

Brazing Dissimilar Metals with a Novel Composite Foil— Johns Hopkins University

Project Details:

Timothy P. Weihs, Principal Investigator

Johns Hopkins University
Department of Materials Science and Engineering
3400 North Charles St
Baltimore, MD 21218
Phone: 410-516-4071
E-mail: weihs@jhu.edu

David Ollett, Project Manager

National Energy Technology Laboratory
626 Cochran's Mill Road
Pittsburgh, PA 15236-0940
Phone: 412-386-7339
E-mail: david.ollett@netl.doe.gov

Sarah Kleinbaum, Technology Area Development Manager

U.S. Department of Energy
1000 Independence Avenue, SW
Washington, DC 20585
Phone: 202-586-8027
E-mail: sarah.ollila@ee.doe.gov

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Executive Summary

Reactive brazing is a novel technique in the joining industry that uses reactive materials to produce substantial amounts of heat locally to join components. In this project, we created mechanically processed dilute thermite foils (Redox Foils) that upon ignition self-propagate to produce molten metal capable of joining dissimilar metal combinations. Due to the transient nature of the reaction, there is limited thermal damage to the base materials. Also, novel component combinations, that cannot be joined via tradition furnace brazing (such as magnesium alloys to steel), can be produced. Redox Foils are produced by mechanically processing and consolidating constituent powders. By adjusting the fabrication pathway and chemistry, the reaction products can be tailored to join specific material combinations. In addition to producing mechanically processed foils, we produce

vapor processed foils with controlled microstructures to understand some of the mechanisms of the reaction.

Over the course of the program, we worked to identify and enhance the properties of the Redox Foils so that they could produce strong braze bonds of dissimilar metals (steel, Al, and Mg alloys). In a first step, the reactivity of the powders, from which the foils were made, was enhanced by ball milling Al and metal oxide powders before consolidation. In a second step, Redox Foils were made by physical vapor deposition to identify what level of dilution is needed to prevent the formation of Cu vapor during the reaction of the Redox Foils. In a third step, we incorporated diluent powders within the milling process to improve homogeneity within the final foils. In addition, finite element model simulations of heat transfer were also combined with detailed microstructure studies to identify what level of homogeneity is needed to avoid the generation of Cu vapor. Lastly, we include Ag powders as a diluent to form a lower melting temperature braze. Unfortunately, none of these steps led to Redox Foils that could produce bonds with shear strengths greater than 10 MPa. The generation of oxygen vapor appears to be generating porous bond lines that are still relatively weak. To circumvent this vapor generation, we investigated Ti:2B reactive scaffolds that provide a heated framework to enhance braze flow and minimize porosity. However, BM Ti:2B powders suffered ~8% mass loss due to surface adsorbed water resulting in porous and weak bonds.

As an alternative solution, we developed Ti-C-Cu based reactive braze foils that rely on TiC formation reactions to melt the Cu braze material. In this system, the foils did not produce gas or vapor upon reaction but did form the desired TiC product with molten Cu. Unfortunately, the reaction temperatures and the duration of Cu melting were insufficient to produce effective bonds. The goal of achieving bond strengths of 20 MPa or higher was not achieved.

Objectives and Accomplishments

- **Objective:** optimize the chemistry, microstructure, and fabrication of heat generating, composite foils so as to increase their ability to provide strong and chemically stable bonds between Al 6061, Mg AZ31 and steel components;
- **Accomplishment:** the chemistry and the microstructure of the foils were optimized but we were unable to produce strong (> 20MPa in shear) and chemically stable bonds
- **Objective:** optimize the parameters used in bonding dissimilar metals so as to enhance the mechanical properties and corrosion resistance of the joints;
- **Accomplishment:** the pressure applied during bonding was optimized to some degree but an optimized foil was never achieved to complete this objective
- **Objective:** characterize the mechanical and corrosion properties of the best joints by producing statistically significant data sets;
- **Accomplishment:** this objective was not undertaken given sufficiently strong bonds were not obtained.

Introduction:

Reactive materials have been used to join metals for over 100 years ever since Hans Goldschmidt discovered that reactive aluminum and iron oxide could produce molten iron capable of joining railroads.^{1,2} This was called the thermite process, where aluminum reduces a metal oxide creating molten metal, alumina, heat, and often gaseous products. Initial joining use of these chemistries involved powdered mixtures and a mold so that the molten braze created by the reduction-oxidation reaction can flow into joints. More recently, reactive multilayer foils using intermetallic formation reactions have been used as a heat source.³⁻⁵ These joints do not produce their own braze, and therefore require pre-wetting of solder or braze layers to enable joining. Reactive joining provides a fast, efficient bonding approach, allowing one to use high temperature brazes that cannot be used on certain alloys.

This project aimed to combine the concepts of the two types of reactive joining described above. By utilizing a thermite composition, the exothermic reaction can create its own braze without requiring any pre-coated solder or braze layers on the components. Further, by creating a fully dense foil, the joint can be formed without any mold or complicated fixture. The braze is created at the location of the joint as shown in **Error! Reference source not found.** and does not need to flow into the joint area, as is the case with typical thermite joining. To reduce the amount of gas produced by thermite reactions, the mixture is diluted with excess metal. Adding diluent decreases the reaction velocity, decreases the total amount of heat, and decreases the reaction temperature. Adding diluent also has the benefit of increasing the quantity of molten metal braze in the products as compared to undiluted thermites.⁶

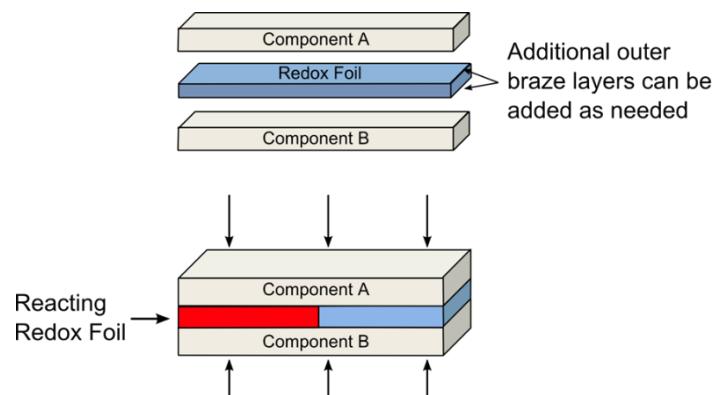


Figure 1: A schematic representation of bonding with a Redox Foil. After ignition, a reaction within the foil self-propagates through the bond interface.

The chemistry and microstructure of the Redox Foil determines how rapidly a given exothermic reaction will propagate within the foil. The chemistry also determines the characteristics of the braze that is formed. By engineering the reaction properties of the foil, we can tailor the reaction for joining many dissimilar metal combinations. Because the reactions propagate quickly (on the order of 1 m/s), the heat is produced for a short period of time, and very locally. This allows for brazing of dissimilar combinations that

cannot be joined with traditional furnace brazing (such as joining steel to magnesium alloys).

Approach:

To develop a Redox Foil capable of joining dissimilar metals, we produced two different types of foils. The first foil is made by mechanically processing constituent powders (Redox Foil),^{6,7} and the other is fabricated by vapor phase processing (PVD).^{5,8} The Redox Foil, is the economical solution that can be easily scaled for automotive applications. PVD foils, on the other hand, have well-defined geometries for scientific inquiry. These ideal microstructures are critical for understanding the processes that occur during propagation, and aid in engineering the necessary microstructure which we emulate in the Redox Foils. In the early stages of the effort, we determined that the Al:Cu₂O system is the most promising system for joining, with the diluent typically Cu, but some foils with Ag dilutions were also prepared, as will be described.

The Redox Foil fabrication process involves three steps. First constituent powders are ball-milled to produce nanocomposite powders. This step was added in FY 2015 to reduce the reactant spacing between the aluminum fuel and the oxide. Initially, only the Al and metal oxide were milled together prior to consolidating into a dense Redox Foil. These foils are labeled BM. However, due to analysis from the PVD foils in FY 2016, it was determined that the Cu diluent needs to be more uniformly incorporated into the final Redox Foil. Therefore, the diluent was added to the ball milling process prior to the consolidation step. These foils are labeled BM+D. After milling, the powders are packed into a tube and then compacted by swaging, a radial reduction technique. Finally, the swaged tubes are rolled flat and the tube encasing the powders is removed leaving the fully dense Redox Foil.

The PVD foils are made using magnetron sputtering. The sputtering chamber contains three targets, Al, Cu₂O-Cu, and Cu. Inside the chamber, substrates are rotated past each target producing layered foils of a planar geometry.

We employed a variety of experimental techniques to analyze the microstructure and reaction of the foils. Characterize microstructure we used cross-sectional optical microscopy (OM) and scanning electron microscopy (SEM). To characterize the propagating reactions in the foils we used high speed videography coupled with emission spectroscopy. High speed videos allowed us to determine propagation velocities, a key metric for how fast the reaction is producing heat. The emission spectroscopy was used to identify if vapor species are produced by the reactions, as well as to approximate reaction temperatures. Slow heating experiments, including differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), were also used to characterize the thermal properties of reactive materials and resulting braze. Finally, the Redox Foils were used to join Al 3003, Mg AZ31, and hot stamped boron steel (HSBS), and the shear strengths of resulting bonds were tested.

Results and Discussion:

The initial Redox Foils were made using single phase Al, Cu, Ni, NiO, CuO, and Cu₂O powders, and during bonding these foils generated significant gas and ejected particles.⁵ Given both gas production and particulate ejection are detrimental to the strength of the bonds being formed with these foils, we attempted to reduce both phenomena by diluting the foils with excess Ni or Cu. Figure 2 displays the normalized mass ejection fraction as a function of dilution for the three oxide chemistries examined. Normalized mass ejection is defined as the mass of the ejected material collected divided by the mass of the original Redox Foil for the experiment. For all three systems, as dilution increases, the average particulate ejection decreases. For the Al:NiO:Ni system, the particle ejection becomes negligible once dilution increases above 10% by mass, whereas for both CuO systems there is still considerable mass ejection even as dilution is increased to 40 wt%. The Al:Cu₂O system ejects less mass than Al:CuO system and drops to essentially no mass ejection at 40 wt% dilution.

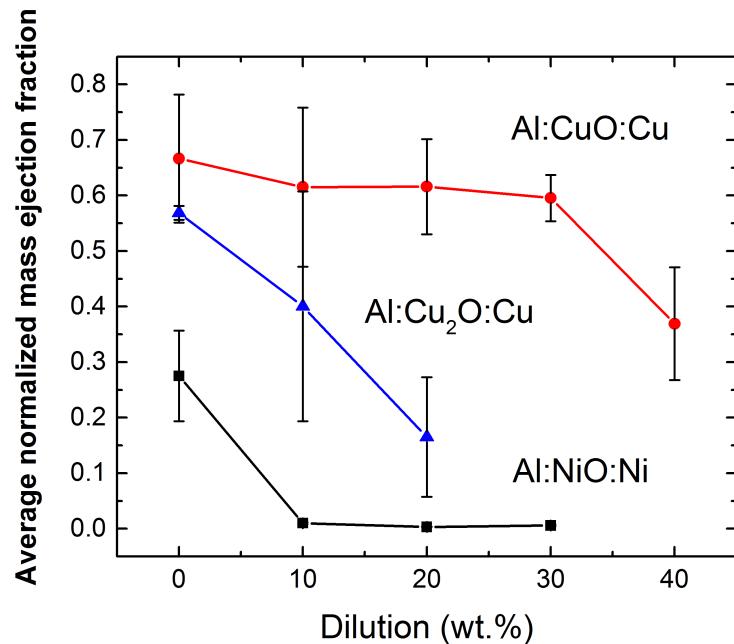


Figure 2: The average normalized mass ejection as a function of dilution for different weight percents of Al:NiO, Al:CuO, and Al:Cu₂O foils, where the diluent is the metal from the starting oxide.

While excess Ni or Cu lowers the reaction temperature of the foils and minimizes gas production and particle ejection, it also slows reaction propagation, increasing the chance the reactions will quench during bonding. To assess this impact of dilution, we performed velocity measurements on samples from the Al:NiO, Al:CuO, and Al:Cu₂O systems. The results are plotted in Figure 3. Trends are similar to those seen for mass ejection. Al:CuO foils appear relatively insensitive to dilution, with average velocity values between 1-2 meters per second (m/s) until 40 wt% Cu, while velocity in Al:NiO foils drops off considerably after only 10 wt% Ni dilution. Differences in velocity between the Al:NiO and

Al:CuO systems increase by nearly an order of magnitude as the respective diluents are added, while the Al:NiO and Al:Cu₂O system approach similar values at high dilutions. In addition, we determined the amount of dilution that could be added to the Al/NiO/Ni, Al/Cu₂O/Cu, and Al/CuO/Cu foils and still have the foils self-propagate across a bonding configuration. We found that the Al/NiO/Ni and Al/Cu₂O/Cu systems could only be diluted 10% before quenching in a bond, while the very reactive Al/CuO/Cu system could be diluted 40wt% before quenching.

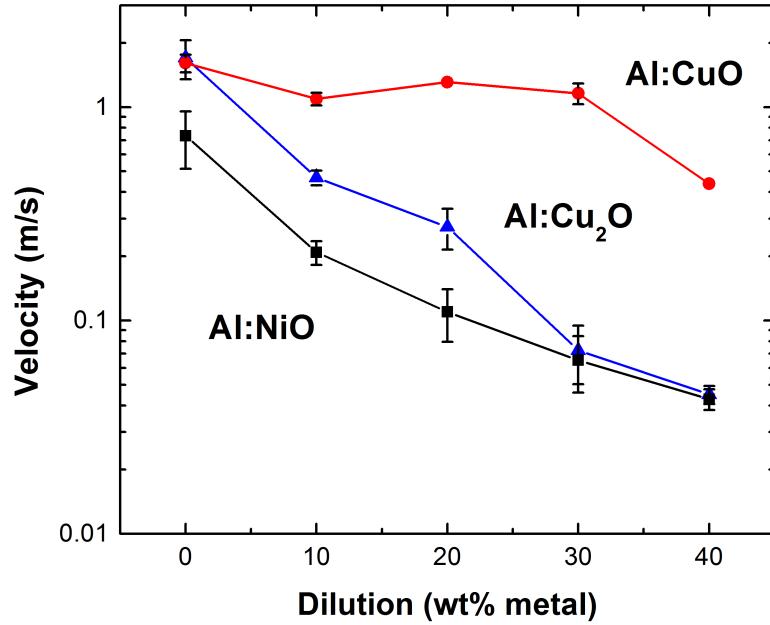
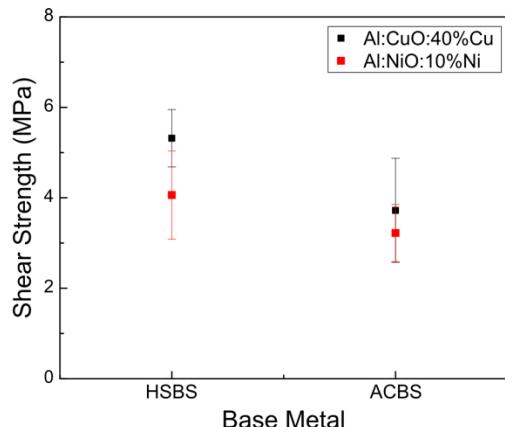
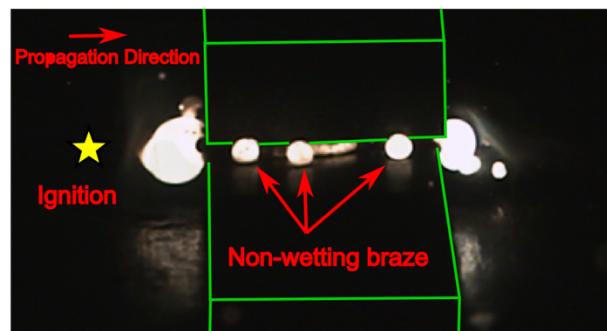


Figure 3: Average propagation velocities of Al:NiO, Al:CuO, and Al:Cu₂O foils as a function of dilution.

In addition to assessing the properties of the initial Redox Foils, preliminary bonds were made using these foils. The Al:CuO foils created porous braze interfaces due to the mass ejection caused by the gas generated by the thermite reaction. Even the heavily diluted case of Al:CuO:40%Cu resulted in substantial particulate ejection from the bond interface. Despite these limitations, the Al:CuO:40%Cu foil was still able to bond all substrates, including Al 6061, Mg AZ31, HSBS, and ACBS. The Al:NiO foils did not produce any noticeable particulate ejection, but the strength of the resulting bonds was less than that of the Al:CuO system as depicted in Figure 4(a). There are two reasons that the NiO-based foils did not perform as well as the CuO-based foils. First, the Al:NiO systems produced more alumina, by volume than the Al:CuO system, due to their lower reactivity and smaller degrees of dilution that still allow propagation within a bond. Second, the molten nickel from the thermite reaction does not wet the bonding substrates as well as the molten copper. This is shown in Figure 4(b) where a high speed camera captures the molten nickel balling up on the surface of the aluminum substrate.



a)



b)

Figure 4: a) Shear strengths for bonding HSBS and ACBS with Al:CuO:40%Cu and Al:NiO:10%Ni. b) A frame from high speed video showing molten braze from Al:NiO:10%Ni not wetting the aluminum bonding substrates; bonding substrates have been outlined in green for clarity.

To make the diluted Redox Foils more reactive and to reduce the risk of quenching, we focused on producing more reactive powders by forming composite powders via ball-milling of the initial, single phase powders as shown schematically in Figure 5. Initials experiments were performed using Al and NiO powders and a clear reduction in reactant spacing can be seen in Figure 6. This led to increased reaction propagation velocities compared to Redox Foils prepared from single-phase powders as shown in Figure 7. For the Al:Cu₂O system, we found that ball milling increases the average propagation velocity by a factor of 3 in 20 wt% diluted foils and a factor of nearly 7 in 40 wt% diluted foils. All ball-milled powder Redox Foils propagated faster than their single-phase counterparts. We also tested ball-milled Redox Foils in a joining configuration to determine whether the reactions would quench in the bonding interface. Quenching tests were performed in bonds where the same component alloys were joined together (Mg AZ31 to Mg AZ31 and Al 6061 to Al 6061) using conventional and ball-milled Redox Foils. The results are shown in Figure 8. In all cases, the highest dilution that could be fully propagated through a bond interface was increased by at least 20 wt% when bonding with ball-milled Redox Foils.

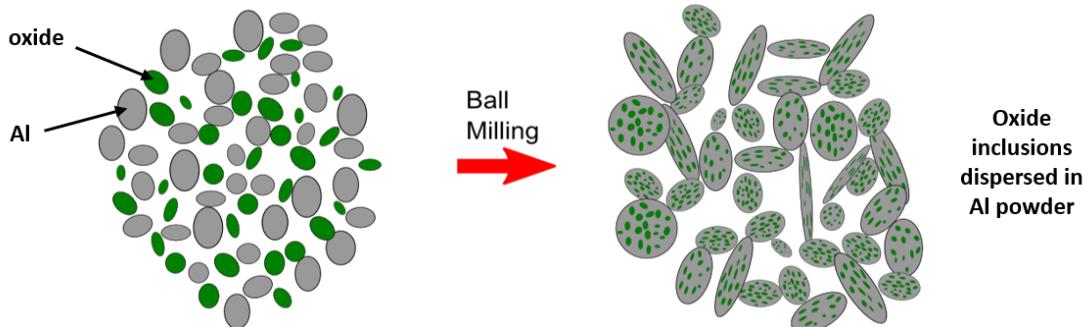


Figure 5: Schematic of powder evolution during ball milling process. Collisions between the milling media and single-phase powders create composite powders containing oxide fragments dispersed in softer aluminum powders.

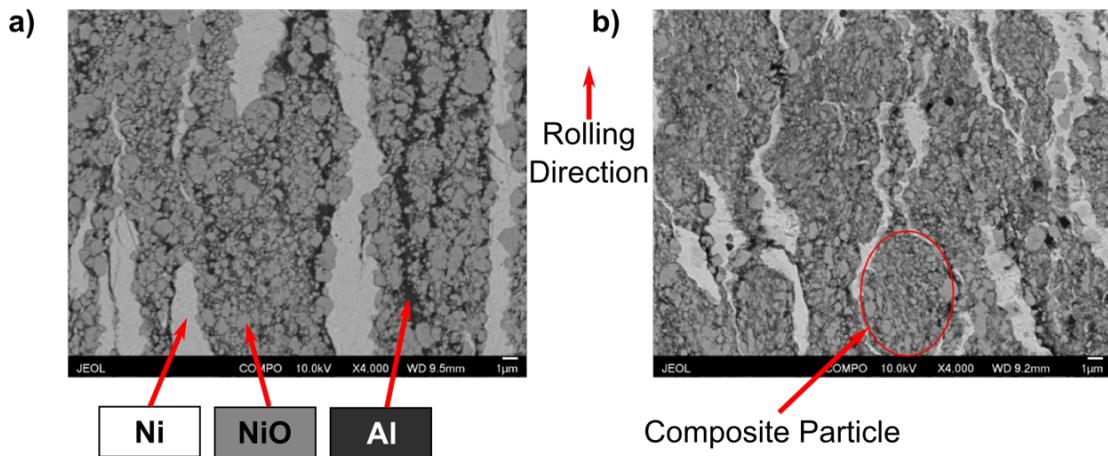


Figure 6: Scanning electron micrographs of Al:NiO:Ni Redox Foil fabricated from (a) single-phase powders, and (b) ball-milled composite powders.

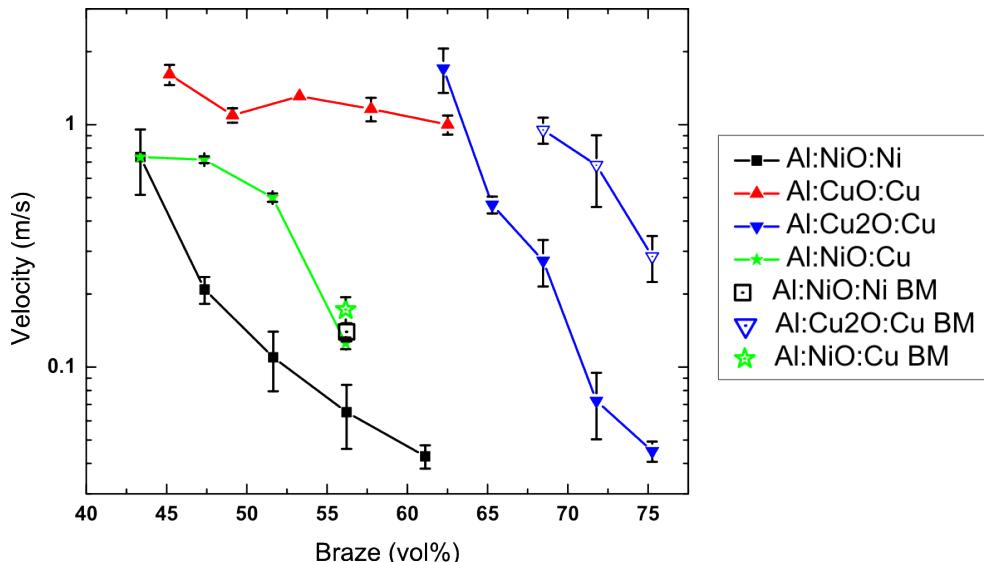


Figure 7: A comparison of propagation velocities for thermite systems produced from single-phase powders and ball-milled (BM) composite powders. Velocities are plotted as a function of expected braze percent by volume, where the balance is the expected alumina content.

While the Redox Foils that were made utilizing BM powders propagated faster than the initial Redox Foils made with single phase powders (Figures 8 and 9(a)), we observed that many of the BM-based foils disintegrated during propagation, resulting in lots of mass ejection from the reaction front. To investigate the cause of the mass ejection, we obtained emission spectra during the reactions to identify gaseous species. The emission spectra for Al:Cu₂O:Cu BM-based foils are presented in Figure 9(b) (red traces). For the 20wt% and 30wt% foils, there are multiple peaks including broad peaks at 490 nm and 500 nm. These correspond to CuO and possibly AlO emission. The sharper peak at 510

nm corresponds to Cu emission. The 40wt% BM-based foil does not show any peaks and has a smooth emission curve. These results indicate that the lower dilution BM-based foils produce Cu vapor during the propagation process. This vapor can create pressure that causes much of the material to be ejected. The ejection of material is detrimental to the joining process as it creates pores in the resulting braze. An example of a dissimilar bond made with a Al:Cu₂O:20Cu BM foil is given in Figure 10. While the strength of the resulting bond reach as high as 10 MPa in shear strength, these bonds include substantial porosity. These pores are weak points that can significantly limit the strength of the resulting bonds.

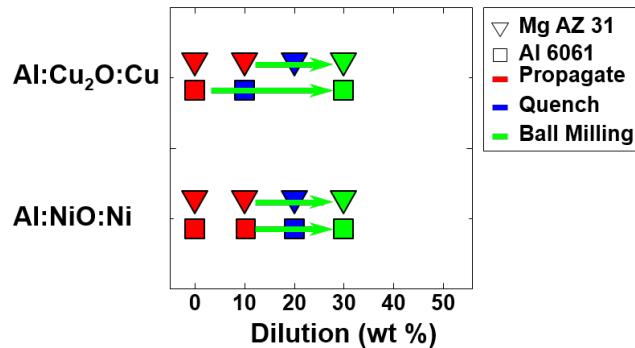


Figure 8: Quenching limits for Al:Cu₂O:Cu and Al:NiO:Ni systems using conventional and ball-milled powders. Foils created from ball-milled powders could be subjected to higher levels of dilution before quenching in the bond interface.

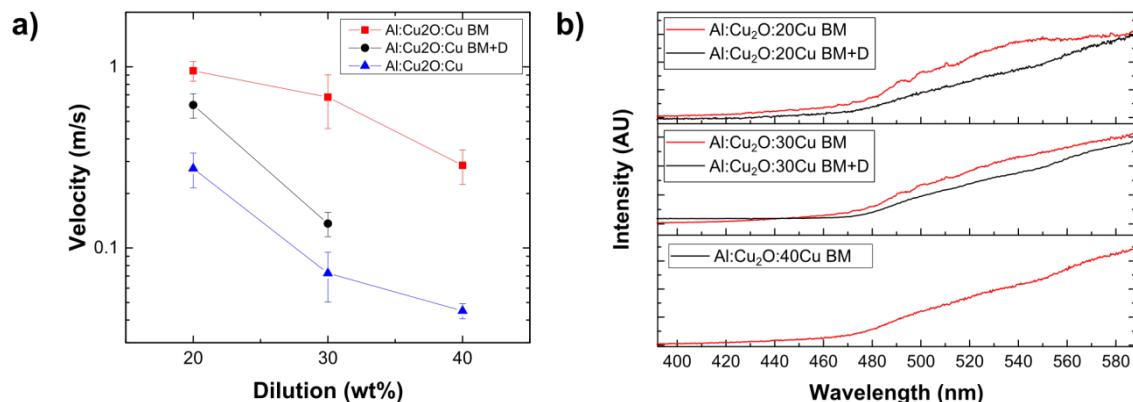


Figure 9: a) Propagation velocity of the Al:Cu₂O:Cu system for three different processing paths, conventional (FY2014), BM (FY2015), and BM+D (FY2016). b) Emission spectroscopy as a function of wavelength for BM (red) and BM+D (black) foils of the Al:Cu₂O:Cu system.

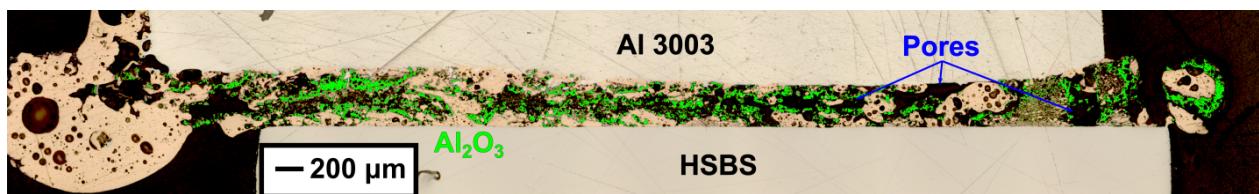


Figure 10: Cross section of dissimilar Al 3003/HSBS bond made with Al:Cu₂O:20Cu BM Foils; the alumina has been false colored green for clarity.

To understand the gas production, we fabricated PVD foils of Al:Cu₂O chemistry and added different amounts of Cu diluent into the foils.⁸ Five different foils were fabricated, with Cu layer thicknesses of 0 nm (Bilayer), 25 nm, 50 nm, 75 nm, and 100 nm. The Al and Cu₂O layer thickness remained constant throughout, so dilution increases with Cu thickness. Note that as the Cu layer thickness (dilution) increases, the peaks in the emission spectra decreased, as shown in Figure 11. The bilayer had very prominent emission peaks, and the highspeed video displayed lots of gas and particulate spray. The 25 nm foil, had some spray and a few peaks. The other foils showed no sign of emission peaks and no sign of spray or gas vapor. These model PVD foils suggested that Cu vapor production can be suppressed if the diluent is evenly distributed throughout the foil.

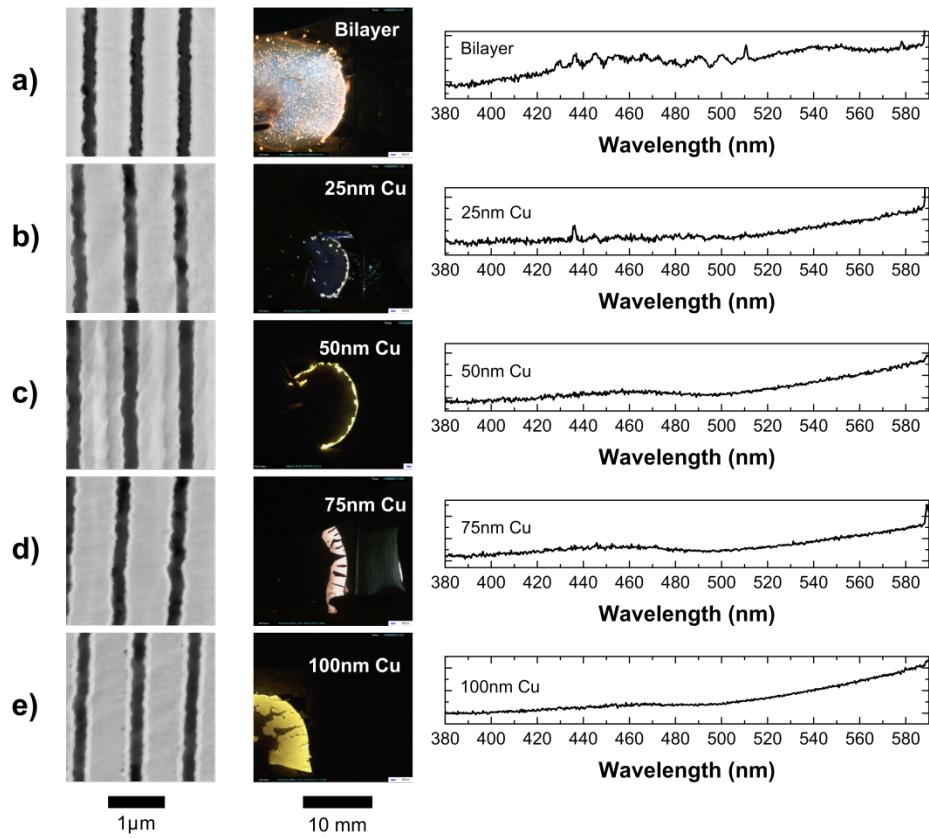


Figure 11: SEM image, high speed video snapshot, and emission spectroscopy of a) bilayer PVD foil and PVD foils with Cu interlayers of thickness b) 25 nm, c) 50 nm, d) 75 nm, and e) 100 nm. In the SEM images, dark is Al, grey is Cu₂O-Cu, and the thin white layer between the two is the Cu layer.

To assess the distribution of diluent within the Redox Foils produced using ball-milled powders, we performed an extensive analysis of the distribution of diluent within the BM Redox Foils.⁹ Image analysis was performed on Al:Cu₂O:Cu BM Redox Foils to understand the length scales present in the microstructure. The results are summarized in Figure 12 where the ratio of thermite to diluent is plotted vs the thermite length scale. Larger ratios correspond to smaller levels of dilution. The size of the circle corresponds to the area fraction of length scales within a given ratio. In addition, we performed finite element model (FEM) heat transfer simulations to determine the critical thermite lengths and ratios that are required to suppress Cu gas formation during propagation. The FEM

results are summarized in Figure 13. Based on the simulations it was determined that for 20wt%, and 30wt% dilutions, over half of the foil area was capable of producing vapor using the analysis from the simulations. Not surprisingly, both of these foils produced Cu vapor. The 40wt% sample, though, was predicted to have fewer dangerous microstructural length scales, and it did not produce Cu vapor. Therefore, to produce gasless propagation, we concluded that a finer spacing and more homogenous distribution of diluent in the microstructure was needed.

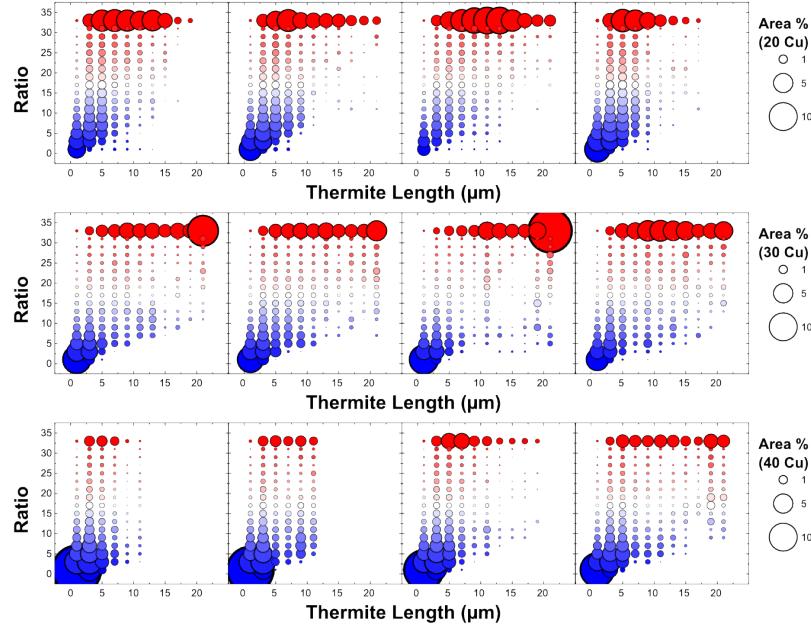


Figure 12: Microstructural analysis of BM Redox Foils. Each graph represents analysis on a different region of foil. Top row is 20wt% Cu; middle row is 30wt% Cu; and bottom row is 40wt% Cu.

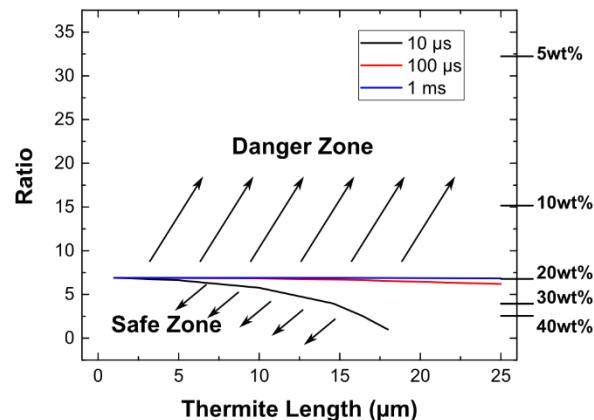


Figure 13: Results from FEM simulations determining what ratio and length scales are required in order to suppress gas formation

In order to accomplish this in the mechanically processed foils, the Cu diluent was ball-milled with the Al and Cu₂O powders to produce three-phase composite particles.⁹ With this fabrication, the diluent is more intimately mixed with the Al and Cu₂O. We see finer Cu pieces evenly dispersed in the resulting BM+D Redox Foil microstructures (Figure

14). Adding the diluent during milling does suppress the Cu vapor production as desired. The emission spectra of BM+D foils do not exhibit Cu peaks (Figure 9(b)), suggesting that the homogenization of diluent did eliminate gaseous Cu products as was seen with the PVD foils. However, adding Cu during the ball-milling state also reduced the propagation velocities compared to BM foils (Figure 9(a)).

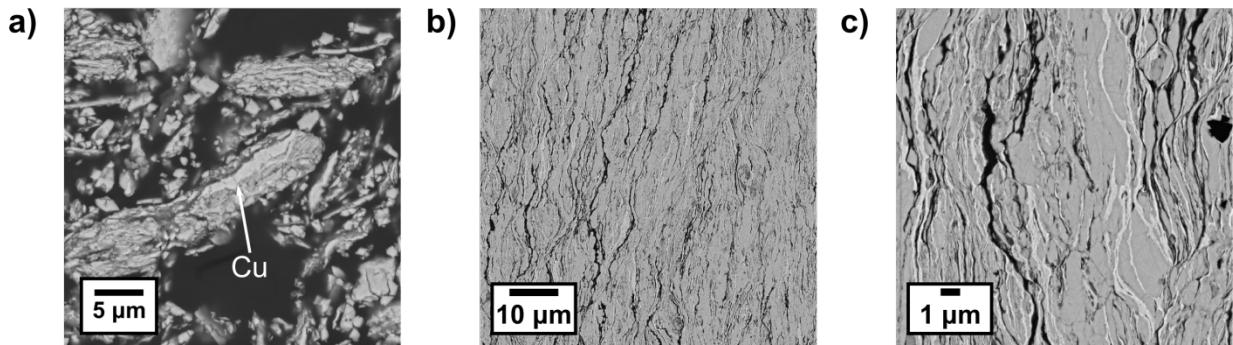


Figure 14: SEM cross sections of a) BM+D powder with Cu inclusion highlighted and images of Al:Cu₂O:30Cu BM+D Redox Foil at low magnification, b), and high magnification, c).

While the BM+D Redox Foils with more uniform distribution of Cu produce less Cu vapor, the strengths of the bonds made with Al:Cu₂O:Cu BM+D foils goes down as dilution increases. At 20wt% dilution, the fracture occurs within the braze, whereas for the 30wt% dilution, the fracture location moves from within the braze to the substrate interface. Strengths and fracture surfaces are shown in Figure 15. This change in fracture location indicates that the molten Cu produced by the reaction did not adequately wet the substrates at higher dilutions. We believe the higher dilution of 30wt% reduces the reaction temperature, and therefore the braze remains molten for a shorter period of time, which is detrimental to wetting of the substrate.

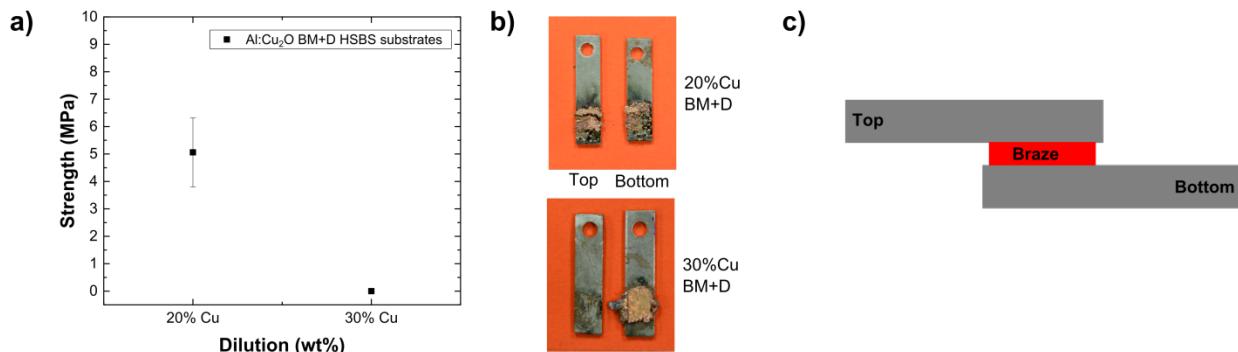


Figure 15: a) Shear strengths of Al:Cu₂O:Cu BM+D foils joining HSBS with representative fracture surfaces in b) and a schematic of the lap shear joint for fracture location in c).

To overcome the wetting issue as you increase the amount of dilution, we substituted Ag for Cu as the diluent. This produced an alloy braze that has a lower solidification temperature. The lower melting temperature should increase the amount of time the braze is molten. The Ag substitution was done with both BM and BM+D fabrication methods. In both cases, the Ag diluted sample melted at a lower temperature than the Cu diluted

sample (Figure 16), suggesting that Ag diluted Redox Foils stays molten for a longer period of time, which we thought would promote wetting of the surfaces.

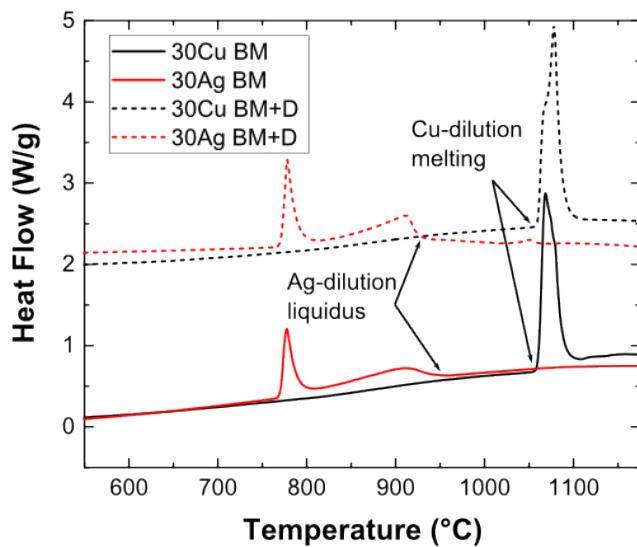


Figure 16: DSC traces of the second heating of Redox Foils indicating that the melting temperatures of the resulting braze is lower when diluted with Ag as opposed to Cu.

However, even with these improvements of metal vapor suppression and braze melting temperature reduction, bonds formed with Ag diluted Redox Foils and Cu diluted BM+D Redox Foils still exhibit porosity. Data from the PVD samples suggests that there may be some form of gas generation other than metal vapor formation. Figure 17 shows SEM pre and post reaction cross sections of a 100 nm PVD foil that provided no evidence of Cu vapor on reaction. The post reaction image contains large pores, which we suspect are formed by vapor not detected via emission spectroscopy (not metal vapor). We have also performed TGA experiments for both PVD foils and Redox foils which show a 1% mass loss at low temperatures under slow heating conditions. We attributed the mass loss to oxygen release, which may also occur at the faster rates and higher temperatures of propagating foils. This sort of oxygen release has been seen for other thermite systems,¹⁰ and must be overcome in order to produce non-porous braze with limited mass ejection during propagation.

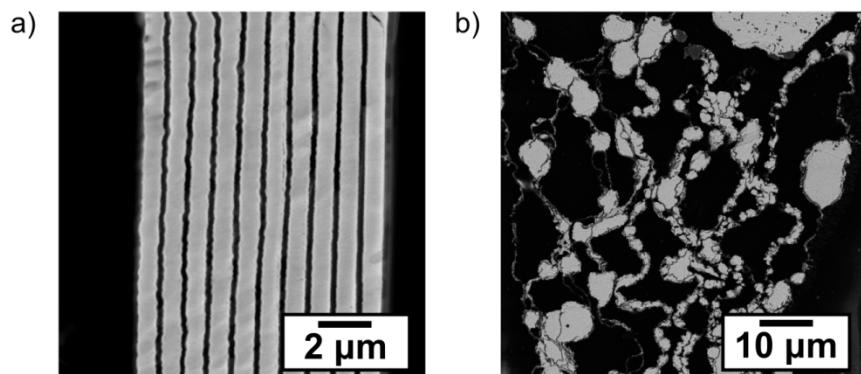


Figure 17: SEM of a) an initial 100 nm PVD foil showing regular layer spacing and a total thickness of approximately 15 μm. b) SEM of a reacted foil with large pores causing an increase in foil thickness.

To minimize the issue of gas generation, that is attributed to oxygen release, we explored the use of high energy formation reactions that could augment the thermite reactions by creating a hot scaffold into which molten braze could flow. We ball milled and compacted Ti:2B powders that have very high adiabatic temperatures and higher melting temperatures, and can form a porous TiB_2 scaffold. We combined the Ti:2B pellets with our traditional thermite powder systems to leverage the best qualities of both reactive systems. The Ti:2B has a high heat output upon reaction, forming TiB_2 , which creates a hot, porous, and solid matrix. The thermite acts as an additional heat source while providing molten braze material that solidifies at temperatures approximately 2000°C below the melting point of TiB_2 . These metallic products (Cu and Ag) are able to flow into the hot pores of the TiB_2 matrix, decreasing porosity and increasing the degree of connectivity of the metal braze throughout the bond thickness. More molten metal is contributed from the local heating of the substrates (Al 3003), which allows for further pore filling. We fabricated trilayer pellets with thermite outer layers and a Ti:2B core, as depicted in Figure 18(a), and we demonstrated the ability to produce joints with such trilayers as shown in Figure 18. Unfortunately, because B powders are often porous and can be very hydroscopic, the Ti:2B powder compacts produced significant vapor upon reaction and significant mass losses were observed in TGA scans of the elemental starting powders. The bonds formed using these trilayer structures all showed low strengths as seen in Figure 19.

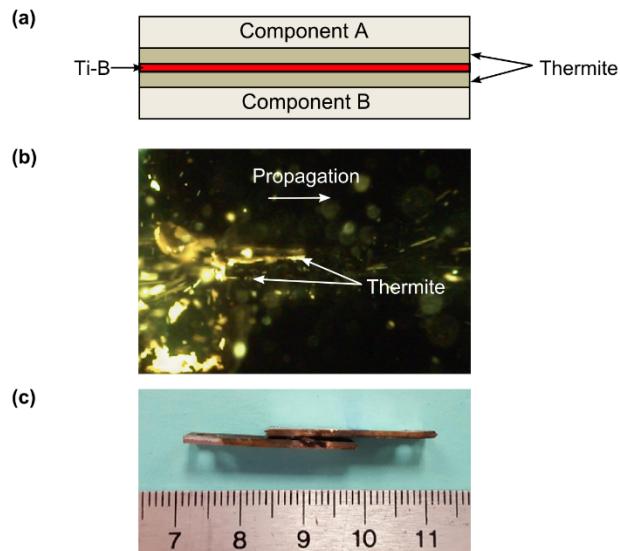


Figure 18: (a) Schematic representation of bonding with a trilayer pellet and (b) video of such a pellet propagating between two Al 3003 substrates producing the joint shown in (c).

As an alternative to the Ti:2B system, we synthesized Ti-C-Cu powders using ball milling to leverage the equally exothermic Ti:C reaction. We investigated a Cu-rich, 0.63CuTiC and a Cu-lean, 0.44CuTiC composition using special WC coated milling vials. Cross-sections of the powders showed limited mixing of Ti, C, and Cu and DTA scans revealed the formation of TiC, but only at high scan temperatures. We pressed the Cu-rich 0.63 CuTiC ball milled powders into pellets, incorporating soft indium powders into the compacts in some cases to minimize porosity. While the pellets could be ignited and did

form TiC and Cu or CuIn brazes, the reactions typically quenched as they propagate between steel samples for bonding. In the few cases where the reactions propagated across the bond interface, the resulting molten braze failed to wet the steel samples and bonding was not accomplished. Thus, reactive foils based on thermite reactions and formation reactions could not produce bonds stronger than 10 MPa in simple shear.

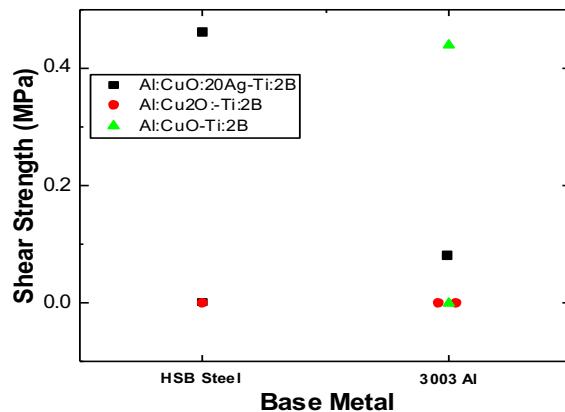


Figure 19: Preliminary bonding results for various combinations of thermite and Ti:2B powders.

Conclusions:

After establishing baseline bonding performance for mechanically fabricated Redox Foils, we identified and undertook multiple strategies for improving the performance of these foils during bonding. We also used sputter deposited thermite foils as model materials to identify the appropriate extent of dilution to avoid the generation of Cu vapor, as well as other sources of gas generation. We ball-milled Al and NiO powders, Al and CuO powders, and Al and Cu₂O powders to make them more reactive. We also added Cu powders during the ball-milling of the last chemistry to enable a more uniform distribution of diluent within the Al/Cu₂O/Cu foils. All of these steps lead to improvements. Reactivity and reaction velocities were improved and Cu gas generation was minimized. We also lowered the melting temperature of the resulting braze by adding Ag powders to the Redox Foils. However, gas generation via oxygen release was identified as a final, remaining source of vapor and could not be eliminated. This gas generation lead to voiding in the bond interfaces and weak bonds. We then utilized mixtures of Ti/B and Ti/C/Cu powders to produce Reactive Foils without the generation of oxygen vapor. However, these foils could not be made reactive enough to propagate through and fully wet components during bonding. In the end, we could not meet our goals for bond strength in dissimilar metal bonds.

References:

1. Goldschmidt, H. Process of Joining Metal Pieces. Google Patents January 6, 1903.

2. Wang, L. L.; Munir, Z. A.; Maximov, Y. M. Review Thermite Reactions: Their Utilization in the Synthesis and Processing of Materials. *J. Mater. Sci.* 1993, **28**, 3693–3708.
3. Wang, J.; Besnoin, E.; Duckham, A.; Spey, S. J.; Reiss, M. E.; Knio, O. M.; Weihs, T. P. Joining of Stainless-Steel Specimens with Nanostructured Al/Ni Foils. *J. Appl. Phys.* 2004, **95** (1), 248–256.
4. Duckham, A.; Spey, S. J.; Wang, J.; Reiss, M. E.; Weihs, T. P.; Besnoin, E.; Knio, O. M. Reactive Nanostructured Foil Used as a Heat Source for Joining Titanium. *J. Appl. Phys.* 2004, **96** (4), 2336.
5. Weihs, T. P. *Fabrication and Characterization of Multilayer Films and Foils*; 2014.
6. Kinsey, A. H.; Slusarski, K.; Woll, K.; Gibbins, D.; Weihs, T. P. Effect of Dilution on Reaction Properties and Bonds Formed Using Mechanically Processed Dilute Thermite Foils. *J. Mater. Sci.* 2016, **51** (12), 5738–5749.
7. Woll, K.; Gibbins, J. D.; Slusarski, K.; Kinsey, A. H.; Weihs, T. P. The Utilization of Metal/metal Oxide Core-Shell Powders to Enhance the Reactivity of Diluted Thermite Mixtures. *Combust. Flame* 2016, **167**, 259–267.
8. Kinsey, A. H.; Slusarski, K.; Krumheuer, E.; Weihs, T.P. *Enhanced reaction velocity and diluent homogenization in Redox Foils using arrested reactive milling thermite powder*, *J. of Mat. Sci.*, 2017, **52**, 11077–11090.
9. Kinsey, A.H.; Behrou, R., Guest, J. K.; and Weihs, T. P. *Critical heat dissipation length scales in fully dense thermite foils*, *Combustion and Flame*, 2018, **190**, 432–440.
10. Zhou, L.; Piekiel, N.; Chowdhury, S.; Zachariah, M. R. Time-Resolved Mass Spectrometry of the Exothermic Reaction between Nanoaluminum and Metal Oxides: The Role of Oxygen Release. *J. Phys. Chem. C* 2010, **114** (33), 14269–14275.

Products:

Journal Papers:

1. K. Woll, J.D. Gibbins, K. Slusarski, A.H. Kinsey, T.P. Weihs, *The utilization of metal/metal oxide core-shell powders to enhance the reactivity of diluted thermite mixtures*, *Combust. Flame*, **167**, 259–267 (2016).
2. A.H. