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# Single and Double Reaction Layer Formation Using Reduced Active Element Containing Brazing Filler Metals

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## Abstract

Active braze filler metals allow nonmetals to be joined to metals and nonmetals without the use of metallization coatings. This is accomplished by including sufficient active element to form a continuous reaction layer on each nonmetal surface resulting in strong, hermetic brazements. The reaction layer is made possible by the inclusion of small quantities, usually 1-3 weight percent, of a Group IVA metal into the braze filler metal composition. Because active filler metal compositions are limited and designed to work with various materials systems, the amount of active element is often more than required resulting in thick, brittle reaction layers or reactions with base materials that lead to excessive braze filler metal flow. Reduced quantities of the active elements titanium and zirconium have been added to standard braze filler metals to determine the quantities required to form continuous reaction layers without compromising tensile strength or promoting excess filler metal wetting/flow.

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## Introduction

Active brazing is different than conventional brazing. Conventional brazing is performed on metallic substrates using a filler metal that melts at a temperature lower than that of the substrates. To join metals to nonmetals it is necessary to provide a continuous metallic surface on the nonmetal in order to promote wetting, thus enabling the braze filler metal to form a chemical/structural bond. Active brazing uses the "active element" within it to form a metallic surface on the nonmetal while in the molten state which is subsequently joined to the metallic substrate by the remainder of the filler metal. Figure 1 shows a simplified sketch that illustrates these concepts for a metal brazed to a nonmetal using conventional and active braze filler metals. A closer inspection of both assemblies post-brazing would reveal that a metal layer had reacted with the nonmetal forming a metallic interface with which the liquid brazing filler metal had wetted and formed a metallurgical bond. However, as shown in Figure 2, the manners in which the two different brazing methods accomplish this vary greatly in both the number and complexity of the required steps. Perhaps most importantly, for the conventional brazing process the metallic surface is applied to the nonmetal substrate prior to brazing while the active brazing method forms the required reaction layer and metallic surface *in-situ*.

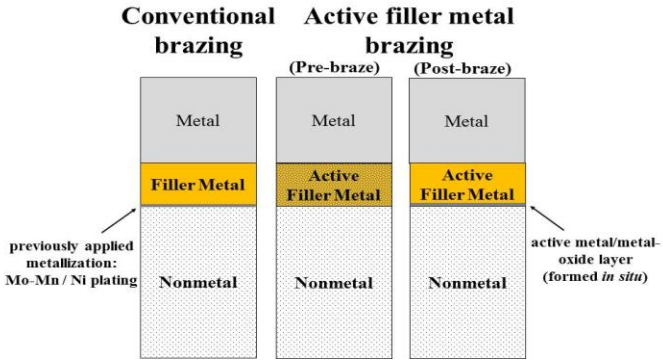


**Figure 1.** Schematic showing conventionally brazed and active filler metal brazed metal/nonmetal sample.

While Figure 2 does clearly indicate that the active brazing process is much simpler overall to perform than the conventional brazing method for metal-nonmetal or nonmetal-nonmetal assemblies, in practice it is not possible or practical to braze everything using the active brazing method. As has been previously reported [1-3] not all metal-nonmetal brazement designs are feasible for active metal brazing, such as those that require the liquid filler metal to be drawn between the faying surfaces by capillary action or those that do not allow the brazing filler metal to be preplaced between the brazement faying surfaces.

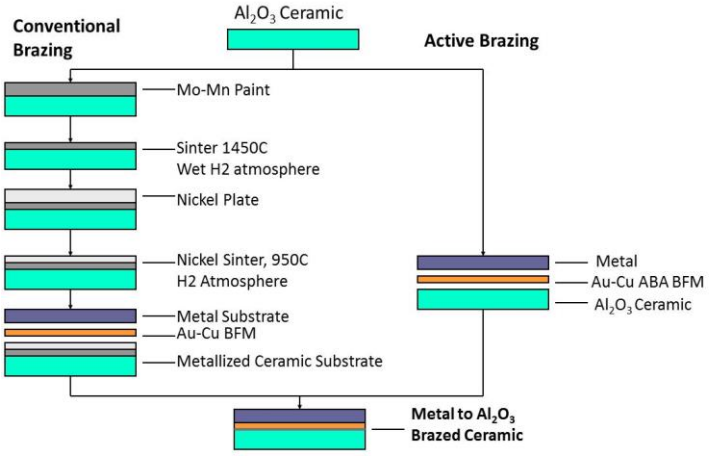


**Figure 2.** Conventional and active brazing comparison.

Active brazing is a viable alternative to conventional brazing whenever traditional metallization techniques are difficult to perform, i.e. small features, irregular shapes, large ceramic piece parts, etc. Also, active brazing is suitable when there are low numbers of parts being built or small-lot production, where automated processes are not cost-effective, or practical to set-up. Third, the active brazing alternative can be used when the joint geometry permits pre-placement of the braze filler metal (butt, lap, shear joints, etc.). And finally, the active filler metal approach is simplest to implement when filler metals are available in active alloy compositions as that matches the conventional composition counterparts.

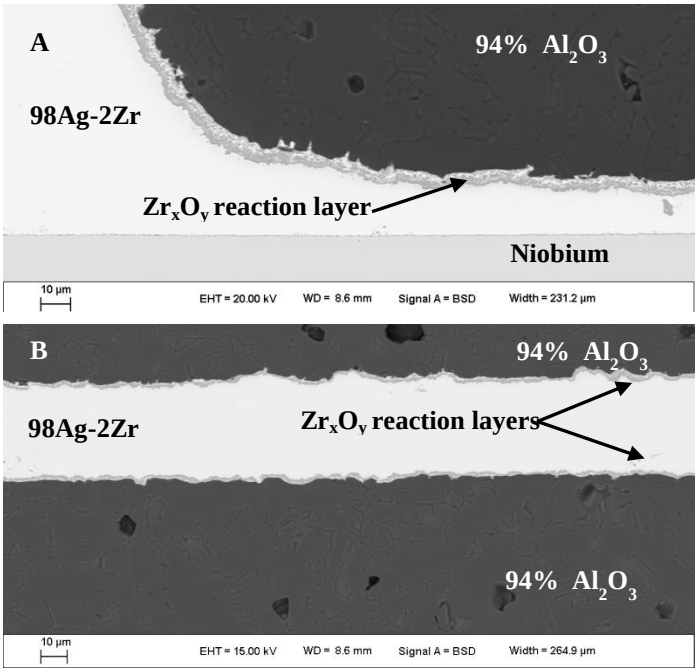


**Figure 3.** SEM images showing (A) one thick, single, continuous reaction layer in a 94% $Al_2O_3$ -Nb sample; and (B) two reaction layers formed on 94% $Al_2O_3$ interfaces using 98Ag-2Zr active brazing filler metal.

After performing a survey of available filler metal compositions it becomes quite clear that the last point is one of the primary limiting factors as to why more users do not consider replacing conventional brazing plus metallization with active brazing processes. The quantity of commercially available active filler metal compositions is limited to only a few compositions versus far more conventional alloy types to cover the 600°C - 1200°C temperature range of brazing applications [4, 5]

Certainly, it is a case of supply-and-demand. It is not cost effective for a supplier to develop a product that has a limited market. On the other hand, the users cannot develop actively brazed products when suitable filler metals are not available. Because of this situation, the user is forced to apply an active filler metal that is not optimized for the brazement, thereby posing a potential reliability concern. For example, brazing metals to nonmetals with a filler metal produces a joint having one reaction layer as seen in Figure 3A. However, the active braze alloy was optimized for *two* reaction layers in joints between nonmetals. The reaction layers are considerably thinner in the latter case as shown in Figure 3B. Excess active element leads to the formation of too thick of a reaction layer (Figure 3A) that jeopardizes joint strength and hermeticity. Excessive reactions can lead to excessive braze filler metal flow ("run-out").

