°C.

tensile stress; the overall tensile strength (stress) was represented as the mean and  $\pm$  one standard deviation.

Quantitative measurements of the  $Ti_xO_y$  layer thickness (at the filler metal/ $Al_2O_3$  interface) were made using 1000X optical micrographs. Six measurements were performed on a minimum of two separate micrographs per sample.

## Results

### Effect of Process Parameters on Ti Scavenging

Figure 3 shows a plot of the natural logarithm of the leak rate as a function of brazing temperature for a brazing time of 5 min. Although the graph suggests a small improvement in hermeticity with higher brazing temperatures, the linear least-squares analysis indicates a minimal statistical significance to this trend. Similarly, hermeticity did not exhibit a significant dependence on brazing time for a given brazing temperature. In all cases, cross sections showed the lacework phase to be present and the  $Ti_xO_y$  reaction layer generally to be absent from the Ag-Cu-Ti/ $Al_2O_3$  interface. Therefore, it appeared that altering the process parameters (within an acceptable range for this filler metal) did not effectively curtail titanium scavenging so as to allow the consistent fabrication of hermetic joints.

The joint pull strengths were evaluated as a function of brazing parameters. For reference, a pull strength of  $64 \pm 4$  MPa ( $9.4 \pm 0.6$  ksi) was measured for  $Al_2O_3/Al_2O_3$  joints made without an Fe-29Ni-17Co interlayer. Pull strengths as a function of brazing temperature for time periods of 5 min are shown in Fig. 4. A

Table 1 — Hermeticity as a Function of Brazing Parameters (5000-Å Molybdenum-Coated Fe-29Ni-17Co Spacer and 100% Molybdenum Spacer)

Peak Process Temp. (°C)	Peak Process Time (min)	Hermetic Joints 5000 Å Mo (fraction)	Hermetic Joints 100% Mo (fraction)
810	1	0/3	—
830	5	0/3	—
850	1	4/4	4/4
850	3	3/4	4/4
850	5	3/4	4/4
850	10	2/4	4/4
875	1	3/4	4/4
875	5	3/4	4/4

trend of increased joint strength with higher brazing temperature could be detected in the plot; albeit, the  $R^2$  value of the linear regression (0.43) indicated a very low correlation. The opposite trend was observed when joint strength was plotted against brazing time (per given brazing temperature). And, similarly, the  $R^2$  value of the linear regression analysis indicated a relatively poor correlation. Because joint strengths were considered satisfactory for this application when in the range of 40–60 MPa (5.8–8.7 ksi), many of the aforementioned tests showed adequate strength. Nevertheless, those same joints were not hermetic (which also implies that pull strength does not provide an effective metric for hermeticity).

The fracture morphology of the pull tested samples showed separation at the Ag-Cu-Ti/ $Al_2O_3$  interface. Also, a limited extent of the failure path was observed within the  $Al_2O_3$  substrate, one to two grains away from the interface. This latter morphology was caused by interlocking

between the filler metal and pores in the  $Al_2O_3$  structure. Fracture was not observed at the Ag-Cu-Ti/Fe-29Ni-17Co interface, nor was it associated with the lacework phase.

Ancillary experiments were performed in which braze joints were assembled using the commercially available titanium-clad, Ag-Cu (eutectic) filler metal. This filler metal has a higher titanium content of 4.5 wt-% vs. 1.6 wt-% for the active filler metal. The purpose of these experiments was to test the alternative solution that using a higher titanium concentration could support the development of both a  $Ti_xO_y$  reaction layer and the lacework phase, thereby allowing the formation of a hermetic joint. This approach proved to be valid. Prototype joints exhibited a 2- $\mu$ m-thick  $Ti_xO_y$  reaction layer at the filler metal/ $Al_2O_3$  interface. Unfortunately, the titanium-clad filler metal exhibited only limited wetting and spreading, resulting in poor joint hermeticity and low mechanical strength. Therefore, the use of the tita-

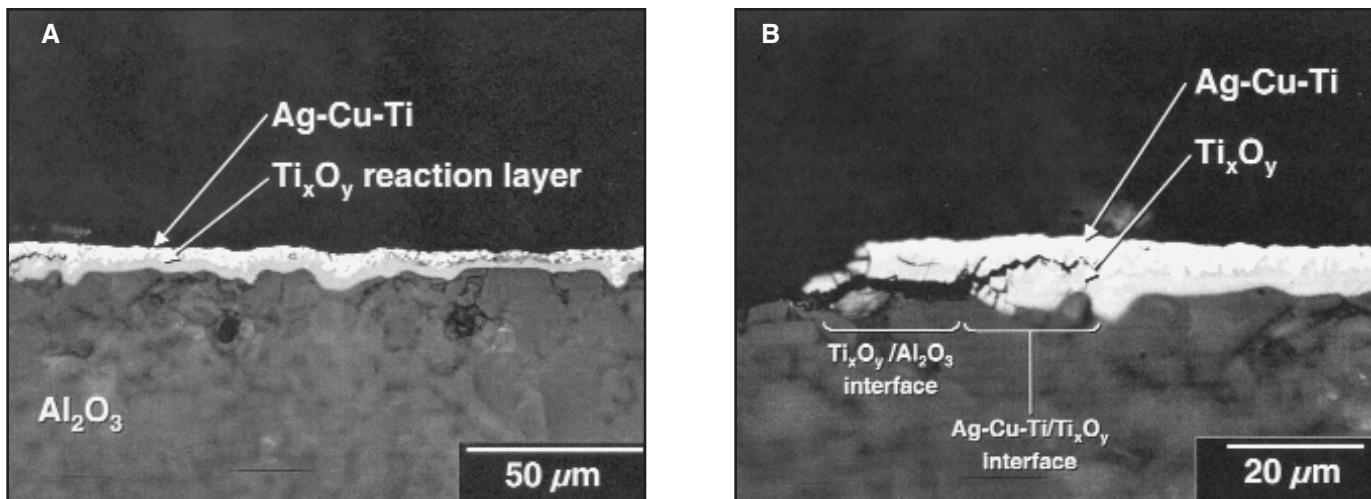


Fig. 10 — Optical micrographs of cross sections showing details of the Ag-Cu-Ti/Al<sub>2</sub>O<sub>3</sub> failure mode from pull tested braze joints made with the 100% molybdenum spacer. A — Fracture in the filler metal near the Ag-Cu-Ti/Ti<sub>x</sub>O<sub>y</sub> interface; B — fracture at the Ti<sub>x</sub>O<sub>y</sub>/Al<sub>2</sub>O<sub>3</sub> interface. The sample was brazed at 850°C for 5 min.

