Understanding the Run-Out Behavior of a Ag-Cu-Zr Braze Alloy

The run-out process is explored when used to join alumina to an Fe-Ni-Co alloy

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The run-out phenomenon occurs when a significant portion of the molten filler metal exits the gap region and accumulates on an exterior, base material surface. It can cause excessive void formation, plus wastes filler metal and generates residual stresses that crack brittle base materials. This behavior was observed in active braze joints made with 97Ag-1Cu-2Zr (wt-%) filler metal when joining alumina (Al_2O_3) ceramic to Kovar™ (a trademark of Carpenter Technologies, Reading, Pa.).

The proposed mechanism for run-out is an instability in the wetting and spreading of molten filler metal. The driving force for run-out was the reaction between the Fe, Ni, and Co constituents of Kovar™ with elemental Al released by the reduction-oxidation reaction between Zr and Al_2O_3.

Based on this study, a modification to the filler metal composition, or use of a barrier coating on the Kovar™ surface, provide the most promising mitigation strategies against run-out.

Run-Out Phenomenon

Braze joint optimization requires that the amount of filler metal supplied to the gap be closely controlled. Too little filler metal results in voids and nonfilled regions in the brazement that jeopardize both strength and hermeticity. On the other hand, an excessive quantity of molten braze alloy can be rejected from the gap, only to collect on an exterior surface as run-out; this not only causes unsightly cosmetic defects and impedes visual as well as x-ray inspection, it may also interfere with next-assembly fitup or mechanical functions.

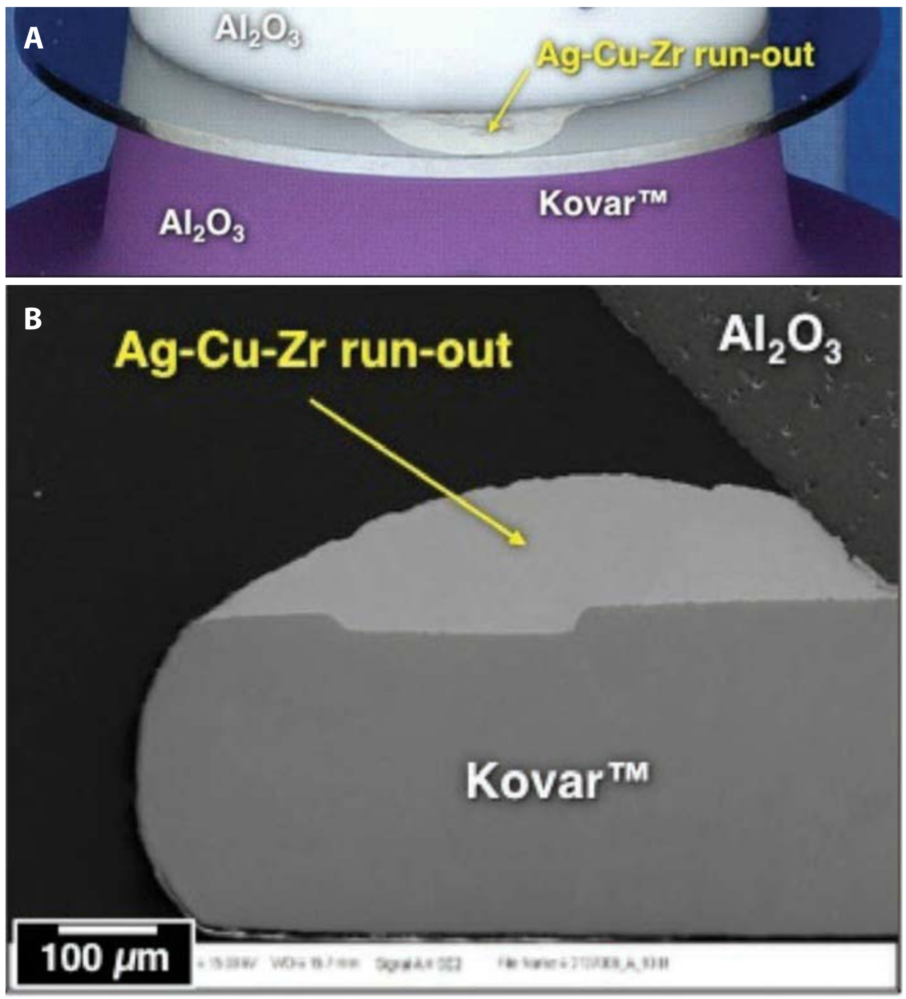


Fig. 1 — A — This photo shows run-out by an Ag-Cu-Zr active braze alloy being used to join two Al_2O_3 base materials to a Kovar™ spacer; B — a SEM photo shows run-out by means of a metallographic cross section.

The run-out filler metal may wet to ancillary structures, as shown in Fig. 1, or simply freeze to nonwettable surfaces. A particularly problematic consequence, whether by wetting or freezing to surfaces, is the generation of residual stresses in the base material. This phenomenon is illustrated in Fig. 2. The run-out of an Au-Cu-Ni-Ti filler metal caused cracking in the ceramic member of the assembly.