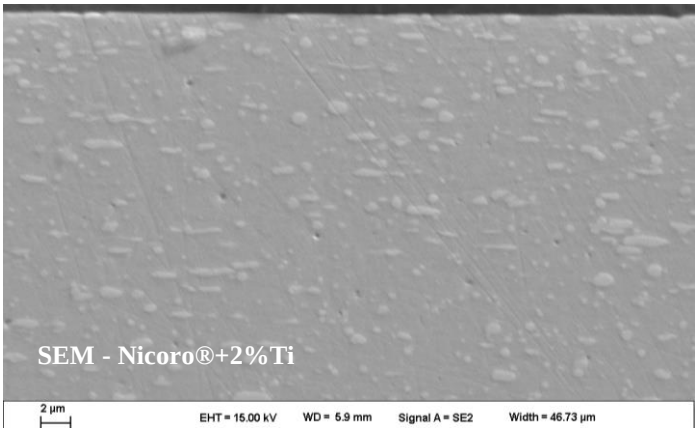


**Figure 4.** SEM image of as-fabricated 62Cu-35Au-2Ti-1Ni active braze filler metal.

The fabrication process for active brazing filler metals is much the same as those used for conventional filler metal alloys, the result being the active element is distributed throughout the bulk of the brazing filler metal as shown in Figures 4 and 5. Figure 4 is a image captured by a scanning electron microscope (SEM) of a commercially available 62Cu-35Au-2Ti-1Ni (weight percent) active brazing filler metal.

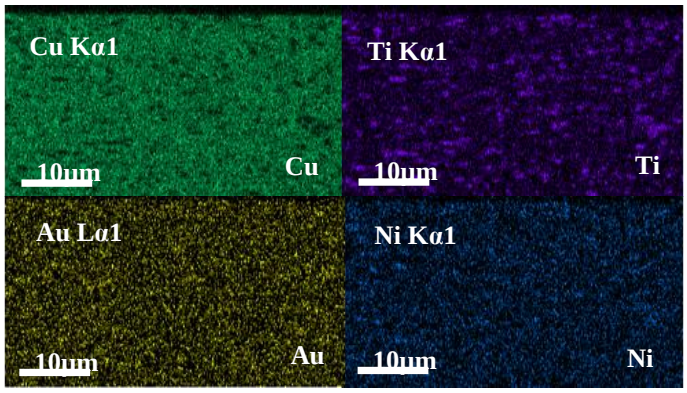


**Figure 5.** SEM/EDS elemental maps of bulk as-fabricated 62Cu-35Au-2Ti-1Ni active braze filler metal.

Figure 5 displays energy dispersive spectroscopy (EDS) images captured on an SEM. The EDS images give a qualitative assessment of the elements that are present in a sample and how those elements are dispersed in the microstructure. During the brazing process an active element would react with the nonmetal or oxide surface(s). Figure 6 is an SEM image of two 94% alumina samples that were brazed using the same 62Cu-35Au-2Ti-1Ni active braze filler metal and subsequently cross-sectioned and polished by metallographic techniques. The lighter phases seen at the braze filler metal/alumina ceramic interfaces and within the bulk filler metal are titanium rich. Figure 7 makes this more readily

apparent as the EDS maps clearly show the unreacted titanium within the bulk filler metal as well as titanium that successfully migrated through the liquid filler metal to the oxide ceramic surface where it reacted to form the $Ti_xO_y$ reaction layer that gives the brazement the both strength and hermeticity. Excess titanium active element not used to form the reaction layer with the nonmetal surface(s) may remain within the bulk filler metal, forming $Ti_xNi$ and $AuTi_x$ compounds, or reacting with the metal substrate.

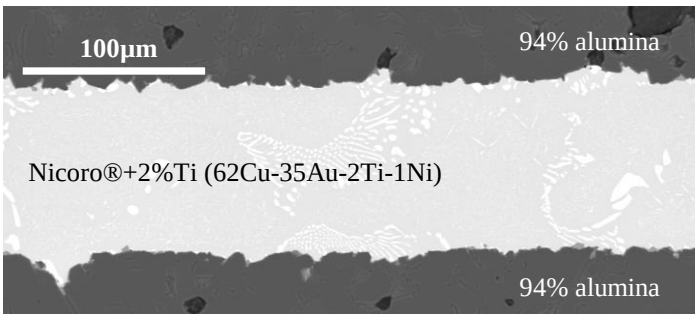


**Figure 6.** SEM Image, Vacuum brazed 94% $Al_2O_3$ using 62Cu-35Au-2Ti-1Ni active braze filler metal

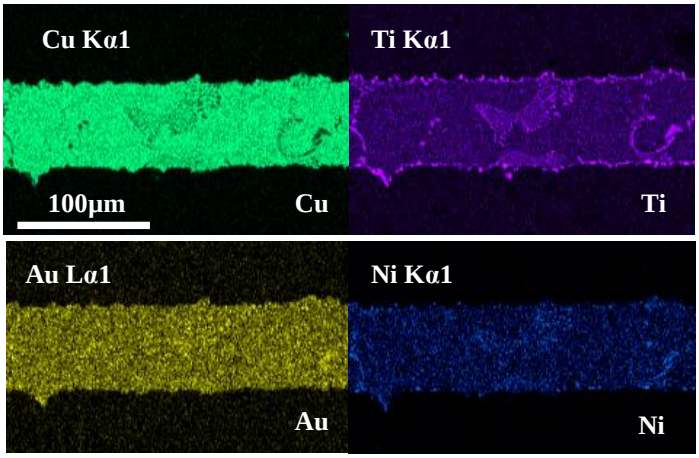


**Figure 7.** SEM/EDS elemental maps, Nicoro®+2%Ti active braze filler metal.

Closer inspection of the EDS maps in Figure 7 show this phenomena where the remaining or excess titanium within the bulk filler metal has reacted with the nickel also present in the filler metal, which though not deleterious in these samples has been shown to produce undesired effects for other material combinations. Specific active element/metal substrate combinations have been shown to react excessively with the base metals, effectively reducing the active element available to generate a desirable reaction layer at the nonmetal [6, 7].

## Braze filler metal selection and modification

In order to determine the optimum quantity of active element required for ceramic to ceramic brazements as well as metal to ceramic brazed assemblies, varying amounts of the active elements titanium and zirconium were deposited onto conventional brazing filler metal using the physical vapor deposition method, direct current (DC) sputtering. A noble protective layer of either silver or gold was deposited over the active element layer to prevent unwanted oxidation when exposed to air. For the first trials, sputtered layer thicknesses of 0.5µm were selected for both the active element and the noble metal. These initial thicknesses were chosen because previous efforts to join metals to nonmetals using a thin-film metallization system demonstrated [8] (shown in Figures 8 and 9) that hermetic, high-strength metal-nonmetal brazements can be made using sputter deposited active element layers only 0.25µm - 0.5µm thick deposited directly onto the faying surfaces of bare alumina ceramic substrates. It was hypothesized that a similar thickness of active element deposited onto the brazing filler metal would be sufficient to form a sufficient reaction layer at the alumina ceramic interface.