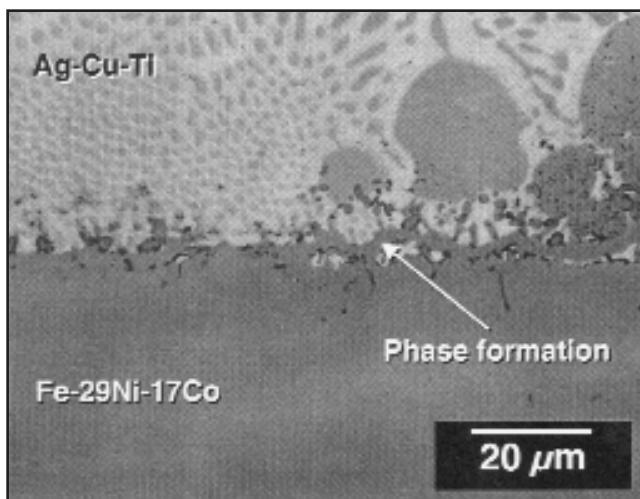


Fig. 11 — Optical micrograph showing a cross section at the Ag-Cu-Ti/(Mo) Fe-29Ni-17Co interface of the joint made with the Fe-29Ni-17Co spacer having a 1000-Å molybdenum coating. The joint was brazed at 850°C for 5 min.

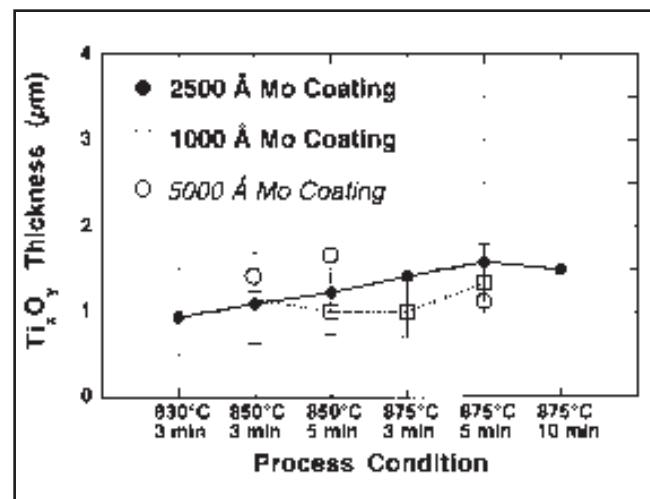


Fig. 12 — The Ti<sub>x</sub>O<sub>y</sub> reaction layer thickness as a function of the brazing process for specimens assembled with Fe-29Ni-17Co spacers having a 2500- or 1000-Å molybdenum barrier layer.

nium-clad product did not provide a viable option for this application and, as such, was pursued no further.

#### Molybdenum Barrier Layer on the Fe-29Ni-17Co Spacer

##### 5000-Å Molybdenum Coating and the 100% Molybdenum Spacer Specimens

Test specimens were fabricated with a 5000-Å molybdenum-coated Fe-29Ni-17Co spacer or with a 100% molybdenum spacer. The hermeticity data are listed in Table 1. The 5000-Å molybdenum coating resulted in a significant improvement in hermeticity. Hermeticity degraded for a brazing time of 5 min at either 810°C (1490°F) or 830°C (1526°F) or when the brazing time was extended to 10 min for a

temperature of 850°C. Therefore, the hermeticity appears to have been optimized for a process window of 850°C, 875°C, and 1 min, 5 min.

Shown in Fig. 5A is an optical micrograph of a joint made with a 5000-Å molybdenum coating on the Fe-29Ni-17Co spacer. The brazing parameters were 850°C and 5 min. The large-scale lacework phase was absent. However, intermittent breaches in the molybdenum layer were observed. Collocated with those small breaches were small particles having a contrast similar to the lacework phase. Nevertheless, a Ti<sub>x</sub>O<sub>y</sub> reaction layer had formed at the Ag-Cu-Ti/Al<sub>2</sub>O<sub>3</sub> interface, as shown in Fig. 5B.

The Ti<sub>x</sub>O<sub>y</sub> layer thickness as a function of brazing time (850°C) is shown in Fig. 6. The layer thickness was not particularly

sensitive to brazing times exceeding 3 min. A specimen brazed at 875°C for 5 min (not shown in Fig. 6) exhibited a  $1.15 \pm 0.39 \mu\text{m}$  thick reaction layer, which was thinner than the plateau thickness level in Fig. 6, suggesting a possible breakdown of the molybdenum layer at the higher brazing temperature and resumption of titanium scavenging.

It was necessary to determine whether the Ti<sub>x</sub>O<sub>y</sub> reaction layer thicknesses recorded in Fig. 6 represented the usage of all of the available titanium contained in the filler metal. Therefore, a theoretical Ti<sub>x</sub>O<sub>y</sub> layer thickness was calculated based upon the following assumptions: 1) The entire Ti content of the filler metal contained in the braze joint clearance was converted to the Ti<sub>x</sub>O<sub>y</sub> reaction layer; 2) the filler metal joint clearance thickness

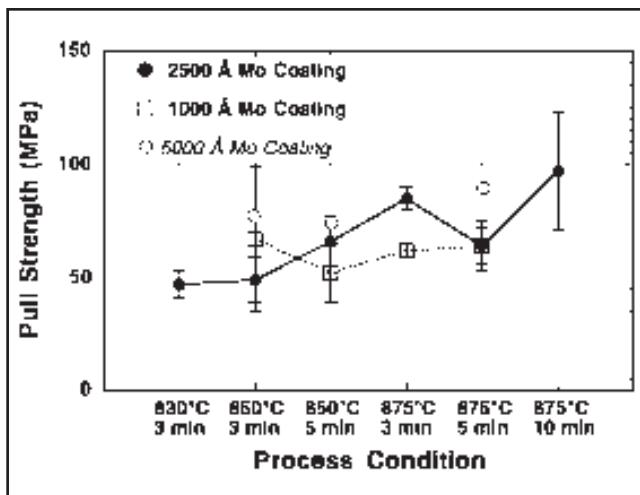


Fig. 13 — Pull strength as a function of brazing conditions for specimens assembled with 2500- $\text{\AA}$  and 1000- $\text{\AA}$  molybdenum-coated Fe-29Ni-17Co spacers.

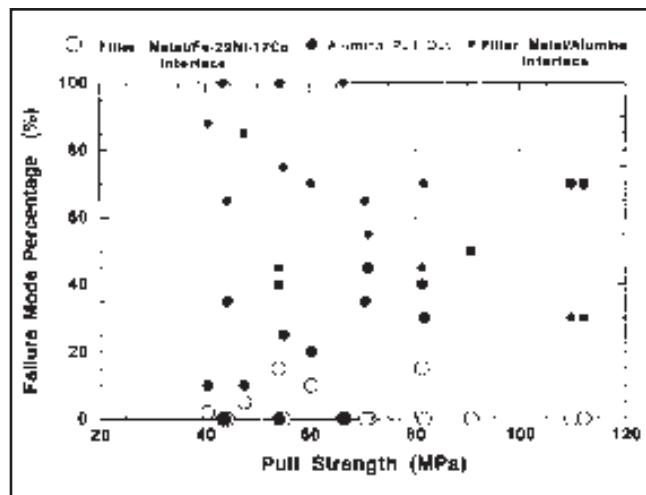


Fig. 14 — Failure mode as a function of pull strength for specimens having the 2500- $\text{\AA}$  molybdenum-coated Fe-29Ni-17Co spacer and which were brazed at 850 and 875°C.

