American Welding Society®

SUPPLEMENT TO THE *WELDING JOURNAL*, JANUARY 2022
Sponsored by the American Welding Society

WELDING
RESEARCH

Interface Reactions Responsible for Run-Out in Active Brazing: Part 4

Based upon the developing correlation between x , the concentration of Al in the filler metal; z , the concentration of Al in the reaction layer; and run-out from the previous Parts 1–3 studies, the current Part 4 investigation was undertaken to determine whether reduced values of x and, thus, lower concentrations of z , could be identified that no longer supported run-out in the braze joint configuration

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Abstract

This study examined the interface reaction between Ag- x Al filler metals having $x = 0.2, 0.5$, or 1.0 wt-% and Kovar™ base materials. The present investigation used the braze joint test sample configuration. The brazing conditions were 965°C (1769°F), 5 min; 995°C (1823°F), 20 min, and a vacuum of 10^{-7} Torr. Run-out was absent from all test samples. Combining these results with those of the Part 2 study that used high-Al, Ag- x Al filler metals ($x = 2.0, 5.0$, and 10 wt-%) established these conditions for run-out: Ag- x Al filler metals having $x \geq 2.0$ wt-% Al, which result in reaction layer compositions, and $(\text{Fe, Ni, Co})_y\text{Al}_z$, having $z \geq 26$ at.-% Al. The limited occurrences of run-out lobes resulted from the surface tension effect that quickly reduced the driving force for additional run-out events. The interface reactions were controlled by a driving force that was an expressed function of filler metal composition (Ag- x Al) and brazing temperature, as opposed to simply thermally activated rate kinetics. The differences of reaction layer composition and thickness confirmed that the interface reactions differed between the braze joint and sessile drop configurations. Collectively, the findings from the Parts 1–4 investigations concluded that the most-effective means to mitigate run-out is to place a barrier coating on the Kovar base material that will prevent formation of the $(\text{Fe, Ni, Co})_y\text{Al}_z$ reaction layer.

Keywords

- Run-Out
- Active Braze Joints
- Interface Reactions

Introduction

Run-out behavior was observed in 97Ag-1Cu-2Zr (wt-%, abbreviated Ag-Cu-Zr) active filler metal braze joints made between Al_2O_3 (alumina) ceramic and Kovar™ base material (Refs. 1, 2). Microanalysis confirmed that aluminum (Al), which was released by the reduction-oxidation (redox) reaction between Zr, the active component of the filler metal, and alumina, formed an aluminide reaction layer $(\text{Fe, Ni, Co})_y\text{Al}_z$, with the Kovar base material that correlated with the run-out's unstable wetting and spreading behavior. Those early studies determined that controlling run-out through the brazing parameters was not possible. They also established the important role of molten filler metal surface tension on both the propensity and the extent of run-out.

Subsequent studies, the results of which were described in the Parts 1–3 studies, were performed to uncover the details of the run-out mechanism to develop an effective mitigation strategy (Refs. 3–5). The test methodologies were based on a simplified, binary filler metal composition, Ag- x Al. The Cu addition did not have a role in the run-out behavior of the Ag-Cu-Zr active braze alloy and, thus, it was omitted from the filler metals. These braze alloys allowed for the controlled additions of Al as an independent variable. The base material was Kovar. Test samples were created with either a sessile drop or a braze joint configuration.

<https://doi.org/10.29391/2022.101.001>

Fig. 1 — Aluminum concentration (at.-%) in the reaction layer is shown as a function of the nominal Al content (wt.-%) in the high-Al filler metal for the braze joint geometry (Ref. 4).

The Part 1 study examined the wetting and spreading of Ag-xAl filler metals in the sessile drop geometry (Ref. 3). The braze alloys were referred to as the high-Al filler metals and they had values of x equal to 0, 2, 5, or 10 wt.-%. Run-out was not observed, although largely uniform wetting and spreading increased with the Al content of the filler metal. Also, the brazing conditions did not have a significant effect on the extent of wetting and spreading as was similarly observed with run-out by the Ag-Cu-Zr active braze alloy (Ref. 1).

The Part 2 study investigated the wetting and spreading behavior of the same high-Al Ag-xAl filler metals but in the Kovar-to-Kovar braze joint configuration. All test specimens showed run-out. This finding established that run-out required the braze joint geometry, which lent further evidence that the molten filler metal surface tension could impede, but not altogether prevent, the run-out, as was also observed with the Ag-Cu-Zr active braze alloy. Again, the brazing parameters had a negligible effect on run-out.

The magnitude of the run-out events increased with Al content (x) in the filler metal. The electron probe microanalysis (EPMA) technique determined the interface reaction layer composition, $\text{Fe, Ni, Co}_y\text{Al}_z$, as a function of the Al concentration (x) in the Ag-xAl filler metal. Those data are shown in Fig. 1 for the following two extreme brazing conditions: 965°C (1769°F), 5 min and 995°C (1823°F), 20 min. The amount of Al in the reaction layer (z) increased with Al in the filler metal (x), which correlated phenomenologically to a greater propensity for run-out.

A second trend observed in Fig. 1 was that the Al concentration in the reaction layer was greater for the less severe brazing conditions, which is unexpected if the reaction layer formation adheres to traditional, thermally-activated rate kinetics. A similar trend was observed with the high-Al filler metal, sessile drop samples in Part 1. This behavior implies that the reaction layer composition was explicitly a function of brazing temperature as

Fig. 2 — A — SEM image shows the braze joint of one annulus from the Ag-0.2Al braze joint formed at 965°C (1769°F) and 5 min; B — high-magnification view shows the interface microstructure. The blue arrow indicates a location without a discernible reaction layer.

well as Ag-xAl composition. This trend resulted from a pseudo equilibrium state that often underlies interfaces.

The Part 3 study examined the wetting and spreading behavior of sessile drops made with Ag-xAl filler metals having reduced Al concentrations $x = 0.2, 0.5$, and 1.0 wt.-% Al. These alloys were referred to as the low-Al filler metals. Run-out was not observed, as expected of the sessile drop configuration. Nevertheless, these Ag-xAl filler metals resulted in decreases of Al concentration, z , in the reaction layer.