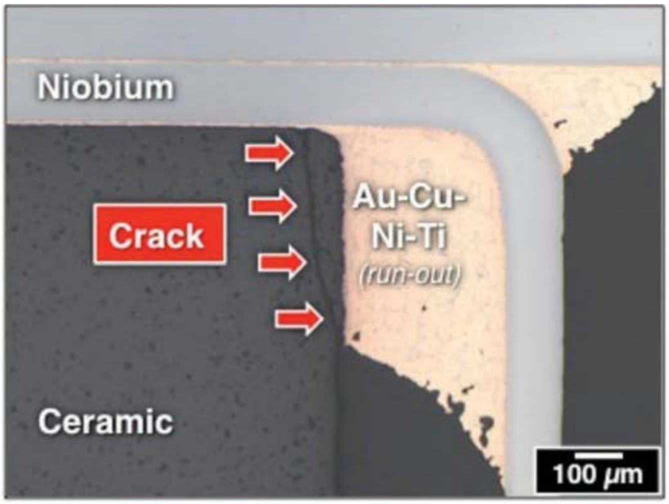


Fig. 2 — Optical micrograph shows cracking in the ceramic member caused by run-out of the Au-Cu-Ti-Ni filler metal.

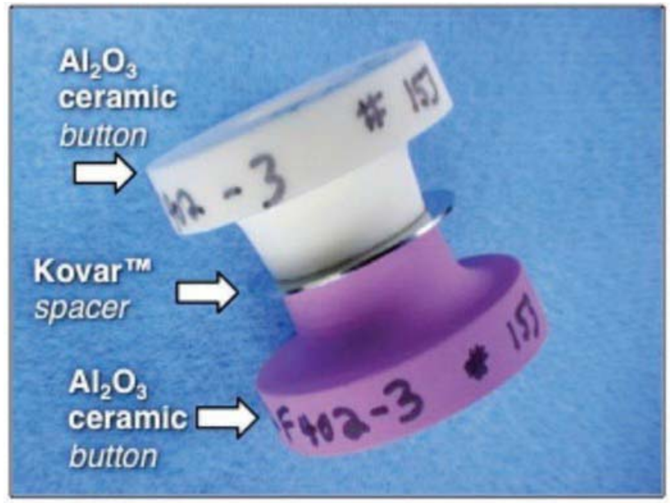


Fig. 3 — This photo shows the tensile button assembly. There are two Al_2O_3 ceramic buttons brazed to either side of the Kovar™ spacer.

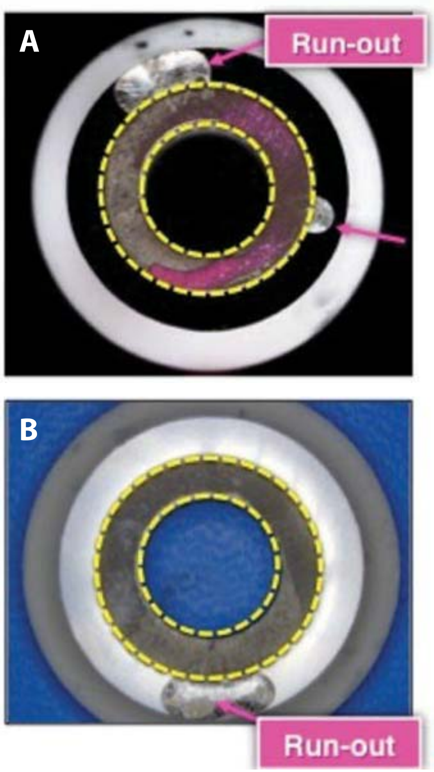


Fig. 4 — A, B — Photographs show run-out experienced by the Kovar™ spacer/Ag-Cu-Zr/Al_2O_3 braze joint. The tensile button assemblies were brazed at 965°C (1769°F) for 20 min in 600-torr Ar prior to being pulled apart. The ceramic faying surfaces are between the dashed circles.

The detrimental effects of run-out have long been recognized by the brazing industry. Several mitigation approaches have been explored to control it, which include the following:

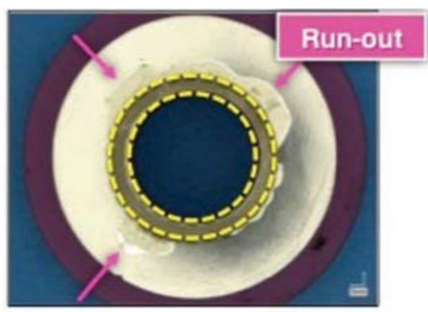


Fig. 5 — Photograph shows run-out (arrows) experienced by the Kovar™ spacer/Ag-Cu-Zr/Al_2O_3 joint that was brazed with a reduced amount of filler metal. The process conditions were 985°C (1805°F) for 5 min in a 600-torr Ar atmosphere.

