MICROSTRUCTURE AND PERFORMANCE OF KOVAR/ALUMINA JOINTS MADE WITH SILVER-COPPER BASE ACTIVE METAL BRAZE ALLOYS[1]

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ABSTRACT

Poor hermeticity performance was observed for Al_2O_3-Al_2O_3 ceramic-ceramic joints having a Kovar™ alloy interlayer. The active Ag-Cu-Ti filler metal was used to braze the substrates together. The Ti active element was scavenged from the filler metal by the formation of a (Fe, Ni, Co)$_x$Ti phase (x = 2-3) that prevented development of a continuous Ti_xO_y layer at the filler metal/Al_2O_3 interface. Altering the process parameters did not circumvent the scavenging of Ti. Molybdenum barrier layers 1000, 2500, or 5000 Å thick on the Kovar™ surfaces successfully allowed Ti_xO_y formation at the filler metal/Al_2O_3 interface and hermetic joints. The problems with the Ag-Cu-Ti filler metal for Kovar™/Al_2O_3 braze joints led to the evaluation of a Ag-Cu-Zr filler metal. The Zr (active element) in Ag-Cu-Zr filler metal was not susceptible to the scavenging problem.

INTRODUCTION

Ceramic materials are used in a wide range of technologies. High temperature stability allows ceramics to be well suited for fuel cells or for the hot section of internal combustion and turbine engine systems (Ref. 1). Engineered ceramics are also making more inroads into electronic and electro-optical applications (Ref. 2). Because ceramics often do not have the range of characteristics that would allow them to be stand-alone structures, they are used in conjunction with metal or metal alloy materials to support product function. Therefore, techniques must be used to join together ceramics and metallic alloys in order to complete the intended design (Ref. 3). *Filler metal* joining techniques have found widespread application in metal-ceramic joining. Metallization layers as well as so-called *active filler metals* are used to promote filler metal wetting and spreading over the ceramic surface.

Thermal expansion mismatch between the metal and the ceramic base materials can generate residual stresses within the joint that are sufficiently large to crack the ceramic (Ref. 4). Unlike glass to metal sealing – where a precise match between the glass and metallic coefficient of thermal expansion (CTE) are required – the broader temperature range needed for metal/ceramic brazing, and other engineering requirements, generally precludes alloy selection which would obtain a precise CTE match to the ceramic. In general, the braze alloy in a metal/ceramic braze joint is expected to help mitigate the thermal expansion mismatch by means of creep or stress relaxation processes (Ref. 5). Shear-type metal/ceramic braze joint geometries promote stress

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relaxation, while the "tortuous path" geometries lead to high residual stresses because of triaxial stresses which cannot be relaxed via creep deformation processes (Ref. 6).

As an example of the issues discussed above, Kovar™ (Fe-29Ni-17Co, wt.%) has thermal expansion characteristics comparable to alumina ceramic up to 450°C (Ref. 7). The CTE of the Kovar™ alloy is 5.3 ppm/°C (30-450°C), which is somewhat less than the value of 7.2 ppm/°C for 94% alumina ceramic over the same temperature range (Refs. 4, 8). However, at higher temperatures, the absence of magnetostrictive forces in Kovar™ lead to a substantial increase in its CTE behavior. The magnitude of mismatch strains encountered in Kovar/94% alumina ceramic braze joints depend on the braze solidification temperature, and can in many cases be accommodated by eutectic Silver-Copper braze alloys (eutectic composition: 72Ag-28Cu, $T_{eut.}$ = 780°C) (Ref. 5). For the current study, we have examined the use of an active filler metal based on near-eutectic silver-copper alloy. The filler metal is the 63.3Ag-35.1Cu-1.6Ti composition (Cusil ABA™) (Ref. 7), which contains Ti as the "active" element that promotes wetting of the Al_2O_3 surface.