**Table 1** – Active element sputtered thickness equivalent

| Brazing Filler Metal | Thickness inches (µm) | Weight percentage of active element | Sputtered layer equivalent, (µm) |
|---|---|---|---|
| BVAg-0 +0.626Zr | 0.002 (50.8) | 0.6 | 0.50 |
| BVAg-0+0.4Zr | 0.003 (76.2) | 0.4 | 0.50 |
| BAu-3 +0.35Ti | 0.002 (50.8) | 0.35 | 0.50 |
| BAu-3 +0.235Ti | 0.003 (76.2) | 0.235 | 0.50 |
| 98Ag-2Zr | 0.002 (50.8) | 2.0 | 1.68 |
| 98Ag-2Zr | 0.003 (76.2) | 2.0 | 2.52 |
| Nicoro®+2%Ti | 0.002 (50.8) | 2.0 | 2.90 |
| Nicoro®+2%Ti | 0.003 (76.2) | 2.0 | 4.35 |

The two commercially fabricated active brazing filler metals evaluated in this study are 98Ag-2Zr (weight percent) and Nicoro®+2%Ti (62Cu-35Au-2Ti-1Ni, weight percent), provided by the Wesgo Metals Division of Morgan Advanced Ceramics[1]. A series of calculations were performed to correlate active element sputtered layer thickness to weight percentage, the results of which are displayed in Table 1. It has been reported that approximately fully dense metallic zirconium films have been formed using DC magnetron sputtering methods [9]. The calculations used for this study assume that the sputtered layers for zirconium and titanium will be fully (100%) dense. With this knowledge, 0.5µm thick

[1] Nicoro® is a registered trademark of MTC-Wesgo Metals.

titanium and zirconium active element layers were DC sputtered onto one side only of 0.002” (50.8µm) or 0.003” (76.2µm) thick silver (99.99%) or BAu-3 (35Au-62Cu-3Ni) conventional brazing filler metal materials.

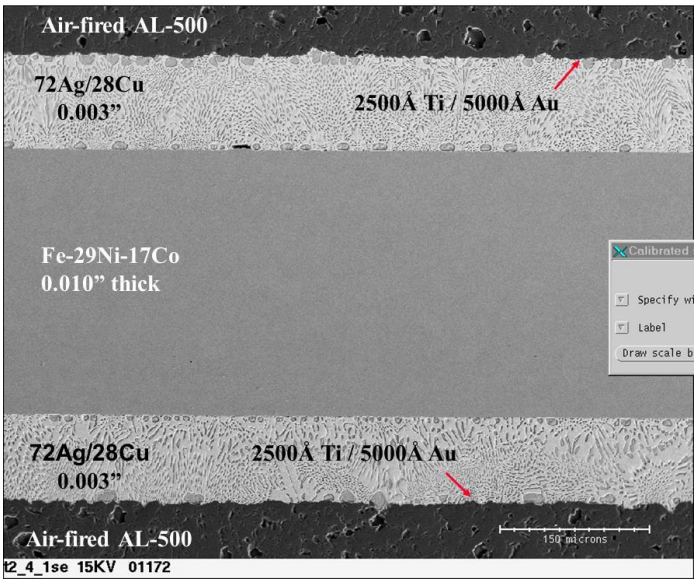


**Figure 8.** Metal/$Al_2O_3$ brazement using thin-film metallization deposited directly onto the alumina ceramic.

The different weight percentages displayed in Table 1 for similar titanium or zirconium thickness additions are due to the differences in their respective densities as well as whether the brazing filler metals are gold-based or silver-based, which greatly affects the bulk filler metal density.

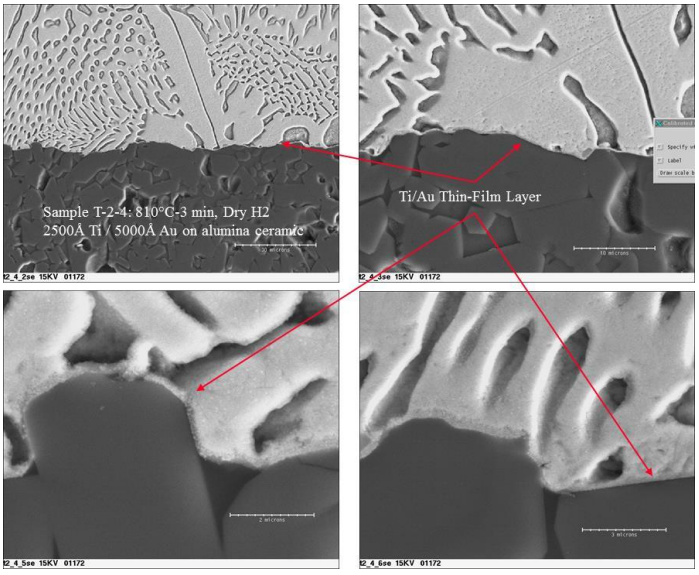


**Figure 9.** $Al_2O_3$ brazement showing Ti/Au thin-film layer metallization deposited directly onto the alumina ceramic.

## Double reaction-layer test samples

Brazing preforms correctly sized for ASTM-F19 tensile buttons were punched from the materials listed in Table 1. The tensile specimens were fabricated without a metal interlayer in order to evaluate the effectiveness of forming two simultaneous reaction layers at the ceramic interfaces.

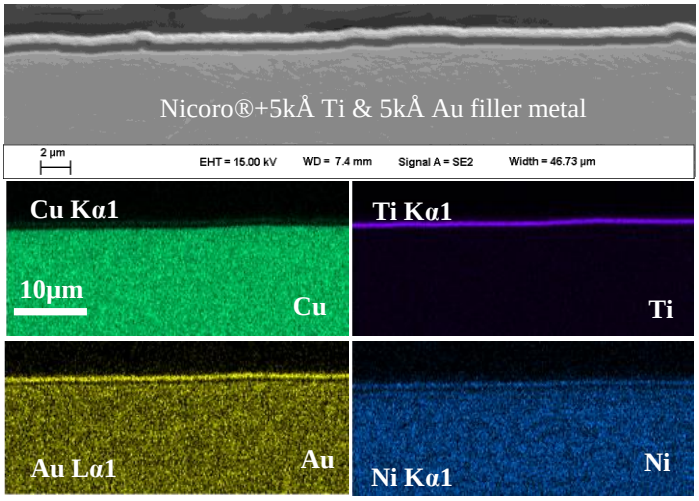


**Figure 10.** SEM image (upper) and EDS maps (lower) showing sputtered thin-film layers on BAu-3 braze filler metal.

Filler metal preforms having outer diameters of 0.625” (1.59cm) and 0.400” (1.01cm) inner diameters were fabricated with the sputtered titanium or zirconium (plus noble metal coating). The corresponding SEM images and EDS maps of the modified filler metals are shown in Figures 10 & 11.

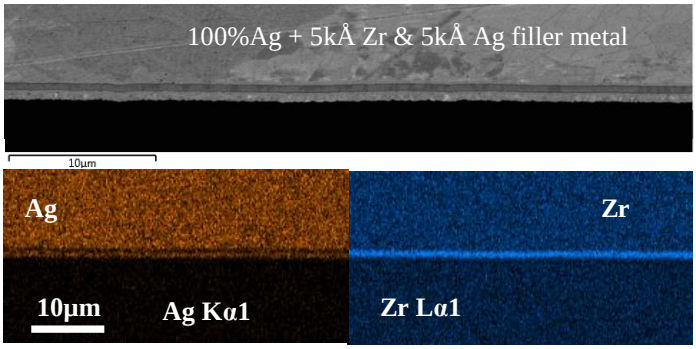


**Figure 11.** (Upper) SEM image; (Lower) EDS maps showing sputtered thin-film layers on pure silver braze filler metal.

Brazing test sample preparation and geometries. Three types of sample geometries were chosen to test the modified brazing filler metals: ASTM F-19 ceramic test specimens made from 94% alumina; 94% alumina discs; and 94% alumina cylinders brazed to metal discs, either commercially pure niobium or the Fe-29Ni-17Co alloy, Kovar® [11]. The proprietary 94ND10 alumina ceramic samples had a roughness value, $R_A$, less than 0.8µm (32µin). ASTM-F19 tensile buttons and the alumina cylinder-metal disc assemblies were helium mass-spectrometer leak tested to assess hermeticity. A positive leak check result, i.e. no detectable helium leak, is an indication that a continuous reaction layer formed on the alumina surface(s). Additionally, the ASTM-F19 samples brazed with the modified braze filler metals were tensile tested and compared to the samples made using commercially available active filler metals (four samples per filler metal composition). The 94% alumina cylinders brazed to either commercially pure niobium

or Kovar were also analyzed to determine how effective the modified filler metals were at forming a single continuous reaction layer.