- Reduce the peak brazing temperature to increase the viscosity of the molten filler metal. Unfortunately, filler metal viscosity is relatively insensitive to peak temperature (except in the presence of a pasty range).
- In light of the previous point, a second approach is to add one or more alloying elements to the filler metal to create a wider pasty range.
- Modify the geometry of the base material surface by adding corners that would be expected to slow or halt the flow of molten filler metal.

All of these measures have been met with little or no success. The lack of effectiveness implies that run-out is not simply a physical displacement or "squishing-out" of molten filler metal. Rather, there are other driving forces responsible for this phenomenon.

Characterization of Run-Out for the Target Application

The Ag-Cu-Zr active braze alloy was considered for an application that joined Kovar™ to Al_2O_3 ceramic. The tensile button configuration was used to assess braze joint performance (Ref. 1). A photo of the tensile button assembly is shown in Fig. 3.

Two Al_2O_3 "buttons" were brazed to a Kovar™ "spacer." The spacer had 0.038-mm (0.0015-in.) dimples that controlled the thicknesses of both gaps. The Ag-Cu-Zr filler metal was preplaced in the gap with the form of an annular ring. Its footprint was the same as that of the Al_2O_3 faying surface with a 10.2-mm (0.400-in.) inner diameter and 15.9-mm (0.625-in.) outer diameter. The preform was 0.051 mm (0.002 in.) thick.

Two varieties of Al_2O_3 ceramic were used in this study; however, the slight compositional variations responsible for their different colors had a negligible effect on wetting or mechanical properties.

Shown in each of Fig. 4A and B are two, post-pull tested tensile buttons taken from different assemblies. Both samples were brazed at 965°C (1769°F) for 20 min in a 600-torr Ar atmosphere. The yellow dashed circles indicate the boundaries of the ceramic faying surface area. The specimens exhibited significant filler metal run-out. Although two run-out "lobes" formed

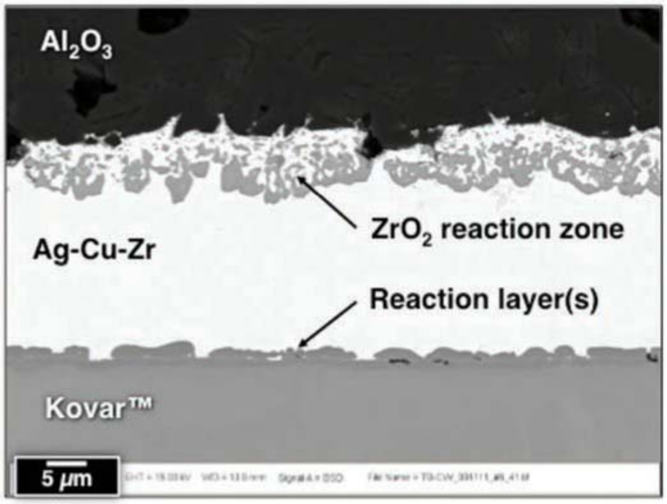


Fig. 6 — SEM photo shows the general microstructure of the braze joint formed between the Kovar™ and Al_2O_3 ceramic base materials using the Ag-Cu-Zr active filler metal. The process conditions were 985°C (1805°F), 5 min, and 600-torr Ar atmosphere.

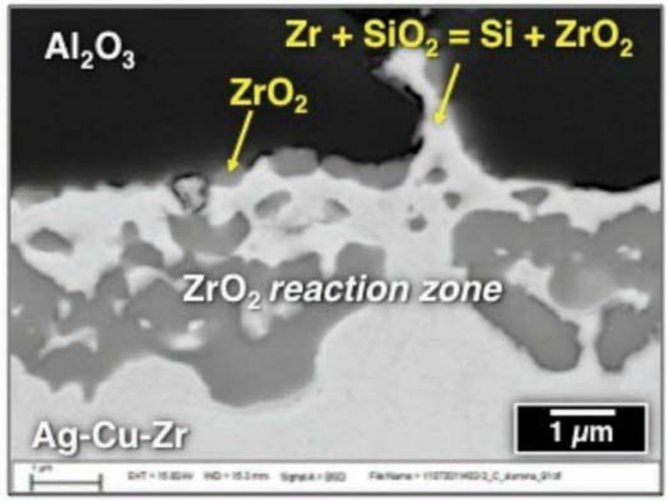


Fig. 7 — High-magnification SEM image shows the immediate Ag-Cu-Zr/Al_2O_3 interface and formation of the ZrO_2 particles.

in Fig. 4A, most often, there is only a single lobe per side of the Kovar™ spacer, as shown in Fig. 4B.

An experiment was performed to confirm that run-out was not simply the squishing-out of excess filler metal from the joint. A smaller footprint of filler metal was placed in the same tensile button braze joint by reducing the outer diameter of the Ag-Cu-Zr preform from 15.9 mm (0.625 in.) to 12.7 mm (0.500 in.). The tensile button was assembled with a single such preform, thereby reducing the filler metal volume by a total of 60%. The buttons were brazed at 985°C for 5 min (600-torr Ar).

