Interface Reactions Responsible for Run-Out in Active Brazing: Part 3

The present study documented the wetting and spreading behavior of Ag-xAl filler metals where the Al content, x, was reduced to values in the range of $0.2 < x < 1.0$ wt-%

BY P. T. VIANCO, C. A. WALKER, D. DE SMET, A. KILGO, B. M. MCKENZIE, AND R. L. GRANT

ABSTRACT

This study examined the interface reaction between sessile drops of the Ag-xAl filler metals having $x = 0.2, 0.5$, and 1.0 wt-% and Kovar™ base material as an avenue to understand the run-out phenomenon observed in active filler metal braze joints. The brazing conditions were combinations of 965°C (1769°F) and 995°C (1823°F) temperatures and brazing times of 5 and 20 min. All brazing was performed in a vacuum of 10^{-7} Torr. Microanalysis confirmed that a reaction layer developed ahead of the filler metal to support spontaneous wetting and spreading activity. However, run-out was not observed with the sessile drops because the additional surface energy created by the sessile drop free surface constrained wetting and spreading. The value of z in the reaction layer composition, $(\text{Fe, Ni, Co})_{\text{Al}_z}$, increased with x of the Ag-xAl sessile drops for both brazing conditions. Generally, the values of z were lower for the more severe brazing conditions. Also, the reaction layer thickness increased with the Al concentration in the filler metal but did not increase with the severity of brazing conditions. These behaviors indicate that the interface reaction was controlled by the chemical potential rather than the rate kinetics of a thermally activated process. The determining metrics were filler metal composition (Ag-xAl) and brazing temperature. The findings of the present study provided several insights toward developing potential mitigation strategies to prevent run-out.

KEYWORDS

- Run-Out • Active Brazing • Sessile Drop
- Interface Reactions

Introduction

Run-out behavior was observed in 97Ag-1Cu-2Zr (wt-%, abbreviated Ag-Cu-Zr) active filler metal braze joints made

between alumina (Al_2O_3) ceramic and Kovar™ base materials (Refs. 1, 2). Microanalysis confirmed that aluminum (Al), which was released by the reduction-oxidation reaction between the zirconium (Zr) active component of the filler metal and alumina base material, participated in an aluminide reaction with the iron (Fe), nickel (Ni), and cobalt (Co) constituents of the Kovar base material. The aluminide interface reaction was intrinsic to the run-out phenomenon. Two additional findings were made from those early studies: 1) the molten Ag-Cu-Zr filler metal's surface tension had a significant effect on the extent of run-out, and 2) the phenomenon was not sensitive to the brazing parameters.

Subsequent experiments simplified the test methodology by replacing the Ag-Cu-Zr filler metal with simpler binary Ag-xAl filler metals (Refs. 3, 4). The study in Ref. 3 examined the wetting and spreading of Ag-xAl filler metals having $x = 0, 2, 5$, and 10 wt-% in the sessile drop configuration. Wetting and spreading increased slightly with the Al content of the filler metal, but the sessile drop configuration did not generate run-out. Also, the wetting and spreading behavior remained largely insensitive to brazing temperatures and time.

The investigation in Ref. 4 documented the behavior of the Ag-xAl filler metals in the Kovar-to-Kovar braze joint configuration using the same values of x and brazing parameters. All test specimens showed run-out. The implication of that observation for the present study was that it further substantiated the role of the free surface of a sessile drop toward mitigating the run-out phenomenon.

Those prior studies sought a possible correlation between run-out, the filler metal composition Ag-xAl, and the composition of the $(\text{Fe, Ni, Co})_{\text{Al}_z}$ reaction layer that formed at the filler metal/Kovar interface. The experiments in Ref. 3 established a correlation between the Al content of $2 \leq x \leq 10$ wt-% in the Ag-xAl filler metal and the Al concentration, z , in the $(\text{Fe, Ni, Co})_{\text{Al}_z}$ reaction layer — Fig. 1. The graph showed that z increased with x . However, the data also illustrated a second trend. The less severe brazing conditions (965°C [1769°F], 5 min) resulted in higher Al concentrations

Fig. 1 — Aluminum concentration (at.-%) in the reaction layer is shown as a function of the nominal Al content (wt.-%) in the filler metal for the sessile drop configuration. The blue and red plots represent the brazing processes of 965°C (1769°F), 5 min and 995°C (1823°F), 20 min, respectively.

(z) in the reaction layer than did the more severe brazing parameters (995°C [1823°F], 20 min). Thus, the Al concentration, z, did not behave in a manner expected of thermally activated rate kinetics, which would have generated the reverse trend.

The present Part 3 study documented the wetting and spreading behavior of Ag-xAl filler metals where the Al content, x, was reduced to values in the range of $0.2 < x < 1.0$ wt.-%. These compositions formed a lower bound that overlapped with the 0.7–0.9 wt.-% Al concentration range measured in the Ag-Cu-Zr filler metal joints, which exhibited run-out (Ref. 1). Although run-out was not expected from the sessile drop geometry, the reaction layer morphology and composition, (Fe, Ni, Co)₂Al₃, were joined to the findings obtained from the Ref. 3 study of high-Al Ag-xAl sessile drops to identify trends that would further inform the understanding of run-out and potential methods to prevent it.

Experimental Procedures

Base Material

Kovar base material (29Ni-17Co-0.3Mn-0.2Si-0.02C-bal. Fe, wt.-%) was used in the as-received condition and without further surface treatment (Ref. 2). The sessile drop test specimens were fabricated from disks measuring 19.2 mm (0.75 in.) in diameter and 0.56 mm (0.022 in.) in thickness.

Filler Metal

The filler metal began with 100Ag sheet. Aluminum additions were made by evaporating an Al coating onto one surface of the sheet with thicknesses that resulted in the Ag-xAl

filler metal compositions having x = 0.2, 0.5, and 1.0 wt.-%. The Ag-xAl filler metal preforms measured 3.0 mm (0.13 in.) in diameter and 51 μ m (0.002 in.) thick.

Brazing Process

The sessile drop samples were made at one of four combinations of brazing temperatures, 965°C (1769°F) or 995°C (1823°F), and brazing times of 5 or 20 min. After an initial review of the sessile drop specimens, the decision was made to limit the microanalysis activities to samples fabricated at the two extreme process conditions: 965°C (1769°F), 5 min and 995°C (1823°F), 20 min, unless the findings from these cases warranted further evaluations of the other two conditions. All brazing operations were performed under a high vacuum of more than 10^{-7} Torr to prevent oxidation of the Al coating. The drawback of using the high vacuum was evaporation of Ag from the exposed surface of the sessile drop. Filler metal evaporation was only significant for test samples made with the 995°C (1823°F), 20-min brazing parameters. Nevertheless, the prior studies confirmed the interface reactions take place so quickly that they were unaffected by the loss of filler metal (Ref. 1).

The sessile drop test samples were fabricated by having the side of the preform with the Al film placed away from the Kovar surface. This configuration required the Al to cross the molten filler metal to reach the Kovar interface, as would be the case in an active filler metal braze joint. Duplicate test samples were fabricated with each of the sessile drop and braze joint configurations as well as for each brazing condition.