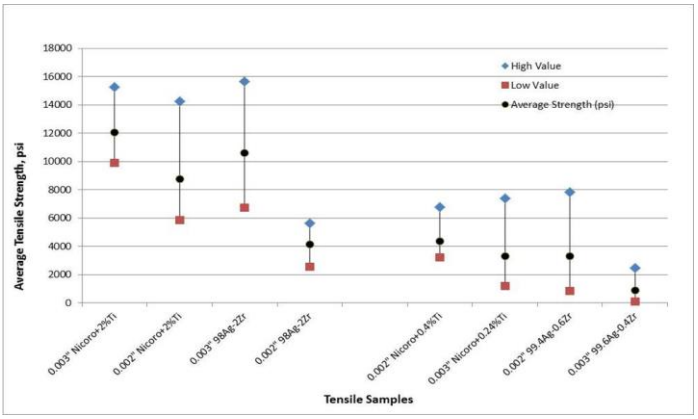


**Figure 12.** Tensile test comparison of 0.5µm thick Ti and Zr thin-films and standard active brazing alloys.

Brazing equipment, brazing process parameters and test equipment. The vacuum brazing process was performed in an R.D. Brew top-loading high-vacuum furnace, using a 10" cryogenic pump for the primary pump. A NIST-traceable calibrated ionization gauge tube is used to monitor absolute pressure during the brazing thermal-cycle. Furnace rate of rise is less than 1.5 E-08 Torr/s (4.8E-04 Pa-l/s).

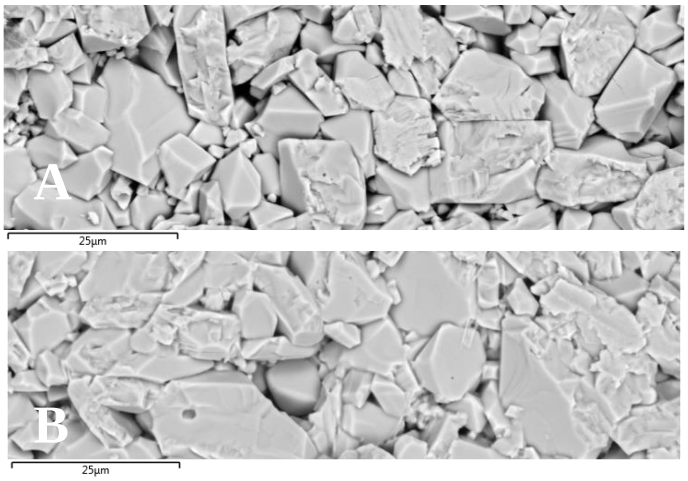


**Figure 13.** (A) 94% $Al_2O_3$ in the as-received condition; (B) 94% $Al_2O_3$ air-fired at 1200°C for 1 hour.

The temperature cycle is not started until the vacuum furnace base pressure is less than 5E-06 Torr. The thermal cycle used was as follows: 10°C/min from room temperature to $T_X$, soak for 10 minutes; ramp at 5°C/min to $T_{Peak}$, soak 5 minutes; Cool at 25°C/min to $T_Y$, soak 0 minutes; cool to room temperature at a rate ≤10°C/min. $T_X$ is 975°C for the gold-based filler metal and 925°C for the silver based material; $T_{Peak}$ is 1035°C for the gold-based filler metal and 985°C for the silver based material while $T_Y$ is 950°C for the gold-based filler metal and 925°C for the silver based material. Following the cooling to room temperature and subsequent unloading and post-brazing visual inspection, the tensile button and metal-ceramic cylinder assemblies were leak checked using a Pfeiffer QualyTest™ Select HLT 265[2] helium mass-spectrometer leak detector (MSLD) capable of detecting leaks as low as 5E-12 atm-cc/sec (~5E-10 Pa-l/s). Any detectable helium leak was determined to have failed the leak test. Following visual inspection and leak testing, the ASTM-F19 tensile buttons were pull tested using a 22 kip MTS servohydraulic test frame at a crosshead speed of 8.38E-06m/s (3.3E-04 in/sec) in accordance with AWS standards [10]. The tensile strength was determined using the cross-sectional area of the tensile button faying surfaces, 1.11E-04$m^2$ (1.80E-01$in^2$).

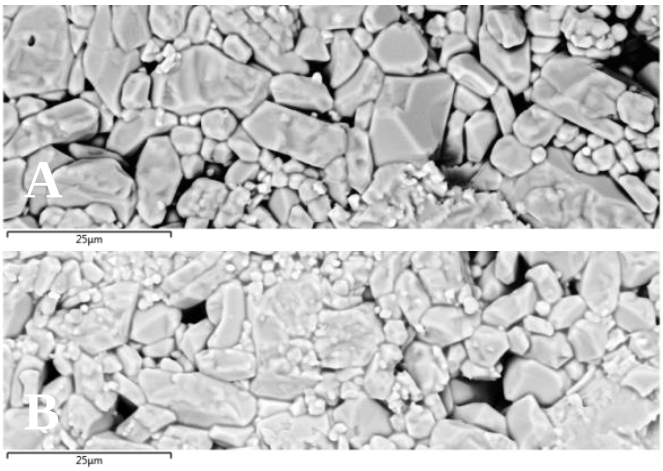


**Figure 14**. (A) 94% $Al_2O_3$ resintered at 1575°C for 2 hours (air); (B) 94% $Al_2O_3$ resintered at 1500°C for 1 hour (wet $H_2$).

Post-brazing leak testing and tensile testing revealed anomalies not typically observed when using the commercially fabricated active brazing filer metals. Eleven of the sixteen samples brazed with the commercially manufactured active braze filler metals failed the helium leak test.

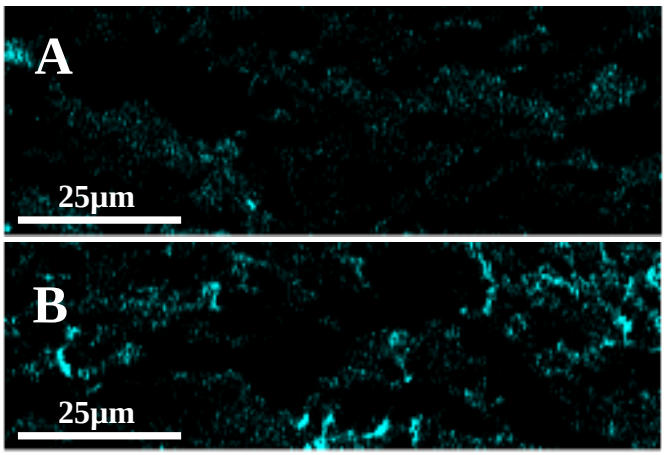


**Figure 15.** (A) EDS map showing the silica present on the surface in the as-received condition; (B) EDS map showing the silica present in the sample air-fired at 1200°C for 1 hour.