Figure 5 shows a photograph of the post-pull tested sample. The run-out still occurred as identified by the arrows. The lobes confirmed that this phenomenon is a result of an instability in the wetting and spreading behavior of molten Ag-Cu-Zr on the Kovar™ base material.

This report describes a study with the objective being to further investigate this hypothesis and to develop potential mitigation steps that will prevent it in the future.

Review of the Material Systems

The materials system is the same as that previously exemplified.

The filler metal is the active braze alloy, 97Ag-1Cu-2Zr (wt-%, abbreviated Ag-Cu-Zr). The T_s is 940°–950°C (1724°–1742°F) and T_l is 960°–970°C (1760°–1778°F). The filler metal preforms had these dimensions: 10.2-mm (0.400-in.) inner diameter, 15.9-mm (0.625-in.) outer diameter, and 0.051 mm (0.002 in.) thickness.

The base materials were Kovar™ and 94% Al_2O_3 ceramic. The nominal braze process had a peak temperature of 985°C (1805°F), time duration of 5 min at peak temperature, and a 600-torr Ar atmosphere.

The braze joint microstructure is exemplified by the SEM image in Fig. 6. Besides the filler metal and base materials, the brazements were characterized by distinct reaction structures at the two interfaces.

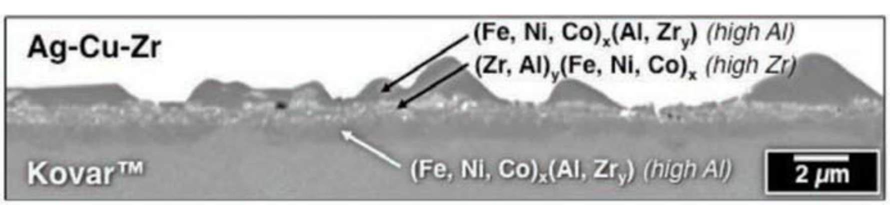


Fig. 8 — SEM image shows the reaction sublayers that form at the Kovar™/Ag-Cu-Zr interface.

Interface Reactions

Cross-Section Microstructure

A reaction zone developed near the Ag-Cu-Zr/Al_2O_3 interface — Fig. 6. The high-magnification, SEM image in Fig. 7 shows the ZrO_2 particles that developed at the immediate Ag-Cu-Zr/Al_2O_3 interface and then migrated a short distance into the filler metal.

The ZrO_2 particles were a product of this reduction-oxidation (redox) reaction between Zr and Al_2O_3 ceramic:

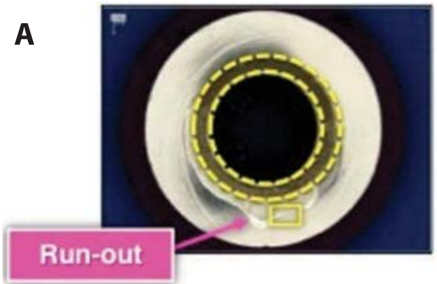
$$3Zr + 2Al_2O_3 = 4Al + 3ZrO_2 \qquad (1)$$

However, this reaction is not spontaneous as determined by a balance of equilibrium free energies. There are three other mechanisms that could drive the Zr/Al_2O_3 redox reaction into spontaneity, including the following:

1. Zr/SiO_2 (grain boundary phase) redox reaction
2. Free energy of solution as elemental Al enters the molten Ag-Cu-Zr filler metal
3. Aluminide reactions at the Kovar™/Ag-Cu-Zr interface.

The first mechanism would not pose a significant effect given the lim-

A



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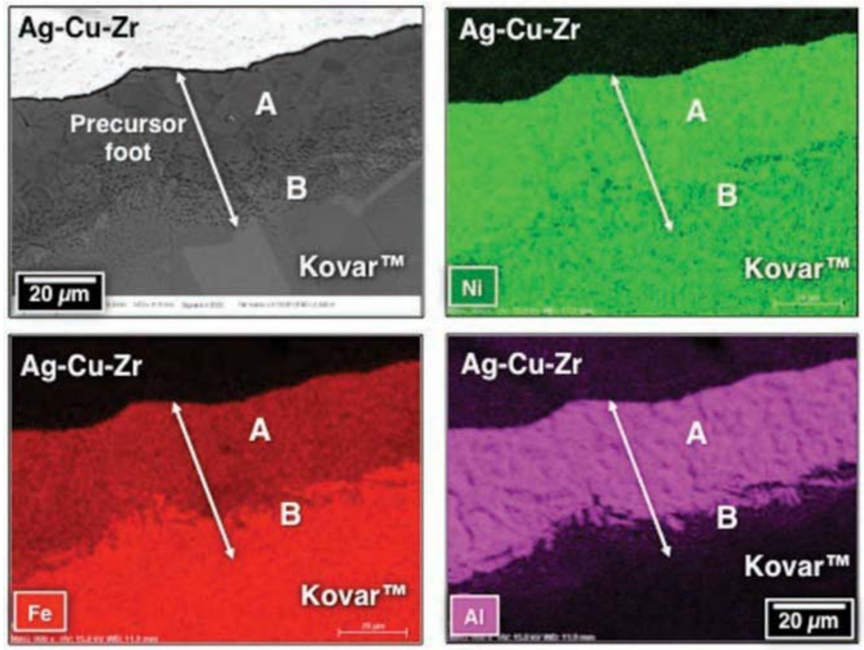
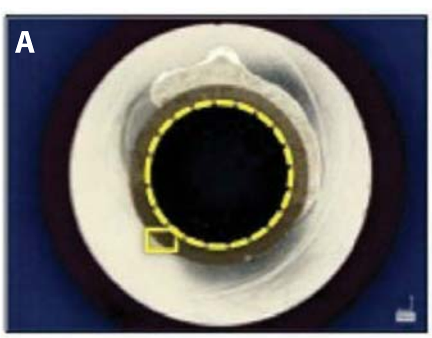