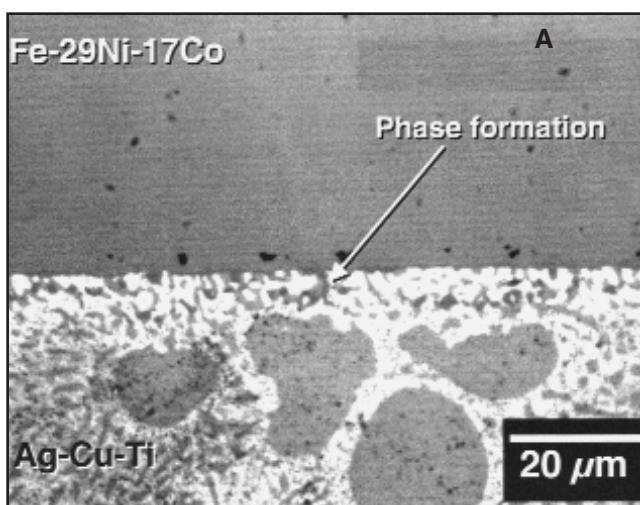


Fig. 15 — Optical micrograph of the joint fabricated with the 250- $\text{\AA}$  molybdenum-coated Fe-29Ni-17Co spacer, viewing specifically; A — the Ag-Cu-Ti/(Mo)Fe-29Ni-17Co interface; B — the Ag-Cu-Ti/Al<sub>2</sub>O<sub>3</sub> interface. Gaps in the layer are indicated by arrows and brackets. The brazing conditions were 850°C for 5 min.

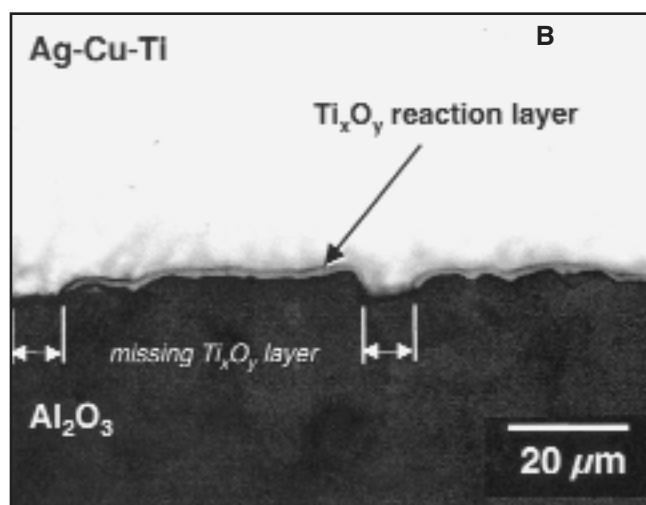
was 51  $\mu\text{m}$  (0.002 in.); 3) the Ti<sub>x</sub>O<sub>y</sub> reaction layer stoichiometry was TiO (Refs. 13–15). The theoretical Ti<sub>x</sub>O<sub>y</sub> thickness was calculated to be 3.4  $\mu\text{m}$  at a single Ag-Cu-Ti/Al<sub>2</sub>O<sub>3</sub> interface.

This theoretical thickness was validated by a joint formed between two pieces of Al<sub>2</sub>O<sub>3</sub> (no Fe-Ni-Co spacer), using a 51- $\mu\text{m}$  (0.002-in.) Ag-Cu-Ti pre-form. The Ti<sub>x</sub>O<sub>y</sub> reaction layer thickness was  $1.9 \pm 0.6 \mu\text{m}$  on each of the two Ag-Cu-Ti/Al<sub>2</sub>O<sub>3</sub> interfaces. Doubling this thickness to represent a single interface gives a value of 3.8  $\mu\text{m}$ , which is very close to that predicted by the theoretical calculation. This exercise provided two important results: 1) The validation experiments determined that nearly all of the titanium in the Ag-Cu-Ti active filler metal would be used to form the Ti<sub>x</sub>O<sub>y</sub> reaction layer in

the absence of scavenging; 2) In the actual experiments using the molybdenum-coated spacer, a significant portion of titanium from the filler metal was, in fact, not being used to develop the Ti<sub>x</sub>O<sub>y</sub> reaction layer.

Braze joints were also fabricated with a 100% molybdenum spacer. All specimens were hermetic (Table 1). The lacework phase was entirely absent from the joint. A Ti<sub>x</sub>O<sub>y</sub> reaction layer formed at the Ag-Cu-Ti/Al<sub>2</sub>O<sub>3</sub> interface. The reaction layer thicknesses, which were measured only for the 850°C, 3 min, and 5 min brazing conditions, were  $3.5 \pm 0.7 \mu\text{m}$  and  $3.4 \pm 0.6 \mu\text{m}$ , respectively. These values were very similar to those predicted in the absence of scavenging, indicating there were no other titanium "sinks" associated with molybdenum.

Next, braze joint pull strengths were evaluated. As a baseline, the pull strength of Al<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> braze joints without the Fe-29Ni-17Co spacer was  $64 \pm 4 \text{ MPa}$  ( $9.4 \pm 0.6 \text{ ksi}$ ). Figure 7 shows pull strength as a function of brazing time for specimens having the 5000- $\text{\AA}$  molybdenum-coated Fe-29Ni-17Co spacer or 100% molybdenum spacer; the brazing temperature was 850°C. In addition, specimens brazed at 875°C for 5 min had a pull strength of  $88 \pm 3 \text{ MPa}$  ( $13 \pm 4 \text{ ksi}$ ). Data scatter was slightly greater with the 5000- $\text{\AA}$  molybdenum coating than with the 100% molybdenum spacer. The molybdenum-coated Fe-29Ni-17Co spacer samples brazed at 3, 5, and 10 min exhibited mean strengths comparable to the above reference value, yet only 50% of the joints made with the 10-min brazing time were hermetic (Table



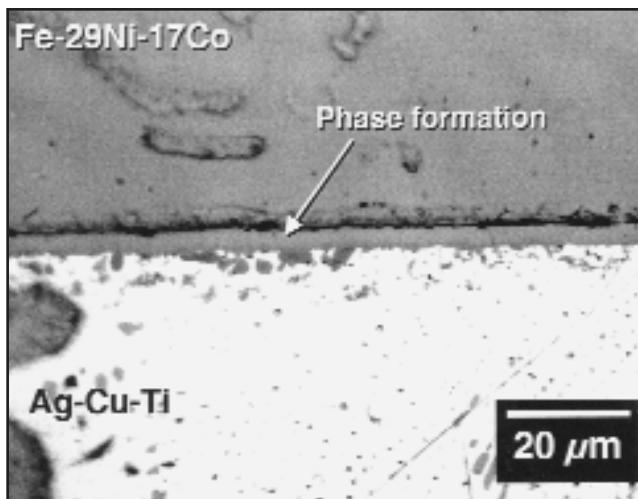


Fig. 16 — Optical micrograph of the Ag-Cu-Ti/(Mo)Fe-29Ni-17Co interface in a specimen assembled with the 100-Å molybdenum-coated Fe-29Ni-17Co spacer. Brazing conditions were 850°C for 5 min.