Data Analysis

Scanning electron microscopy (SEM) in conjunction with energy dispersive x-ray (EDX) analysis were used to qualitatively assess the sessile drop surface morphology and chemistry, respectively. Upon completion of the surface analysis, the sessile drop samples were subjected to metallographic cross sections. The cross-section microstructures were initially evaluated by the same SEM and EDX techniques.

The electron probe microanalysis (EPMA) technique was used to determine, quantitatively, the compositions of the reaction layers as well as those of the remaining filler metal and adjoining Kovar base material. Elemental concentrations were expressed as a mean and error term of one standard deviation. The equipment was operated at an accelerating voltage of 15 keV and a beam current of 20 nA. The step interval was 0.2 μ m for the sessile drop samples and 1.0 μ m for the braze joint samples due to the greater profile length. In the event that a greater resolution was required for analysis, the EPMA traces were repeated using 0.2 μ m steps. The absolute resolution limit was $\pm 0.5 \mu$ m, or roughly a circular area of one micron diameter due to sampling volume effects at this acceleration voltage. The concentration resolutions were ± 0.1 wt.-% and ± 0.5 at.-% for the elements present in these samples. The analysis details were provided in Part 2 with respect to the procedures used to compute the compositions.

Concentration profiles were obtained in the following manner. A total of six concentration profiles were acquired between three traces made on each of the duplicate sessile

Fig. 2 — Photographs show the Ag-xAl sessile drop samples with $x = 0.2, 0.5$, and 1.0 wt-%. The samples were fabricated at 965°C (1769°F), 5 min and 995°C (1823°F), 20 min.

drop specimens. The traces began in the filler metal and terminated in the Kovar base material.

The EPMA technique was also used to determine the quantity of Al that remained in the filler metal as well as the concentrations of Fe, Ni, and Co resulting from dissolution of the Kovar base material. These analyses were performed in the filler metal away from the interface(s). An absolute detection limit (error) for the Al in the filler metal was established by measuring the Al signal in the Kovar base material far from the interface and associated diffusion zone. The elemental concentrations were small in the filler metal, approaching the resolution limit of the EPMA technique. Nevertheless, several trends were deciphered from those assessments.

Lastly, the reaction layer thicknesses were measured from the sessile drop cross sections. Data were collected representing all four brazing conditions and the three Ag-xAl compositions. Five thickness data were taken at each of the three locations near the sessile drop center for a total of 15 measurements. The reaction layer thickness was represented by the mean and an error bar of ± 1 standard deviation.

Results

Visual Inspection

Figure 2 shows photographs of the sessile drop samples for each of the three Ag-xAl compositions and process conditions of 965°C (1769°F), 5 min and 995°C (1823°F), 20 min. The sessile drop samples did not exhibit run-out. In the case of specimens brazed at the intermediate process conditions, wetting and spreading occurred to similar extents as shown in Fig. 2 without anomalies, including the absence of run-out.

Surface SEM and EDX Analyses

The sessile drops were examined by SEM and EDX analysis techniques. Particular attention was given to the edges, which are associated most closely to the wetting and spreading behavior¹. Data are presented for the two extreme brazing conditions: 965°C (1769°F), 5 min and 995°C (1823°F), 20 min. The sessile drop morphologies of the two intermediate brazing conditions transitioned between these two limiting cases. Detailed observations are described, below, according to filler metal composition.

Ag-0.2Al Filler Metal

Figure 3A shows a portion of the Ag-0.2Al alloy sessile drop that was formed with the brazing parameters 965°C (1769°F) and 5 min. The yellow box indicates the region viewed at higher magnification in Fig. 3B. Region “B” identifies the bulk filler metal, and region “A” is the precursor film that preceded the bulk filler metal. Ahead of the precursor film was an approximately ten-micron-wide band that was the reaction layer. Cracks were absent from the reaction layer. The corresponding EDX maps are shown in Fig. 4 for Ag, Al, Fe, Ni, and Co. The reaction layer was comprised of Al, Fe, Ni, and Co; it was richer in Ni and depleted in Fe vs. the nominal Kovar composition. Cobalt was nearly equivalent between the reaction layer and base material. Similar surface structures were observed with high-Al filler metals (Ref. 3). Therefore, even with the reduced Al content, a reaction formed ahead of the filler metal.

Figure 5 shows the edge of the sessile drop resulting from the Ag-0.2Al filler metal brazed at 995°C (1823°F) and 20

¹ It was noted that the small Al concentrations also altered the solidification microstructure of the Ag-xAl alloys. The brazing parameters had a lesser effect on this property.

Fig. 3 — A — SEM photograph shows a portion of the Ag-0.2Al sessile drop fabricated at 965°C (1769°F) and 5 min. The yellow box indicates the region examined at higher magnification; B — high-magnification image shows the precursor layer, “A,” and bulk filler metal, “B,” together with the exposed reaction layer.

Fig. 4 — EDX x-ray maps show the elemental distributions of Ag, Al, Fe, Ni, and Co at the edge of the Ag-0.2Al sessile braze at 965°C (1769°F) and 5 min.

min. The reaction layer exhibited small peaks that were topological rather than being caused by differences in chemistries. The wider expanse of the exposed reaction layer resulted from the increased degree of Ag evaporation. Otherwise, the Ag-0.2Al sessile drop exhibited the same “B” and “A” regions, as observed in Fig. 3.

Ag-0.5Al Filler Metal

The Ag-0.5Al sessile drop morphology that was formed with the brazing conditions of 965°C (1769°F) and 5 min is shown at low magnification in Fig. 6A. The additional Al content resulted in a serrated outline to the precursor layer that was accompanied by a similarly shaped reaction layer ahead of the former. The size scale of the serrations was too small to

signify run-out. The sessile drop edge (yellow box) is shown at higher magnification in Fig. 6B. The surface topography was similar to that of the Ag-0.2Al filler metal.

The Ag-0.5Al sessile drop that was formed by the brazing conditions of 995°C (1823°F) and 20 min. The sessile drop had the same morphology as that shown in Fig. 6, including the serrated pattern along the edge of the precursor film (“A”).

Ag-1.0Al Filler Metal

Figure 7A shows an SEM image of the Ag-1.0Al sessile drop after brazing at 965°C (1769°F) for 5 min. Wetting and spreading was similar to the other two filler metals. A high-magnification SEM photograph is shown in Fig. 7B of the sessile drop edge taken at the yellow box location in Fig. 7A. A well-defined

Fig. 5 — SEM photograph shows the edge of the Ag-0.2Al sessile drop that was formed under the 995°C (1823°F), 20-min brazing conditions. Regions “A” and “B” identify the precursor layer and bulk filler metal, respectively.

precursor layer (“A”) developed between the bulk filler metal (“B”) and the reaction layer. The width of the reaction layer was 30–40 μm, which was wider than the reaction layers observed for the Ag-0.2Al and Ag-0.5Al sessile drops in Figs. 3B and 6B, respectively. The EDX data showed the same qualitative composition as observed with those other filler metals.

Small particle-like structures were observed in the precursor layer (“A”) of Fig. 7B. The EDX analysis indicated their composition to be similar to that of the reaction layer. The EPMA will show, later in this report, that Fe, Ni, and Co dissolved from the Kovar base into the filler metal, albeit at very small concentrations (< 0.8 wt-%). Therefore, the particles in Fig. 7B were a result of the reaction between the dissolved Fe, Ni, and Co and Al in the filler metal.

