Strong, Electrically-Conductive Silver-Based Braze Joints & Electrical Contacts Between Chromia- and/or Alumina-Protected Stainless-Steel

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Motivation and Objectives

Dense oxide scales can protect stainless steels from oxidation in high temperature environments. Cr and Al are commonly used to form protective oxide scales [1,2]. However, adding Cr can introduce volatile phases which can contaminate other device components [3,4]. In contrast, Al additions produce non-volatile Al_2O_3 scales. Unfortunately, Al_2O_3 scales block electron transport and can make it difficult for brazes to wet and adhere to stainless steel.

As shown in Figure 1, recently our group developed a Particle Interlayer Directed Wetting and Spreading (PIDWAS) brazing technique to produce dense, well-adhered Ag-Ni braze joints/circuits on ceramic substrates [5]. This approach could also be useful for brazing oxide-protected steel. Unfortunately, Ni particles in the PIDWAS interlayer are oxidized at high temperature to form mechanically weak NiO that somewhat compromises joint strength. Further, many Ni-Al intermetallics are known to be brittle, and may also compromise the strength of Ag-Ni to Al_2O_3-protected stainless steel (AFA) joints/electrical contacts.

Hence, the **objectives** of this project are to:

(1) Identify new PIDWAS interlayer materials that could be used to braze Al_2O_3- or Cr_2O_3- protected stainless steel

(2) Prevent Al_2O_3 formation in the braze joint

(3) Compare the mechanical stability, longevity, and electrical performance of PIDWAS brazes to conventional Ag brazes and electrical contact pastes.

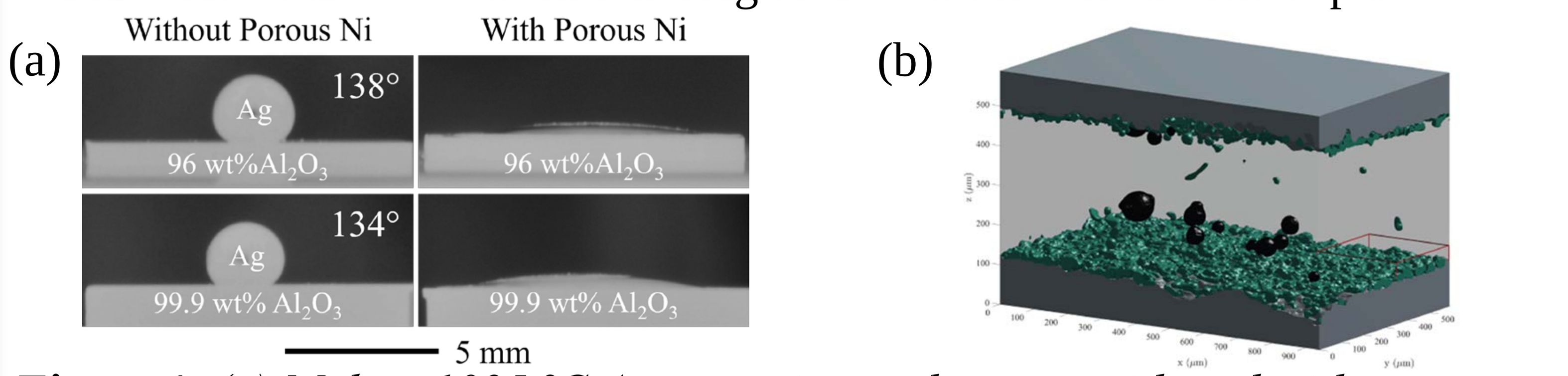


Figure 1. (a) Molten 1025 °C Ag on various substrates with and without a screen-printed Ni interlayer, and (b) a 3D X-Ray tomography microstructural reconstruction of an As-Produced Al_2O_3|Ag-Ni|Al_2O_3 joint where Ni is green, Ag is transparent, pores are black, and Al_2O_3 is gray, from Ref. [5].