Fig. 9 — A — Photo shows a tensile button that was pull tested to reveal run-out on the Kovar™ spacer; B — SEM image shows the "precursor foot" that developed ahead of the filler metal fillet. The EDX maps show the Fe, Ni, and Al constituents.

ited quantity of SiO_2 present in the ceramic. The second scenario could potentially occur since the Ag-Al binary alloy phase diagram exhibits a eutectic composition of 71Ag-29Al (wt-%) that has a low eutectic temperature, at 567°C (1053°F), and extensive composition range in the δ phase (Ag terminal phase) that favors Al dissolution into the filler metal (Ref. 2).

The third scenario could also generate a significant driving force by the reaction between Al, which is released by the redox reaction at the Ag-Cu-Zr/Al_2O_3 interface, with the Fe, Ni, or Co constituents of Kovar™. Such reactions would readily form highly stable, covalent (intermetallic) compounds (Ref. 3).

The reaction at the Kovar™/Ag-Cu-Zr interface is illustrated by the SEM image in Fig. 8. There is the high Al, $(Fe, Ni, Co)_x(Al, Zr)_y$ layer that borders with the bulk filler metal. Below it is the high Zr, $(Zr, Al)_y(Fe, Ni, Co)_x$ layer. Lastly, the high Al was repeated adja-



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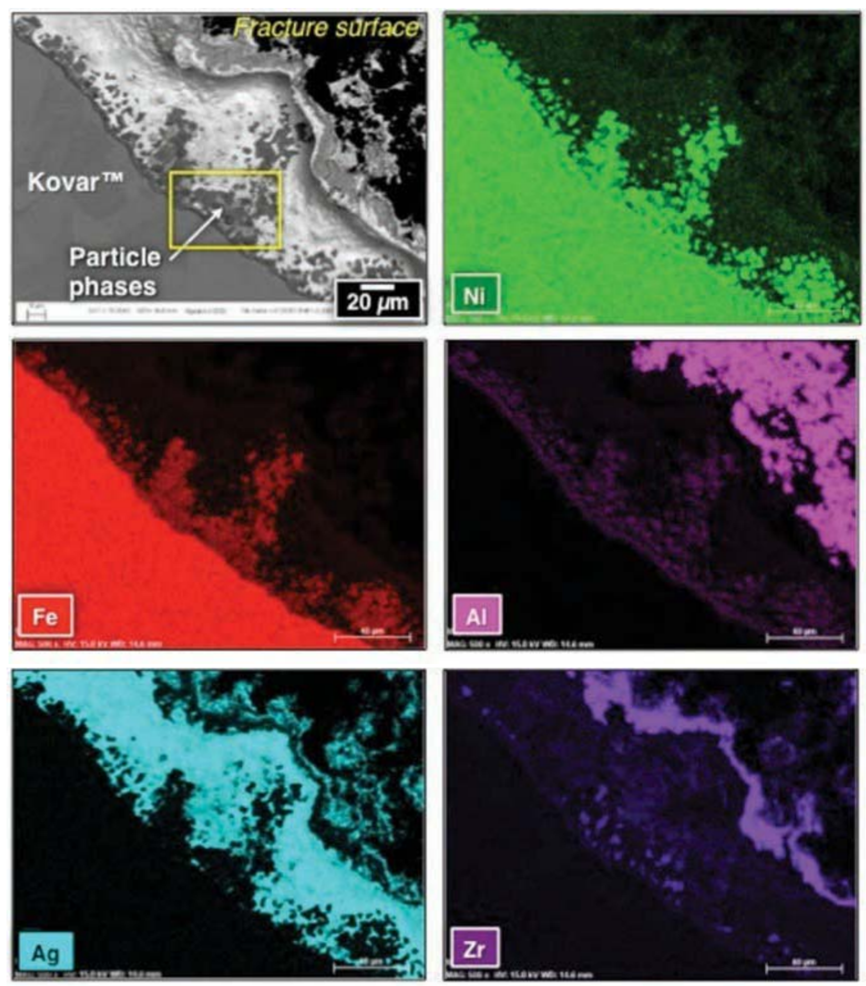

Fig. 10 — A — Photo shows a tensile button and the area (yellow box) where run-out was absent; B — SEM/BSE image as well as Zr, Al, Fe, Ni, and Ag EDX maps at the fillet edge.