Nearly the entire Ag-1.0Al sessile drop — bulk layer “B” and precursor layer “A” — evaporated under the 995°C (1823°F), 20-min brazing conditions. The sessile drop edge is shown in Fig. 8. The regions “A” and “B” were identified by correlation with the respective reaction layer morphologies underneath them. The EDX analysis confirmed that the reaction layer composition was consistent across its entire footprint. Lastly, as was documented for all combinations of filler metals and brazing parameters, cracks were not observed in the reaction layer structures.

Cross Section SEM, EDX, and EPMA

The cross-section analysis had three objectives: 1) document the interface reaction microstructure as a function of brazing conditions and filler metal composition; 2) determine the reaction layer compositions, quantitatively, using the EPMA technique; and 3) measure the reaction layer thicknesses.

Ag-0.2Al Filler Metal

The SEM image in Fig. 9A shows the edge of the sessile drop that was formed by the Ag-0.2Al filler metal when brazed at 965°C (1769°F) and 5 min. Regions “A” and “B”

Fig. 6 — A — Low-magnification SEM/backscattered electron (BSE) image shows the sessile drop formed by the Ag-0.5Al filler metal under the brazing conditions of 965°C (1769°F) and 5 min. The yellow box indicates the edge shown in B; bulk filler metal (“B”) and precursor layer (“A”) are identified in the picture.

correspond to the similarly labeled structures in Fig. 3B. A continuous reaction layer formed along the Ag-0.2Al/Kovar interface, although it had a variable thickness. Cracks were not observed in the layer. A high-magnification view of the very edge is shown in Fig. 9B. At this particular location, the reaction layer extended only ≈ 2 μm in front of the precursor layer (“A”). Nevertheless, these images confirmed the surface SEM data (Figs. 3, 4) that the reaction layer formed ahead of the molten filler metal at this low-Al concentration, making it capable of controlling the wetting and spreading behavior of the molten filler metal.

The interface microstructure and chemistry were documented at the center of the sessile drop by the SEM image and EDX maps in Fig. 10. The reaction layer was continuous under the filler metal but still exhibited a variable thickness. The EDX analysis showed that the reaction layer was comprised of Al, Fe, Ni, and Co (not shown). It was richer and poorer in Ni and Fe, respectively, than the Kovar base material as documented earlier by surface SEM of the sessile drop edge — Fig. 4. The Al signal also extended into the base material at several locations (white brackets).

A backscattered electron (BSE) channeling contrast image

Fig. 7 — SEM images show the features of the sessile drop formed by the Ag-1.0Al filler metal under the 965°C (1769°F), 5-min brazing conditions: A — Low-magnification view of the sessile drop; B — high-magnification image (yellow box in Fig. 7A) showing the sessile drop edge.

Fig. 8 — SEM photograph shows the reaction layers at the edge of the Ag-1.0Al sessile drop fabricated at 995°C (1823°F) for 20 min. The filler metal had completely evaporated away.

of a second location along the interface is shown in Fig. 11. Recrystallization zones were observed in the Kovar base material. Those zones, which varied in size, corresponded to areas of heightened Al concentration. A similar microstructure was observed in the base material of the previous studies based on the high-Al filler metals (Refs. 3, 4). Lastly, an intermittent white layer, which was Fe rich and observed in those earlier investigations, was observed between the reaction layer and base material.

A representative EPMA trace is provided in Fig. 12, which shows the Fe, Ni, Co, and Al concentration profiles across the Ag-0.2Al/Kovar interface. A significant accumulation of Al accompanied reduced Fe, Ni, and Co peaks between the 7.8- and 9.0-μm positions. This region was referred to as the interdiffusion zone (I.Z.). The I.Z. was not considered to be a part of the reaction layer because the high Ag concentration implied that it was a part of the filler metal. Iron, Ni, and Co showed concentration gradients beyond the I.Z. and into the filler metal region.

An Al diffusion gradient existed in the Kovar base material between 10 and 11.8 μm (blue lines and arrow). This region was associated with a recrystallization zone. The con-

Table 1 — Fe, Ni, and Co Concentrations in 100% Ag Filler Metal after Brazing the Kovar™/100 Ag/Kovar™ Joint

Brazing Conditions	Elemental Concentrations Remaining in the 100 Ag Filler Metal - Braze Joint Configuration (wt-%)		
	Fe	Ni	Co
965°C (1769°F), 20 min	0.34 ± 0.38	0.18 ± 0.17	0.15 ± 0.15
995°C (1823°F), 5 min	0.25 ± 0.05	0.14 ± 0.04	0.12 ± 0.03
995°C (1823°F), 20 min	0.23 ± 0.09	0.13 ± 0.05	0.12 ± 0.08

centrations of Fe, Ni, and Co were lower in the regions of Al diffusion vs. the nominal Kovar base material. The more pronounced minimum in the Ni concentration profile was caused by its depletion as it contributed to the nearby reaction layer (R.L.). The Fe-rich reaction layer was not intercepted by this trace.

The reaction layer thickness approached the resolution limit of the EPMA technique ($\pm 0.50 \mu\text{m}$). Its composition was determined from only two data points (black arrows) per each of the traces. The reaction layer composition was as follows:

$$(\text{Fe, Ni, Co})_{79 \pm 2} \text{Al}_{21 \pm 2} \approx (\text{Fe, Ni, Co})_4 \text{Al}$$

Following the format used in Parts 1 and Part 2 of this study, the Fe, Ni, and Co concentrations were grouped into a single constituent because the primary interest was in the Al concentration (Refs. 3, 4).

The composition of the remaining Ag-0.2Al filler metal was also determined from the EPMA data. Besides Ag, the other predominant elements were as follows (wt-%): Al, 0.07 ± 0.01 ; Fe, 0.23 ± 0.08 ; Ni, 0.15 ± 0.05 ; and Co, 0.13 ± 0.04 . The baseline Al concentration, which was measured in the Kovar base material away from the interface microstructures, was $0.003 \pm 0.007 \text{ wt-%}$, which established the statistical significance of the Al measurements in the filler metal.

Fig. 9 — A — SEM image shows the edge of the sessile drop formed by the Ag-0.2Al filler metal at 965°C (1769°F) and 5 min. The “A” and “B” labels correspond to the precursor layer and bulk filler metal, respectively; B — high-magnification image of the yellow box in Fig. 9A.

Fig. 10 — SEM image and corresponding Fe, Ni, and Al EDX maps of the interface microstructure under the center portion of the Ag-0.2Al sessile drop formed at 965°C (1769°F) and 5 min. The white brackets indicate an Al signal in the base material.

The analysis turned to the Ag-0.2Al sessile drop brazed at 995°C (1823°F) and 20 min. Figure 13A shows the SEM images in both SEM/BSE and secondary electron (SEM/SE) modes as well as the Al and Ag EDX maps obtained from the center of the cross section. The Ag EDX map marked the remaining filler metal. The reaction layer, which was signified by the elevated Al signal (white arrows), developed only in-

termittently along the interface. The SEM/SE image identified a region, highlighted by polishing relief (yellow arrow and lines) that did not have a reaction layer. At that location, Al diffused into the Kovar base material but without a detectable recrystallization zone. The Fe-rich reaction layer was not observed in these samples.