Theoretical Search Criteria and Results

A new PIDWAS interlayer element for AFA brazing must:

- Have a melting point > than Ag (so it doesn't disappear during brazing)
- Form an intermetallic with Al (to chemically getter/trap the Al)
- Have that intermetallic be ductile (to promote high fracture strength)
- Be slight solubility in Ag (to ensure Ag wets it)

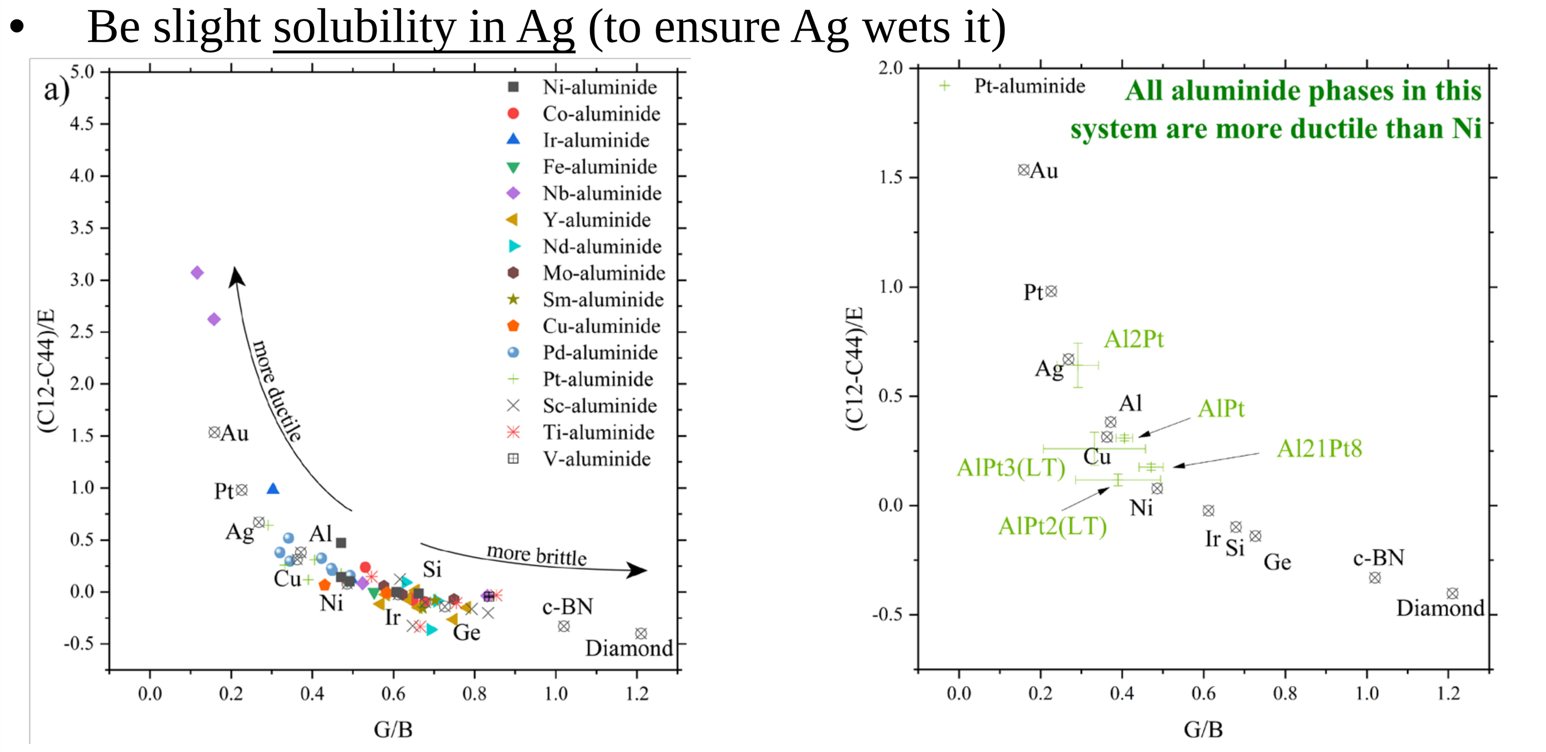


Figure 2. An aluminide ductility analysis of select metal and candidate metal aluminide phases made considering the Pugh criteria (the ratio of the shear modulus, G, and bulk modulus, B) and the Pettifor criteria (the ratio between the differences in the C_{12} and C_{44} stiffness tensor coefficients and the Young's modulus, E), based on the approach of Ref. [6].