The Al_2O_3/Kovar™/Al_2O_3 joints were required to be hermetic for the proposed application. However, prototype assemblies based upon the ASTM F19 "tensile button" configuration, and made with the Ag-Cu-Ti filler metal, failed to meet hermeticity requirements, in spite of their having acceptable tensile strengths. Scanning electron micrographs of the F19 joint structure at low and high magnifications are shown in Fig. 1. The low magnification image in Fig. 1a shows a "lace work" phase apparent in the filler metal field near the Kovar™ interlayer (see arrows). Higher magnification photos shown in Figs. 1b and 1c revealed interesting details regarding the metal/ceramic interface. In some locations, voided interfaces were observed with only intermittent patches of interface containing a Ti-based reaction layer (designated in this paper as the "Ti_xO_y layer" for brevity) at the filler metal/ceramic interface (see Fig. 1b). On the other hand, some regions of the filler metal/ceramic interface revealed somewhat continuous layers of the Ti_xO_y layer (see Fig. 1c). Energy dispersive x-ray analysis dot maps of the "lace work" phase (not shown) showed it to be comprised of Fe, Ni, Co, and Ti. The x-ray dot maps also revealed that only a spotty Ti signal was detected at the filler metal/Al_2O_3 interface. There was no significant Ti remaining in the filler metal. Electron microprobe analysis (EMPA) was performed on the lace work phase. The phase appears to have a stoichiometry that varies between (Fe, Ni, Co)$_3$Ti and (Fe, Ni, Co)$_2$Ti. Therefore, the microstructural evidence indicates that the loss of hermeticity in the Kovar™/Al_2O_3 braze joints was caused by the scavenging of Ti from the filler metal through the formation of (Fe, Ni, Co)-Ti line compounds. As a result, there was virtually no Ti available for reaction at the filler metal/Al_2O_3 interface.

The micrographs obtained for the Al_2O_3/Kovar™/Al_2O_3 joint should be compared with those in Fig. 2, showing an Al_2O_3/Al_2O_3 braze made without the Kovar™ interlayer, which was processed using indentical process parameters. The "lace work" phase was absent and there was a continuous Ti_xO_y layer at the filler metal/ceramic interface. This type of braze joint was hermetic, and had adequate tensile button strength. The Al_2O_3/Al_2O_3 braze joints results further indicated that the loss of hermeticity in joints made with Kovar™ interlayers were attributable to Fe/Ni/Co dissolution from the Kovar™ into the braze joint, and the resulting scavenging reaction discussed above.
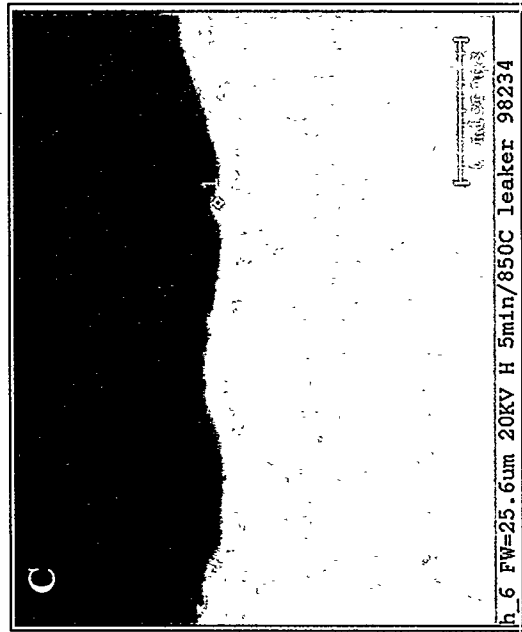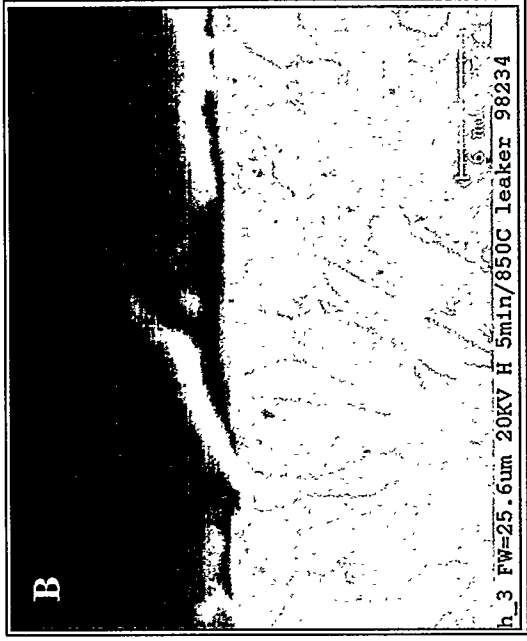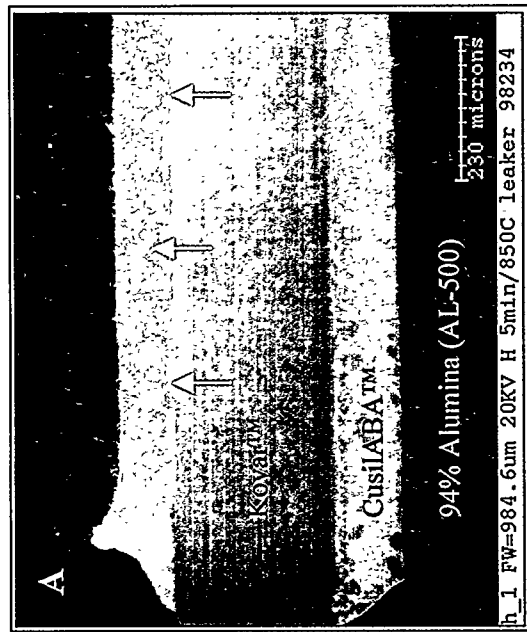
Fig. 1 Scanning electron micrographs of an Al_2O_3/Kovar[TM] /Al_2O_3 joint brazed with the Ag-Cu-Ti filler metal. The process conditions were 850°C and 5 min. (a) Low magnification view showing the entire braze joint, with the "lace-work" phase indicated by arrows in the top joint. (b) High magnification view of a region with virtually no Ti_xO_y reaction product at the braze/ceramic interface and numerous possible leak paths. (c) High magnification view of a region with reasonably continuous Ti_xO_y reaction product at the braze/ceramic interface.