The EPMA results are shown in Fig. 13B. Only an inter-

Fig. 11 — BSE channeling contrast image shows the recrystallization microstructure in the Kovar base material. The filler metal was Ag-0.2Al and the brazing conditions were 965°C (1769°F) and 5 min.

diffusion zone was observed at the interface. Significant Al diffusion occurred into the adjacent Kovar base material (blue arrow and lines) that correlated with the area denoted by the yellow arrow and lines in Fig. 13A. The absence of a strong minimum by the Ni signal in this region correlated with the absence of a defined reaction layer. This observation confirmed the earlier point made with respect to Fig. 12. That is, Ni depletion in the adjacent Kovar base material resulted, explicitly, from formation of the reaction layer and was not simply a consequence of Al diffusion into the Kovar base material.

The Fe, Ni, Co, and Al concentrations (wt-%) were determined at the center of the remaining filler metal; those values were as follows: Fe, 0.17 ± 0.06 ; Ni, 0.12 ± 0.04 ; Co, 0.10 ± 0.03 ; and Al, 0.07 ± 0.01 . Figure 14 shows the Al concentration as a function of nominal filler metal composition and brazing parameters. Referring to the Ag-0.2Al results, the Al concentration was nearly identical to that measured following brazing at 965°C (1769°F) and 5 min.

The Fe, Ni, and Co concentration data were compiled in Fig. 15. The sessile drop samples could not be fabricated with the Ag-0Al (i.e., 100Ag) filler metal due to an absence of wetting and spreading activity. However, braze joint samples could be made with the Ag-0Al filler metal for three of the four brazing conditions; the exception was the 965°C (1769°F) and 5-min case. Those results are listed in Table 1; however, only the data obtained from the 995°C (1823°F), 20-min conditions were directly applicable to the current EPMA results. Therefore, only those Fe, Ni, and Co concentrations (wt-%) were included in Fig. 15². Note: Because the concentrations in Table 1 resulted from a braze joint that had two base material interfaces, the mean values and error terms were divided by two and then plotted in the graph.

Statistically, the concentrations of Fe, Ni, and Co in the Ag-0.2Al filler metal were the same as those of the Ag-0Al braze alloy for the 995°C (1823°F), 20-min conditions. Furthermore, the Fe, Ni, and Co concentrations were similar between the

Fig. 12 — EPMA traces show the Al, Fe, Ni, and Co concentration profiles across the interface at the center of the Ag-0.2Al sessile drop formed at 965°C (1769°F) and 5 min. The abbreviations I.Z. and R.L. refer to the interdiffusion zone and reaction layer, respectively. The black arrows point to the data used to determine the reaction layer composition. The blue arrows and lines indicate the extent of diffusion of Al into the Kovar base material.

two brazing conditions. The expectation was that the concentrations would increase under the higher brazing temperatures and longer time when assuming that the dissolution process was based upon thermally activated rate kinetics.

Metallographic cross sections were made of specimens fabricated with the two intermediate brazing conditions: 965°C (1769°F), 20 min and 995°C (1823°F), 5 min. Both interface microstructures were well represented by the data in Figs. 9–12 and Fig. 13, respectively. Such similarities prevailed for the other filler metal compositions that are described below.

Ag-0.5Al Filler Metal

The SEM/BSE channeling contrast image of the interface microstructure belonging to the Ag-0.5Al sessile drop when brazed at 965°C (1769°F) for 5 min is shown in Fig. 16. The layer had a variable thickness but was continuous along the entire interface. Recrystallization zones, which varied from negligible to approximately 5 μm wide, were observed in the Kovar base material. The corresponding EDX analysis confirmed an elevated Al concentration in those zones. A continuous Fe-rich reaction layer formed in these test specimens. Defects such as cracks and delamination were not observed in the reaction layer.

A representative EPMA plot is provided in Fig. 17. The Al signal correlated with the recrystallization zone (blue lines and arrow); here, it was approximately 2–3 μm wide. A well-defined reaction layer was identified in the EPMA graph. The reaction layer exhibited gradients in the Fe, Ni, and Al signals; the Fe concentration increased while those of Ni and Al decreased when progressing from the I.Z. boundary toward the base material. The Co concentration remained unchanged across the reaction layer.

² The concentrations of dissolved Fe, Ni, and Co in Table 1 were not statistically different as a function of brazing conditions. This was an unexpected trend if one assumed the dissolution process to be based upon thermally activated rate kinetics.

Fig. 13 — A — SEM/BSE and SEM/SE modes as well as Ag and Al EDX maps show the interface microstructure at the center of the Ag-0.2Al sessile drop formed by the brazing conditions of 995°C (1823°F) and 20 min; B — the EPMA traces show the Al, Fe, Ni, and Co concentration profiles across the interface. The blue arrows and lines show an Al diffusion gradient into the Kovar base material.

was too thin to obtain a composition by EPMA.

The Al concentration of the Ag-0.5Al filler metal was nearly the same as that remaining in the Ag-0.2Al filler metal for the same brazing process — Fig. 14. The Fe, Ni, Co, and Al concentrations were as follows (wt-%): Fe, 0.3 ± 0.1 ; Ni, 0.20 ± 0.08 ; Co, 0.16 ± 0.06 ; and Al, 0.09 ± 0.01 . Although the mean concentrations of Fe, Ni, and Co had increased vs. the Ag-0.2Al filler metal results (Fig. 15), the differences were not statistically significant.

The SEM/BSE channeling contrast image is shown in Fig. 18A of the Ag-0.5Al sessile drop brazed at 995°C (1823°F) and 20 min. The reaction layer was continuous and had a relatively uniform thickness. A few voids were observed in the layer (black arrow). An Al diffusion zone, which was like that in Fig. 13A, was observed in the Kovar base material; it was distinguishable by a grain structure that differed from those of either a recrystallization zone or the base material.

The high-magnification SEM/BSE channeling image in Fig. 18B shows a grain structure within the reaction layer. The two boundaries identified by the blue arrows had microstructures that were similar to that of the Fe-rich

The single reaction layer had the following composition:

The Al concentration was slightly higher than that of the Ag-0.2Al filler metal (21 ± 2 at.-%) for the same brazing conditions.

The Fe-rich reaction layer was clearly defined by a peak in the Fe concentration profile in Fig. 17 (red arrow). The peak was accompanied by a minimum in the Ni concentration and a step in the Al concentration at the beginning of the recrystallization zone. Cobalt exhibited only a shallow increase here. As in the prior studies, the continuous Fe-rich layer

Fig. 14 — Plot shows the Al concentration remaining in the sessile drop filler metal as a function of the latter's nominal Al content and brazing conditions.

Fig. 16 — BSE channeling image of the interface microstructure at the center of the Ag-0.5Al sessile drop formed by the brazing conditions of 965°C (1769°F) and 5 min.

reaction layer. Other grain boundaries exhibited the typical contrast. Small voids appeared in the reaction layer. Cracks were not observed in the reaction layers.