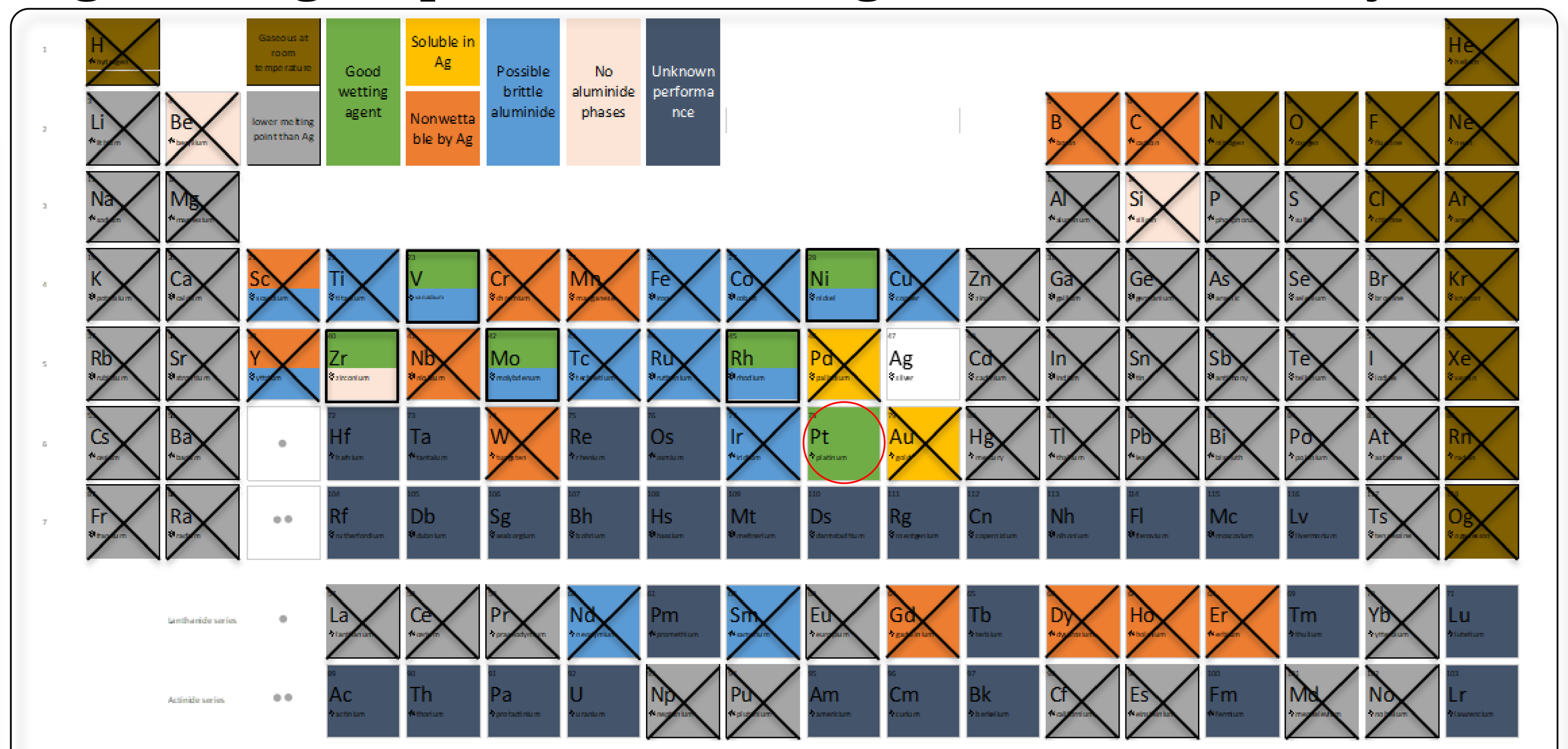
