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Understanding the Run-out Behavior of a Ag-Cu-Zr Braze Alloy When Used to Join Alumina to an Fe-Ni-Co Alloy

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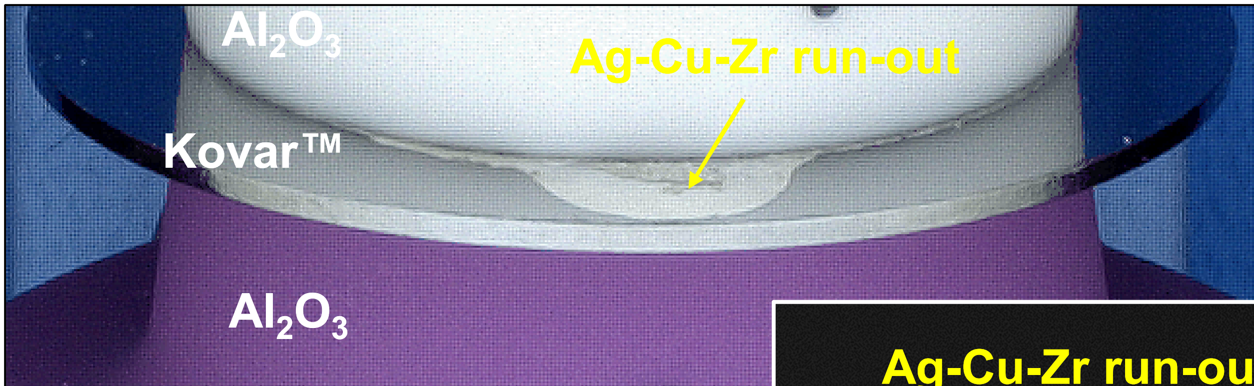
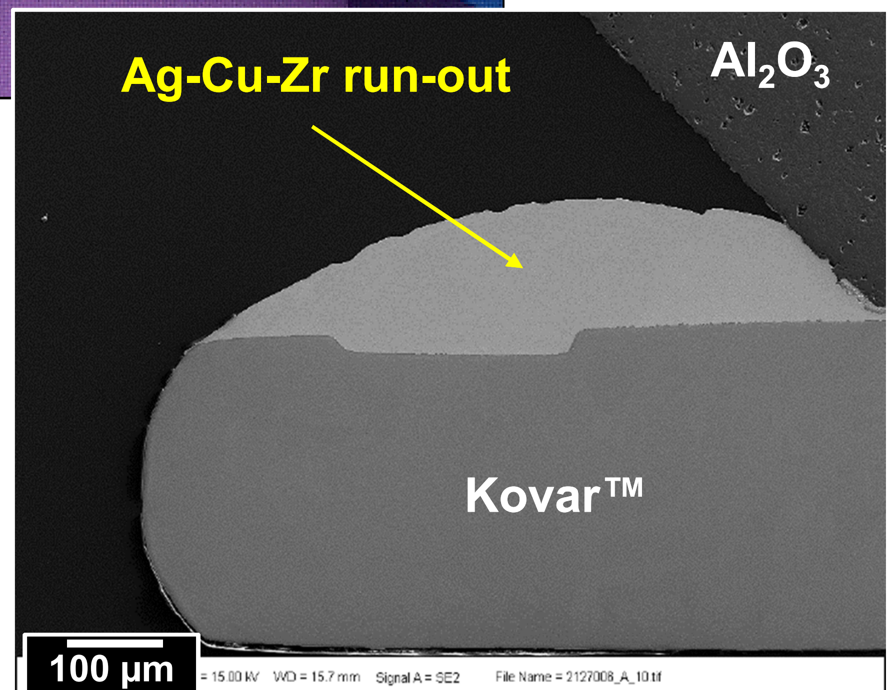
Problem

- **Filler metal run-out** can jeopardize the manufacturing, function, and long-term reliability of braze joints.



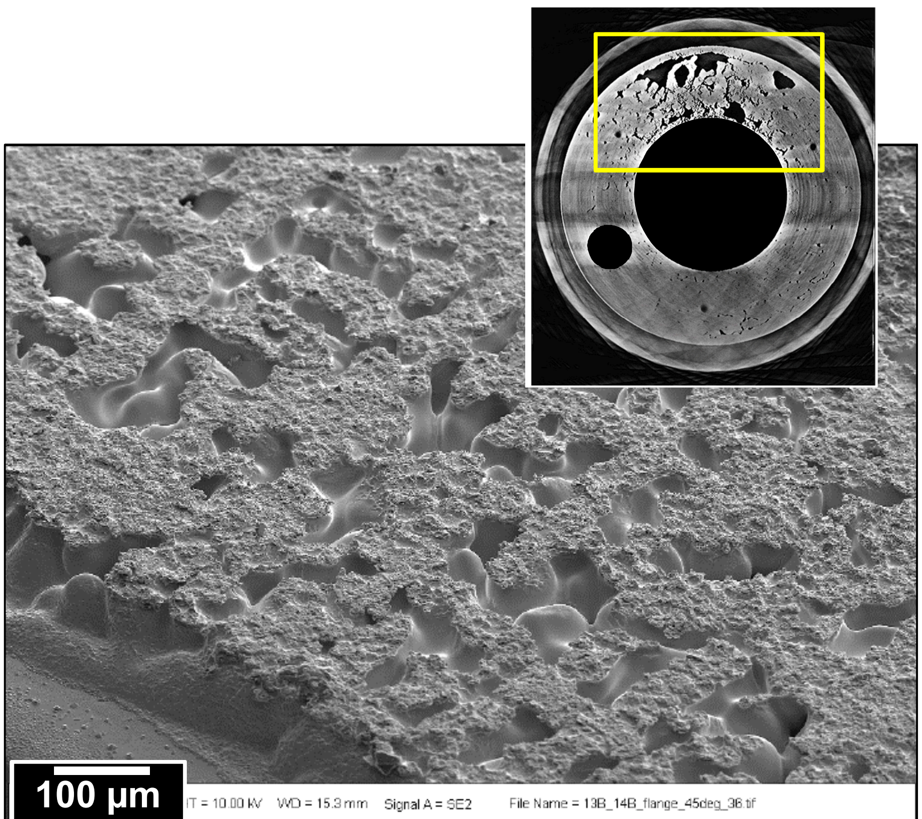


- **Run-out can also degrade cosmetic appearance as well as impede the x-ray inspection of braze joints.**