Additionally, as displayed in Figure 12, there are wide disparities in strengths of the tensile buttons fabricated using commercially manufactured active braze filler metals. Figure 12 also shows that with the exception of the 50.8µm thick

[2] QualyTest™ is a trademark of INFICON AG Liechtenstein

98Ag-2Zr brazing filler metal, the tensile strengths of the ASTM F-19 tensile buttons brazed with the modified braze filler metals were considerably lower than the samples brazed with the commercially produced filler metals. Further investigations into possible causes of the variation of tensile strength revealed that improper sintering parameters were used; this step is typically performed in air on the ceramics prior to brazing. The peak temperature of 1200°C is lower than the recommended 1575°C. Also, a 1 hour period was used instead of the standard 2 hours.

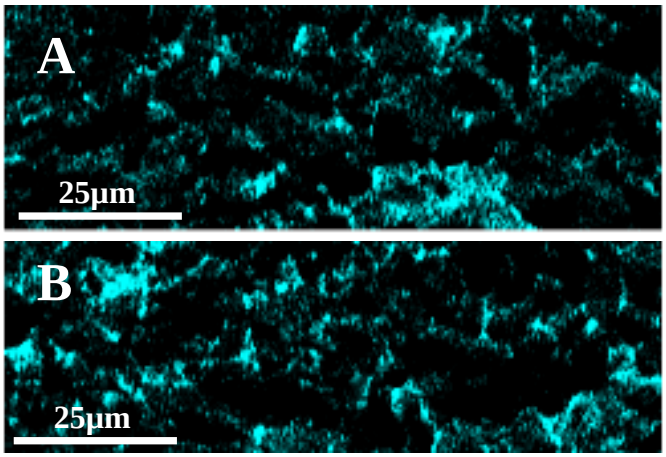


**Figure 16.** (A) EDS map showing the silica present on the surface after air-firing at 1575°C for 2 hours; (B) EDS map showing silica present wet $H_2$ firing at 1500C for 1 hour (B).

Previous studies [1] have shown that resintering 94% alumina ceramic at the recommended temperatures at 1575°C in air (2 hours) or 1500°C in wet hydrogen of 28°C dew point (1 hour) result in hermetic and strong brazements [14,15]. These conditions heal surface damage introduced on the faying surfaces during final grinding or polishing operations. An explanation for the poor brazement performance of the tensile button samples resintered at the 1200°C temperatures is that the resintering temperature was too low to melt and reflow the glassy phase between the alumina grains. As seen in Figure 13 the there is little difference between upper image A, which shows the as-received alumina, and lower image B, which was obtained from alumina fired at 1200°C,. Figure 14 shows high magnification SEM images of the surfaces of alumina pieces that had been resintered at 1575°C (A) and 1500°C (B). The effects of the greater firing temperatures are obvious as both the upper and lower images in Figure 14 show the alumina grains having smoothed, rounded edges as compared to the angular edges in Figure 13. Similarly, when comparing silicon EDS maps of the same four samples, the differences between the as-received sample (Figure 15A) and the sample air-fired at 1200°C (Figure 15B) are minimal while Figure 16A and B indicate that much more silicon has migrated to the sample surfaces.

Metallographic analysis of the two reaction layer samples brazed with the modified braze filler metals confirmed that the primary cause of the poor helium leak test performance and tensile test results were insufficient, noncontiguous reaction layer formation at the alumina ceramic/braze filler metal interfaces. As seen in Figure 17, the initial titanium trial layer thickness, 0.5µm, deposited on the gold-based brazing filler metal was insufficient to form a continuous reaction layer on either of the ceramic-filler metal interfaces.

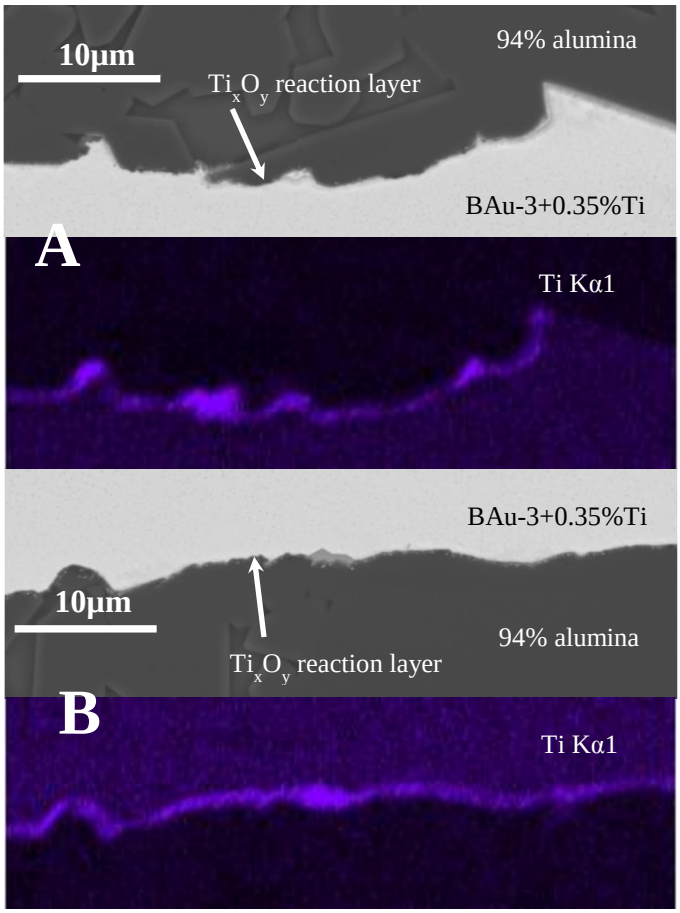


**Figure 17. (A) I**nterfaces of a 94% $Al_2O_3$/94% $Al_2O_3$ assembly brazed with BAu-3+0.35%Ti brazing filler metal. (B) Titanium (Kα1) EDS map of active-braze reaction.

The 50.8µm thick brazing filler metal, while having the same titanium deposition thickness as the 76.2µm thick brazing foil has 50 weight percent more active element (0.35% vs. 0.235%). While only the 50.8µm thick sample is shown (Figure 17) in both cross-sectioned thicknesses, the ceramic faying surface adjacent to the sputtered titanium layer appeared to have a more continuous layer than was formed on the faying surface away from the thin-film deposition. This was expected as the limited supply of titanium should react readily with the nearest oxide surface. Visual examination of the ASTM-F19 tensile specimens post-testing revealed that in all cases, the alumina button away from the sputtered film was the side where failure initiated. This failure mode was confirmed at a later date using an SEM analysis. The examination of samples brazed using the modified brazing filler having 0.5µm of zirconium and 0.5µm of silver applied to the 50.8µm and 76.2µm pure silver filler metal shows unique differences from the BAu-3 filler metal modified with titanium. Figure 18 shows that the ceramic faying surface in contact with the side of the filler having the zirconium coating formed a nearly continuous $Zr_xO_y$ reaction layer with the

alumina ceramic surface. On the other hand, the opposite interface has little or no $Zr_xO_y$ reaction layer.