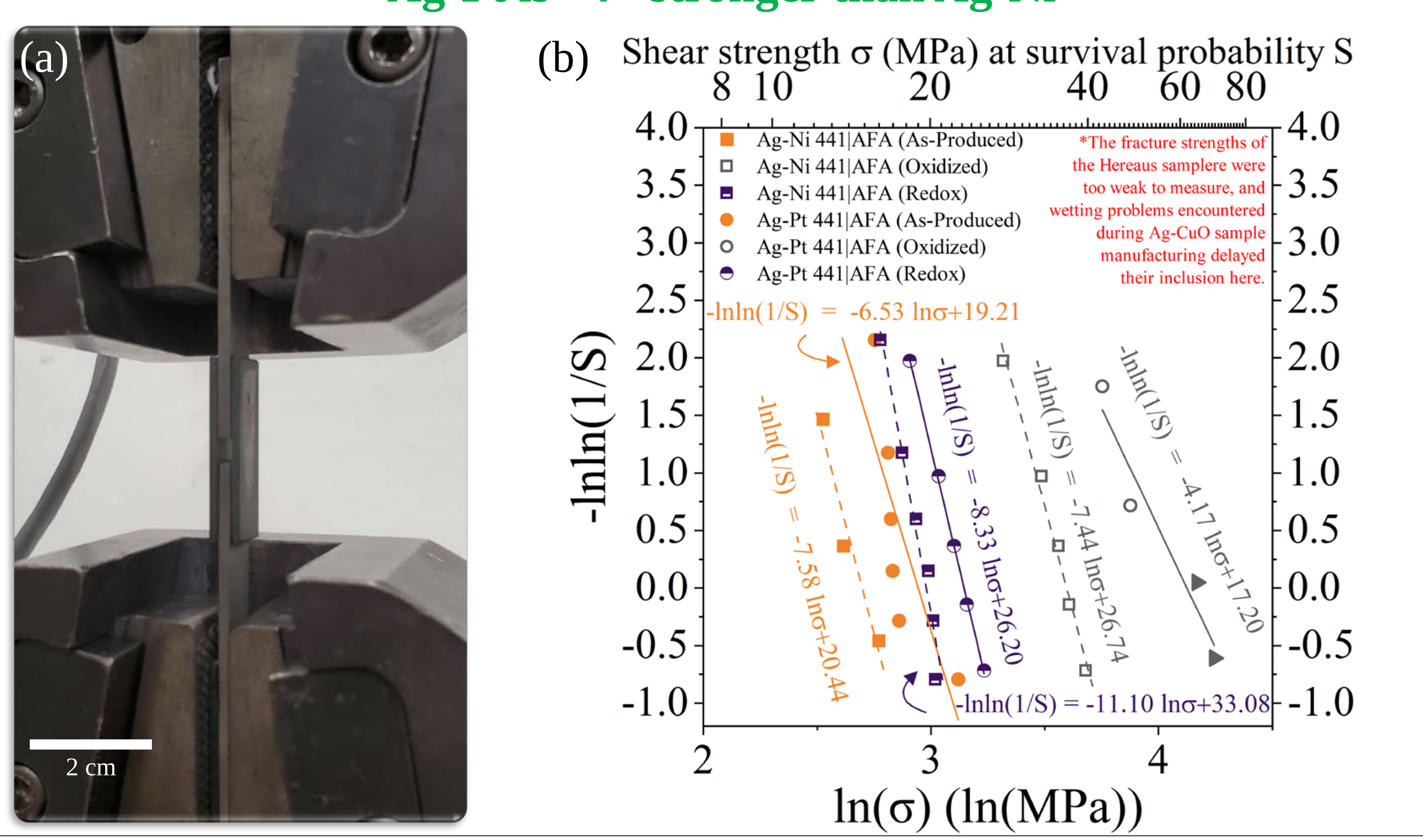


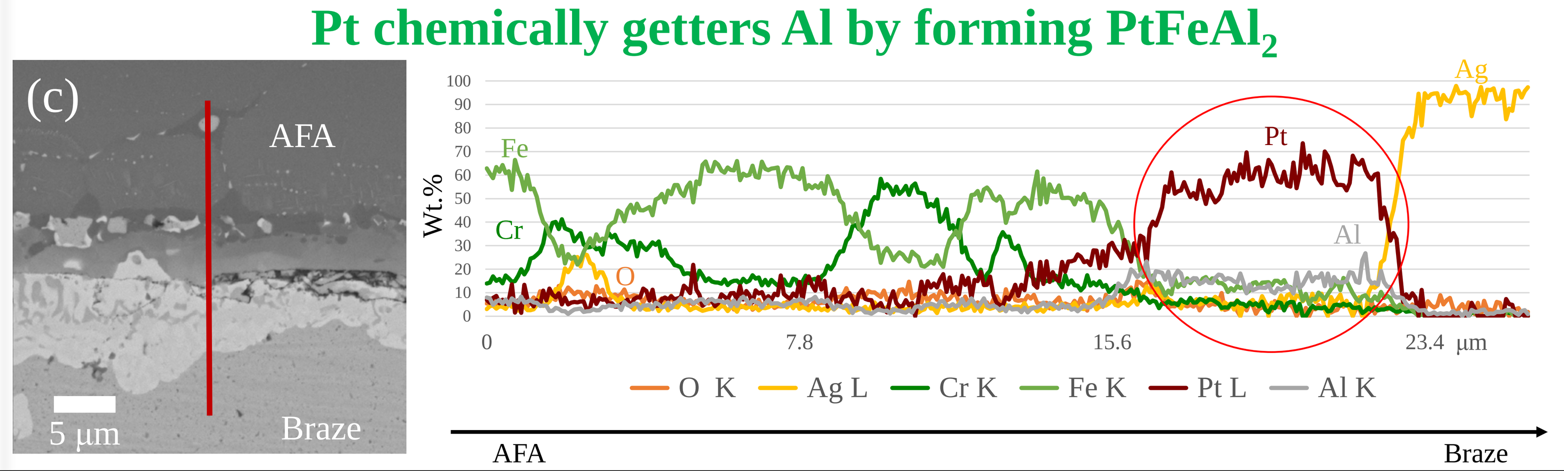
Figure 3. Elements that meet the search criteria in the periodic table.

Results

Ag-Pt is ~4× stronger than Ag-Ni



Pt chemically getters Al by forming $PtFeAl_2$



NiO reduction prevents H_2 penetration deeper into the joint and gives H_2O space to occupy