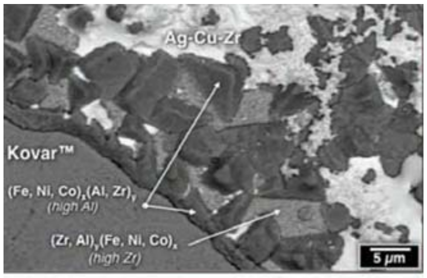

Fig. 11 — A high-magnification SEM (BSE) image shows the fillet edge and particle phase compositions.

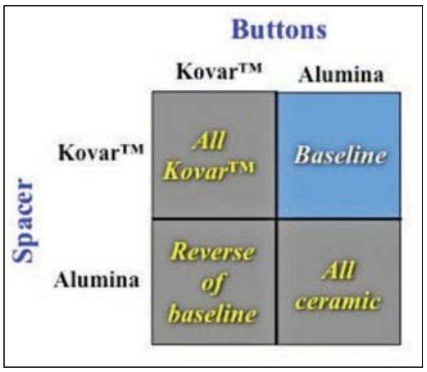

Fig. 12 — Schematic shows the four variants of individual tensile button and spacer material based on Kovar™ or Al_2O_3.

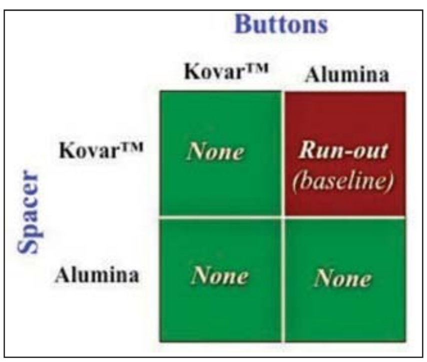

Fig. 13 — Schematic shows the observations of run-out for the four variants of spacer and button base materials.

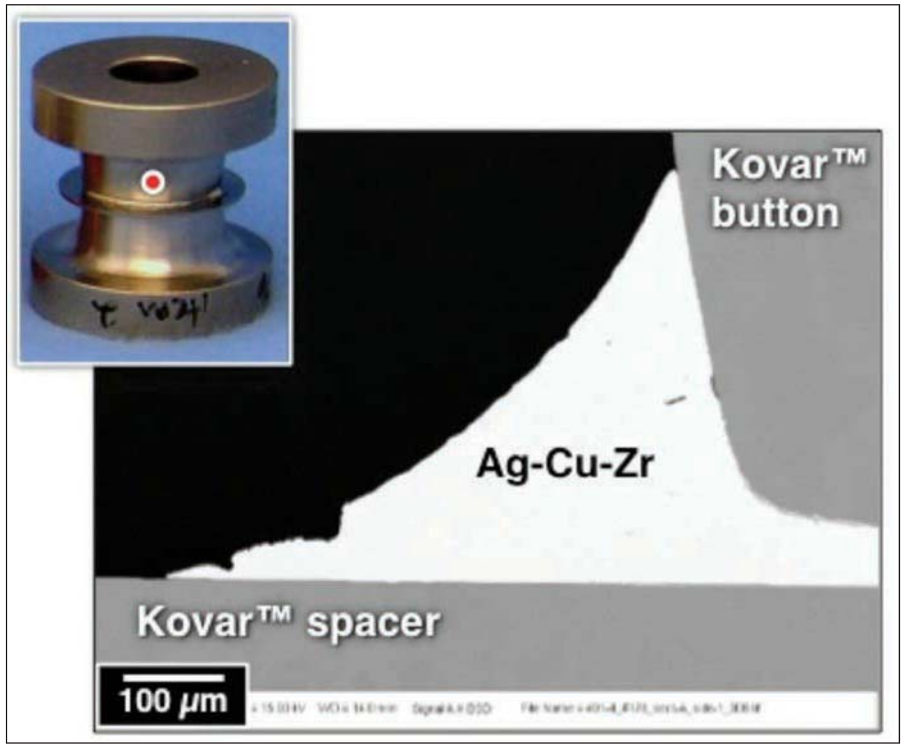

Fig. 14 — SEM image shows the cross section of the expected fillet that formed at the red dot of the inset photo for the all-Kovar™ test sample.

cent to the Kovar™ base material. The presence and morphologies of the sublayers varied sample to sample as well as location to location along the same interface.

The Cu constituent of the Ag-Cu-Zr braze alloy did not have a detectable presence in any of the interface reactions. The filler metal retained its 2 wt-% Cu and became, effectively, an Ag-Cu alloy. Also, both Zr and Al were absent from the filler metal.

Wetting Front Microstructure

The interface reactions were investigated with respect to their roles in the wetting and spreading of molten Ag-Cu-Zr filler metal on the Kovar™ surface.