Representative EPMA plots are presented in Fig. 19. Figure 19A shows the concentration profiles across the filler metal, interface, and Kovar base material. The red arrow identifies the Fe-rich reaction layer. The Fe and Ni profiles exhibited opposite fluctuations in the recrystallization zone, which was identified by the blue arrow and lines (Al signal). The fluctuations had not been previously observed and did not include either the Co or Al signals.

An enlarged portion of the EPMA graph is provided in Fig. 19B, which shows the details of the interface microstructure. An I.Z. extended into the filler metal. Two reaction layers were observed, which were labelled R.L. #1 and R.L. #2. They had the following compositions:

Fig. 15 — Plot shows the concentrations of Fe, Ni, and Co in the remaining sessile drop filler metal as a function of the latter's nominal composition and brazing conditions.

Fig. 17 — Graph shows the EPMA traces of Al, Fe, Ni, and Co taken across the interface at the center of the Ag-0.5Al sessile drop formed at 965°C (1769°F) and 5 min. The red arrow indicates the Fe-rich reaction layer. The blue arrows indicate Al diffusion into the Kovar base material.

The R.L. #2 composition was normalized against the Ag signal. The thicker R.L. #1 had a composition similar to the reaction layer that formed at 965°C (1769°F) and 5 min. The Al concentration was slightly higher in R.L. #2 than in R.L. #1 as expected because of the former's closer proximity to the filler metal. The Fe concentration varied the most between the two reaction layers, with it being higher in R.L. #1 (31 ± 1 at.-%) than in R.L. #2 (26 ± 2 at.-%) because it was closer to its Kovar base material. The lower Fe content in R.L. #2 was compensated by higher concentrations of both Al (above) and Ni (R.L. #2, 31.3 ± 0.5 at.-% Ni vs. R.L. #1, 29.7 ± 0.7 at.-% Ni). Lastly, the broad peaks under the red arrow indicate the Fe-rich reaction layer that was less distinct due to its intermittent nature (Fig. 18B).

The remaining Ag-0.5Al filler metal had the following Fe, Ni, Co, and Al concentrations (wt.-%): Fe, 0.22 ± 0.07 ; Ni, 0.15 ± 0.05 ; Co, 0.13 ± 0.04 ; and Al, 0.08 ± 0.01 . Referring to Fig. 14, the Al concentration was statistically unchanged

Fig. 18 — SEM/BSE channeling images show the interface microstructure belonging to the Ag-0.5Al sessile drop brazed at 995°C (1823°F) and 20 min: A — Low-magnification view (black arrow identifies a large void); B — high-magnification image showing details of the interface microstructure, including the reaction layer grain boundaries (blue arrows), the appearance of which resemble the Fe-rich reaction layer (white arrow).

Fig. 19 — A — EPMA profiles of Al, Fe, Ni, and Co taken across the interface at the center of the Ag-0.5Al sessile drop formed at 995°C (1823°F) and 20 min. The red arrow indicates the Fe-rich reaction layer. The blue arrows and lines indicate the presence of Al in the recrystallization zone; B — enlarged EPMA plot focused on the reaction layer microstructure.

vs. that measured in this filler metal after brazing at 965°C (1769°F) and 5 min. Moreover, it was equivalent to Al concentrations remaining in the Ag-0.2Al filler metal for both brazing conditions. The concentrations of Fe, Ni, and Co were plotted in Fig. 15. As was observed with the Ag-0.2Al filler metal, the mean concentrations were lower than those measured after brazing at 965°C (1769°F) and 5 min; but, statistically, the values were the same. Nevertheless, the higher brazing temperature and longer brazing time did not cause an anticipated increase of Kovar dissolution.

Ag-1.0Al Filler Metal

The SEM/BSE channeling contrast image of the interface microstructure that formed at the center of the Ag-1.0Al sessile drop when brazed at 965°C (1769°F) and 5 min is shown in Fig. 20. The reaction layer exhibited a dark gray tone nearer to the filler metal (green oval) and a light gray tone in the remainder of the layer (magenta oval), suggesting the presence of different phases. That assumption was

further supported by the EDX analysis results. The darker gray section had higher Al and Ni concentrations as well as a reduced Fe content. Numerous grain boundaries were observed in the reaction layer. A continuous Fe-rich reaction layer formed between the reaction layer and Kovar base material. Recrystallization zones were prevalent in the base material. Cracks and delamination defects were not observed in the reaction layer.

The representative EPMA trace is shown in Fig. 21. The interface microstructure was composed of an I.Z. that exhibited significant elemental fluctuations. Two reaction layer phases were identified as R.L. #1 and R.L. #2. The two phases were distinguished by their respective Fe concentration gradients. A positive Fe gradient increased from R.L. #2 to R.L. #1. Concurrently, a negative slope by the Al concentration profile increased in magnitude from R.L. #2 to R.L. #1. Nickel exhibited mixed concentration profiles, having positive and negative gradients in R.L. #2 and R.L. #1, respectively. Lastly, the Co trace was largely unchanged between both reaction layers.

Fig. 20 — BSE channeling image shows the interface microstructure belonging to the Ag-1.0Al sessile drop formed at 965°C (1769°F) and 5 min. The green and magenta ovals show the dark and light gray tones, respectively, that indicated two phases.

Fig. 22 — High-magnification SEM/BSE channeling image shows the interface microstructure belonging to the Ag-1.0Al sessile drop formed by the brazing conditions of 995°C (1823°F) and 20 min. The black arrows identify grain boundaries having a morphology similar to the Fe-rich reaction layer. Cyan circles identify several of the numerous voids in the reaction layer.

The compositions are shown, below, for R.L. #1 and R.L. #2:

The two compositions were statistically different despite a higher variability for the R.L. #1 due to the steep concentration gradients of Fe, Ni, and Al.

The Al signal indicated a relatively small recrystallization zone at this location (blue lines and arrow). The continuous Fe-rich reaction layer was identified by the red arrow. As observed previously, the Fe peak was accompanied by a minimum in the Ni signal and a downward step in the Al signal when progressing from the R.L. #1 layer into the recrystallization zone.

The concentrations of Fe, Ni, Co, and Al were measured

Fig. 21 — This graph shows the EPMA traces of Al, Fe, Ni, and Co taken across the interface at the center of the Ag-1.0Al sessile drop formed at 965°C (1769°F) and 5 min. The red arrow indicates the Fe-rich reaction layer. The blue arrows and lines mark off the diffusion of Al into the Kovar base material.

in the remaining Ag-1.0Al filler metal. Those values were as follows (wt-%): Fe, 0.22 ± 0.07 ; Ni, 0.15 ± 0.05 ; Co, 0.13 ± 0.04 ; and Al, 0.29 ± 0.01 . Referring to Fig. 14, the Al content exhibited a sharp increase over that of the Ag-0.5Al filler metal for similar brazing conditions. This trend suggests that the interface reaction and associated Al diffusion into the base material had reached a limiting condition, thereby leaving behind a greater percentage of Al in the filler metal.

Lastly, referring to Fig. 15, the mean concentrations of Fe, Ni, and Co decreased slightly in the Ag-1.0Al filler metal when compared to the Ag-0.5Al filler metal. However, the differences were not statistically significant. These data, when compared to the plot of remaining Al shown in Fig. 14, suggest that there is not a correlation between base material dissolution and the interface reactions and diffusion processes that are responsible for the Al left in the filler metal.