Based upon the developing correlation between x , z , and run-out from the previous Parts 1–3 studies, the current Part 4 investigation was undertaken to determine whether reduced values of x and, thus, lower concentrations, z , could be identified that no longer supported run-out in the braze joint configuration. The same low-Al, Ag-xAl filler metals were used having $0.2 < x < 1.0$ wt.-% Al. Note that these compositions formed a lower bound that overlapped with the 0.7–0.9 wt.-% Al concentration measured in the Ag-Cu-Zr filler metal, which was responsible for run-out by that active braze alloy (Ref. 1).

Fig. 3 – A – EPMA trace shows the Al, Fe, Ni, and Co concentrations across the braze joint formed by the Ag-0.2Al filler metal and 965°C (1769°F) and 5 min brazing conditions; B – enlarged EPMA map shows the concentration details on one of the interfaces.

Experimental Procedures

Base Material

Kovar base material (29Ni-17Co-0.3Mn-0.2Si-0.02C-bal. Fe, wt-%) was used in its as-received condition and without further surface treatment (Ref. 2). The braze joint test specimens were constructed with two Kovar annular flanges. Each flange had an outside diameter of 25.4 mm (1.00 in.); an inside diameter of 6.4 mm (0.25 in.); and a thickness of 0.51 mm (0.020 in.).

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 Ag-xAl filler metal compositions having $x = 0.2, 0.5,$ and 1.0 wt-% Al. The Ag-xAl filler metal preforms were sheared into the same annular footprint as that of the Kovar flanges. The preform thickness was 51 μm (0.002 in.).

Brazing Process

The test specimens were made using one of four combinations of brazing temperatures, 965°C (1769°F) or 995°C (1823°F), and brazing times of 5 min or 20 min. All brazing operations were performed under a high vacuum of better than 10^{-7} Torr to prevent oxidation of the Al coating. The potential drawback of using a high vacuum is the evaporation of Ag from the filler metal. However, such evaporation was negligible for the braze joint configuration. Furthermore, observations compiled from the previous studies that used test samples in the sessile drop configuration established that the interface reactions take place so quickly, they are unaffected by a loss of filler metal (Refs. 1, 3–5).

Fig. 4 – Plot shows the Al concentration remaining in the braze joints as a function of the nominal Al content in the filler metal and brazing conditions.

The braze joint specimen was formed by placing two Ag-xAl filler metal preforms between the two Kovar flanges. Two preforms were used to provide sufficient Al for reactions at two filler metal/Kovar base material interfaces. The surfaces of the filler metal preforms having the Al coating were positioned next to one another along the centerline of the joint clearance. This arrangement required the Al to diffuse across the molten filler metal to reach the Kovar base material interfaces. The braze joint clearance was not controlled because the earlier studies indicated that the interface reactions were not sensitive to this property. This behavior was confirmed,

Fig. 5 — Plots show the concentrations of Fe, Ni, and Co that remained in the braze joint filler metals as a function of the nominal Al content initially in the Ag-xAl alloy and brazing conditions: A — 965°C (1769°F), 5 min; B — 995°C (1823°F), 20 min.

Fig. 6 — SEM backscattered electron channeling image shows the interface microstructure of the Ag-0.5Al braze joint fabricated at 965°C (1769°F) for 5 min. The white arrows identify two instances of an anomalous structure in the reaction layer.

a postiori, in the present study. Generally, the clearance varied between 50 and 150 μm .

Duplicate test samples were fabricated for each brazing condition.

Data Analysis

A brief description is provided of the data analysis; the details are described in Ref. 4. The test specimens were subjected to metallographic cross sections that were made along the flange diameter. Microanalysis activities, which included scanning electron microscopy (SEM), energy dispersive x-ray (EDX) analysis, and electron probe microanalysis (EPMA), were limited 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 warranted additional evaluations of the other two conditions. The EPMA technique determined, quantitatively, elemental concentrations in the reaction layers as well as compositions of the remaining filler metal and Kovar base material adjoining the interface.

The reaction layer thicknesses were measured for all four brazing conditions and Ag-xAl compositions. The diametrical cross sections exposed two segments of braze joint annulus. At the center of each segment, five thickness measurements were taken that included both interfaces for a total of 20 data per sample. Each reaction layer thicknesses were represented by the mean and an error bar of $\pm$ one standard deviation.

Results

Visual Inspection

Run-out was not observed for all three filler metals and all brazing conditions. This observation was in contrast to the extensive run-out observed with braze joint specimens fabricated with the high-Al filler metals (Ag-xAl, $x = 2, 5$, and 10 wt-% Al) (Ref. 4).

Cross Section Analysis

Several observations were relevant across all of the test specimens. Those findings were as follows: First, voids as well as wetting defects, such as nonwetting or dewetting, were absent. Second, capillary flow was excellent through the joint clearances. Third, cracks or delamination defects were not observed in the interface microstructures and, specifically, in the reaction layers.

More-detailed findings are categorized according to filler metal composition in the discussion below.

Fig. 7 — A — SEM shows the Ag-0.5Al filler metal braze joint fabricated at 995°C (1823°F) and 20 min; B — high magnification, backscattered electron channeling photograph shows the details of the interface microstructure. The blue arrows identify interface regions having only an I.Z.

Fig. 8 — EPMA trace shows the Fe, Ni, Co, and Al concentration profiles across the Ag-0.5Al/Kovar braze joint interface. The brazing conditions were 995°C (1823°F) and 20 min. The black arrow indicates the single data point used to determine the reaction layer composition. The blue arrows identify Al diffusion into the adjacent Kovar base material that accompanied the recrystallization zone.

Fig. 9 — EPMA trace shows the Fe, Ni, Co, and Al concentration profiles across the Ag-1.0Al/Kovar base material interface. The brazing conditions were 965°C (1769°F) and 5 min. The black arrow indicates the data point from which was determined the reaction layer composition. The red arrow identifies the Fe-rich reaction layer. The blue arrows identify Al diffusion into the adjacent Kovar base material that accompanied the recrystallization zone.

Ag-0.2Al Filler Metal

Figure 2A shows the braze joint formed by the Ag-0.2Al filler metal and 965°C (1769°F), 5 min brazing conditions to illustrate the excellent capillary flow that characterized all test specimens. The interface microstructure is represented by the SEM/BSE channeling contrast image in Fig. 2B. The reaction layer was less than 1 μm thick and was not always continuous along the interface, e.g., the location indicated by the blue arrow. Nevertheless, at those locations where the reaction layer was absent, the filler metal was still capable of wetting the Kovar base material. Recrystal-

lization zones developed in the latter adjacent to the interface. Figure 3A shows a representative EPMA plot of Al, Fe, Ni, and Co profiles across the braze joint. Aluminum peaks were observed at both Ag-0.2Al/Kovar base material interfaces. The enlarged plot in Fig. 3B shows that the Al peak was not associated with a definable reaction layer. Rather, the peak was a result of the formation of an interdiffusion zone (I.Z.) at the interface. The I.Z. was not considered to be a reaction layer because of the high concentration of Ag, which implied that it was a structure associated with the filler metal. The I.Z. had an Al concentration of 3 ± 2 at.-%

Fig. 10 — SEM backscattered electron channeling images show the interface microstructure of the braze joint formed by the Ag-1.0Al filler metal with the brazing conditions of 995°C (1823°F) and 20 min. Inset photograph illustrates the extent of the recrystallization zone. The high magnification image shows details of the interface microstructure, including void development in the recrystallized base material (cyan bracket).

in Fig. 3B. The Al peak was documented to reach values as high as 22 at.-%; however, the structure was still not a reaction layer.

The Al concentration in the remaining Ag-0.2Al filler metal was 0.07 ± 0.05 wt.-% at the midpoint of the joint clearance. Because the absolute error was 0.001 ± 0.008 wt.-% (which was applicable for all test specimens), the Al concentration was statistically significant. Therefore, roughly two-thirds of the available Al was used to create the interface microstructures (i.e. and/or reaction layers) so that the mechanisms responsible for the development of those microstructural features were not restricted by Al availability. The Al concentration in the remaining filler metal was plotted as a function of nominal filler metal Al content (x of Ag- x Al) and brazing conditions in Fig. 4 for all of the test samples.

The Fe, Ni, and Co concentrations were also recorded in the remaining filler metal. Figure 5A is a compilation of not only the findings obtained from the Ag-0.2Al filler metal but all of the filler metals used to make the joints brazed at 965°C (1769°F) and 5 min. The remaining Ag-0.2Al alloy had these Fe, Ni, and Co concentrations (wt.-%): Fe, 0.1 ± 0.2 ; Ni, 0.09 ± 0.09 ; and Co, 0.08 ± 0.07 . The concentrations were very small, which was also a finding obtained from the sessile drop test samples in Part 3 (Ref. 5). These results confirmed the premise that dissolution (erosion) of the Kovar base material was very limited by the molten Ag- x Al filler metals. Lastly, the data in Fig. 5A also confirmed an earlier observation that the proportions of Fe, Ni, and Co consistently matched their relative concentrations in the Kovar base material.

The interface microstructure was analyzed for the Ag-0.2Al braze joints fabricated at 995°C (1823°F) and 20 min. Although an intermittent reaction layer could be discerned in the SEM images,

it was too thin for the EPMA to determine its composition with statistical significance. Interdiffusion zones supported the successful wetting, spreading, and capillary flow of molten filler metal. The microanalysis data (EDX analysis and EPMA) confirmed that Al diffusion took place into the Kovar base material, which was accompanied by the recrystallization zones.

The remaining Ag-0.2Al filler metal had the following elemental concentrations (wt.-%): Al, 0.07 ± 0.07 ; Fe, 0.07 ± 0.05 ; Ni, 0.06 ± 0.03 ; and Co, 0.05 ± 0.04 . Referring to Fig. 4, the Al concentration was identical to that in the braze joints made at 965°C (1769°F) and 5 min.

The Fe, Ni, and Co concentrations are shown in Fig. 5B. The concentrations were still relatively small. In fact, the values did not differ statistically from those measured after brazing at 965°C (1769°F) for 5 min (Fig. 5A). This result was somewhat unexpected. The anticipated result was that the more severe brazing conditions would cause a greater degree of Kovar dissolution into the filler metal.

Lastly, in the case of either set of brazing conditions, a correlation could not be established between the Al concentration and the concentrations of Fe, Ni, and Co elements that remained in the Ag-0.2Al filler metal.

Ag-0.5Al Filler Metal

The Ag-0.5Al braze joints, when fabricated at 965°C (1769°F) and 5 min, developed a uniform reaction layer (Fig. 6). However, the layer remained too thin to determine its composition accurately by EPMA. Numerous voids were observed in the reaction layer

Fig. 11 — EPMA trace illustrates the Fe, Ni, Co, and Al concentrations across an Ag-1.0Al/Kovar base material interface formed by the brazing conditions of 995°C (1823°F) and 20 min. The black arrow indicates the data point representing the reaction layer composition and the red arrow indicates the Fe-rich reaction layer.

as well as anomalous structures identified by the white arrows. The lighter gray tone suggested an increased presence of Fe, Ni, and/or Co. However, the limited layer thickness prevented both qualitative and quantitative elemental assessments by EDX and EPMA, respectively, from identifying further details of those structures. A recrystallization zone was prevalent in the adjoining Kovar base material.

The EPMA measured the Al, Fe, Ni, and Co concentrations in the remaining filler metal; those concentrations were (wt-%): Al, 0.07 ± 0.02 ; Fe, 0.14 ± 0.14 ; Ni, 0.09 ± 0.08 ; and Co, 0.08 ± 0.06 . The Al concentration was nearly identical to that measured in the Ag-0.2Al braze joint for the same brazing conditions (Fig. 4). That similarity also extended to the Fe, Ni, and Co concentrations (Fig. 5A).

The Ag-0.5Al specimens that were brazed at 995°C (1823°F) for 20 min were examined. The reaction layer was not continuous (Fig. 7A). Nevertheless, the high magnification image (Fig. 7B) confirmed that the filler metal wetted the base material at the I.Z.s (blue arrows) between the reaction layer segments. An intermittent, Fe-rich reaction layer developed between the reaction layer and recrystallization zone. Scattered voids were also observed in both the reaction layer and recrystallization zone.

Seven of the 12 EPMA traces did not identify a reaction layer where they crossed the interfaces. Interdiffusion zones were observed at those locations. The remaining five EPMA traces crossed distinct reaction layers. A representative EPMA trace of the latter case is shown in Fig. 8. Only one data point (black arrow) qualified as representing a reaction layer in each of those five EPMA traces. The following $(\text{Fe, Ni, Co})_{76 \pm 4}\text{Al}_{24 \pm 4} \approx (\text{Fe, Ni, Co})_3\text{Al}$ composition was compiled from those data:

Fig. 12 — Reaction layer thickness is plotted as a function of nominal Al concentration in the filler metals for each of the four brazing conditions. Representative error bars are provided for the two conditions: 965°C (1769°F), 5 min and 995°C (1823°F), 20 min.

The extensive recrystallization zone was clearly evident in the Kovar base material (Fig. 7B). The zone is also indicated in the EPMA trace by the blue arrow that signifies the Al diffusion that accompanied the recrystallization behavior.

The Al, Fe, Ni, and Co concentrations were measured in the remaining filler metal. Those values were: (wt-%): Al, 0.06 ± 0.03 ; Fe, 0.22 ± 0.05 ; Ni, 0.12 ± 0.02 ; and Co, 0.11 ± 0.03 . The Al concentration was nearly identical to the value measured when the Ag-0.5Al alloy was brazed at 965°C (1769°F) and 5 min. In fact, the Al concentration was also the same as the concentrations recorded for the Ag-0.2Al filler metal and both brazing conditions.

The Fe, Ni, and Co concentrations (Fig. 5B) were unchanged from those measured for the Ag-0.5Al after brazing at 965°C (1769°F) for 5 min (Fig. 5A). On the other hand, the Ag-0.5Al braze joints exhibited Fe, Ni, and Co concentrations that were statistically higher than those remaining in the Ag-0.2Al filler metal for the same brazing conditions of 995°C (1823°F) and 20 min. Regardless, the concentrations were still very low, approaching the detection limit of the EPMA technique.

Ag-1.0Al Filler Metal

The interface microstructure of the Ag-1.0Al filler metal, which was brazed at 965°C (1769°F) and 5 min, was very similar to that shown in Fig. 6 (Ag-0.5Al filler metal and the same brazing conditions) except that the reaction layer was slightly thicker. The EPMA plot, a representative of which is shown in Fig. 9, yielded a single data point (black arrow) from which to compute the reaction layer composition. A thin I.Z. formed next to the filler metal. The red arrow marks the Fe-rich reaction layer that developed, albeit only intermittently, between the primary reaction layer and Kovar base material. The EPMA trace showed that the Fe peak was

Fig. 13 — The Al concentration, z , in the braze joint reaction layer, $(\text{Fe, Ni, Co})_y\text{Al}_z$, is plotted as a function of nominal Al concentration, x , in the Ag- x Al by combining data from this study with that from Ref. 4 (high-Al Ag- x Al filler metals).

accompanied by a minimum in the Ni trace. The blue arrow shows the extent of Al diffusion into the base material, which coincided with the recrystallization zone.

The compilation of EPMA reaction layer concentrations (black arrow) culminated into the following reaction layer composition:

The Al, Fe, Ni, and Co concentrations were recorded in the remaining filler metal. Those values were as follows: (wt-%): Al, 0.10 ± 0.02 ; Fe, 0.06 ± 0.04 ; Ni, 0.04 ± 0.04 ; and Co, 0.04 ± 0.04 . Referring to Fig. 4, the Al concentration was statistically the same as values measured for the Ag-0.2Al and Ag-0.5Al filler metals and the same brazing parameters. The mean concentrations of Fe, Ni, and Co decreased, proportionally, for all three elements; however, the differences were not statistically significant vs. the other two filler metals.

The interface microstructure, which was formed by the Ag-1.0Al filler metal when brazed at 995°C (1823°F) for 20 min, is represented by the SEM/BSE channeling contrast images in Fig. 10. The inset image illustrates the reaction layer and extensive recrystallization zone along the interface. The high magnification image (yellow box) highlights the details of the interface microstructure. Large, individual voids, as well as strings of smaller voids (cyan bracket), were observed within the recrystallization zone. The Fe-rich reaction layer formed intermittently along the interface between the primary reaction layer and Kovar base material. In general, the interface microstructure was similar to that observed by this filler metal when brazed at 965°C (1769°F) and 5 min except for an increased development of the recrystallization zone.

The corresponding EPMA data are shown in Fig. 11. A single data point (black arrow) was obtained from each trace across the thin reaction layers. The computed composition was as follows:

This composition was statistically equivalent to that generated by the Ag-1.0Al filler metal using the 965°C (1769°F), 5 min. brazing conditions. The red arrow indicates the Fe-rich reaction layer, which was accompanied by the minimum in the Ni profile. Aluminum diffusion into the Kovar base material (blue arrow) coincided with the recrystallization zone.

The Al, Fe, Ni, and Co concentrations, which remained in the filler metal, were as follows (wt-%): Al, 0.07 ± 0.01 ; Fe, 0.09 ± 0.04 ; Ni, 0.05 ± 0.04 ; and Co, 0.06 ± 0.03 . Referring to Fig. 4, the Al concentration was statistically the same as, not only the measurements obtained from the other filler metals brazed at 995°C (1823°F) and 20 min but also when compared to all filler metals brazed at the less severe conditions, 965°C (1769°F) and 5 min. Clearly, the remaining braze alloy Al concentrations were not sensitive to either the nominal Ag- x Al filler metal composition or to the brazing parameters.

The Fe, Ni, and Co concentrations remained very small (Fig. 5B). As in the previous cases, the proportions of Fe, Ni, and Co coincided with their relative concentrations in the Kovar base material. The Fe, Ni, and Co concentrations were identical to those measured for the other two filler metals after brazing at 965°C (1769°F) and 5 min (Fig. 5A). The trend was less consistent under the current brazing conditions (Fig. 5B). Fluctuations caused the Ag-1.0Al concentrations to be less than those observed for the Ag-0.5Al filler metal but similar to the values measured for the Ag-0.2Al alloy. The expectation was that the more severe brazing conditions (Fig. 5B) would have caused a greater degree of Kovar dissolution and, thus, higher concentrations of Fe, Ni, and Co in the remaining filler metal than the less-severe brazing parameters would have (Fig. 5A). The inability to discern this predicted trend by the Ag-1.0Al filler metal and other two Ag- x Al compositions stemmed largely from the resistance of Kovar to dissolution that resulted in the low Fe, Ni, and Co concentrations and associated data scatter. Therefore, the trends observed within each of, or between, Fig. 5A and B, could not be attributed to any one or more specific mechanisms.

Reaction Layer Thickness

The reaction layer thicknesses are plotted in Fig. 12 as a function of nominal Al concentration, x , in the Ag- x Al filler metal. The data are shown for all four brazing conditions. Error bars are provided for the two conditions: 965°C (1769°F), 5 min and 995°C (1823°F), 20 min. Similar data scatter was observed for the other two conditions, the error bars of which were omitted for clarity. Once a significant reaction layer was formed, the thickness increased with Al content in the filler metal. However, the thickness did not increase as a function of the severity of the brazing parameters. In fact, the mean thickness values showed the opposite trend: The thickest layers were generated by the least severe conditions (965°C [1769°F], 5 min). The two intermediate process conditions, 965°C (1769°F), 20 min and 995°C (1823°F),

Fig. 14 — Graphs combine the Fe, Ni, and Co concentrations measured in the present study of low-Al filler metal braze joints with those from the previous study of high-Al filler metal braze joints (Part 2) for the two brazing conditions: A — 965°C (1769°F), 5 min; B — 995°C (1823°F), 20 min.

5 min, produced nearly identical layer thicknesses across the filler metal compositions.

Discussion

The following analyses incorporate findings obtained from all of the earlier studies that examined sessile drop and braze joint test specimens made with either the low-Al, Ag-xAl filler metals ($x = 0.2, 0.5$, and 1.0 wt-%) or with the high-Al, braze alloys ($x = 2, 5$, and 10 wt-%) (Refs. 3-5). The discussion is divided into the following sections: (a) reaction layer composition effects; (b) Al concentrations in the remaining filler metal; (c) Fe, Ni, and Co concentrations in the remaining filler metal; and (d) reaction layer thicknesses. A final section compares these same properties between the low-Al filler metal braze joints examined in the present study with those of the low-Al sessile drop test samples discussed in the Part 3 study. The objective of the latter analysis was to document the effects of sample configuration on the interface reaction and microstructures.

Run-Out and Reaction Layer Composition

The SEM and EDX analysis studies of the sessile drops fabricated from both low-Al and high-Al filler metals determined that the aluminide reaction layer developed ahead of the filler metal. The same finding was confirmed in the case of the braze joint test specimens, based on metallographic cross sections. This property gave the Ag-xAl filler metals (and the Ag-Cu-Zr active braze alloy) the ability to spontaneously wet and spread on the Kovar surface, a necessary mechanism for run-out to take place.

All of the high-Al Ag-xAl filler metal compositions generated significant run-out in the braze joint configuration but not in the sessile drop geometry. This observation confirmed the capacity of the molten filler metal surface tension to curtail the driving

force for run-out. This scenario was responsible for run-out being limited to one or two lobes per braze joint (Ref. 5).

The braze joint geometry posed the risk for run-out. Therefore, the results of the present study were combined with those from the high-Al braze joints test specimens in Part 2 (Ref. 4). The following boundary conditions were established for braze joint run-out, based on Ag-xAl composition:

- Run-out is absent when $x \leq 1.0$ wt-% Al.
- Run-out is present when $x \geq 2.0$ wt-% Al.
- A transition zone exists in the $1.0 < x < 2.0$ wt-% Al range. The transition zone resulted from the inability to establish either the presence or absence of run-out because experiments were not performed at the intermediate Ag-xAl compositions.

The above boundary conditions were correlated to the Al concentrations, z , in the corresponding $(\text{Fe, Ni, Co})_y\text{Al}_z$ reaction layers. Those boundary conditions were as follows:

- Run-out is absent when $z \leq 20$ at.-% Al.
- Run-out is present when $z \geq 26$ at.-% Al.
- A transition zone exists in the $20 < z < 26$ at.-% Al range. The z values were an average calculated by combining the data from both brazing conditions since the values were not statistically different between them.

The correlation between x and z is shown graphically in Fig. 13. A measurable reaction layer was only produced under the 965°C (1769°F) and 5 min brazing conditions when the filler metal had $x \geq 1.0$ wt-% Al. The reaction layers' limited thickness and inconsistent presence along the interface led to the large bar associated with the Ag-1.0Al lower boundary composition. The values of z subsequently increased monotonically with x . The smaller error bars resulted from thicker, more consistently present reaction layers. Measurable values of z were first obtained from the Ag-0.5Al filler metal when the brazing conditions were 995°C (1823°F) and 20 min. Again, the large error bars resulted from the few measurements caused by limited development of the reaction layers. The values of z fluctuated between 0.5 wt-%

Fig. 15 — Reaction layer thickness is plotted as a function of nominal Al concentration of the filler metal for each of the four brazing conditions. Data in the present study and the results obtained from the high-Al braze joints in the Part 2 report are combined. Representative error bars are provided for the two conditions: 965°C (1769°F), 5 min and 995°C (1823°F), 20 min.

Fig. 16 — Graph shows the reaction layer Al concentration, z , as a function of low-Al Ag- x Al composition for both test sample configurations: the braze joint (present study) and sessile drop (Part 3 study). Results are presented for the 965°C (1769°F), 5 min and 995°C (1823°F), 20 min brazing condition.

Al and 2.0 wt-% Al before increasing monotonically with x when $x \geq 2.0$ wt-% Al.

A trend occurred when $x \geq 2.0$ wt-% Al (Fig. 13). The value of z was greater in test samples brazed under the less severe parameters, 965°C (1769°F) and 5 min. The expected outcome, based simply on thermally activated rate kinetics, was that the higher brazing temperature of 995°C (1823°F) and longer brazing time of 20 min would introduce more Al into the reaction layer composition since plenty of Al was available (Fig. 4). The behavior in Fig. 13 lent further evidence that the driving force for the interface reaction was controlled by a pseudo equilibrium that, in turn, was determined, explicitly, by the brazing temperature and filler metal composition (Ag- x Al).

The SEM and EDX data were compared to the boundary conditions established above. As alluded to in the results section, reaction layer development was either absent or intermittent for $x \leq 1.0$ wt-% Al. However, when the braze joints were fabricated with the high-Al filler metals having $x \geq 2.0$ wt-%, the SEM images in Part 2 showed reaction layers having a consistent presence and uniform thickness along the respective interfaces. For this reason, a scenario was proposed whereby the thin, sometimes intermittent reaction layers generated by the low-Al, Ag- x Al filler metals ($x \leq 1.0$ wt-% Al) physically impeded the unstable wetting and spreading action required for run-out. Evidence to the contrary of this hypothesis was that those same SEM images showed these filler metals to wet and spread over the I.Z.s. located between segments of reaction layer. Nonwetting or dewetting were not observed at the I.Z. sites, but, if either defect was present, it would have potentially impeded run-out. In other words, the intermittent presence of the reaction layer that accompanied the low-Al filler metals was unlikely to have prevented run-out in the braze joints.

Interestingly, this conclusion also corroborated the unsuccessful attempts to stop run-out of the Ag-Cu-Zr active braze alloy by introducing physical obstructions to wetting and spreading in the form of grooves scribed into the Kovar surface.

The above boundary conditions, which were based upon x and z associated with the binary Ag- x Al filler metals, were compared to filler metal concentrations of Al measured in the original study of the alumina/Ag-Cu-Zr/alumina active braze joints (Ref. 1). The EPMA data indicated that 0.7–0.9 wt-% Al was generated by the redox reaction between Zr and alumina at the interface. Those samples exhibited run-out. In the present study, the braze joints made with Ag- x Al filler metals of $x \leq 1.0$ wt-% Al did not exhibit run-out. The assumption is made that run-out would not take place in the transition zone of $1.0 \leq x \leq 2.0$ wt-% Al. Therefore, the occurrence of run-out by the Ag-Cu-Zr active braze alloy would have required a local perturbation in the molten filler metal composition to bring $x \geq 2.0$ wt-% and concurrently, a reaction layer having $z \geq 26$ at.-%. Referring back to Fig. 13, when consideration is given to the values of x in the range, $0.5 \leq x \leq 1.0$ wt-% Al, the error bars accompanying the values of z were capable of allowing the latter to meet or exceed the 26 at.-% Al boundary condition. Therefore, run-out was still feasible in the Ag-Cu-Zr active braze joint even though the average value of x across the braze joint, 0.7–0.9 wt-% Al, was below the minimum concentration of 1.0 wt-% required for run-out in the current experiments.

Aluminum in the Remaining Filler Metal

Figure 4 shows the concentration of Al that remained in the Ag- x Al filler metals after completion of the brazing processes. The remaining Al levels implied that sufficient Al was available

Fig. 17 — Reaction layer thickness plotted as a function of filler metal Al concentration for both the sessile drop and braze joint specimens of this study. All four brazing conditions are represented in the data. Error bars accompany only the 995°C (1823°F), 20 min brazing condition for clarity; they are representative of the other conditions.

Fig. 18 — Plot shows the Al concentration remaining in the sessile drop test samples as a function of the Al content, x , in the Ag- x Ag filler metal and brazing conditions reproduced from the Part 3 study.

to support the formation of both the I.Z.s and interface reaction layers as well as Al diffusion into the Kovar base material.

The more notable observation obtained from Fig. 4 is that the concentration of residual Al was constant to within experimental error across a nearly five-fold range of x concentrations in the Ag- x Al filler metals. The fact that the Al concentration did not increase with x implies that the driving force for I.Z. formation, (Fe, Ni, Co)_yAl_z reaction layer formation, and Al diffusion into Kovar increased with x . When similar data were included from studies of the high-Al, Ag- x Al filler metal braze joints, the remnant Al concentrations jumped to 1.8 and 4.5 wt-% for the Ag-5Al and Ag-10Al alloys brazed at 965°C (1769°F), 5 min and to nearly 8 wt-% when the Ag-10Al filler metal was brazed at 995°C (1823°F) and 20 min. These data indicate that the Ag-5Al filler metal and, particularly, the Ag-10Al alloy drew closer to a significant oversupply of Al. Otherwise, the Al concentrations of the other high-Al, Ag- x Al alloy/brazing parameter combinations were less than 1.0 wt-%. Yet, all of these test samples generated run-out. Therefore, the quantity of Al that remained in the filler was not, in and of itself, a determining factor for run-out. Rather, Al's role in run-out was affecting the composition of the (Fe, Ni, Co)_yAl_z reaction layer.

Iron, Ni, and Co in the Remaining Filler Metal

The concentrations of Fe, Ni, and Co dissolved in the Ag- x Al filler metals during brazing were plotted as a function of x (0.2, 0.5, and 1.0 wt-%) in Fig. 5A and B for the two respective brazing conditions. Several observations were compiled from these data. First, the concentrations were very low, approaching the sensitivity limit of the EPMA technique. Thus, dissolution was not particularly significant. Second, the dissolution process did

not cause fractionalization of the base material elements. The Fe, Ni, and Co concentrations remained largely in proportion to their nominal concentrations in the Kovar base material. Third, the concentrations were more variable for the less severe brazing conditions (Fig. 5A), as indicated by the wider error bars.

The understanding was that the concentrations of Fe, Ni, and Co were small and fell within the measurement error. Nevertheless, an examination of the mean concentrations vs. brazing conditions provided additional insight into the interface reactions. For example, the concentrations did not show the expected trend of being greater after the more severe brazing conditions. This unexpected trend may indicate an inherent insensitivity of the dissolution process to the brazing conditions. A second analysis was performed by combining the data in Fig. 5A and B with the data obtained from the high-Al, Ag- x Al braze joints made in Part 2. The resulting plots are shown in Fig. 14A and B for the two respective brazing conditions. Iron, Ni, and Co dissolution increased for the Ag-2.0Al and Ag-5.0Al filler metals, more so under the 995°C (1823°F), 20 min brazing condition. Although this apparent jump in the degree of Kovar dissolution could not be mechanistically correlated to run-out exhibited by these high-Al, Ag- x Al filler metals ($x \geq 2.0$ wt-%), the coincidence of the two phenomena suggests that a transition took place in pseudo equilibrium, driving the interface reaction as a whole.

A correlation was not observed between the Fe, Ni, and Co concentrations vs. x of the low-Al, Ag- x Al braze alloys (Fig. 5A and B) as well as between those concentrations and the quantity of Al that remained in the filler metal after brazing (Fig. 4). The expectation that such a correlation was possible stemmed from the SEM/EDX data of the sessile drop samples in Part 3. Those analyses indicated that dissolved Fe, Ni, and Co combined with

the Al in the filler metal, creating aluminide particles. That association appears to have been neither a controlling factor in the dissolution of Kovar base material, nor did it significantly impede Al from developing the $(\text{Fe, Ni, Co})_y\text{Al}_z$ reaction layer at the filler metal/Kovar interface.

The Fe, Ni, and Co concentrations dropped in the Ag-10Al filler metal, most dramatically so for the 995°C (1823°F), 20 min brazing condition. The Part 2 study identified an aluminide reaction within the filler metal, but in this case, it formed a substantial quantity of large, $(\text{Fe, Ni, Co})_y\text{Al}_z$ particles. Those particles removed Fe, Ni, and Co from the filler metal, thereby accounting for the decrease in the elemental concentrations. Of course, the formation of those particles also removed Al from the filler metal. Nevertheless, the propensity for run-out was not diminished by the latter mechanism.

Reaction Layer Thickness

In general, the reaction layers were relatively thin (Fig. 12), having thicknesses less than three microns. The limited thicknesses were responsible for the absence of cracks in the layers. The more striking trend was that the reaction layer thickness was greater for the least severe brazing conditions. This behavior is counterintuitive to the premise that the interface reactions were controlled by thermally activated, rate kinetics. One explanation was that the reaction layers formed under the 965°C (1769°F), 5 min brazing condition, which contained a lower concentration of Al and had a larger lattice size that led to a greater thickness. Unfortunately, the lattice parameters have not been identified for the $(\text{Fe, Ni, Co})_y\text{Al}_z$ stoichiometries to confirm this hypothesis.

A second explanation was that, in fact, the interface reactions were not determined simply by thermal activation. Rather, reaction layer development was controlled by the same aforementioned pseudo equilibrium condition that was expressly a function of Ag-xAl composition and brazing temperature and, thus, was not based on thermally activated rate kinetics or equilibrium phase predictions.

The thickness data in Fig. 12 were combined with the same data obtained from the high-Al braze joints investigated in Part 2; the resulting plot is shown in Fig. 15. The trend of thickness vs. brazing conditions, which prevailed in Fig. 12, changed with the Ag-2.0Al filler metal. Any thickness dependence on brazing conditions remained unclear with the Ag-5.0Al braze alloy. Lastly, a trend emerged with the Ag-10Al filler metal whereby the reaction layer thickness increased with the severity of the brazing conditions¹.

A limited correlation, if any at all, was expected between the reaction layer thickness and run-out. Run-out is a wetting and spreading phenomenon. Such processes are sensitive to the immediate filler metal/reaction layer interface but not to the quantity of reaction layer underneath that interface. By and large, this hypothesis was substantiated by Fig. 15 in the following manner: A statistically significant minimum was observed for the Ag-2.0Al braze alloy and 965°C (1769°F), 5 min brazing conditions. A low-

er-than-expected reaction layer thickness, albeit not statistically significant, was observed for this filler metal when the brazing temperature was increased to 995°C (1823°F) for the same 5 min. On the other hand, the reaction layer composition (Fig. 13) did not exhibit anomalies that corresponded with the thickness anomalies described above for the Ag-2.0Al filler metal (Fig. 15). The reaction layer composition provided a wetting and spreading condition that supported run-out by this braze alloy.

Braze Joint vs. Sessile Drop Configurations

A comparison was made between the observations compiled from the present study of low-Al filler metal braze joints with the findings described in Part 3 that were obtained from the low-Al sessile drop test specimens (Ref. 4). This analysis provided additional insights into the interface reaction that underlies the run-out phenomenon.

The assessment began by comparing reaction layer compositions, $(\text{Fe, Ni, Co})_y\text{Al}_z$, between the two geometries. The value of z was plotted as a function of filler metal composition in Fig. 16. Although detailed trends did not occur consistently as a function of brazing conditions, two general behaviors emerged from the data: (a) z increased with x and (b) the reaction layers, which formed in the braze joints, were slower to develop with increasing x , and when present, they had a lower value of z than the sessile drop reaction layers. These trends indicate that the chemical potential driving the interface reaction was sensitive to the sample configuration.

A comparison was also made of the reaction layer thickness between the braze joint and sessile test sample geometries. Those data are shown in Fig. 17. The reaction layer thickness increased with Al content, x , in the filler metal for both geometries. The mean layer thicknesses were consistently less for the braze joint samples vs. the sessile drop specimens. A qualitative assessment of the sample configurations confirmed that the quantity of filler metal was only slightly greater within the braze joints when compared to the center locations of the sessile drops where the measurements were taken. Thus, filler metal amount did not appear to be a significant factor in the sensitivity of thickness to specimen geometry. However, the presence of two interfaces in the braze joints, as opposed to a single interface in the sessile drops, cannot be ruled out as a contributing factor that altered the interface pseudo equilibrium between the two geometries. Furthermore, the absence of a consistent role by the brazing conditions on layer thickness lent further evidence which, when combined with the sample configuration effect, indicated that reaction layer development was not controlled simply by thermally activated rate kinetics.

The next analysis compared the postbrazing, Al concentration in the remaining filler metals between the braze joint and sessile drop samples. The sessile drop data that were reproduced from the Part 3 study are shown in Fig. 18. Those results were compared to the findings of the current braze joint study provided in Fig. 4². The Al concentrations were the same between the two configura-

1. The Part 2 SEM images showed those reaction layers, which exceeded approximately 5 μm , also developed cracks.

2. Recall that two preforms were used to form the braze joints so as to provide the same quantity of Al per interface as was provided by the single preform used to make the sessile drops.

tions for the Ag-0.2Al and Ag-0.5Al filler metals and both brazing conditions. A sharp increase of Al concentration was observed in the Ag-1.0Al sessile drop test samples that was not observed with the braze joints for the common brazing condition of 965°C (1769°F) and 5 min. A melting properties analysis was performed in Part 3, which concluded that the elevated Al content remaining in the Ag-1.0Al sessile drop was unlikely to have resulted from a distillation effect caused by a partial evaporation of the molten filler metal. Rather, the Ag-1.0Al filler metal marked a transition in the driving force responsible for the interface reaction such that the latter did not utilize an increased proportion of Al from the filler metal needed to maintain a similar level of residual Al after brazing. This behavior was not observed in the braze joint configuration.

The final comparison was made of the Fe, Ni, and Co concentrations in the filler metals between the braze joint geometry (Fig. 5A and B of the present study) and sessile drop configurations (Fig. 15 of the Part 3 study). In both cases, the concentrations approached the detection limits of the EPMA technique such that the absolute error coupled with the point-to-point variations limited the statistical significance of trends observed within, or between, either data set. Nevertheless, a general observation was made whereby the concentrations of Fe, Ni, and Co were lower for the braze joint geometry versus the sessile drop configuration. In fact, this trend was statistically significant in the case of the Ag-1.0Al filler metal and brazing conditions of 965°C (1769°F) and 5 min. This behavior was counterintuitive. Higher elemental concentrations were expected in the braze joints because there were two interfaces from which to dissolve the Kovar base material for filler metal quantities in the braze joints that did not differ significantly between the two geometries. Rather, as was the case of the Al concentration findings, the corresponding Fe, Ni, and Co concentrations suggest that the dissolution mechanism was controlled by a pseudo equilibrium condition that was also sensitive to the test sample geometry.

Conclusions

1. The present study examined the interface reactions in braze joint test samples made between the binary Ag-xAl filler metals ($x = 0.2, 0.5$, and 1.0 wt-%) and Kovar base material. The brazing conditions were combinations of 965°C (1769°F) or 995°C (1823°F), and brazing times of 5 or 20 min. All brazing operations were performed under a high vacuum of better than 10^{-7} Torr.

2. Metallographic cross sections confirmed that the $(\text{Fe, Ni, Co})_y\text{Al}_z$ reaction layer formed ahead of the filler metal, thereby supporting spontaneous wetting and spreading that is required for run-out.

3. Run-out was not observed with any of the filler metal compositions or brazing conditions.

4. The Ag-0.2Al filler metal developed primarily interdiffusion zones (I.Z.s) or, at best, intermittent segments of reaction layer that were too thin to provide a measurable composition.

5. The Ag-0.5Al filler metal developed intermittent reaction layers for the 965°C (1769°F), 5 min brazing condition. The layer fabricated under the 995°C (1823°F), 20 min brazing condition was sufficiently thick to obtain a composition:

6. The Ag-1.0Al filler metal produced reaction layers of measurable compositions for both brazing conditions:

7. The present, low-Al filler metal data were combined with the high-Al filler metal data to establish boundary conditions for run-out based on x and z of Ag- x Al and $(\text{Fe, Ni, Co})_y\text{Al}_z$ compositions respectively:

- Run-out is absent when: $x \leq 1.0$ wt-% Al or $z \leq 20$ at.-% Al
- Run-out is present when $x \geq 2.0$ wt-% Al or $x \geq 26$ at.-% Al
- Transition zones: $1.0 < x < 2.0$ wt-% Al or $20 < z < 26$ at.-% Al.

8. Sufficient Al remained in the filler metals to support interface reactions and diffusion into the Kovar base material. The remaining Al concentration was insensitive to either the original Ag- x Al composition or the brazing conditions. When these findings were combined with data from the high-Al filler metals studied in Part 2, a correlation was not found between Al concentration and the occurrence of run-out.

9. Kovar dissolution was very limited in the low-Al, Ag- x Al filler metals. The Fe, Ni, and Co concentrations were largely insensitive to Ag- x Al composition, the Al concentrations in the remaining filler metal, and the brazing parameters. Even when including the high-Al, Ag- x Al filler metal results of Part 2, the conclusion was made that Kovar dissolution did not have a controlling role in the run-out phenomenon.

10. The reaction layer thickness remained less than $3 \mu\text{m}$ and did not exhibit cracks or delamination. The layer thickness increased with x of the Ag- x Al filler metal under all brazing conditions. However, the thickness values were greater for the least severe brazing parameters which was not expected, based on the assumption that growth was controlled by thermally activated rate kinetics. When data sets were combined between this study and Part 2, an explicit correlation was not observed between reaction layer thickness and run-out.

11. A comparative analysis was performed between the braze joint geometry (this study) and sessile drop geometry (Part 3), which identified differences in reaction layer composition and thickness as well as differences of Al, Fe, Ni, and Co concentrations in the postbrazed filler metal that indicated a sensitivity by the driving force or pseudo equilibrium of the interface-reaction-to-test-specimen configuration.

12. The findings of the present study, when combined with those documented in the previous investigations (Parts 1–3), established the following premises of the run-out phenomenon and potential mitigation strategy:

- The aluminide interface reaction, which controls the run-out phenomenon (besides the role of molten filler metal surface tension) was not predictable based on thermally activated rate kinetics. The pseudo equilibrium condition and associated driving force caused the interface reaction to not behave predictably as a function of brazing temperature and time. A contributing factor was the extreme rapidness of the interface reaction.
- Reducing the Al concentration, x , to less than or equal to 1.0 wt-% in the binary Ag- x Al filler metals halted the run-out phenomenon. However, the Al concentration must be controlled to even lower levels to minimize the probability that a local perturbation

bation in the Al concentration could cause the latter to exceed 2.0 wt-%, thus leading to a run-out event.

■ Controlling the quantity of Al released into the filler metal by reducing the concentration of the active element, Zr, in the Ag-Cu-Zr filler metal was proven to be unsuccessful in ancillary experiments. The minimum Zr concentration that was required to provide a strong, hermetic braze joint still resulted in run-out.

■ Based on the above observations, the promising mitigation approach to prevent run-out by the Ag-Cu-Zr active braze alloy is through the introduction of a barrier layer on the Kovar base material surface prior to brazing. Atomic layer deposition of a thin alumina coating has proven to be successful toward preventing run-out on Kovar (Ref. 6). A candidate elemental layer is molybdenum (Mo), which was successful at preventing adverse filler metal/Kovar interactions and still providing braze joints that met hermeticity and strength requirements (Refs. 7, 8).

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 United States Government.

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