1). The 1-min brazing time resulted in a lower strength, but with all joints being hermetic. These results reiterate the lack of direct correlation between pull strength and braze joint hermeticity.

A detailed comparison was made between the  $Ti_xO_y$  layer thickness data in Fig. 6 and strength data in Fig. 7. Specifically, those braze joints fabricated with the 5000-Å molybdenum-coated Fe-29Ni-17Co spacer were assessed. Similar trends were observed for both properties, suggesting a possible correlation between  $Ti_xO_y$  layer thickness and joint strength.

The fracture surface morphology was evaluated for pull test specimens assembled with the 5000-Å molybdenum-coated Fe-29Ni-17Co spacer. Three failure modes were observed: 1) separation at the Ag-Cu-Ti/(Mo)Fe-29Ni-17Co interface; 2) separation at the Ag-Cu-Ti/ $Al_2O_3$  interface; and 3) fracture within the  $Al_2O_3$  substrate that was called "Al<sub>2</sub>O<sub>3</sub> pull-out." The extent of each fracture mode was measured as a percentage of the total fracture area. The results are shown in Fig. 8 and include data from samples brazed at 850 or 875°C. The predominant failure mode was separation at the Ag-Cu-Ti/(Mo)Fe-29Ni-17Co interface and occurred either alone or in combination with a lesser presence of one or both of the other two modes. Metallographic cross sections determined that the Ag-Cu-Ti/(Mo)Fe-29Ni-17Co interface failure was actually a mixture of separation at the Ag-Cu-Ti/Mo interface and fracture at the Ag-Cu-Ti/lacework phase interface where the molybdenum coating had been breached. A noticeably higher occurrence of fracture at the Ag-Cu-Ti/ $Al_2O_3$  interface was observed (at the expense of the Ag-Cu-Ti/(Mo)Fe-29Ni-17Co interface

failure) in samples assembled at the higher brazing temperature.

The pull strengths of specimens assembled with the 100% molybdenum spacer were also included in Fig. 7. Brazing times of 3 and 10 min caused lower strengths than comparable samples having the 5000-Å molybdenum-coated Fe-29Ni-17Co spacer; the two specimen types had similar strengths for the 5-min brazing time. Clearly, the dependence of mean pull strength on brazing time was not monotonic. However, the data suggested the pull strength decreased slightly with brazing time.

The failure mode analysis of the pull test specimens made with the 100% molybdenum spacer are shown in Fig. 9 (which includes all process conditions). The data appeared to have separated into two groups. The larger population showed failure at the Cu-Ag-Ti/ $Al_2O_3$  interface. Specifically, the fracture path was located either in the Ag-Cu-Ti filler metal immediately adjacent to the Ag-Cu-Ti/ $Ti_xO_y$  interface, as illustrated in Fig. 10A; at the Ag-Cu-Ti/ $Ti_xO_y$  interface, as shown in Fig. 10B; or along the  $Ti_xO_y$ / $Al_2O_3$  interface, as is also represented in the latter micrograph. A small group of samples had higher pull strengths and failed primarily by the alumina ( $Al_2O_3$ ) pull-out mode. When the pull test results were segregated

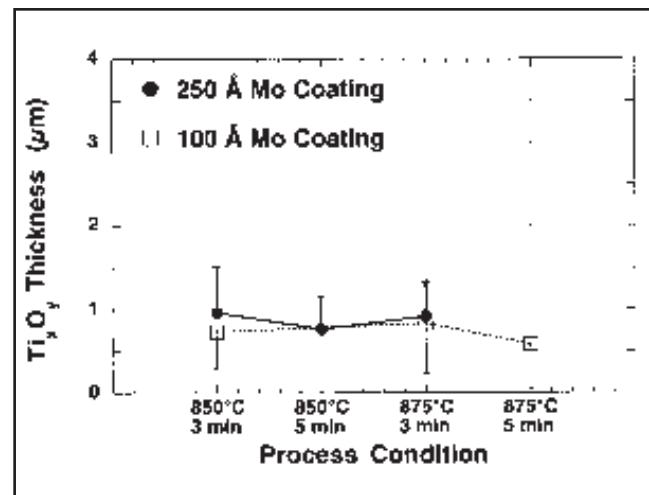


Fig. 17 — The  $Ti_xO_y$  reaction layer thickness as a function of the brazing process for specimens assembled with Fe-29Ni-17Co spacers having a 250- or 100-Å molybdenum barrier layer.

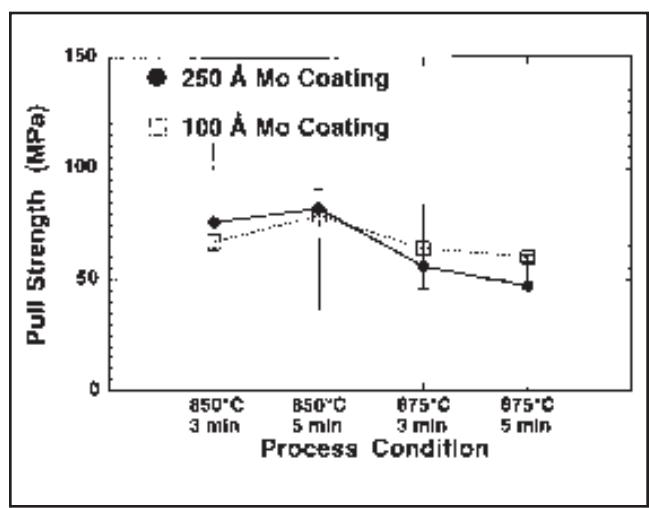


Fig. 18 — Pull strength as a function of process conditions for specimens brazed with 250- or 100-Å molybdenum-coated Fe-29Ni-17Co spacers.

according to the brazing temperature, it was observed that samples fabricated at 850°C were distributed into both regimes in Fig. 9, while those assembled at 875°C were found only in the low-strength regime. This trend suggested that the higher brazing temperature had degraded the Cu-Ag-Ti/ $Al_2O_3$  interface.