The interface microstructure result from the Ag-1.0Al sessile drop brazed at 995°C (1823°F) and 20 min was examined. The corresponding SEM/BSE channeling contrast image is shown in Fig. 22. The filler metal was almost completely lost to evaporation; only a few patches remained on the base material (rounding caused the bright edge of the layer). The reaction layer exhibited numerous grain boundaries, several of which exhibited the same morphology as the high-Fe reaction layer (black arrows). A relatively thick Fe-rich reaction layer developed adjacent to the Kovar base material. Also, recrystallization zones extended well into the latter. Although small voids were observed in the reaction layer (cyan circles), cracking was absent.

Figure 23A shows a representative EPMA trace. An interdiffusion zone and two reaction layer chemistries were identified in the EPMA data. The R.L. #1, which comprised a majority of the reaction layer, exhibited an increasing Fe concentration that was accompanied by decreasing concentrations of both Ni and Al. The Co signal showed no significant change across the reaction layer. Figure 23B highlights the features of the R.L. #2. Iron and Ni showed reduced concentrations while Co and Al signals showed small peaks when compared to R.L. #1. The Fe-rich reaction layer (red arrow) exhibited the expected fea-

Fig. 23 — A — EPMA trace shows the Al, Fe, Ni, and Co concentration profiles taken across the interface at the center of the Ag-1.0Al sessile drop formed at 995°C (1823°F) and 20 min. The red arrow indicates the Fe-rich reaction layer. The blue arrows and lines mark off the diffusion of Al into the Kovar base material; B — enlarged EPMA plot shows R.L. #1 and #2 sections.

tures: an Fe peak, a minimum in the Ni signal, no change to the Co signal, and a sharp drop-off of the Al signal proceeding into the recrystallization zone (blue arrows and lines).

The following compositions were determined for the reaction layers:

The two compositions are only slightly different from each other as initially indicated by the SEM image in Fig. 22. The R.L. #1 composition was very similar to that of R.L. #1 formed by Ag-1.0Al when brazed at 965°C (1769°F) and 5 min. However, the R.L. #2 concentration of Al (27 ± 1 at.-%) was significantly lower than that of the same reaction layer (31 ± 2 at.-%) formed under the less-severe brazing conditions, despite an ample supply of Al provided by the filler metal. Lastly, both R.L. #1 and #2 compositions were very similar to the respective layers created by the Ag-0.5Al filler metal at 995°C (1823°F) and 20 min.

The absence of filler metal atop the reaction layer prevented a determination of residual Al, Fe, Ni, and Co concentrations.

Reaction Layer Thickness

Figure 24 shows the reaction layer thickness plotted as a function of the Al concentration in the filler metal. The error bars were provided only for the 965°C (1769°F), 5-min and 995°C (1823°F), 20-min brazing parameters to maintain clarity of the graph. The data spreads were similar for the other two intermediate brazing conditions. The general trend had the layer thickness increase with Al content (x) in the Ag-xAl filler metals. However, at a given filler metal composition, the thickness values did not differ, statistically, between brazing conditions with one exception: the anomalously low value for the Ag-0.2Al filler metal brazed at 995°C (1823°F) for 20 min. Recall that the reaction layer was present only intermittently for that case — Fig. 13A.

Fig. 24 — The reaction layer (total) thickness is plotted as a function of the nominal Al concentration in the filler metal sessile drops. The error bars are representative of all four brazing conditions.

Discussion

Prior Investigations

Prior studies examined the high-Al Ag-xAl binary alloys ($x = 2, 5$, and 10 wt.-%) (Refs. 3, 4). The findings are briefly summarized below because they are important to the discussion of the present study:

1. Run-out did not occur in the sessile drop geometry for all compositions.
2. The Al concentration, z , in the $(\text{Fe, Ni, Co})_y \text{Al}_z$ reaction layer increased with the Al concentration, x , in the Ag-xAl filler metal — Fig. 1.

Fig. 25 — Aluminum concentration, z , in the reaction layer, $(\text{Fe, Ni, Co})_y\text{Al}_z$, is plotted as a function of Al content (x) in the Ag-xAl filler metal for the sessile drop geometry. The data are shown for both brazing conditions.

Fig. 26 — Aluminum concentration, z , in the reaction layer, $(\text{Fe, Ni, Co})_y\text{Al}_z$, is plotted as a function of Al content (x) in the Ag-xAl filler metal and brazing conditions for the sessile drop geometry. Data were included from the earlier study with values of x equal to 2, 5, and 10 wt-% Al.

Fig. 27 — Remaining Al concentration in the filler metal (Ag-xAl) is plotted as a function of nominal Al content, x , across the range of $0.2 \leq x \leq 10$ wt-% Al obtained from the current study and Ref. 3. The brazing conditions were 965°C (1769°F) and 5 min. The error bars are the same size as the symbols in numerous instances.

3. The values of z were lower with the more severe brazing conditions: 995°C (1823°F), 20 min.

4. The reaction layer thickness increased with the Al content in the filler metal, but it was not sensitive to the brazing conditions.

5. Enough Al remained in the Ag-xAl filler metals such that the Al supply was not a constraining factor for the interface reaction or Al diffusion into the base material.

6. The concentrations of Fe, Ni, and Co, which dissolved into the filler metal, were very small. Those concentrations were a function of Ag-xAl filler metal composition but not in a monotonic manner. Iron, Ni, and Co dissolution did not increase with severity of the brazing conditions.

Present Study

Run-out was not observed with the low-Al Ag-xAl sessile drops as well. Very similar topographies and EDX compositional analyses were observed for the reaction layers exposed at the sessile drop edges across the Ag-xAl compositions and brazing conditions. The only exception was the serrated appearance of the Ag-0.5Al sessile drop edges, which were consistent for both brazing conditions. Moreover, these topological features, as well as the qualitative compositional data obtained by EDX, were very similar to those observed with the high-Al Ag-xAl filler metals (Ref. 3). The SEM and EDX data confirmed that, even at these reduced Al concentrations in the filler metal, the reaction layer developed ahead of the filler metal and would thus support the spontaneous wetting and spreading behavior by the molten filler metal that characterizes the run-out phenomenon.

The Al content, z , in the interface reaction layer, $(\text{Fe, Ni, Co})_y\text{Al}_z$, was examined as a function of the initial Al concentration in the filler metal. The focus was placed on the reaction layer in direct contact with the filler metal because it controlled wetting and spreading activity. Those data are plotted in Fig. 25 for both brazing conditions. The brazing conditions of 965°C (1769°F) and 5 min resulted in a monotonic increase of z with increasing x in the Ag-xAl filler metal. Although the same general trend can be said of z for the 995°C [1823°F] and 20-min brazing conditions, it was not monotonic. The Ag-0.2Al filler metal did not produce a discernable reaction layer. The value of z increased to 28 ± 2 at.-% for the Ag-0.5Al filler metal but then did not change significantly for the Ag-1.0Al alloy.