Shown in Fig. 9A is a tensile button having run-out (yellow box). The SEM image in Fig. 9B shows a precursor "foot" that extended approximately 40 μm from the edge of the Ag-Cu-Zr fillet. The composition of the precursor foot was analyzed, qualitatively, by the energy dispersive x-ray (EDX) technique. The Fe, Ni, and Al elemental maps are also shown in Fig. 9B. The region "A" exhibited a very strong presence of Al, Ni, and Fe that indicated the (Fe, Ni)-Al reaction. There is an enrichment of Ni vs. Fe when compared to unreacted Kovar™ at the lower, right-hand region. Region "B" shows the same reaction, albeit, with a lesser presence of Al. Zirconium and Ag were absent from the precursor foot.

The edge of the Ag-Cu-Zr fillet was similarly analyzed where run-out was absent. The tensile button and location (yellow box) are shown in Fig. 10A. The corresponding SEM (BSE) image, together with the EDX maps of Fe, Ni, Al, Ag, and Zr are provided in Fig. 10B.

The Ag map confirmed that these images pertained to the edge of the fillet, not a precursor foot phenomenon. The EDX maps show that particles composed of Fe, Ni, Al, and Zr formed at the very edge of the fillet.

The fillet edge location indicated by the yellow box in Fig. 10B is shown at high magnification in Fig. 11. There were two particle phases that corresponded to the high Al $(Fe, Ni, Co)_x(Al, Zr)_y$ and high Zr $(Zr, Al)_y(Fe, Ni, Co)_x$ compositions noted in the previous cross sections. It was conjectured that the formation of these particles impeded the further wetting and spreading action of the Ag-Cu-Zr filler metal by acting as a sink for Al, thus preventing formation of the precursor foot.

Base Material Geometry

The previous analysis suggests that the reaction between the released Al and Fe plus Ni constituents of Kovar™ underlie the wetting and spreading instability responsible for run-out. The next analysis examined the role of molten Ag-Cu-Zr surface tension.

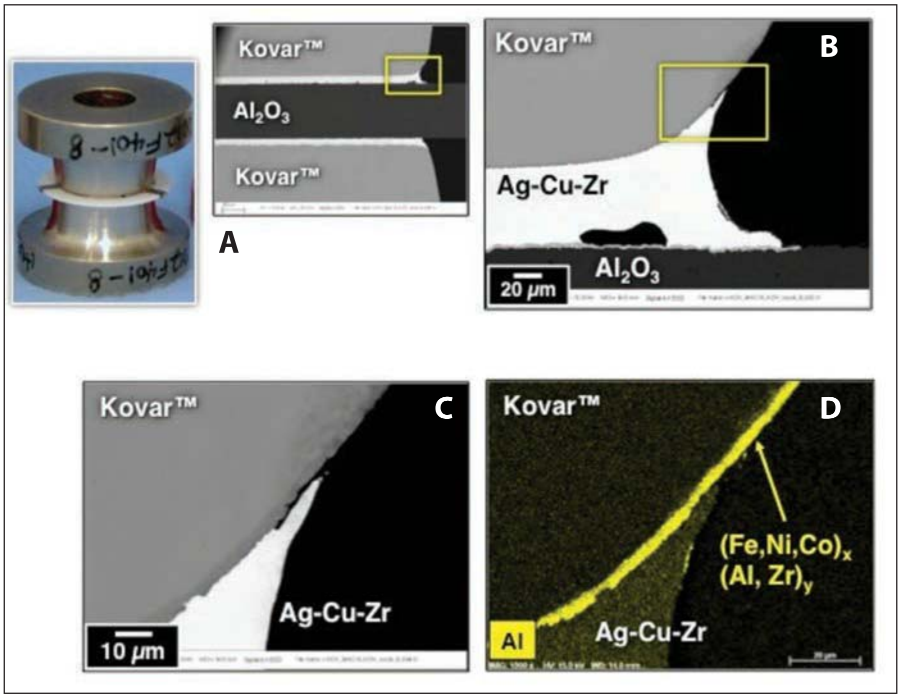

Fig. 15 — A — SEM image shows the cross section of the Ag-Cu-Zr braze joint made between the Al_2O_3 spacer and the Kovar™ buttons; B — the medium magnification image shows the top of the filler metal fillet; C, D — SEM image and EDX map of Al illustrate the extent of the aluminide diffusion/reaction beyond the fillet edge.

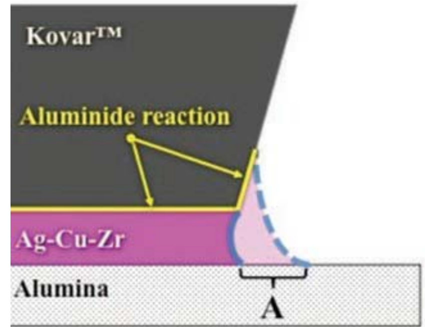

Fig. 16 — Schematic shows the extension of the Ag-Cu-Zr braze alloy fillet, "A," that would be required for the molten filler metal to follow the aluminide diffusion/reaction up the sidewall of the Kovar™ button as run-out.