The following approaches were pursued in an effort to develop a functional (i.e., hermetic with decent F19 tensile button strength) Al_2O_3/Kovar™/Al_2O_3 joint: (1) A series of experiments were performed to determine whether the Ti scavenging of the Ag-Cu-Ti filler metal could be reduced by altering the processing parameters. (2) The use of a Mo barrier layer on the Kovar™ was explored. In each approach, the integrity of the joints were evaluated by optical and electron microscopy techniques and tested for hermeticity and pull strength.
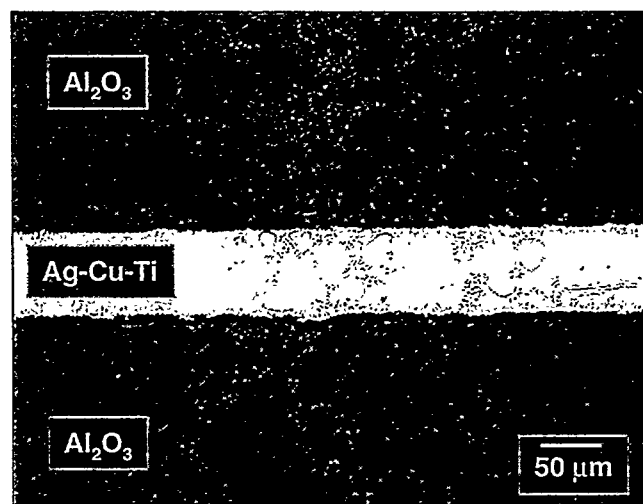
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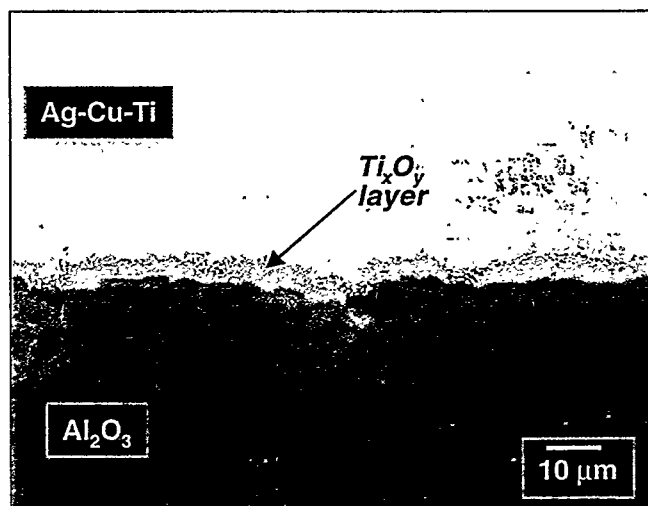
(b)

Fig. 2 Optical micrographs of the Al_2O_3/Al_2O_3 joint made with Ag-Cu-Ti filler metal. There was no Kovar™ interlayer present. The process conditions were 850°C and 5 min.

As a third approach, the active Ag-Cu-Zr filler metal was investigated. Zirconium is attractive as an "active" element because of the negative free energy (thermodynamically spontaneous) of the reduction-oxidation reaction with Al_2O_3 above 600°C (Ref. 10). The Ag-Cu-Zr ternary phase diagram has been published (Ref. 11). Zirconium additions to the eutectic Ag-Cu binary alloy of 1-3 wt.% are present as a Cu_4AgZr line compound phase in the alloy (Refs. 12, 13). Since there is negligible solubility of Zr in either Cu- or Ag-rich phases, the ternary alloy is expected to have lower creep strength than the Ag-Cu-Ti alloy. Reduced creep strength can alleviate residual stress build-up in the joints due to thermal expansion mismatch between the metal and ceramic substrates (Ref. 14). The experimental alloy composition studied was 69.2Ag-28.7Cu-2.1Zr.

EXPERIMENTAL PROCEDURES

Sample geometry

The test sample configuration was the ASTM F19 "tensile button" made of WESGO AL-500 alumina ceramic (Ref. 15). The buttons were air fired at 1575°C for 2 hours prior to the brazing cycle. These specimens were used to obtain hermeticity data, perform microstructural analyses, and determine joint tensile strength. The strength was designated by the maximum load prior to failure using a cross-head displacement rate of 3×10^{-4} in/min (0.00762 mm/min). The maximum load was converted to a tensile stress. At least three tensile button samples per process task were constructed and pull tested. The strength value was represented as the mean of the three data and a $\pm$ error term represented by one standard deviation. In order to alleviate the expense of using the F19 sample configuration for microstructural analysis, a hollow "straight-walled" cylinder test sample geometry was brazed at the same time as the tensile button specimens. These samples had the same inside cavity dimensions as the F19 tensile buttons; they were also air fired prior to brazing, and were brazed with fixturing identical to those used for the tensile buttons. The straight-walled cylinders were evaluated for hermeticity as well as joint microstructure.

Process parameters

Filler metal joints were fabricated according to the following general furnace schedule:

25°C - 730°C; 10°C/min ramp
730°C, 15 min hold
730°C - T_p; 5°C/min ramp
T_p, t_p hold
Tp – 730°C, 10°C/min ramp
730°C – 25°C, furnace cooling ramp

The peak process temperature, T_p, and peak process time, t_p, ranged from 810°C and 5 min to 900°C and 10 min. The samples were fabricated under an Ar partial pressure of 1.0-1.5 Torr unless otherwise stated. Upon completion of the tensile button (or straight-walled cylinder) assembly, the samples were evaluated for hermeticity using commercial He leak detection equipment.

Quantitative analysis of the joint microstructure was comprised of measurements of the Ti_xO_y layer thickness at the filler metal/Al_2O_3 interface. The thickness measurements were made on 1000x optical micrographs taken of the interface. Six (6) measurements were performed per a minimum of two separate micrographs.

RESULTS AND DISCUSSION

### Cu-Ag-Ti – Kovar™ interaction as a function of process parameters

The first set of experiments examined whether the Ti scavenging could be minimized by altering the peak process temperature (T_p) and process time (t_p). Shown in Fig. 3 are plots of the logarithm of the leak rate as a function of: (a) process time for a process temperature of 850°C, and (b) process temperature per a 5 min process time. Although the plots suggest an improvement in hermeticity with reduced process time or increased process temperature, respectively, the linear least-squares analysis had a very low fit (R^2) correlation, indicating a minimal statistical significance in both cases. As indicated in Fig. 3, a few samples were found to be hermetic, and metallographic cross sections of those samples indicated a continuous Ti_xO_y reaction layer, with a limited amount of lace-work phase near the Kovar™ interlayer. However, for the case of most samples, which were non-hermetic, the microstructure was unaffected by process conditions; there was no development of a continuous Ti_xO_y layer at the filler metal/Al_2O_3 interface along with the presence of the lace work phase near the Kovar™ interlayer.

An important observation was made from an analysis of hermeticity versus pull strength. Shown in Fig. 4 is all of the process variation data plotted as pull strength versus the logarithm of the leak rate. Only a very weak correlation ($R^2 = 0.29$) could be drawn by the linear least-squares analysis. The fact is, satisfactory pull strengths were achieved with samples having poor hermeticity, apparently caused by a discontinous Ti_xO_y layer at the filler metal/Al_2O_3 interface. Moreover, metallographic cross sections made of pull tested samples confirmed that a significant portion of the failure path occurred within the Al_2O_3 ceramic. From these observations, we deduced that a discontinuous Ti_xO_y reaction layer can still produce reasonable joint strength, while failing in hermeticity. It was surmised that a continous Ti_xO_y reaction layer is required to establish joint hermeticity.

Mo-coated Kovar™ to reduce Ti scavenging

A reduction in Ti scavenging was realized by sputter depositing a layer of Mo on the Kovar™ interlayer surfaces. The extent of the lace work phase was significantly reduced or eliminated altogether, and a Ti_xO_y layer had developed at the filler metal/Al_2O_3 interface. The micrographs in Fig. 5 illustrate these points with a low magnification view of the joint structure and a close-up of the filler metal/Al_2O_3 interface. The sample was processed at 850°C for 5 min and had 5000 Å of Mo on the Kovar surface.
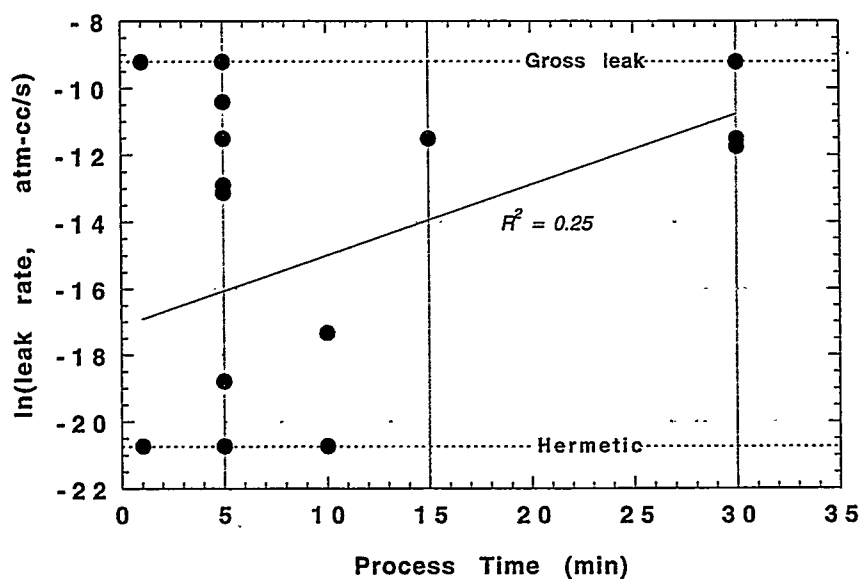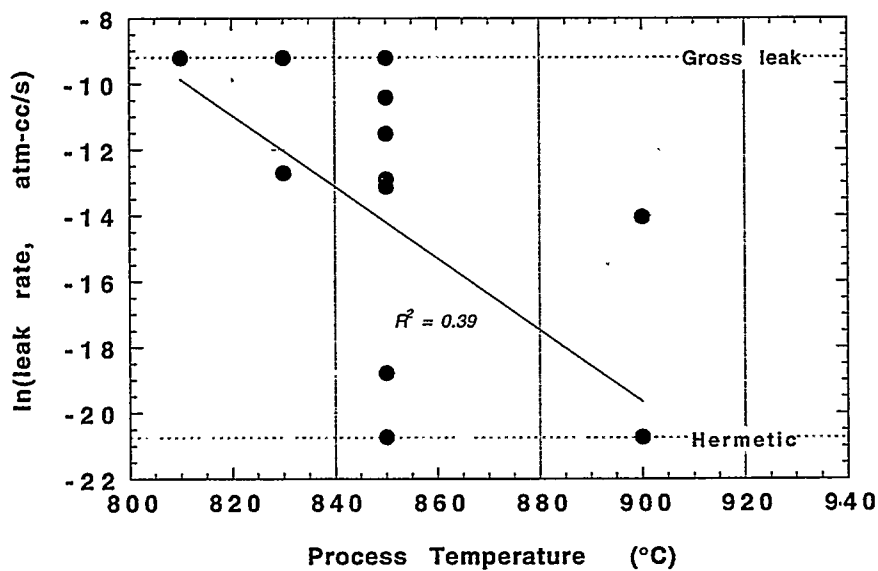
Fig. 3 Logarithm (natural) of the leak rate as a function of (a) process time for a process temperature of 850°C and (b) process temperature for a process time of 5 min. Each sample had the Kovar™ interlayer. The R² value was calculated from a linear least-squares data fit.
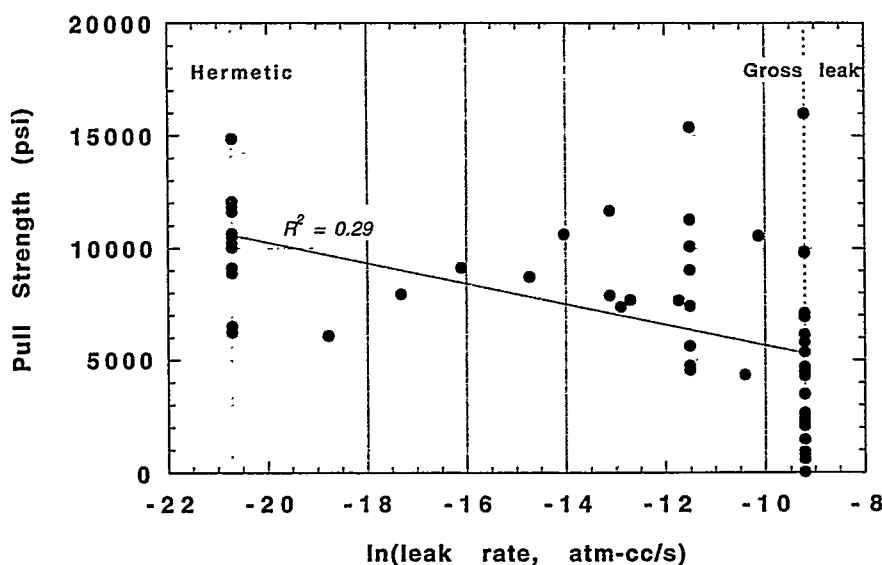
Fig. 4 Pull strength as a function of the logarithm of the leak rate compiled from all of the relevant process variation data. The R^2 value was calculated from a linear least-squares data fit.

The plot in Fig. 6 shows the measured Ti_xO_y thickness for joints made with the Mo-coated Kovar™ (5000 Å) as a function of process time for a process temperature of 850°C. The layer thickness is insensitive to process time for values exceeding 1 min, remaining steady at approximately 1.7 µm.

In parallel with the trials performed with the Mo-coated Kovar™ interlayers, samples were assembled with a 100% Mo interlayer. These experiments determined the fundamental effectiveness of Mo as a barrier to Ti scavenging in the event that the thin Mo-coatings did not survive the brazing cycle. Shown in Fig. 6 are the two Ti_xO_y thickness data after brazing for 3 min and 5 min at 850°C. The Ti_xO_y thickness values were 3.5 µm and 3.4 µm, respectively. These values were nearly twice those which resulted from the use of the Mo-coated Kovar™ as the interlayer.

A computation was performed to determine the theoretical Ti_xO_y layer thickness that would result from similar bond gap thickness and an assumed stoichiometry of TiO for the Ti_xO_y layer. *The computed thickness was 3.3 µm.* This value nearly equals that observed when the Mo interlayer was used. Therefore, simply having the Mo coating over the Kovar™ interlayer did not ensure that *all* of the Ti had diffused to, and reacted at, the filler metal/Al_2O_3 interface. Nevertheless, considering that nearly all joints made with the 5000 Å thick Mo-coated Kovar™ were hermetic and had adequate strength, the observed Ti_xO_y layer thickness range was adequate for the joints to meet functional requirements.
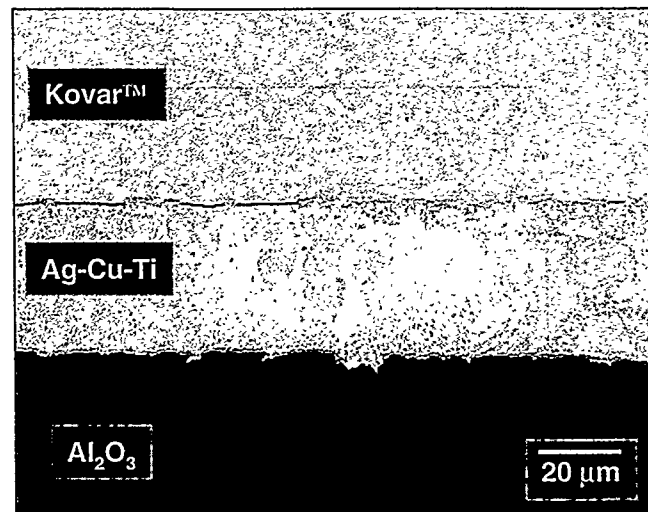
(a)
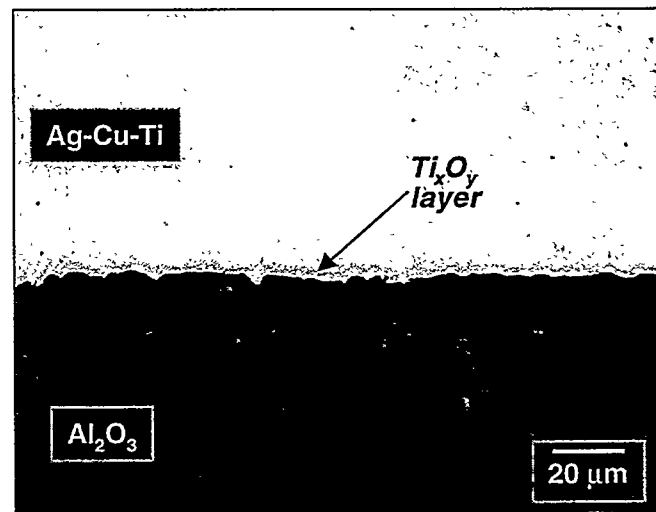
(b)

Fig. 5 Optical micrographs of: (a) the entire braze joint and (b) the filler metal/Al_2O_3 interface from the sample having a 5000 Å Mo layer on the Kovar™. The process conditions were: 850°C and 5 min.

Molybdenum coating thicknesses of 1000 Å and 2500 Å on Kovar™ were also evaluated. Figure 7 plots the measured Ti_xO_y thickness as a function of the Mo coating thickness. The peak process temperature was 850°C. Two process times were evaluated: 3 min and 5 min. The mean layer thickness increased slightly with thicker Mo layers; however, the significance of the trend was obscured by the data scatter. The Ti_xO_y layer thickness showed no apparent dependence upon the peak process time with any of the Mo coating values. Nearly all of the joints made with either the 1000 Å and 2500 Å Mo coatings passed hermeticity testing.
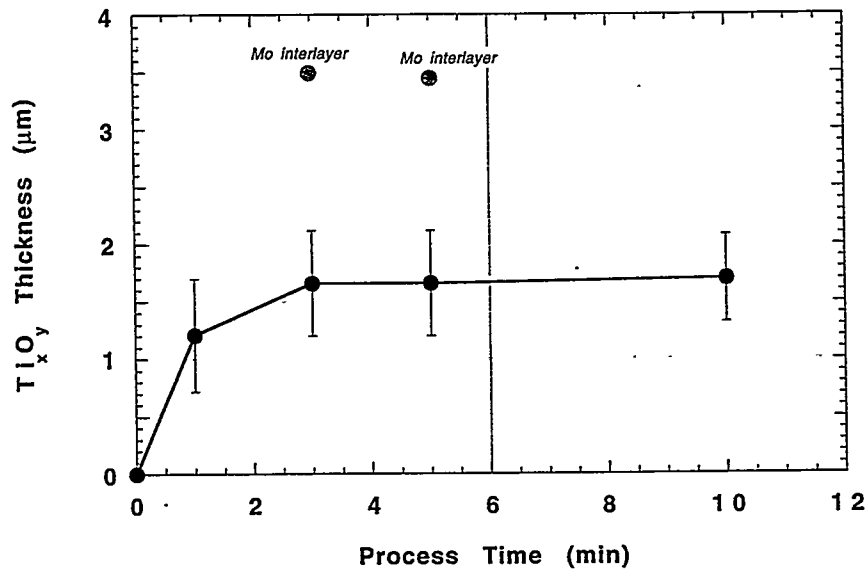
Fig. 6 Plot of the Ti_xO_y layer thickness as a function of process time for Kovar™ interlayers having a Mo coating thickness of 5000 Å. The peak process temperature was 850°C. Also shown are the Ti_xO_y thickness data points that result from the use of a 100% Mo interlayer, at a process temperature of 850°C.
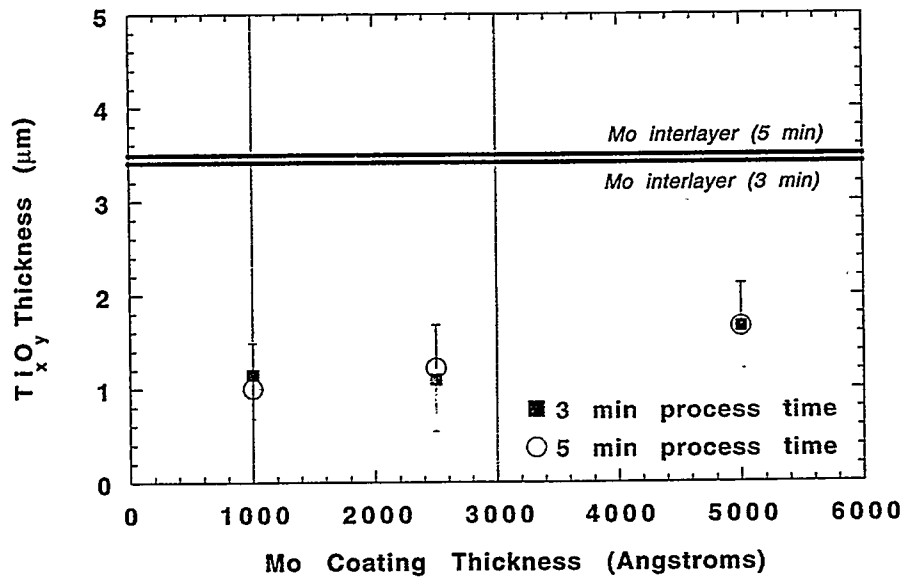

Fig. 7 Plot of the Ti_xO_y layer thickness as a function of Mo coating thickness. The peak process temperature was 850°C. Two peak process times were used: 3 min and 5 min.

Filler metal joints made with 69.2Ag-28.7Cu-2.1Zr alloy

Shown in Table 1 are hermeticity and tensile strength data from eight process groups made with bare Kovar™ interlayers and the Ag-Cu-Zr filler metal. Each group consisted of two tensile buttons and one straight-walled cylinder that were fabricated with the noted peak process temperature and time values.

A process temperature of at least 950°C was required to realize hermetic joints. This point corroborates similar test data in the literature (Ref. 16). Electron microprobe analysis confirmed the Zr to be present as Cu_4AgZr line compound phase in the as-received braze foil. The higher process temperatures were required to drive dissolution of the Cu_4AgZr so as to make the Zr available for reaction at the filler metal/Al_2O_3 interface. Cross sections of samples brazed with the Zr-7 process were examined using electron microprobe analysis, which indicated a continuous layer of ZrO_2 at the alumina interface, and only a minor amount of Zr scavenging near the Kovar interlayer.

Run ID	Peak Process Temp. (°C)	Peak Process Time (min)	Hermeticity	Tensile Strength (psi)
Zr-1	850	5	3/3 leaked	667., 783.
Zr-2	850	10	3/3 leaked	493., 783.
Zr-4	900	1	2/3 leaked	7,426.*
Zr-5	900	3	3/3 leaked	8,282.*
Zr-3	900	5	1/3 leaked	4,583., 4,830.
Zr-6	950	3	2/3 leaked	6,991., 9,297.
Zr-7	950	5	0/3 leaked	8,673., 11,284.
Zr-8	950	10	1/3 leaked	7,977., 9,270.

Table 1. Hermeticity and tensile strength data from eight process groups using the Ag-Cu-Zr alloy with a Kovar interlayer. The (*) sign denotes that the second strength datum was lost during testing. A hermetic joint was that having a leak rate below 1×10^{-9} atm-cc/s.

CONCLUSIONS

1. Poor hermeticity performance was observed for Al_2O_3/Kovar™/Al_2O_3 metal/ceramic braze joints. The active Ag-Cu-Ti filler metal was used to join the three structures. The joints exhibited generally adequate tensile strengths. However, in non-hermetic joints, a continuous Ti_xO_y reaction layer did not form at the filler metal/Al_2O_3 interface. The Ti active element was scavenged from the filler metal via the formation of an (Fe, Ni, Co)-Ti phase, resulting from dissolution of the Kovar™ interlayer into the braze joint.

2. Altering the process parameters did not circumvent the loss of Ti to (Fe, Ni, Co)-Ti phase development when brazing to bare Kovar™. However, molybdenum barrier layers sputtered on the Kovar™ surface did successfully prevent Ti scavenging, resulting in continuous Ti_xO_y layer formation at the filler metal/Al_2O_3 interface and hermetic joints.

3. The use of Zr as the active element in a Ag-Cu-Zr filler metal was found to be essentially immune to the scavenging phenomenon, resulting in strong hermetic joints, albeit, at higher processing temperatures.

ACKNOWLEDGEMENTS

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