A hypothesis was proposed to explain the above behavior for the 995°C (1823°F) and 20-min brazing conditions. Two competing mechanisms were active: 1) reaction layer formation and 2) Al diffusion into the Kovar base material. In fact, Al diffusion occurred extensively into the Kovar base material for both Ag-0.2Al and Ag-0.5Al filler metals (e.g., Fig. 13B and Fig. 19A, respectively). On the other hand, the con-

centration of Al remaining in the filler metal (Fig. 14) indicated there were ample supplies of Al in all the filler metals to support both processes. Therefore, the failure of the Ag-0.2Al filler metal to produce a reaction layer was not for a lack of Al; rather, it was caused by a reduced driving force (chemical potential) for the reaction to take place. A similar scenario may explain the unchanged values of z between the Ag-0.5Al and Ag-1.0Al. Clearly, the data in Fig. 25 demonstrate that the reaction's driving force was a function of both filler metal composition and brazing conditions.

The Al concentration in the reaction layer (z) was further examined as a function of Al concentration, x , in the filler metal by combining the data in Fig. 25 with the corresponding results obtained from the high-Al filler metals (Ref. 3) — Fig. 26. The same general trend was continued across the entire range of filler metal Al concentrations; z increased with x for both brazing conditions. However, the values of z remained lower for the more severe brazing conditions. Since the opposite trend would be expected, based on thermally activated rate kinetics, the results in Fig. 26 confirmed that the chemical potential controlled reaction layer development at the interface.

Next, the findings were analyzed for the remaining Al in the filler metal, beginning with the data in Fig. 14. The Al content exhibited a substantial spike for the Ag-1.0Al sessile drops when brazed at 965°C (1769°F) and 5 min. Evidence was not observed of excessive evaporation having an increased concentration of Al in the filler metal (evaporation was responsible for the loss of the Ag-1.0Al filler metal and thus the absence of a data point in Fig. 14 for the case of the 995°C (1823°F), 20-min brazing conditions). A short analysis, which is presented in Appendix A, further substantiated the unlikelihood of the evaporation mechanism. Rather, the elevated Al concentration resulted from the combination of a higher-starting Al content and the lack of its full consumption by the interface reaction diffusion into the Kovar base material.

The Al concentration (x) data in Fig. 14, which were compiled from the low-Al Ag- x Al filler metals, were combined with similar results obtained from the high-Al Ag- x Al filler metals (Ref. 3) — Fig. 27. A continuous data set could only be compiled for the 965°C (1769°F), 5-min brazing conditions due to the evaporation of the Ag- x Al sessile drops having $x \geq 1.0$ wt-% when brazed at 995°C (1823°F) and 20 min. The significant increase of the remaining Al, which was observed between 0.5 and 1.0 wt-% (Fig. 14), continued to grow with $x > 1.0$ wt-%. This analysis further substantiated the earlier stipulation that the absence of run-out in the sessile drop geometry was not caused by the lack of Al available to form a reaction layer. Rather, the additional surface energy created by the open configuration of the sessile drop mitigated the driving force for the run-out phenomenon.

The concentrations of Fe, Ni, and Co in the Ag- x Al filler metals were plotted in Fig. 15 as a function of x (0.2, 0.5, and 1.0 wt-%). Several general observations were made from the data. First, the concentrations were very low, indicating that the Kovar dissolution was not extensive in the Ag- x Al alloys. Second, the dissolution process did not cause fractionalization of the base material because the Fe, Ni, and Co concentrations remained in-proportion to their nominal values in the Kovar composition. Third, Fe, Ni, and Co dissolution did not increase

Fig. 28 — Iron, Ni, and Co concentrations in the filler metal (Ag- x Al) are plotted as a function of nominal Al content, x , across the range of $0.2 \leq x \leq 10$ wt-% Al obtained from the current study and Ref. 3. The brazing conditions were 965°C (1769°F) and 5 min.

with the more severe brazing conditions.

The Fe, Ni, and Co concentration data in Fig. 15 were combined with results obtained from the previous study of the high-Al sessile drop specimens (Ref. 3) — Fig. 28. A complete data set could only be compiled for the 965°C (1769°F), 5-min brazing conditions due to the evaporation of the Ag- x Al sessile drops having $x \geq 1.0$ wt-% when brazed at 995°C (1823°F) and 20 min. A log₁₀ x -axis was used to include the entire range of filler metal compositions. The Fe, Ni, and Co concentrations were sensitive to the Ag- x Al composition but not in a monotonic manner. Rather, a concentration minimum, which was statistically significant, was observed in Ag- x Al filler metals having x equal to 2.0 and 5.0 wt-% Al. In addition, the nonmonotonic trends in Fig. 28 did not correlate with the Al concentrations remaining in the filler metal (Fig. 27). Therefore, the fact that the Fe, Ni, and Co concentrations did not correlate with either the initial Al concentration of the filler metal (x , Ag- x Al) or the residual Al concentrations after brazing (Fig. 27) implied that, in general, Kovar dissolution was not controlled expressly by the chemical potential for Fe-, Ni-, and Co-aluminide formation. Rather, the driving force of Kovar dissolution was a function of several contributing factors, including filler metal composition and brazing conditions.

Reaction layer thicknesses were plotted in Fig. 24. The layer thickness increased with Al concentration in the filler metal but did not exhibit an increase with severity of the brazing conditions as expected from a thermally activated rate mechanism. This behavior was particularly evident with the Ag-0.2Al filler metal, whereby the reaction layer was continuous when brazed at 965°C (1769°F) and 5 min but was only intermittent when brazed at 995°C (1823°F) and 20 min. Such behaviors suggest that the reaction layer thickness was controlled by unique chemical potentials at the interface that were determined by the filler metal composition

and brazing temperature. The consequence was that the layer thickness did not exhibit the expected increase with brazing temperature or time.

Implications toward Controlling Run-Out

Although run-out did not take place in the sessile drop configuration, this study of the reaction layer development and filler metal properties provided valuable insights toward possible approaches to control run-out. First, the reaction layer will form ahead of the filler metal, even at these low Al concentrations, to support the spontaneous wetting and spreading that is required of run-out.

Second, the extensive analysis of the interface reaction layer, $(\text{Fe, Ni, Co})_y\text{Al}_z$, established several trends. The Al content, z , in the reaction layer, $(\text{Fe, Ni, Co})_y\text{Al}_z$, decreased with the lower initial Al concentration, x , in the filler metal (Ag-xAl). This finding may prove important if, in fact, run-out is correlated to the reaction layer composition. The reaction layer thickness also decreased with x ; however, once the reaction layer forms, its thickness does not have a role in the interface energy that contributes to the wetting and spreading behavior and thus, run-out. An important observation was that both the reaction layer composition and thickness did not respond to the braze parameters in a manner expected of thermally activated rate kinetics. The consequence of this finding was that the interface reaction and its role in run-out cannot be controlled by means of altering the brazing temperature and time.

Third, a correlation was not observed between the concentration of Fe, Ni, and Co dissolved in the filler metal vs. either the composition, $(\text{Fe, Ni, Co})_y\text{Al}_z$, or thickness of the reaction layer. Although these elements combined with Al and formed aluminide particles, their quantity did not significantly affect these interface reaction properties. This result suggested that additions of Fe or Ni to the filler metal would not successfully intercept the Al before it could reach the Ag-xAl/Kovar base material interface and form the reaction layer. In fact, this technique was proved to be unsuccessful in an unpublished study (Ref. 5). Therefore, the most promising approach to mitigate run-out by the Ag-Cu-Zr active brazing filler metal requires preventing the aluminide interface reaction (e.g., the use of a barrier layer on the Kovar surface).