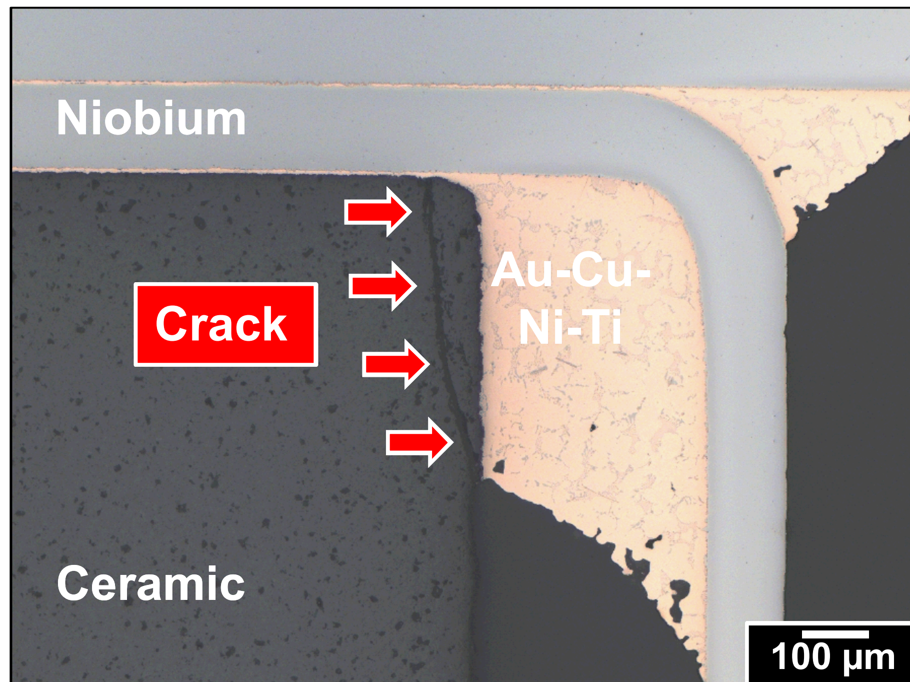
Problem

- **Run-out has been observed to cause these defects:**

- **Excessive voids and solidification shrinkage cause a loss of hermeticity and load-bearing capacity.**

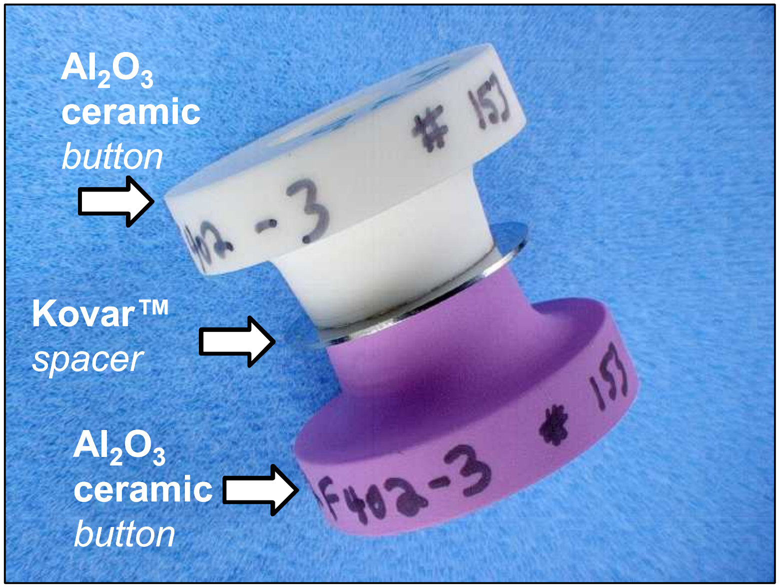


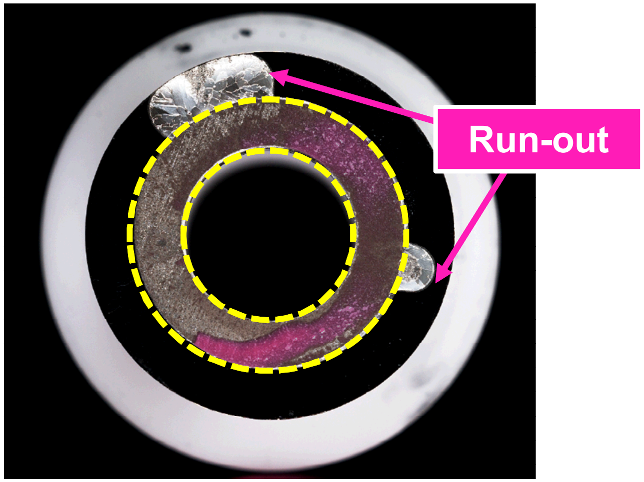
- **Residual stresses that generate cracks in brittle base materials.**



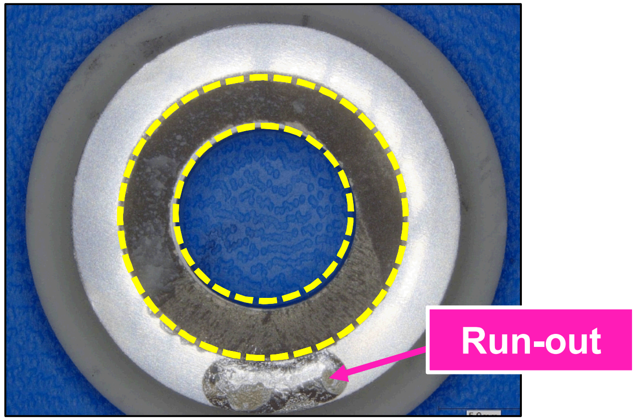
Background Observations

- An analysis was performed of the run-out phenomenon using the ASTM F19-11 tensile test specimen configuration.



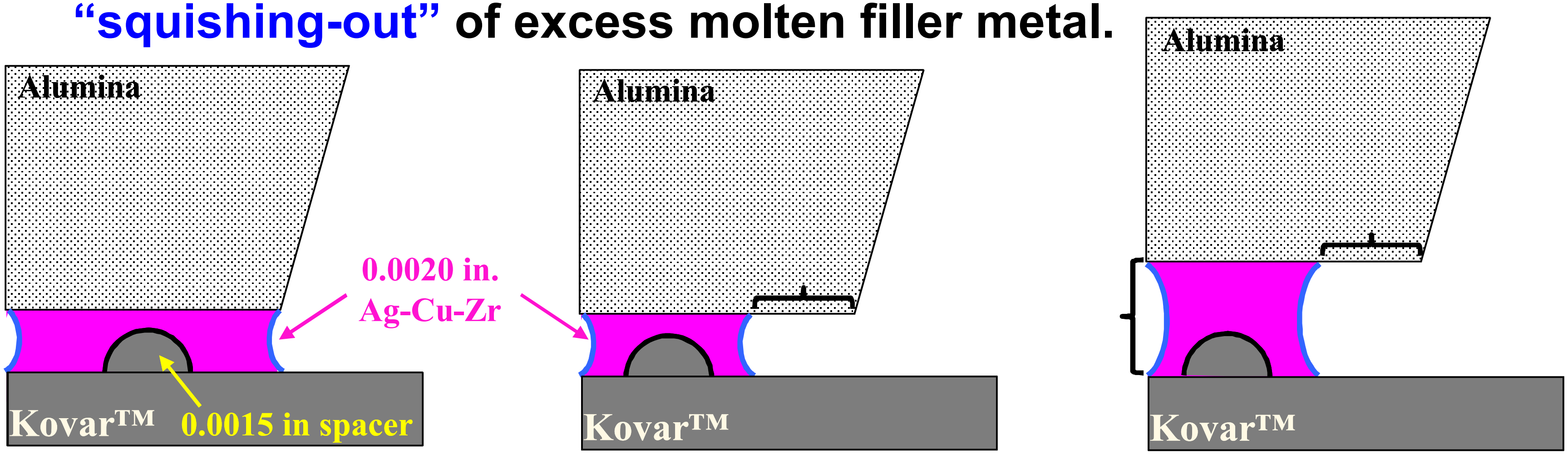


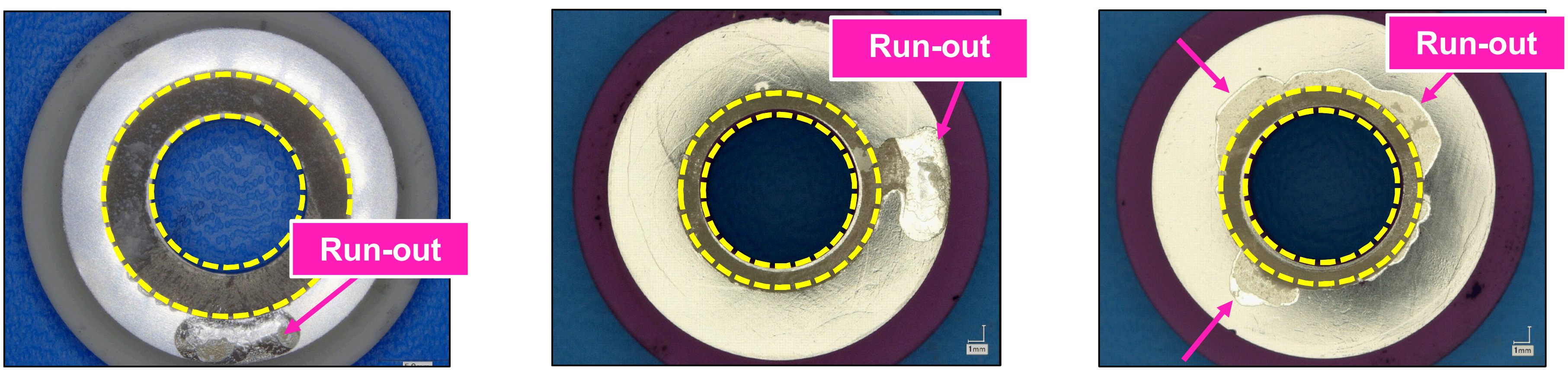
- The post-pull test specimens provided an excellent view of the extent of run-out.



Background Observations

- Run-out was examined as simply the **“squishing-out”** of excess molten filler metal.





- **The run-out was pervasive; it did not behave in a manner that is consistent with the physical displacement of molten filler metal.**

Physical Metallurgy

- The analysis of the run-out phenomenon began by understanding the **braze joint materials system**.

- **Active braze alloy:**

  97Ag - 2Zr - 1Cu (wt.%)

  T_s = 940 – 950° C

  T_l = 960 – 970° C

- **Base materials:**

  95% alumina (Al_2O_3)

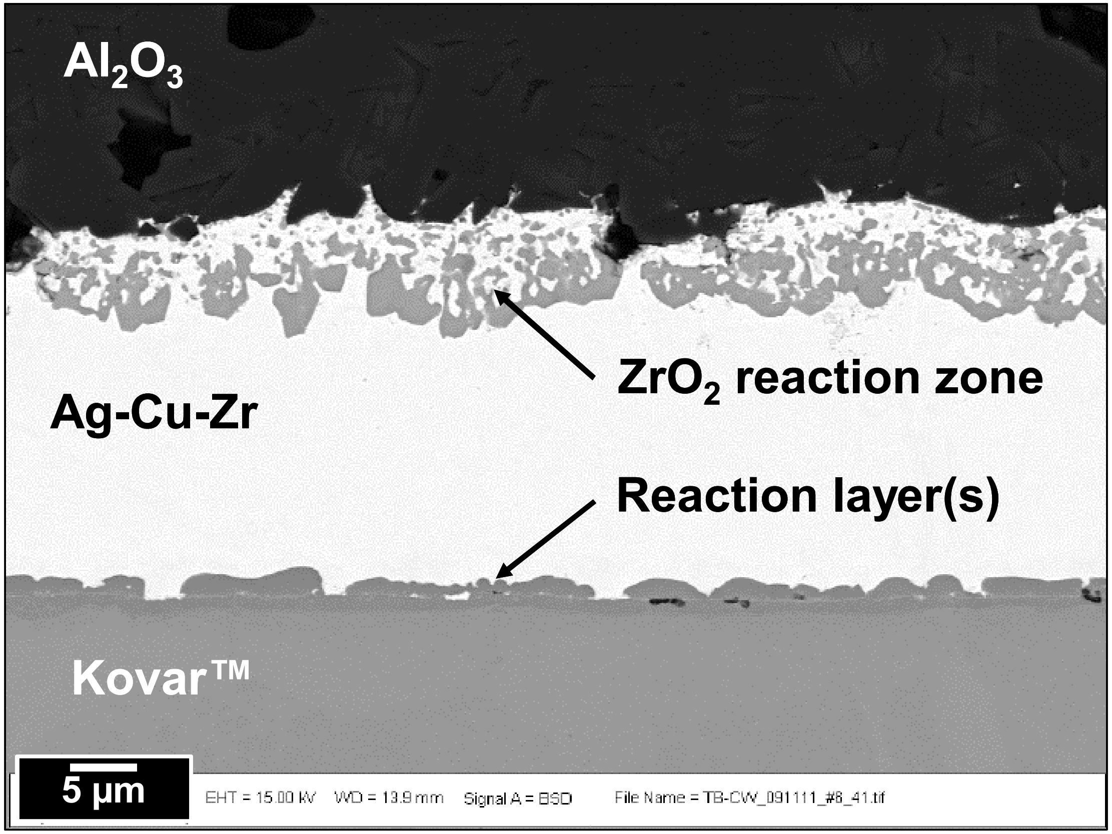
  Kovar™ (Fe-29Ni-17Co)*

- **Nominal brazing process:**

  985° C

  5 min

  600 torr Ar

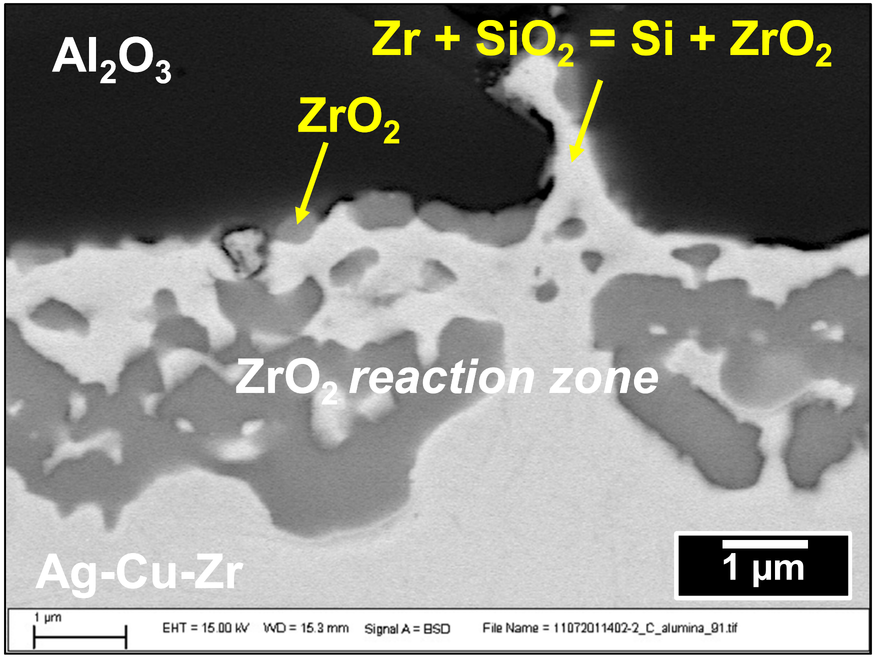


*Kovar™ is a registered trademark of Carpenter Technologies.

Interface Reactions

- Two reduction-oxidation ("redox") reactions take place at the Ag-Cu-Zr / Al_2O_3 interface.

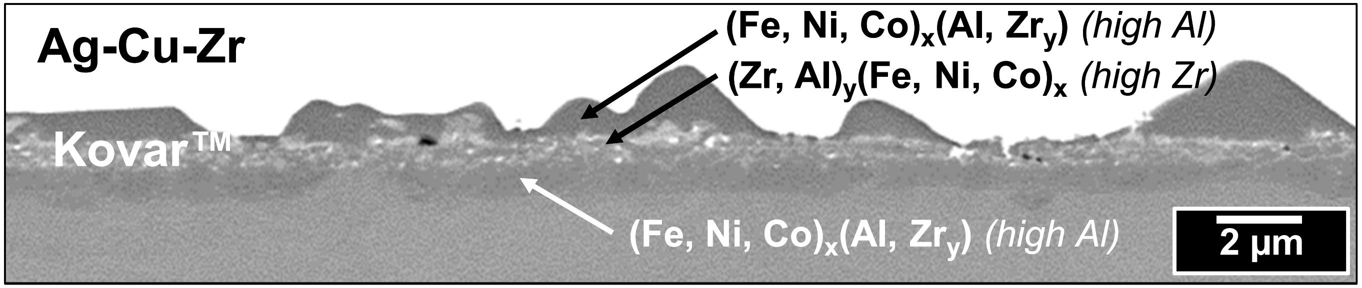
$3Zr + 2Al_2O_3 = 4Al + 3ZrO_2$	$Zr + SiO_2 = Si + ZrO_2$
$\Delta G_f^o = +600\ cal$	$\Delta G_f^o = -46{,}100\ cal$

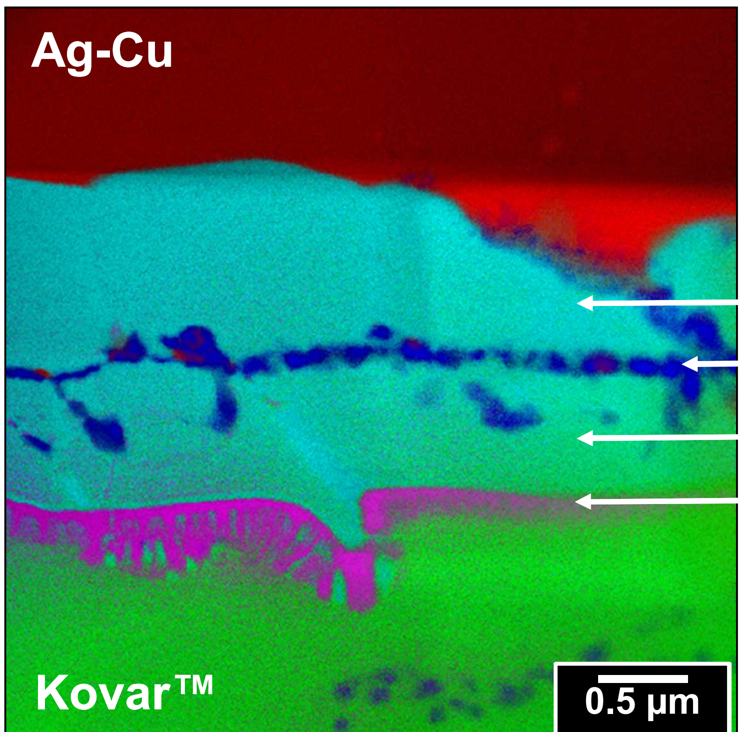


- Supplemental driving forces include free energy of solution of Al in molten Ag-Cu-Zr, or the Ag-Cu-Zr/Kovar™ interface reactions.

Interface Reactions

- Multiple reaction layers form at the Ag-Cu-Zr/Kovar™ interface.





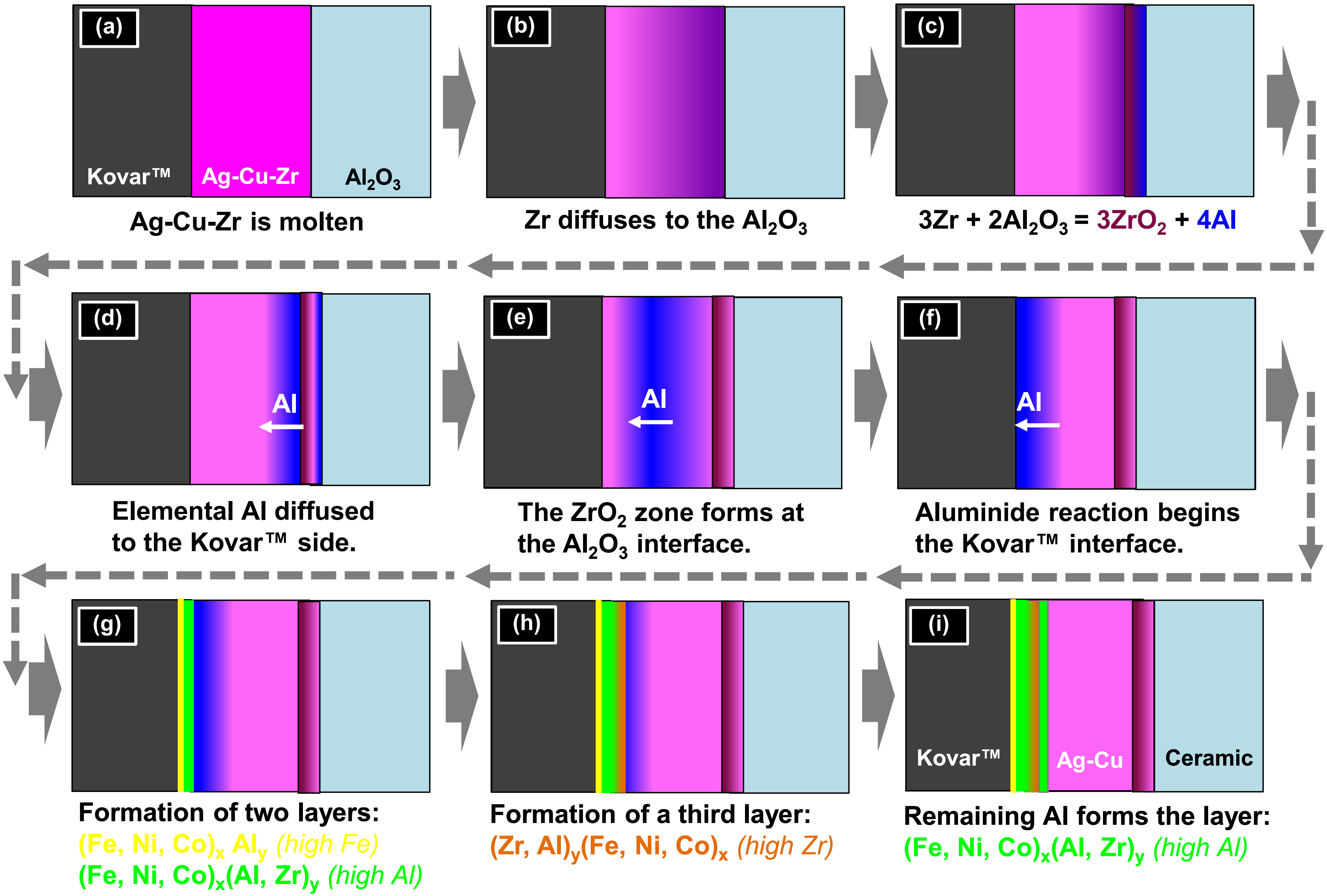
$(Fe, Ni, Co)_x(Al, Zr)_y$ *(high Al)*

$(Zr, Al)_y(Fe, Ni, Co)_x$ *(high Zr)*

$(Fe, Ni, Co)_x(Al, Zr)_y$ *(high Al)*

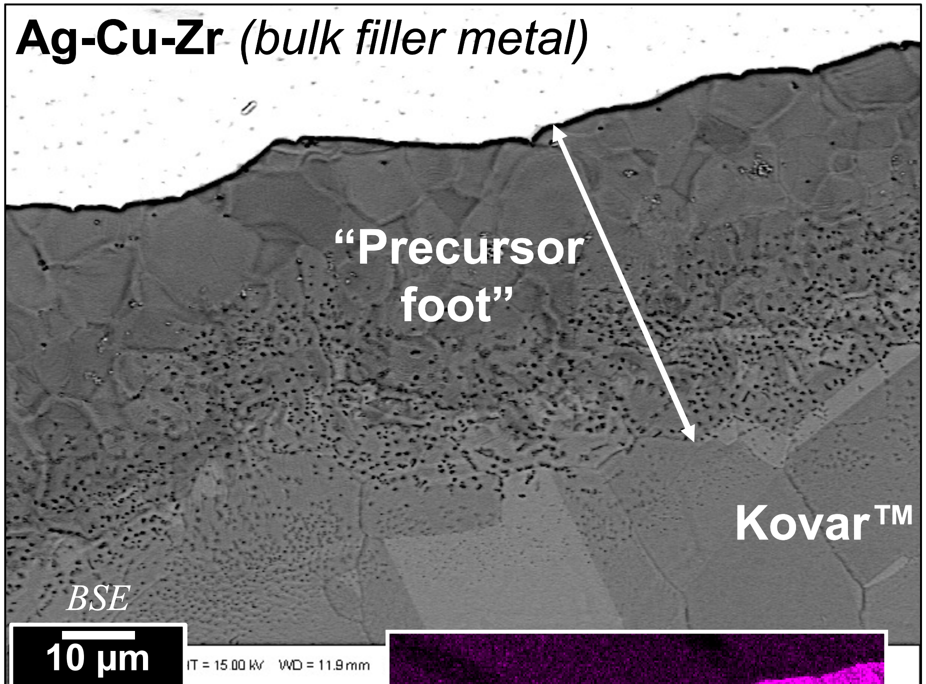
$(Fe, Ni, Co)_x\ Al_y$ *(high Fe)*

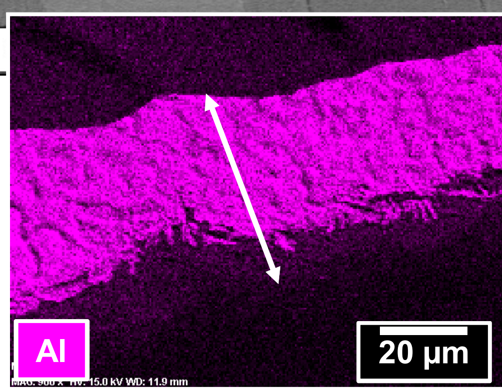
Elemental spectral analysis


(a)
Kovar™
Ag-Cu-Zr
Al_2O_3
Ag-Cu-Zr is molten
(b)
Zr diffuses to the Al_2O_3
(c)
$3Zr + 2Al_2O_3 = 3ZrO_2 + 4Al$
(d)
Al
Elemental Al diffused to the Kovar™ side.
(e)
Al
The ZrO_2 zone forms at the Al_2O_3 interface.
(f)
Al
Aluminide reaction begins the Kovar™ interface.
(g)
Formation of two layers:
$(Fe, Ni, Co)_x\ Al_y$ *(high Fe)*
$(Fe, Ni, Co)_x(Al, Zr)_y$ *(high Al)*
(h)
Formation of a third layer:
$(Zr, Al)_y(Fe, Ni, Co)_x$ *(high Zr)*
(i)
Kovar™
Ag-Cu
Ceramic
Remaining Al forms the layer:
$(Fe, Ni, Co)_x(Al, Zr)_y$ *(high Al)*

Interface Reactions

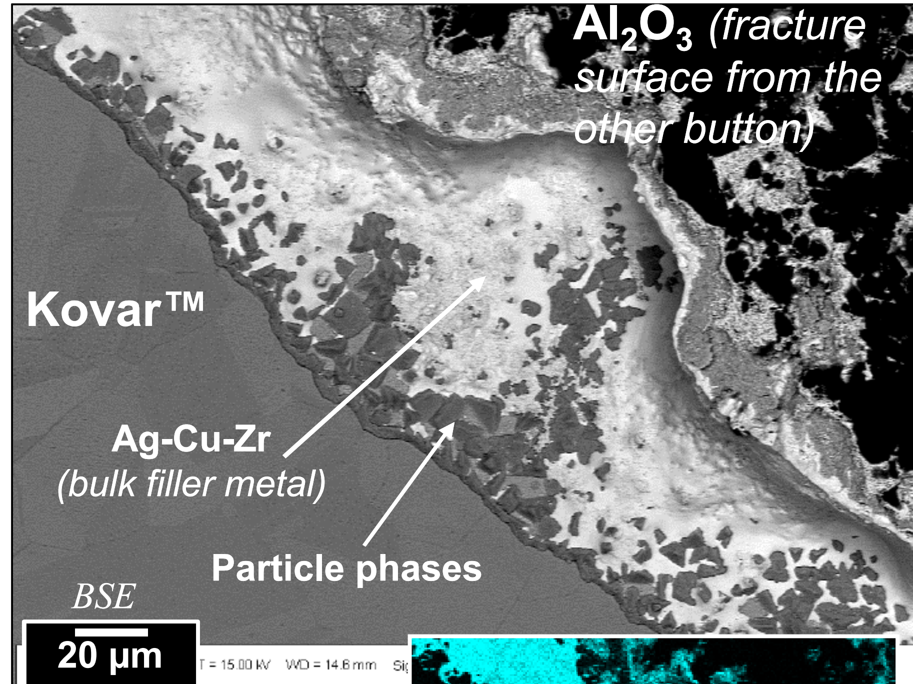
- **Observed differences between the run-out and non-run-out structures on the surface of the filler metal front (toe).**

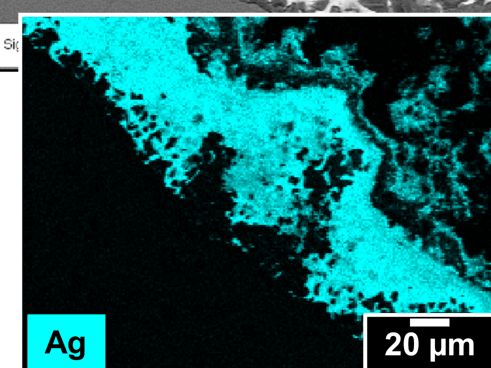




Run-out

EDXA



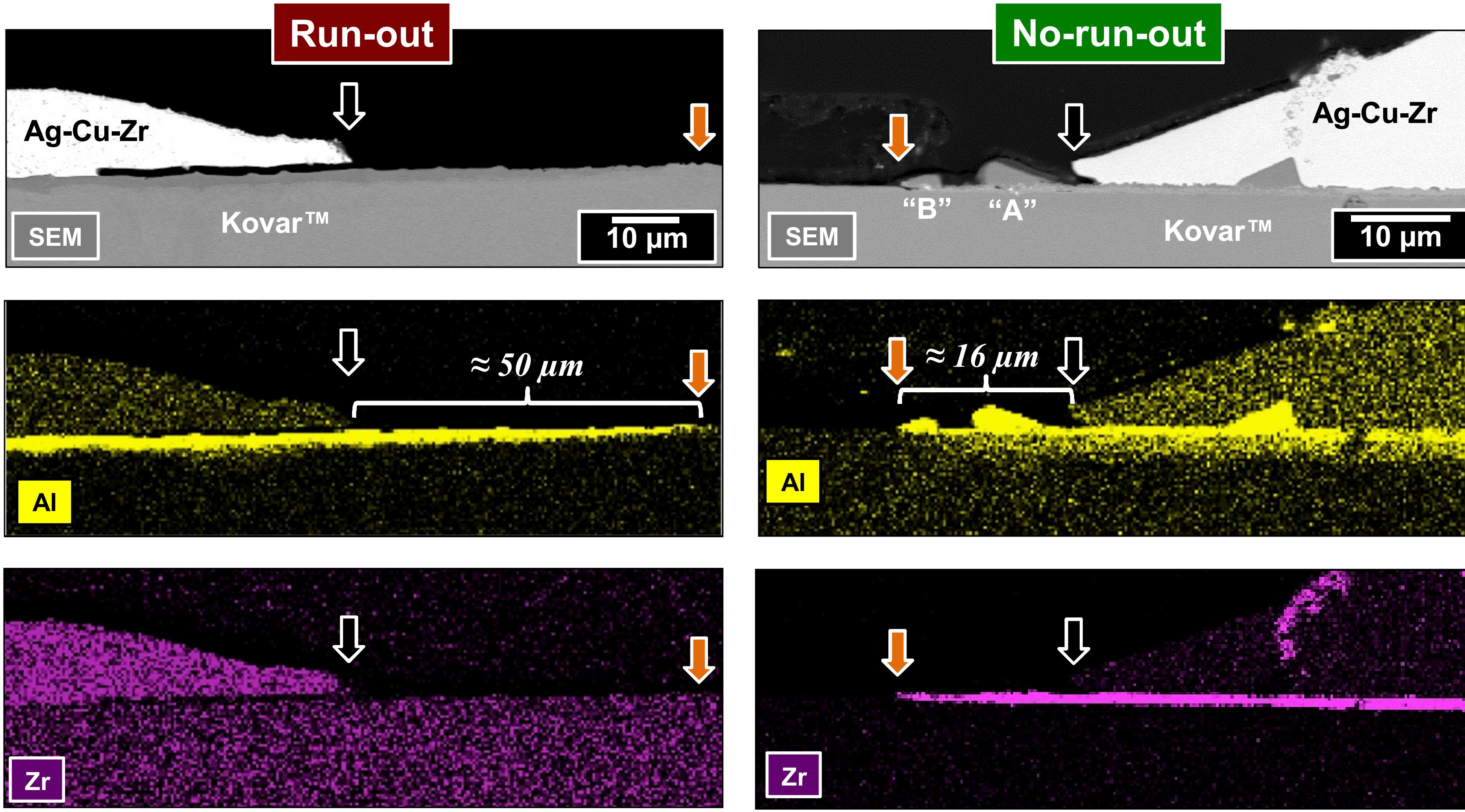


No-run-out

EDXA

Interface Reactions

- The different wetting fronts were also documented by means of **metallographic cross sections made at the filler metal front (toe)**.



An Experiment

- Combinations of different button and spacer materials would highlight those factors that control the run-out phenomenon.
- Duplicate test samples were assembled for each of the four conditions.
  - Each sample was assessed for run-out.
  - Subsequently, the test samples were cross sectioned to document their microstructures.

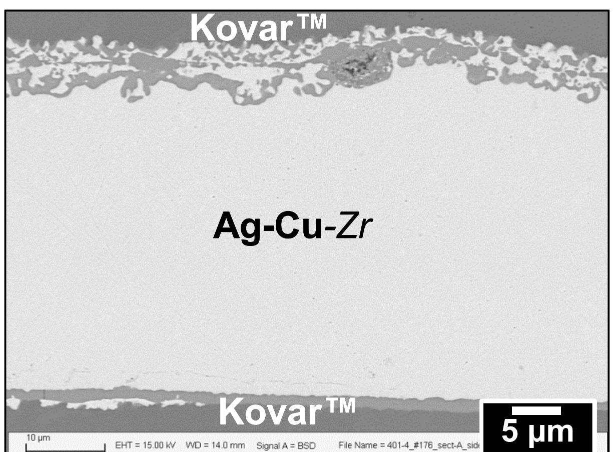
Spacer	Buttons: Kovar™	Buttons: Alumina
Kovar™	*All Kovar™*	*Baseline*
Alumina	*Reverse of baseline*	*All ceramic*