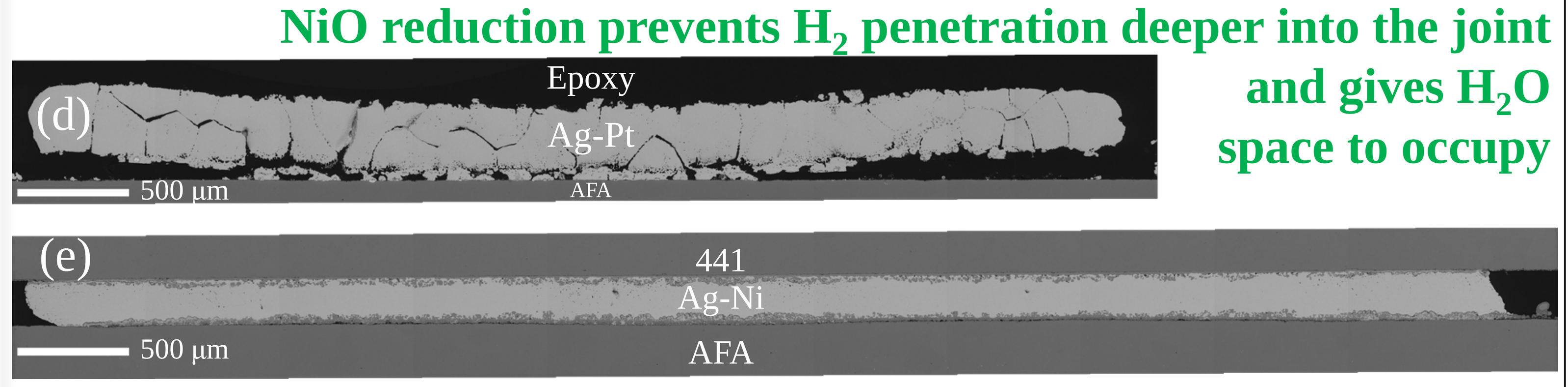


Figure 4. (a) The double shear lap test setup, and (b) the Weibull plot of As-Produced, Air Annealed, and RedOx cycled Ag-Ni and Ag-Pt 441-to-AFA braze joints. The survival probability was calculated by ranking the recorded fracture stresses from low to high such that the survival probability of the j^{th} of N samples was $S_j=1-(j-0.3)/(N+0.4)$[7]. (c) A cross-sectional SEM and energy dispersive spectroscopy scan of an As-Produced Ag-Pt joint at the AFA|braze interface. (d) A cross-sectional SEM image of a Ag-Pt braze after twenty-five 12-hr-in-4%H_2+12-hr-in-air RedOx cycles at 650℃. The sample broke in the braze and detached from the 441. (e) A cross-sectional SEM image of an Ag-Ni braze after twenty-five 12-hr-in-4%H_2+12-hr-in-air RedOx cycles at 650℃.