Conclusions

1. The present study examined the interface reactions of sessile drop test samples made between the binary Ag-xAl filler metals having $x = 0.2, 0.5$, and $1.0 \text{ wt-\% Al}$ and a Kovar base material. The objective was to document the effect of the reduced Al concentrations on reaction layer development to define the role of Al in the run-out phenomenon observed in the Ag-Cu-Zr active braze joints made between Kovar and alumina (Al_2O_3) ceramic.

2. The surface SEM and EDX analyses confirmed that the reaction layer developed ahead of the filler metal and would thus allow for the spontaneous wetting and spreading behavior that characterizes the run-out phenomenon.

3. Run-out was not observed with these low-Al sessile

drops, as was also the case with the high-Al sessile drops, thereby confirming that the additional surface energy created by the sessile-drop-free surface constrained the wetting and spreading to curtail run-out.

4. The interface reaction and diffusion mechanisms were not limited by Al availability in the filler metal, even at these reduced concentrations.

5. The value of z in the reaction layer composition, $(\text{Fe, Ni, Co})_y\text{Al}_z$, increased with x of the Ag-xAl sessile drops for both brazing conditions. The Ag-0.2Al and Ag-1.0Al filler metals experienced z values that were lower for the more severe brazing conditions, indicating that the reaction layer composition was determined by the chemical potential of the interface rather than the rate kinetics of a thermally activated process.

6. The concentrations of Fe, Ni, and Co in the Ag-xAl sessile drops, which resulted from Kovar dissolution during brazing, was low. The concentrations did not correlate with either the filler metal composition (Ag-xAl) or post-brazing residual Al. The latter trends indicate that the dissolution of Fe, Ni, and Co was not driven by an Fe-, Ni-, and Co-aluminide reaction with the Al.

7. The reaction layer thickness increased with the Al concentration in the filler metal, but it did not increase with the severity of brazing conditions. That behavior is consistent with an athermal reaction whereby layer thickness was determined by the pseudo-equilibrium condition at the interface defined by the filler metal composition and brazing temperature.

8. The findings of the present study indicate that the most promising approach to mitigate run-out by the Ag-Cu-Zr active brazing filler metal requires preventing the aluminide interface reaction (e.g., the use of a barrier layer on the Kovar surface.)

Acknowledgments

The authors wish to thank Dr. Rebecca Wheeling for a thorough review of the manuscript. Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia LLC, a wholly owned subsidiary of Honeywell International Inc. for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525. This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the U.S. Government.

References

1. Vianco, P. T., Walker, C. A., De Smet, D., Kilgo, A. C., McKenzie, B. M., Kotula, P. M., and Grant, R. L. 2015. Understanding the run-out behavior of a Ag-Cu-Zr braze alloy when used to join alumina to an Fe-Ni-Co alloy. *Proc. 6th International Brazing and Soldering Conference*. Eds. R. Gourley and C. Walker. Miami, Fla.: American Welding Society.
2. Kovar™ is a registered trademark of Carpenter Technologies, Reading, Pa.

3. Vianco, P. T., Walker, C. A., De Smet, D., Kilgo, A. C., McKenzie, B. M., and Grant, R. L. 2018. Interface reactions responsible for run-out in active brazing: Part 1. *Welding Journal* 97(2): 35-s to 54-s. DOI: 10.29391/2018.97.004

4. Vianco, P. T., Walker, C. A., De Smet, D., Kilgo, A. C., McKenzie, B. M., and Grant, R. L. 2019. Interface reactions responsible for run-out in active brazing: Part 2. *Welding Journal* 98(4): 99-s to 115-s. DOI: 10.29391/2019.98.008

5. An unpublished study investigated this technique of adding as much as 2 wt-% Fe of Ni to the Ag-2Zr-1Cu filler metal. The brazing conditions were 985°C (1805°F), 5 min, and 600 Torr atmosphere as a means of stopping the run-out phenomenon. Braze joint strength and hermeticity were poor with either addition. The Fe and Ni additions simply could not impede the interface reaction.

6. The Engineering ToolBox. Melting and boiling temperatures — Evaporation and melting of common materials.

engineeringtoolbox.com/melting-boiling-temperatures-d_392.html

7. Heat of vaporization of the elements. periodictable.com/Properties/A/VaporizationHeat.an.wt.html

8. Swartzentruber, L. 1984. The Ag-Fe (silver-iron) system. *Bulletin of Alloy Phase Diagrams*, Vol. 5., pp. 560–564. New York, N.Y.: Springer

9. Singleton, M., and Nash, P. 1987. The Ag-Ni (silver-iron) system. *Bulletin of Alloy Phase Diagrams*, Vol. 8., pp. 119–121. New York, N.Y.: Springer

10. Karakaya, I., and Thompson, W. 1986. The Ag-Co (silver-iron) system. *Bulletin of Alloy Phase Diagrams*, Vol. 7, pp. 259–263. New York, N.Y.: Springer

Appendix A

The Ag-1.0Al filler metal was completely evaporated from the sessile drop when brazed at 995°C (1823°F) for 20 min. A similar behavior was observed in Ref. 3 with the high-Al filler metals. The persistence of this phenomenon caused the authors to make a first-order analysis by comparing the relevant physical and thermal properties of Ag and Al. Silver and Al have very similar surface tensions when in the liquid state and under vacuum: 910 ± 10 N/m and 960 ± 60 N/m, respectively (Refs. 6, 7). Their heats of vaporization are also very similar, being 293 kJ/mol for Al and 255 kJ/mol for Ag (Refs. 8–10). Finally, the vaporization (boiling) temperature of Al is 2327°C (4221°F), which is slightly higher than that of Ag, 1959°C (3542°F). Therefore, boiling point depression is expected to be very limited, and particularly so given these low Al concentrations. In summary, this first-order analysis would not predict a significant difference of evaporation rate between these Ag-xAl alloys. Unfortunately, an empirical investigation of this phenomenon was beyond the scope of the present study.

PAUL T. VIANCO (ptvianc@sandia.gov), CHARLES A. WALKER, DENNIS DE SMET, ALICE KILGO, BONNIE M. MCKENZIE, and RICHARD L. GRANT are with Sandia National Laboratories, Albuquerque, N.Mex.

American Welding Society

Welding Journal Now Publishing Direct Object Identifier (DOI) Numbers

Dear members of the welding research community,

Note that in each issue of the *Welding Journal* Research Supplement, we are including Direct Object Identifier (DOI) numbers with each of the papers published in print and online. A direct object identifier is a unique alphanumeric string assigned by a registration agency (we are using *Crossref.org*) to identify content and provide a persistent link to its location on the Internet. Our decision to begin assigning a DOI for each paper comes directly from a request by the research community.

As part of our obligation to *Crossref.org*, we are asked to provide DOI numbers, when available, in the references section of papers. So, if you have submitted a paper to the *Welding Journal* or are planning on submitting a paper, we ask that you update your references to include DOI numbers whenever possible.

Thank you.

Annette Alonso
Publisher, *Welding Journal*