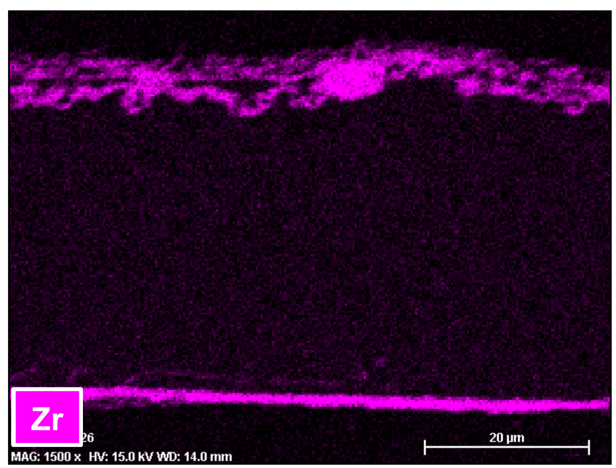
Results: *"All Kovar™"* Braze Joint

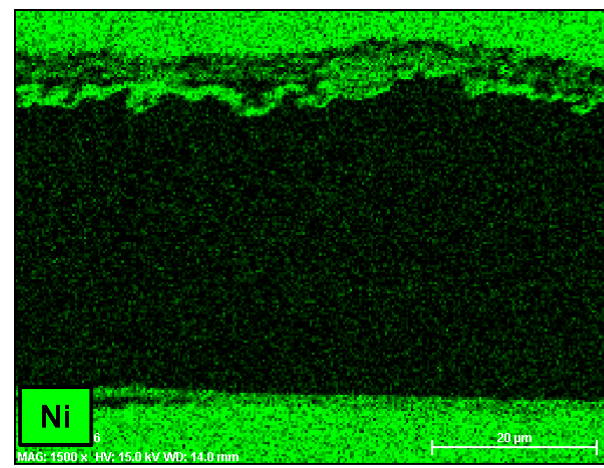
- Run-out was observed *only* under the baseline configuration.

- The absence of run-out from the all-Kovar™ sample implied that Al was required for run-out that came from the redox reaction.
  - The Zr component reacted with the Ni and Fe components of the Kovar™ base materials.

Spacer \ Buttons	Kovar™	Alumina
Kovar™	*None*	***Run-out*** *(baseline)*
Alumina	*None*	*None*

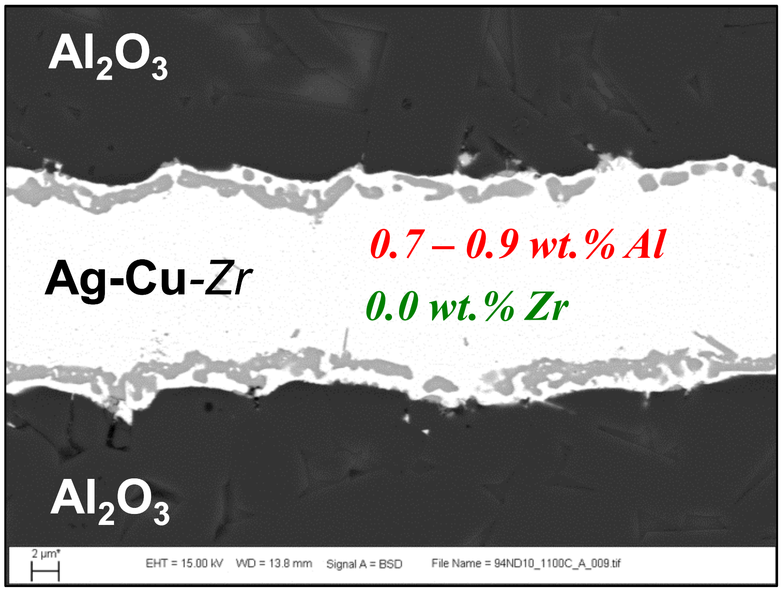






Results: *"All Al_2O_3"* Braze Joint

- **The absence of run-out from the all-Al_2O_3 sample confirmed the explicit requirement that Kovar™ be present in the joint.**



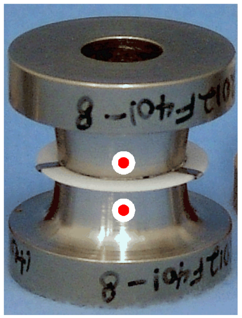
Spacer \ Buttons	Kovar™	Alumina
Kovar™	*None*	*Run-out (baseline)*
Alumina	*None*	*None*

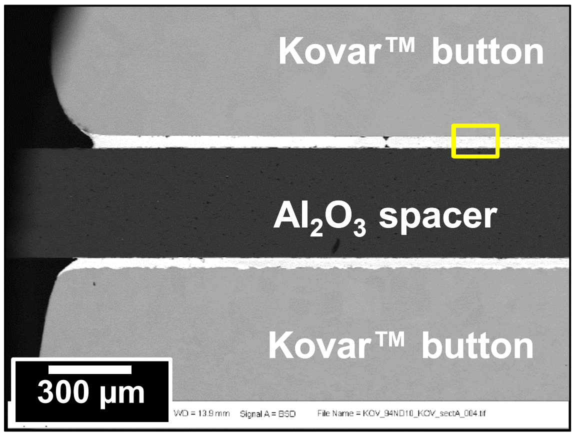
- **Although the aluminide reactions are necessary for run-out, they are not the primary driving force for the redox reaction.**

These results suggest … ***the primary driving force for the Zr/Al_2O_3 redox reaction is the heat of solution by Al entering the Ag-Cu-Zr molten filler metal.***

Results: Kovar™ Button and Al_2O_3 Spacer

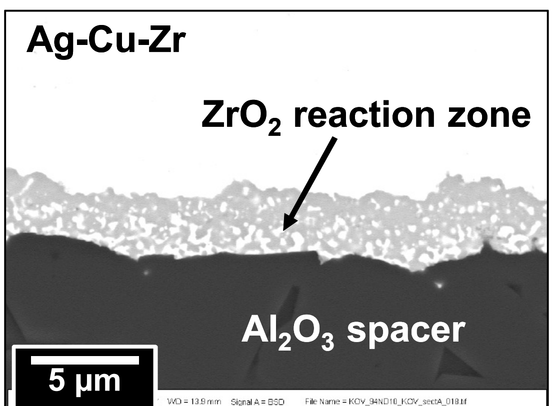
- **The samples having the Kovar™ buttons and Al_2O_3 washer did not exhibit run-out.**

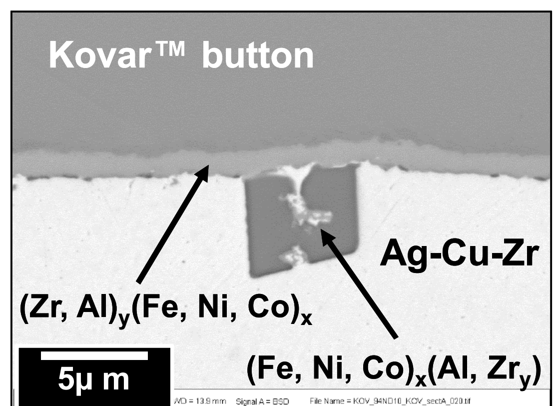




Spacer \ Buttons	Kovar™	Alumina
Kovar™	*None*	***Run-out*** *(baseline)*
Alumina	*None*	*None*

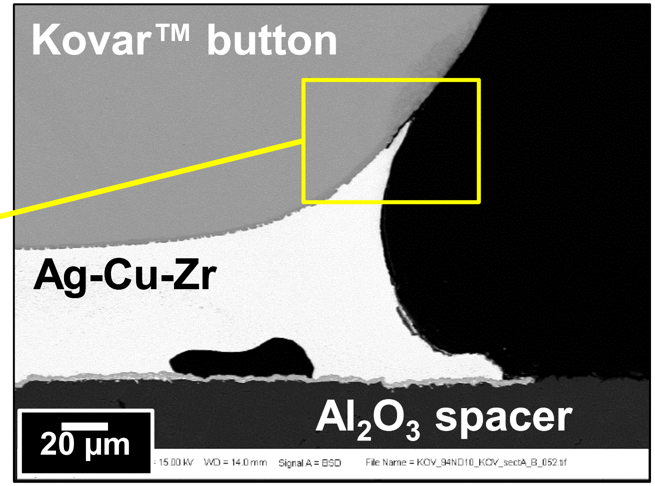
- **The interfaces exhibited the appropriate reactions for run-out:**

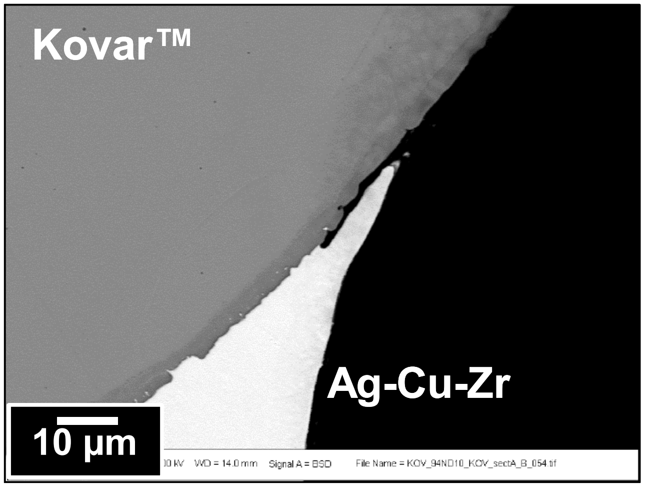


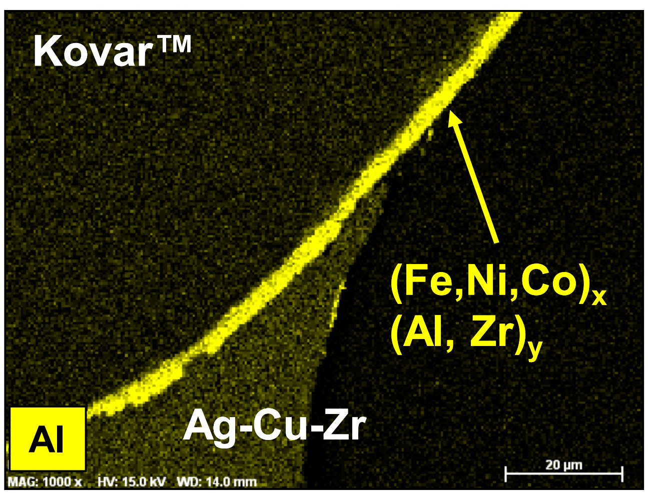


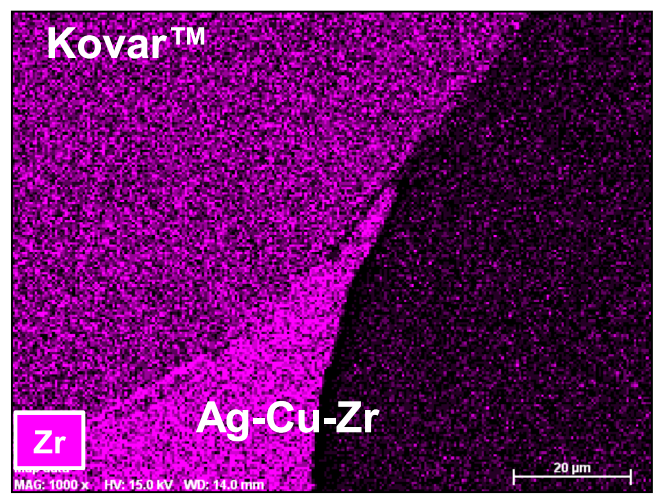
Aluminide Reactions

- The aluminide reactions occurred extensively on the Kovar™ buttons.



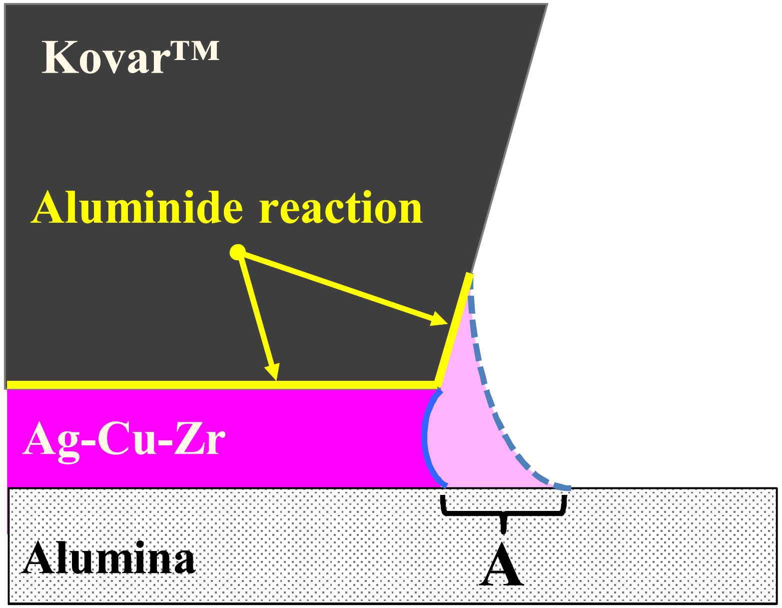






Surface Tension and Geometry

- **The absence of run-out up the wall of the Kovar™ button can be explained by the following scenario:**



- **The aluminide reaction progressed up the button wall in a configuration that been observed to promote run-out.**
- ***However,* the surface tension of the filler metal would require the latter to spontaneously wetting-and-spread a further distance "A."**
- **Because active filler metals cannot readily wetting-and-spread, the surface tension did not "permit" run-out in this geometry.**

Summary

- Filler metal run-out can have a detrimental impact on the performance, reliability, and cosmetic appearance of braze joints.
- The materials system examined in this study included the active filler metal, 97Ag-2Zr-1Cu and the base materials, Al_2O_3 as well as Kovar™ (Fe-29Ni-17Co).
- The primary driving force for run-out is the aluminide reaction between elemental Al, which is released by the Zr/Al_2O_3 redox reaction, and the Kovar™ constituents, primarily Fe and Ni.
- The surface tension of the molten Ag-Cu-Zr has a significant effect on the wetting-and-spreading behavior that transports the (bulk) filler metal in a run-out event.
- The most promising mitigation strategies would impede the aluminide reaction through alloy additions to the Ag-Cu-Zr filler metal, or by placing a coating on the Kovar™ surface.