A comparison was made of mechanical strength and failure mode data between specimens having the 5000-Å molybdenum-coated Fe-29Ni-17Co spacer and those assembled with the 100% molybdenum spacer. The molybdenum-coated Fe-29Ni-17Co spacers resulted in pull strengths of 50 to 90 MPa (7.2 to 13 ksi) and failure primarily at the Ag-Cu-Ti/(Mo)Fe-29Ni-17Co interface. On the other hand, the 100% molybdenum spacer resulted in generally lower pull strengths

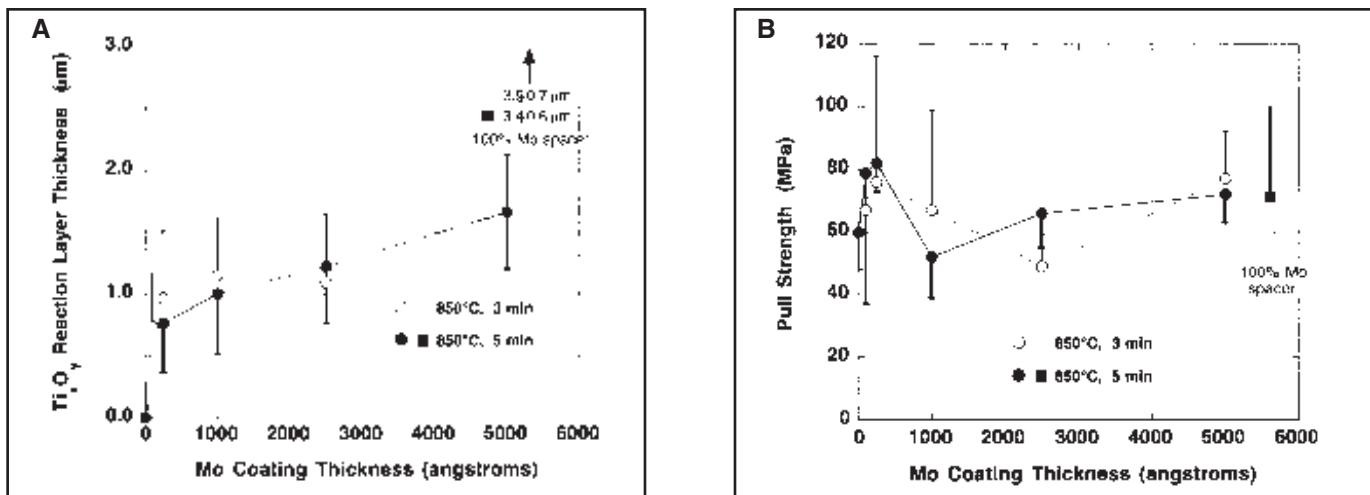


Fig. 19—A—Graph of the  $\text{Ti}_x\text{O}_y$  reaction layer thickness as a function of the molybdenum coating thickness for the 850°C, 3- and 5-min brazing processes; B—pull strength as a function of the molybdenum coating thickness for the 850°C, 3- and 5-min brazing processes. The 100% molybdenum spacer data have been included in both plots.

of 30 to 65 MPa (4.4 to 9.4 ksi) and a dominant failure mode of separation at the Ag-Cu-Ti/ $\text{Al}_2\text{O}_3$  interface. This comparison suggested that the thicker  $\text{Ti}_x\text{O}_y$  reaction layer, which resulted from use of the 100% molybdenum spacer, may have degraded the strength of the Ag-Cu-Ti/ $\text{Al}_2\text{O}_3$  interface. However, this trend was not entirely consistent. The group of “high-strength” data points had  $\text{Al}_2\text{O}_3$  pull-out as a significant fracture mode.

Further strength-failure mode comparisons were performed to understand the relationship between  $\text{Ti}_x\text{O}_y$  layer thickness and braze joint strength. Pull strengths of 35 to 65 MPa (5.1 to 9.1 ksi) were observed for brazed joints made with the uncoated Fe-29Ni-17Co spacers. These strengths are comparable to the low-strength group for specimens made with the 100% molybdenum spacer. Both data sets exhibited fracture primarily at the Ag-Cu-Ti/ $\text{Al}_2\text{O}_3$  interface. Yet there was no  $\text{Ti}_x\text{O}_y$  reaction layer with the uncoated Fe-29Ni-17Co spacer and a 3- to 4- $\mu\text{m}$ -thick  $\text{Ti}_x\text{O}_y$  reaction layer with the 100% molybdenum spacer. On the other hand, braze joints made with the 5000- $\text{\AA}$  molybdenum-coated Fe-29Ni-17Co spacer had consistently higher pull strengths. The Ag-Cu-Ti/ $\text{Al}_2\text{O}_3$  interface was able to support those strengths with only a 1.5- to 2.0- $\mu\text{m}$   $\text{Ti}_x\text{O}_y$  reaction layer thickness. Therefore, it appears that a 1.5- to 2.0- $\mu\text{m}$ -thick  $\text{Ti}_x\text{O}_y$  layer optimized the Ag-Cu-Ti/ $\text{Al}_2\text{O}_3$  interface strength.

A less-than-perfect reduced hermeticity was also observed for joints made with the 5000- $\text{\AA}$  molybdenum-coated spacer. At this point in the analysis, it cannot be stated with certainty that the 1.5- to 2.0- $\mu\text{m}$   $\text{Ti}_x\text{O}_y$  layer failed to provide hermeticity or that the latter was lost at the Ag-Cu-Ti/(Mo)Fe-29Ni-17Co interface.

Table 2—Hermeticity as a Function of Brazing Parameters (2500- and 1000- $\text{\AA}$  Molybdenum-Coated Fe-29Ni-17Co Spacers)

Mo Coating ( $\text{\AA}$ )	Peak Process Temp. (°C)	Peak Process Time (min)	Hermetic Joints (fraction)
2500	830	3	1/3
2500	850	3	3/3
2500	850	5	2/3
2500	875	3	3/3
2500	875	5	3/3
2500	875	10	3/3
1000	850	3	3/3
1000	850	5	3/3
1000	875	3	3/3
1000	875	5	3/3

#### 2500- and 1000- $\text{\AA}$ Molybdenum Coatings

Specimens were assembled using Fe-29Ni-17Co spacers coated with 2500- or 1000- $\text{\AA}$  molybdenum layers. Table 2 shows that in all but two cases having the 2500- $\text{\AA}$  coating, the brazed joints were 100% hermetic. There was no large-scale lacework phase present in the filler metal. However, closer scrutiny of samples having a Ag-Cu-Ti/(1000- $\text{\AA}$  Mo)Fe-29Ni-17Co interface (Fig. 11) revealed formation of a material phase adjacent to the spacer, and the beginnings of its separation from the interface. This morphology represents the same sequence believed to form the lacework phase. A similar artifact was observed with the 2500- $\text{\AA}$  Mo-coated Fe-29Ni-17Co spacer but to a lesser extent.