Test Specimens

Tensile button samples were fabricated that represented one of four variants of the matrix of spacer and base materials shown schematically in Fig. 12.

The upper left-hand cell represents the "all-Kovar™" joint that has the individual buttons and spacer fabricated from Kovar™. To its right is the baseline variant — Al_2O_3 buttons and a Kovar™ spacer. The lower left-hand cell has Kovar™ buttons and an Al_2O_3 spacer, which is reverse to the traditional configuration. Lastly, there is the "all-ceramic" sample that has all of the components constructed of Al_2O_3 ceramic base material.

The parts were brazed with a 50.8-μm- (0.002 in.-) thick Ag-Cu-Zr filler metal preform under these conditions: 985°C (1805°F), 5 min, and 600-torr Ar. The braze joint gap was controlled by dimples on the Kovar™ spacer or ribbon across the Al_2O_3 spacer.

Run-Out Behaviors

Each sample was inspected for run-out. Those results are summarized in Fig. 13. As expected, the baseline sample exhibited run-out. There was an absence of run-out in the all-Kovar™ braze joints. This finding confirmed that the elemental Al released by the Zr/Al_2O_3 redox reaction is required for the run-out phenomenon to take place, further substantiating the point that the latter is not simply a physical displacement ("squishing out") of excess molten filler metal.

The all-Kovar™ samples exhibited reaction layers at both Ag-Cu-Zr/Kovar™ interfaces. Those reactions, which consumed all of the Zr from the filler metal, were heavier in Ni than in Fe. This proportionality is opposite to that of the two elements in the Kovar™ base material. Cobalt was also present in the reaction layers. This sample established that there is a significant driving force for Zr to react with the Kovar™ base material. However, these reactions did not cause run-out. Rather, there was the expected fillet formation around the joint, as shown in Fig. 14.

The analysis turned to the samples having Kovar™ buttons but a ceramic spacer. Cross sections confirmed formation of the ZrO_2 reaction zone. The aluminide layer developed at the Ag-Cu-Zr/Kovar™ interface and extended well up the wall of the button as shown by the series of SEM images and EDX map of Al in Fig. 15.

All of the "ingredients" were present for run-out, yet the phenomenon did not take place.

The absence of run-out was caused by the geometry of the fillet region coupled with the molten filler metal surface tension. This point is described with the assistance of Fig. 16. The solid blue line marks the limit of the filler metal fillet. The fillet shape that would be required to support run-out up the button is described by the dashed trace. However, achieving the latter fillet would require the filler metal to wet an additional distance "A" further out on the Al_2O_3 surface.

The Ag-Cu-Zr active braze alloy cannot spontaneously spread on the ceramic surface. Therefore, the surface tension of the molten filler metal would not permit the latter to follow the reaction layer and create a run-out lobe.

The final variant of this experiment was the all-Al_2O_3 specimen. As expected, the redox reaction took place at both Ag-Cu-Zr/Al_2O_3 interfaces. Run-out was not observed on the Al_2O_3 surfaces, thereby confirming that the Kovar™ base material and, specifically, the aluminide reactions, were required for this behavior.

In the absence of the Kovar™ base material, the Al_2O_3/Ag-Cu-Zr/Al_2O_3 provided the opportunity to determine the quantity of elemental Al generated by the redox reaction. Electron probe microanalysis determined the concentration of elemental Al in the filler metal was in the range of 0.7–0.9 wt-% Al.

Such a relatively small quantity of elemental Al was responsible for the aluminide reactions and run-out phenomenon observed in this brazement.

Last, this sample also provided evidence that identified the likely driving force behind the Zr/Al_2O_3 redox reaction. The absence of the Kovar™ base material eliminated the aluminide reactions as the primary driving force. Therefore, it was concluded that the free energy of solution generated by elemental Al entering the molten filler metal drove the spontaneity of the Zr/Al_2O_3 redox reaction.

Conclusions

1. The run-out behavior degraded the performance of braze joints made between Kovar™ and Al_2O_3 ceramic using the active filler metal, 97Ag-2Zr-1Cu (wt-%). The phenomenon did not respond to mitigation strategies, the cause being "squishing out" of excessive filler metal.

2. At the $Ag\text{-}Cu\text{-}Zr/Al_2O_3$ interface, the redox reaction between Zr and the Al_2O_3 released elemental Al into the molten filler metal. The Al reacted with the Kovar™ constituents, creating the aluminide reaction layer responsible for the wetting and spreading instability that generated run-out.

3. It was also learned that the free energy of solution generated by elemental Al entering the molten filler metal drove the spontaneity of the Zr/Al_2O_3 redox reaction.

4. Most important, however, the findings of this study indicate that the strategies having the greatest promise of successfully mitigating run-out are as follows: braze joint geometry that takes advantage of the molten filler metal's surface tension, filler metal modifications that inhibit the aluminide reaction at the Kovar™ surface, or coatings on the Kovar™ surface that prevent the aluminide reactions. WJ

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