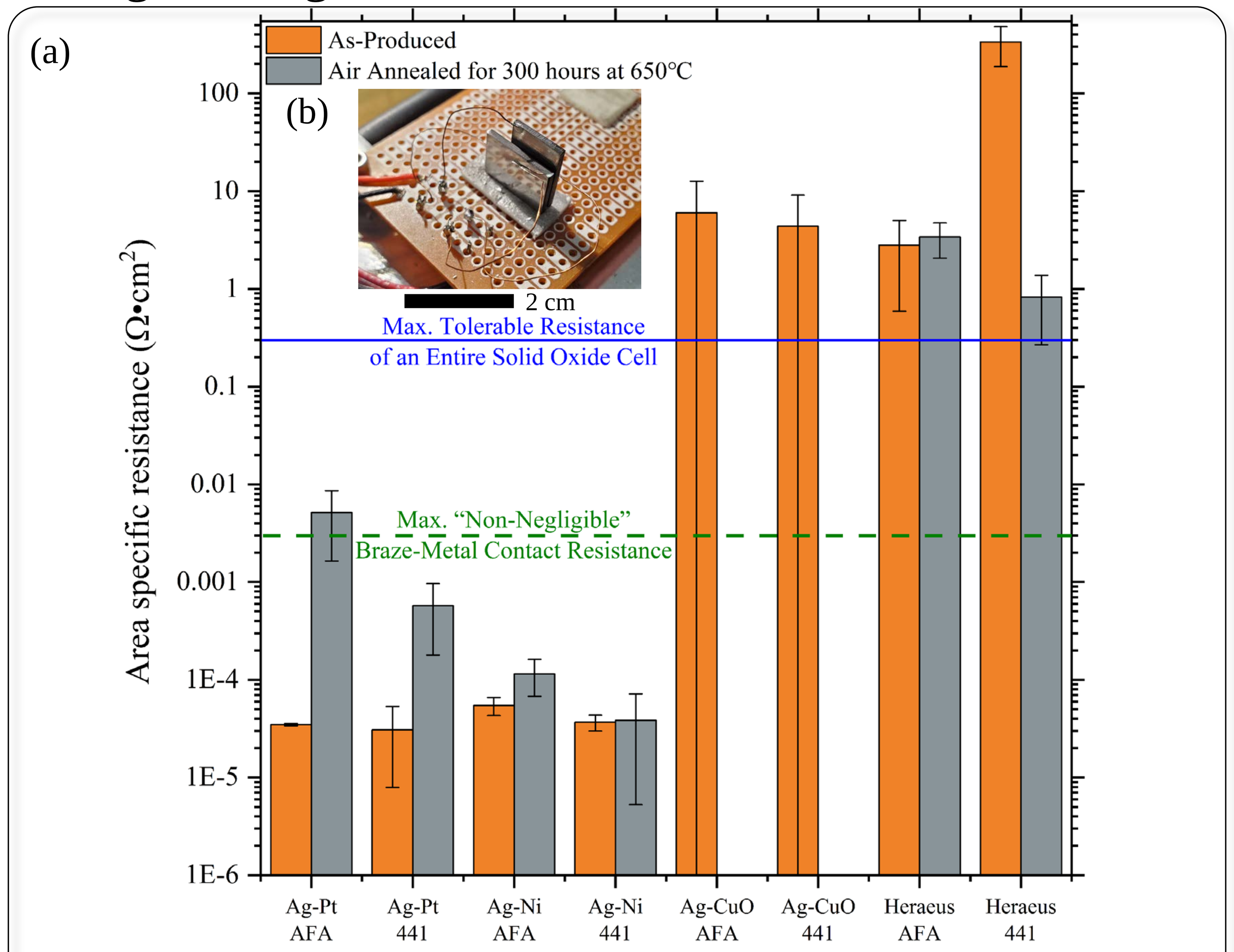


Figure 5. (a) The contact resistance between Ag-Pt, Ag-Ni, Ag-CuO, or Heraeus Ag contact paste and various stainless steel substrates using the 4-point sample geometry shown in (b). The dashed line is defined here as 1% of the ideal area specific resistance for an entire SOFC defined in Ref. [8].

Conclusions

- Both Pt and Ni can be used as PIDWAS interlayer materials, and both can perform "double-duty" by: 1) directing the wetting and spreading of molten Ag, and 2) gettering Al from a stainless steel substrate.
- Even after 300 hours in 650°C air, the braze to stainless steel contact resistance of Ag-Pt and Ag-Ni joints are 1000's of times lower than those of conventional Ag brazes and Ag circuit pastes.
- Ni interlayers can perform "triple-duty" by acting as internal oxygen storage materials that delay the formation of Ag intergranular water pockets during RedOx cycling. Because of this, during RedOx cycling Ag-Ni joints remain largely crack free and exhibit joint strengths that range between their "As-Produced" and "Oxidized" values, while Ag-Pt joints suffer from Ag intergranular fracture that reduces the braze joint strength below its "As-Produced" value.
- Even though Ag-Pt braze joints are not recommended for use in RedOx cycled atmospheres and are ~3 times more expensive than competing braze compositions (a cost which might be lowered through additional microstructural optimization and/or changes in the current \$19/oz. and \$888/oz. prices of Ag and Pt, respectively), Ag-Pt joints are dense, electrically conductive and ~4 times stronger than Ag-Ni braze joints in air.
- When shear strengths of only a few MPa are needed, Ag-Ni joints are recommended over Ag-Pt joints due to their lower cost, better RedOx cycling durability, and lower braze to stainless steel contact resistance.

References

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