A  $\text{Ti}_x\text{O}_y$  reaction layer was formed at the Ag-Cu-Ti/ $\text{Al}_2\text{O}_3$  interface of specimens having either the 1000- or 2500- $\text{\AA}$  molybdenum coatings. Plotted in Fig. 12 is the  $\text{Ti}_x\text{O}_y$  reaction layer thickness as a function of the brazing conditions. (The thickness data from samples having a 5000- $\text{\AA}$  molybdenum coating on the Fe-

29Ni-17Co spacer were also included for comparison.) The harshness of the brazing process increases from the left to the right along the abscissa. The  $\text{Ti}_x\text{O}_y$  reaction layer thicknesses were similar at the least severe brazing conditions. At intermediate brazing conditions, the 2500- $\text{\AA}$  molybdenum coating resulted in a  $\text{Ti}_x\text{O}_y$  layer thickness that increased with process severity while that resulting from the 1000- $\text{\AA}$  molybdenum coating remained largely unchanged. Therefore, the  $\text{Ti}_x\text{O}_y$  reaction layer associated with the 1000- $\text{\AA}$  molybdenum coating remained thinner as compared to that formed with the 2500- $\text{\AA}$  molybdenum-coated spacer.

The above trends were combined into the following scenario. At the least severe brazing process conditions, the molybdenum coatings of either thickness provided similar performances as barrier layers; hence, the resulting  $\text{Ti}_x\text{O}_y$  layers had similar thickness. The 2500- $\text{\AA}$  molybdenum coating maintained its barrier function, thereby allowing the  $\text{Ti}_x\text{O}_y$  layer thickness to increase with higher brazing temperatures and/or times. On the other hand, the

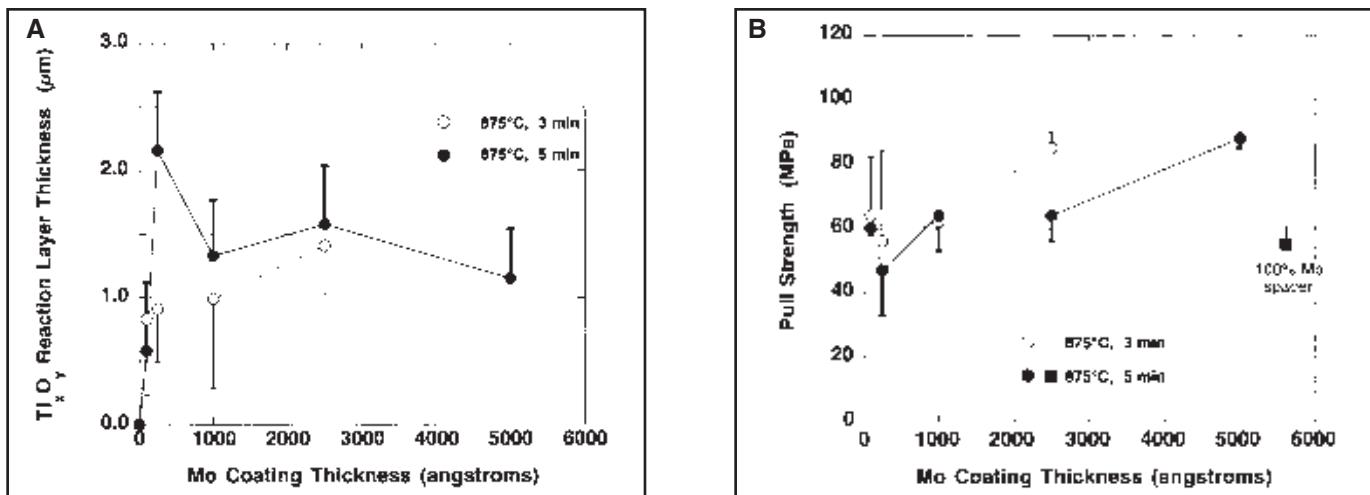


Fig. 20—A—Graph of the  $Ti_xO_y$  reaction layer thickness as a function of the molybdenum coating thickness for the 875°C, 3- and 5-min brazing processes; B—pull strength as a function of the molybdenum coating thickness for the 875°C, 3- and 5-min brazing processes. The 100% molybdenum spacer data have been included in both plots.

Table 3—Hermeticity as a Function of Brazing Parameters (250- and 100-Å Molybdenum-Coated Fe-29Ni-17Co Spacers)

Mo Coating (Å)	Peak Process Temp. (°C)	Peak Process Time (min)	Hermetic Joints (fraction)
250	850	3	3/3
250	850	5	3/3
250	875	3	3/3
250	875	5	3/3
100	850	3	3/3
100	850	5	3/3
100	875	3	3/3
100	875	5	2/3

1000-Å molybdenum coating had a greater tendency to break down under the harsher brazing conditions, thus allowing a greater degree of scavenging to occur, which partially curtailed any growth of the  $Ti_xO_y$  reaction layer. The small increase in  $Ti_xO_y$  thickness associated with the harshest process conditions of 875°C and 5 min indicated the kinetics of the layer growth rate dominated the scavenging mechanism.

Pull strength as a function of brazing conditions is shown in Fig. 13. Generally, strength increased with process severity for the 2500-Å molybdenum-coated spacers. On the other hand, braze joints made with the 1000-Å molybdenum-coated spacers showed pull strengths that were relatively insensitive to process conditions. A comparison of Figs. 12 and 13 indicated that  $Ti_xO_y$  thicknesses and pull strength exhibited similar trends. This correlation was also observed between  $Ti_xO_y$  thicknesses and pull strength for joints made with the 5000-Å molybdenum-coated spacers—Figs. 6, 7.

Pull test failure mode data for joints fabricated with the 2500-Å molybdenum-coated spacers are shown in Fig. 14. The 850 and 875°C brazing temperatures were

represented. The most prevalent fracture location was along the Ag-Cu-Ti/ $Al_2O_3$  interface, followed by pull-out from the  $Al_2O_3$  substrate observed at the highest strength readings. An absence of significant failure along the Ag-Cu-Ti/(Mo)Fe-29Ni-17Co interface indicated that satisfactory adhesion was realized at the Mo/Fe-29Ni-17Co and Mo/Ag-Cu-Ti interfaces, the latter in spite of some local breaches in the coating that allowed the scavenging reaction to locally occur. These results are in sharp contrast to the predominant Ag-Cu-Ti/(Mo)Fe-29Ni-17Co interface failures of joints made with the 5000-Å molybdenum-coated spacer—Fig. 8.