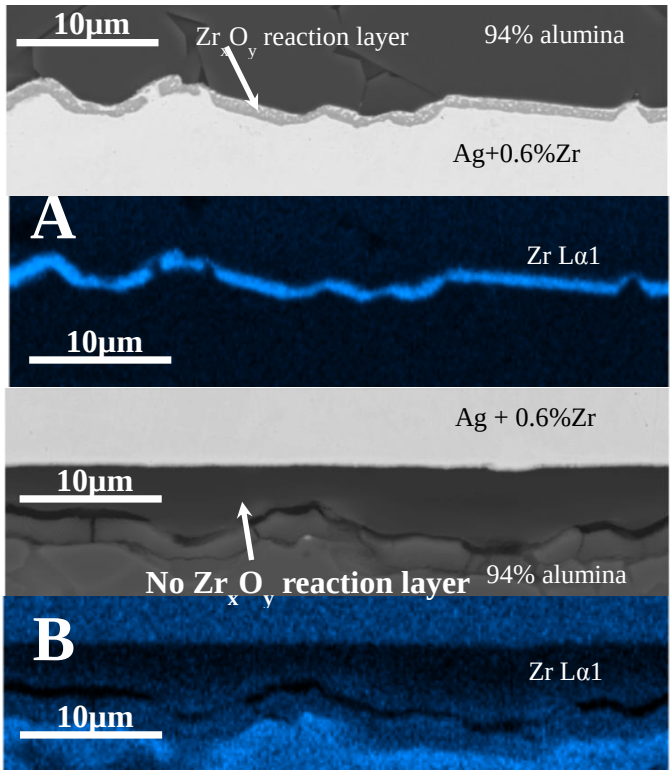


**Figure 18.** (A) Interfaces of a 94% $Al_2O_3$/94% $Al_2O_3$ assembly brazed with Ag+0.6% Zr brazing filler metal. (B) Zr (Lα1) EDS Map of active-braze reaction.

This is in contrast with the modified BAu-3 material where titanium and a $Ti_xO_y$ reaction layer is evident on both faying surfaces of the brazements It is believed that the differences in the atomic sizes of tanium and zirconium and the quantities of the respective element atoms required to make a finite layer thickness explain this observation.

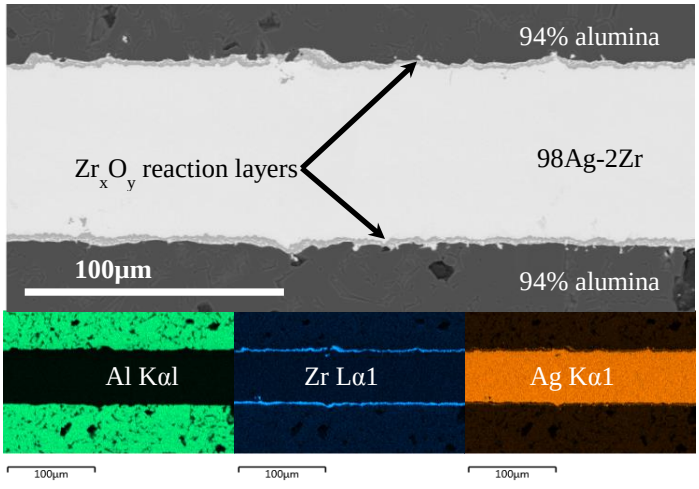


**Figure 19.** Top: SEM image showing both interfaces of a 94% $Al_2O_3$/94% $Al_2O_3$ assembly brazed 98Ag-2Zr active brazing filler metal. Bottom: EDS maps showing Al, Zr, and Ag.

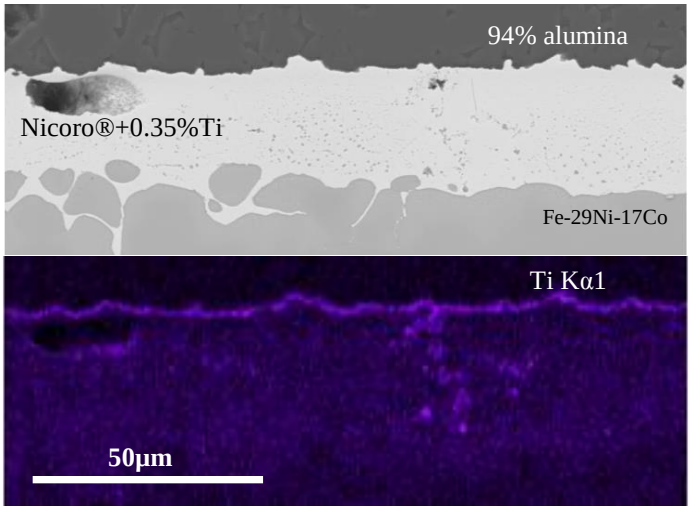


**Figure 20.** Top: SEM image showing interfaces of a 94% $Al_2O_3$/Fe-29Ni-17Co assembly brazed using BAu-3+0.35%Ti active brazing filler metal. Bottom: EDS map showing titanium (Kα1) in the completed brazement.

Recall from Table 1 that a 0.5µm layer of zirconium amounts to a 0.6 weight percentage for 50.8µm thick silver foil and 0.4 weight percentage for the 76.2µm pure silver filler metal compared to 0.35 and 0.235 weight percentages of titanium for the modified 50.8µm and 76.2µm thick BAu-3 braze filler metal. These differences are due to the gold-based filler metal having a higher density than the silver based material and because titanium, used to modify the gold-based material, is less dense than zirconium.

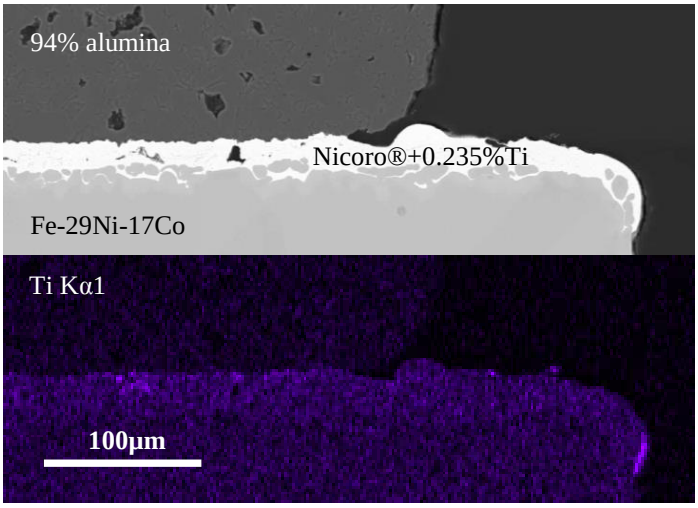


**Figure 21.** Top: SEM image showing the interfaces of a 94% $Al_2O_3$/Fe-29Ni-17Co alloy assembly brazed with BAu-3+0.235%Ti active brazing filler metal. Bottom: EDS map showing titanium in the completed brazement.

This impact is more fully appreciated when comparing the thicknesses of the two active element materials required to make a material equivilent to the commercially manufactured active brazing filler metal materials, which is generally 2 weight percent. To make a 98Ag-2Zr material, a zirconium coating 1.6µm thick is required, slightly more than three time times the material used in this study. When using titanium as

the active element, a thin-film that is 2.9µm thick is required to make the equivilent active braze filler metal counterpart, BAu-3+2%Ti. That thickness is a factor of almost six times greater than what was used initially. Because of the differences in atomic densities of the two materials, 14.1 g/mol Zr versus 10.64 g/mol Ti, for any given deposition thickness, there will be approximately 33 percent more titanium atoms than zirconium atoms. Additional, or excess, titanium active filler metal, is more readily observed than zirconium when comparing ceramic-ceramic samples brazed with the two commercially available active filler metals, 98Ag-2Zr, shown in Figure 19, and Nicoro®+2%Ti, as displayed previously in Figures 6 and 7. Note that Figure 19 shows that even with 2 weight percent of zirconium in the brazing filler metal, all is utilized by the two reaction layers, unlike the titanium in Figures 6 and 7.