Pull test failure mode data for joints made with 1000-Å molybdenum-coated Fe-29Ni-17Co spacers were nearly identical to those of specimens made with the 2500-Å molybdenum-coated spacer.

In summary, the specimens assembled with the 2500- and 1000-Å molybdenum-coated Fe-29Ni-17Co spacers exhibited similar strengths and slightly less  $Ti_xO_y$  layer growth than were observed for braze joints made with the 5000-Å molybdenum-coated spacers. Nevertheless, the

thinner molybdenum coatings resulted in better hermeticity performance. This comparison indicated that the poorer hermeticity performance of braze joints made with the 5000-Å molybdenum-coated spacers was due to breaches at the Mo/Fe-29Ni-17Co spacer interface rather than breaches at the Ag-Cu-Ti/ $Al_2O_3$  interface.

#### 250- and 100-Å Molybdenum Coatings

Braze joints were assembled with Fe-29Ni-17Co spacers having molybdenum coating thicknesses of 250 and 100 Å. The hermeticity data are shown in Table 3. In all but one case, the specimens were 100% hermetic. Figure 15 shows optical micrographs illustrating the Ag-Cu-Ti/(Mo)Fe-29Ni-17Co interface (Fig. 15A) and the Ag-Cu-Ti/ $Al_2O_3$  interface (Fig. 15B) of a braze joint made with a 250-Å molybdenum-coated Fe-29Ni-17Co spacer. This specimen was brazed at 850°C for 5 min. An extended lacework phase did not develop in the filler metal field. The Ag-Cu-Ti/(Mo)Fe-29Ni-17Co interface (Fig. 15A) showed a particulate phase with a gray scale contrast similar to the lacework phase. The Ag-Cu-Ti/ $Al_2O_3$  interface (Fig. 15B) exhibited an intermittent  $Ti_xO_y$  reaction layer. Gaps in the layer are indicated by the arrows and brackets. The morphology shown in Fig. 15 was representative of all brazing temperatures and times.

Use of the 100-Å molybdenum coating on the Fe-29Ni-17Co spacer resulted in the formation of a distinct layer phase at the Ag-Cu-Ti/(Mo)Fe-29Ni-17Co interface. This microstructure is shown in Fig. 16. The layer, which had a contrast similar to that of the lacework phase, indicated a loss in the barrier function by the 100-Å-thick molybdenum coating. Similarly, gaps were observed in the  $Ti_xO_y$  reaction layer at the Ag-

Cu-Ti/Al<sub>2</sub>O<sub>3</sub> interface but with a greater frequency than observed in braze joints having the 250-Å molybdenum-coated spacer — Fig. 15B. This latter morphology was not sensitive to the brazing conditions.

The Ti<sub>x</sub>O<sub>y</sub> reaction layer thickness was plotted as a function of brazing conditions in Fig. 17. Both 250- and 100-Å molybdenum coatings resulted in nearly equivalent Ti<sub>x</sub>O<sub>y</sub> layer thicknesses that were not particularly sensitive to the brazing conditions. The thicknesses were slightly less than the corresponding values created by the 2500- and 1000-Å molybdenum coatings and significantly below those resulting from the 5000-Å molybdenum layer on the spacer.

The pull strengths of joints made with 250- or 100-Å Mo-coated Fe-29Ni-17Co spacers were plotted as a function of brazing parameters in Fig. 18. The 850°C brazing temperature produced joints having mean strengths that exceeded those of joints made with the 2500- and 1000-Å-thick molybdenum-coated spacers (Fig. 13) and were comparable to the strength of joints made with the 5000-Å molybdenum-coated spacer — Fig. 7. However, the 875°C brazing temperature caused the strength values to decrease, particularly for specimens having the 250-Å molybdenum-coated spacers, to levels commensurate with the 2500- and 1000-Å molybdenum coatings.

Pull-tested braze joints exhibited similar failure modes when assembled with either the 250-Å molybdenum-coated spacers or 100-Å molybdenum-coated spacers. The predominant fracture path was a mixture of separation at the Ag-Cu-Ti/Al<sub>2</sub>O<sub>3</sub> interface and the Al<sub>2</sub>O<sub>3</sub> pull-out. The Al<sub>2</sub>O<sub>3</sub> pull-out mode was more prevalent with the stronger joints. The Ag-Cu-Ti/(Mo)Fe-29Ni-17Co interface structure had no significant role in the fracture process of braze joints assembled with either molybdenum coating thickness on the spacer.

#### Relationship between Ti<sub>x</sub>O<sub>y</sub> Reaction Layer Thickness and Joint Hermeticity and Strength

The data presented above were evaluated to determine, explicitly, the role of Ti<sub>x</sub>O<sub>y</sub> reaction layer thickness on the hermeticity and pull strength properties of active braze joints. The correlating factor was molybdenum coating thickness. First, the discussion will address specimens brazed at 850°C for 3 or 5 min, including those samples fabricated with 100% molybdenum spacers.

It was observed that braze joints were 100% hermetic when fabricated with spacers having 100, 250, and 1000-Å thick molybdenum coatings. There was a loss of hermeticity for braze joints made with the 2500- and 5000-Å molybdenum-coated spacers. The Ti<sub>x</sub>O<sub>y</sub> layer thickness increased

with molybdenum coating thickness, as shown in Fig. 19A. A comparison of hermeticity and Ti<sub>x</sub>O<sub>y</sub> layer thickness properties would suggest an inverse relationship between them if it were not for the 100% hermetic braze joints made with the 100% molybdenum spacer. The latter braze joints developed Ti<sub>x</sub>O<sub>y</sub> layer thicknesses that were nearly twice those measured with the molybdenum-coated Fe-29Ni-17Co spacers. These observations lent further evidence that a weakened Ag-Cu-Ti filler metal/(Mo) Fe-29Ni-17Co interface — not the thicker Ti<sub>x</sub>O<sub>y</sub> reaction layer — caused the reduced hermeticity associated with the 2500- and 5000-Å molybdenum coatings. Therefore, in general, the hermeticity of active braze alloy joints improves with increased Ti<sub>x</sub>O<sub>y</sub> layer thickness. Moreover, it can be inferred from this study that a minimum Ti<sub>x</sub>O<sub>y</sub> thickness of approximately 0.75 to 1.0 µm would be required to ensure hermeticity.

A similar analysis was performed on the braze joint strength data. Figure 19B shows pull strength as a function of molybdenum coating thickness. A small maximum was observed with the 250-Å-thick molybdenum coating. Overall, when considering the degree of data scatter, the strength levels exhibited no distinguishing dependence on molybdenum thickness. Similar strength levels resulted from use of a 100% molybdenum spacer. The predominant failure path was at the Ag-Cu-Ti/Al<sub>2</sub>O<sub>3</sub> interface except for braze joints fabricated with the 5000-Å molybdenum-coated spacers where fracture at the Ag-Cu-Ti/(Mo)Fe-29Ni-17Co interface was most often observed. Putting aside the latter exception for the moment and, assuming the only change to the Ag-Cu-Ti/Al<sub>2</sub>O<sub>3</sub> interface was growth of the Ti<sub>x</sub>O<sub>y</sub> reaction layer, a comparison of Figs. 19A and 19B indicated that joint strength was not particularly sensitive to Ti<sub>x</sub>O<sub>y</sub> reaction layer thickness as long as such a layer was present. This insensitivity of the pull strength to Ti<sub>x</sub>O<sub>y</sub> reaction layer thickness was likely caused by the offsetting effects of the layer brittleness, which caused an increased propensity for failure with greater layer thickness, and higher strength as a thicker layer was accompanied by an increased coverage of the substrate. Lastly, the case of braze joints assembled with the 5000-Å molybdenum-coated spacers represented an anomaly by virtue of decohesion at the Ag-Cu-Ti/(Mo) Fe-29Ni-17Co interface.

The above trends were not reproduced with a 875°C brazing temperature, as shown in Fig. 20. First of all, the braze joints were hermetic with the exception of those made with 100-Å molybdenum-coated spacers and brazed for 5 min. An improved hermeticity was most apparent for braze joints made with the 5000-Å

molybdenum-coated spacers, indicating a better integrity of the Ag-Cu-Ti/(Mo) Fe-29Ni-17Co interface. Secondly, the plot in Fig. 20A indicated that the 3-min brazing time produced a largely monotonic increase of Ti<sub>x</sub>O<sub>y</sub> thickness with molybdenum thickness, as was similarly observed for the 850°C brazing temperature — Fig. 19A. On the other hand, the 5-min brazing time caused the Ti<sub>x</sub>O<sub>y</sub> thickness to reach a maximum and then level off or decrease slightly with the molybdenum thickness, which is in contrast to the monotonically increasing thickness observed with the 850°C brazing temperature — Fig. 19A. Third, the Ti<sub>x</sub>O<sub>y</sub> thickness was generally less after a 3-min brazing time than after a 5-min brazing time. This trend is also different from the similar Ti<sub>x</sub>O<sub>y</sub> thicknesses than observed for either 3 or 5 min of brazing at 850°C. In summary, the higher brazing temperature improved the hermeticity of the joints but also significantly altered the growth dynamics of the Ti<sub>x</sub>O<sub>y</sub> layer, particularly in terms of an increased sensitivity to the brazing time.

The pull strength data obtained from samples brazed at 875°C appear in Fig. 20B. Comparing Fig. 20B to Fig. 20A, it appears that the lower Ti<sub>x</sub>O<sub>y</sub> thicknesses (approximately 0.75 to 1.5 µm) associated with the 3-min brazing time resulted in an increase of pull strength with Ti<sub>x</sub>O<sub>y</sub> thickness. On the other hand, a similar comparison of the 5-min data indicated that the thicker Ti<sub>x</sub>O<sub>y</sub> layers (approximately 1.25 to 2.25 µm) resulted in a decrease of pull strength. This latter trend was also applicable to braze joints assembled with a 100% molybdenum spacer for which a very thick Ti<sub>x</sub>O<sub>y</sub> layer (approximately 3.0–3.5 µm) coincided with a relatively low pull strength.

In summary, the following generalizations were developed for braze joint performance as a function of molybdenum thickness on the Fe-29Ni-17Co spacer. The 250-Å molybdenum-coated spacer provided excellent joint hermeticity and pull strength when brazed at 850°C for either 3 or 5 min. The spacers coated with 250 to 5000 Å of molybdenum resulted in hermetic joints with excellent strength when assembled with the higher brazing temperature of 875°C.

The following generalizations were developed with respect to braze joint performance as a function of Ti<sub>x</sub>O<sub>y</sub> thickness. First, it appears that a minimum Ti<sub>x</sub>O<sub>y</sub> thickness of approximately 0.75 to 1.0 µm was required for hermeticity. Second, the analysis of braze joint strength and Ti<sub>x</sub>O<sub>y</sub> thickness culminated in the following trends. An excessively thin Ti<sub>x</sub>O<sub>y</sub> layer (<0.5 µm) reduced the extent of bonded area, resulting in a relatively low pull strength. An excessively thick Ti<sub>x</sub>O<sub>y</sub> layer (>2.5 µm) degraded pull strength as the

probability increased for fracture in that brittle layer. Therefore, optimum joint strength would likely be realized with a  $Ti_xO_y$  reaction layer thickness in the range of 0.75 to 2.0  $\mu m$ .

## Conclusions

1) Poor hermeticity was observed for  $Al_2O_3/Fe-29Ni-17Co$  spacer/ $Al_2O_3$  joints brazed with the active Ag-Cu-Ti filler metal. The joints exhibited satisfactory pull strengths. A  $Ti_xO_y$  reaction layer did not form at the Ag-Cu-Ti/ $Al_2O_3$  interface because titanium was scavenged from the filler metal via the formation of an (Fe, Ni, Co)-Ti phase. Altering the brazing parameters did not mitigate the titanium scavenging mechanism.

2) A molybdenum barrier layer was sputter deposited onto the Fe-29Ni-17Co spacer with thicknesses of 100, 250, 1000, 2500, or 5000 Å. The coatings reduced the extent of titanium scavenging, allowing  $Ti_xO_y$  formation at the Ag-Cu-Ti/ $Al_2O_3$  interface and a significant improvement in hermeticity.

3) The 250-Å molybdenum-coated spacers produced hermetic joints having excellent strength when assembled with an 850°C (1562°F) brazing temperature (for either 3 or 5 min). The higher brazing temperature of 875°C (1607°F) resulted in hermetic joints with excellent strength for all molybdenum coating thicknesses.

4) A minimum  $Ti_xO_y$  thickness of approximately 0.75 to 1.0  $\mu m$  was required for hermeticity. Joint pull strength was not

strongly sensitive to  $Ti_xO_y$  thickness, because of two opposing mechanisms, poor surface coverage when the  $Ti_xO_y$  layer was too thin and brittle fracture with an excessively thick  $Ti_xO_y$  layer. The  $Ti_xO_y$  reaction layer thickness of 0.75 to 2.0  $\mu m$  provided consistently good strength levels.

5) Fracture along the Ag-Cu-Ti/ $Al_2O_3$  interface was the predominant failure mode in all cases, except specimens made with the 5000-Å molybdenum coating. The poor hermeticity and strength of the Ag-Cu-Ti/(5000-Å Mo)Fe-29Ni-17Co interface was mitigated when brazing was performed at the higher temperature of 875°C.

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