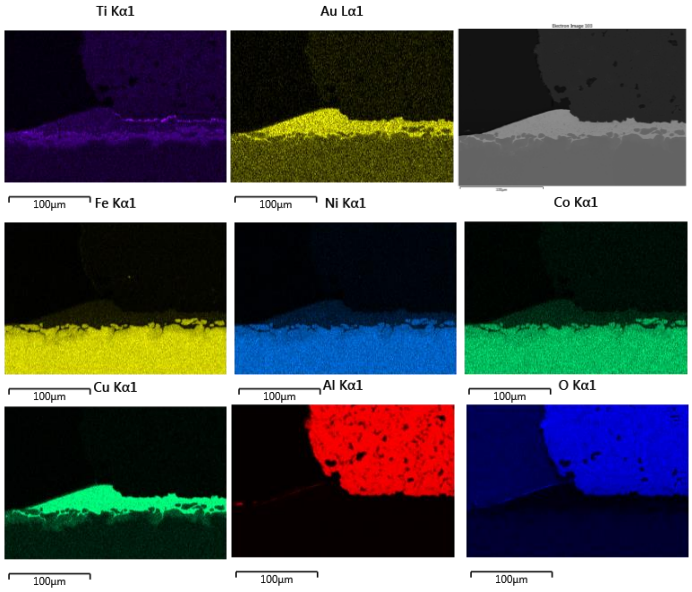


**Figure 22.** SEM image (upper right) showing interfaces of a 94% $Al_2O_3$/Fe-29Ni-17Co alloy assembly brazed with Nicoro®+2%Ti filler metal. Other images are EDS maps showing titanium distribution and base metal dissolution.

## Single reaction-layer test samples

Single reaction layer samples were brazed with the modified braze filler metals and commercial active braze alloys using the same brazing thermal profiles. For each of the filler metal compositions, samples were fabricated using 94% alumina ceramic cylinders and either niobium or Fe-29Ni-17Co alloy washers. The brazing filler metal was preplaced between the metal and ceramic faying surfaces with the sputtered thin-film layers, if applicable, adjacent to the metal surface. Previous experiments have confirmed that the titanium or zirconium active element readily diffused through the molten filler metal and reacted with the oxide surface. Metallographic analysis (Figures 20 -22) showed that the Fe-29Ni-17Co alloy base metal substrates were prone to dissolution by all of the titanium-containing filler metal compositions.

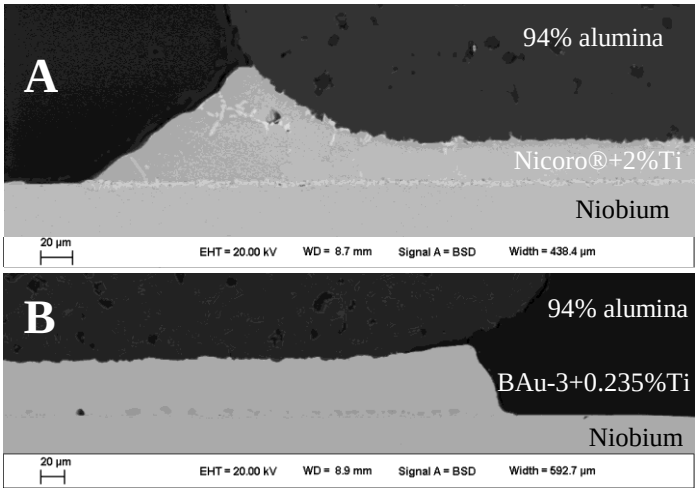


**Figure 23.** SEM back-scattered images showing interfaces of a 94% $Al_2O_3$/Nb assembly brazed using (A) Nicoro®+2%Ti and (B) BAu-3+0.235%Ti active brazing filler metal.

As both BAu-3 filler metal thicknesses used in these samples had the same quantity of titanium added, the amount of Fe-29Ni-17Co alloy erosion appeared similar in the samples. For the two weight percent titanium filler metal, however, the erosion appears to be more severe. As represented in Figure 23, the titanium bearing active brazing filler metals did not appear to have any deleterious effects on the niobium base metal samples evaluated for this study.

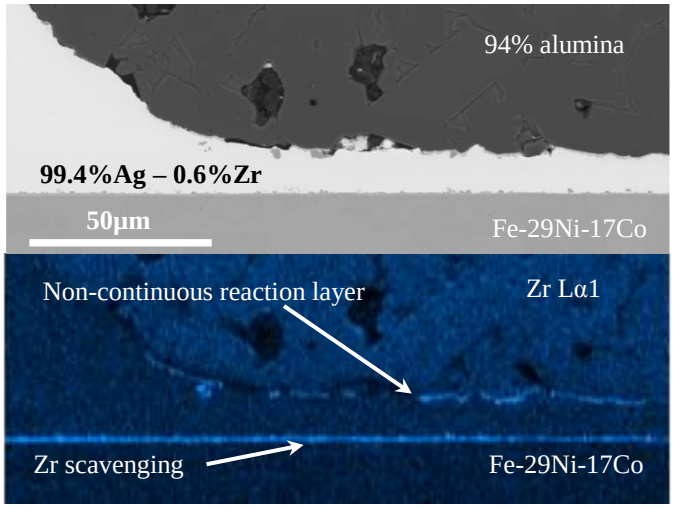


**Figure 24.** Top: SEM image showing a 94% $Al_2O_3$/Fe-29Ni-17Co alloy interface brazed using Ag-0.6%Zr filler metal. Bottom: EDS map showing the incomplete $Zr_xO_y$ reaction layer formation and scavenging of the Zr.

SEM images and EDS maps of the cross-sectioned samples made with the modified BAu-3 brazing filler metals exhibit more nickel segregation and interaction with the niobium surfaces than do the samples made with the Nicoro®+2%Ti active brazing alloy. This behavior is expected since the commercial filler metal contains only one weight percent nickel, versus three weight percent for the modified brazing filler metals.

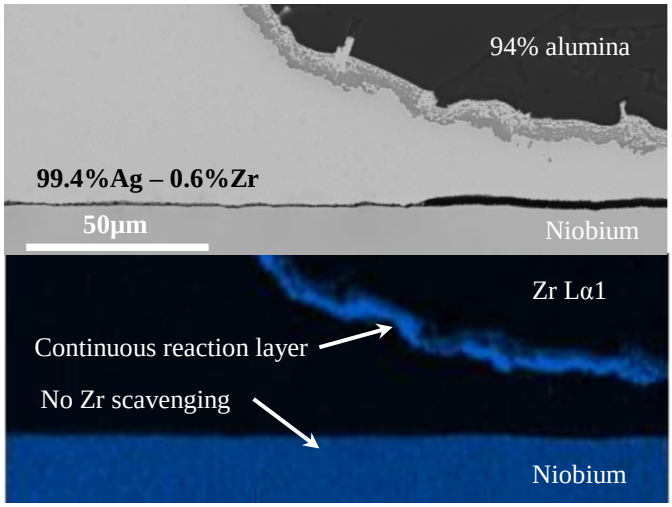


**Figure 25.** Top: SEM image showing a 94% $Al_2O_3$/Nb washer interface brazed with Ag-0.6%Zr filler metal. Bottom: EDS map showing a continuous $Zr_xO_y$ reaction layer formation.

The final samples to be discussed are the alumina ceramic brazed to either Fe-29Ni-17Co or niobium discs using pure silver braze filler metal modified with either 0.4 or 0.6 weight percent zirconium to form the active brazing filler metal, 98Ag-2Zr. The zirconium containing filler metals, both those made by modifying pure silver and the commercial material, displayed minimal erosion of the Fe-29Ni-17Co substrates and none on the niobium base materials as shown in Figures 24-27. The interface reaction layers formed with zirconium tended to be thicker and more continuous than those formed with titanium. Measurements taken using SEM software indicate $Zr_xO_y$ measurements of 4-6µm compared to 2-3µm for the $Ti_xO_y$ reaction layers. Also it was observed that, on the zirconium bearing samples but not the titanium active element brazements, there is a continuous silica layer along the $Zr_xO_y$ reaction layer. This layer is visible in many of the zirconium containing samples, but is most easily seen in the commercial 98Ag-2Zr material as shown in Figures 26 and 27, where SEM/EDS analysis revealed that the alumina ceramic glassy-phase material, silica, had formed a completely continuous reaction with the zirconium, independent of which metal substrate was utilized in the braze joints. The silicon layer is more pronounced on the niobium base metal samples. This is believed to be due to the tendency of a portion of the zirconium to be scavenged by the Fe-29Ni-17Co, shown in Figures 24 and 26, leaving less material to form a reaction with the alumina or silica material.

## Conclusions

Active brazing filler metals were fabricated by depositing thin-films of titanium or zirconium on to conventional brazing filler metals. The sputter-deposited active element layers were prevented from oxidation by depositing a thin layer of noble metal (silver or gold) over them prior to exposure to the atmosphere. The modified BAu-3 active brazing filler metal contained either 0.235 or 0.35 weight percent titanium, while the modified silver active brazing filler metal contained 0.4 or 0.6 weight percent zirconium. Brazed assemblies were fabricated to have two reaction layers by using either 94% alumina ceramic ASTM F-19 tensile buttons or 94% alumina discs. Although $Ti_xO_y$ or $Zr_xO_y$ reaction layers formed on both interfaces of each of the test samples, the samples were not hermetic of either pedigree.

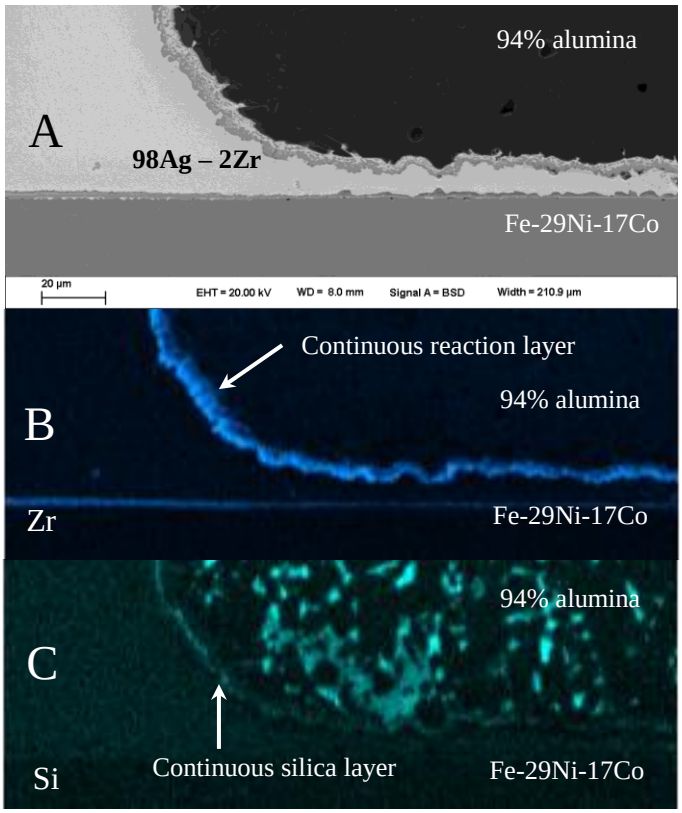


**Figure 26.** (A) SEM image of a 94% $Al_2O_3$/Fe-29Ni-17Co alloy interface brazed using 98Ag-2Zr filler metal. (B & C) EDS maps showing $Zr_xO_y$ and $Si_xO_y$ reaction layers.

SEM/EDS analysis confirmed that the reaction layers formed were not continuous on either of the surfaces, as compared to samples fabricated with commercially manufactured active brazing filler metals containing two weight percent of titanium or zirconium.

The average tensile strengths of the samples brazed using the two weight percent active element were superior to the strengths of those fabricated using the modified filler metals having reduced active element percentages. Future test samples should include greater concentrations of active element and also amended filler metal preparation methods as the analysis of the metallographic cross-sections also showed the tendency of the sputter deposited active element to preferentially form a thicker, more continuous reaction layer on the faying surface it was positioned adjacent to during the prebrazing fixturing process.

Of the samples fabricated so as to form a reaction layer at only a single interface, those utilizing Fe-29Ni-17Co metal substrates were shown to scavenge both of the active elements, titanium and zirconium, more readily than the commercially pure niobium metal. While scavenging and base metal erosion

was observed on all the titanium containing filler metals, positioning the titanium or zirconium away from the metal substrate during brazement fixturing process should reduce observed scavenging and base metal erosion. Regarding the two active elements, titanium was found to be more likely to be scavenged, or react unfavorably with the base metals than did zirconium.

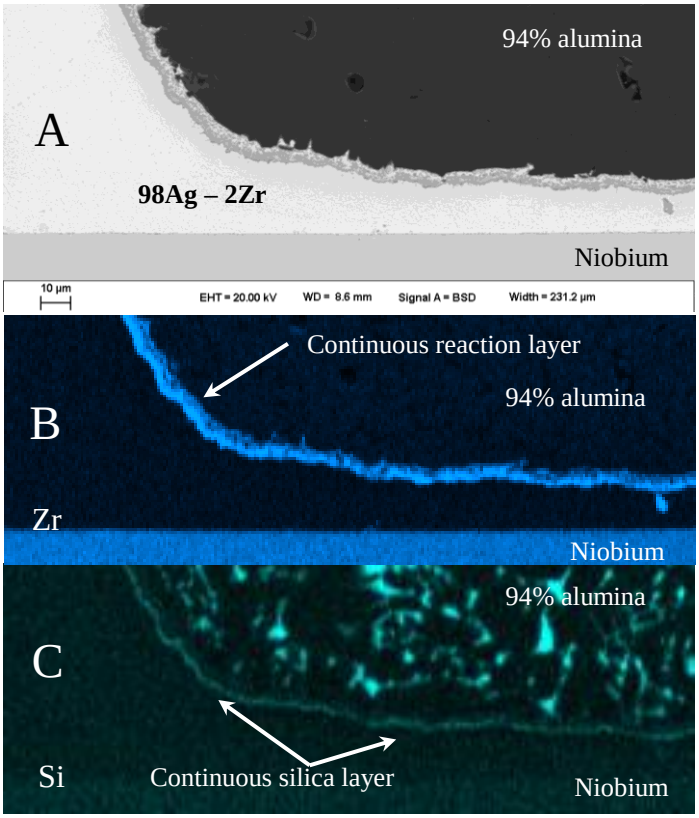


**Figure 27.** (A) SEM image showing a 94% alumina ceramic/Nb washer assembly brazed using 98Ag-2Zr filler metal. (B & C) EDS maps showing complete reaction layer formation of $Zr_xO_y$ and $Si_xO_y$ on the alumina surface.

While not quantified as part of this study, the materials combination observed to have the greatest amount of base metal erosion and active element scavenging was 94% alumina ceramic and Fe-29Ni-17Co brazed with titanium containing filler metal. Conversely, the samples showing the least base metal erosion and scavenging were 94% alumina ceramic and niobium brazed with zirconium containing filler metal. This latter combination also appeared to form a more continuous reaction layer with the silica material within the alumina ceramic glassy phase. Mixed helium leak detection results and overall poor tensile button strengths of the tensile buttons confirmed the importance of properly resintering alumina ceramic substrates following the grinding and/or polishing process prior to brazing. Firing temperatures of 1500°C for one hour (wet hydrogen) and 1575°C (air) for two hours, were adequate to reflow the glassy phase of the alumina ceramic samples used in this study.

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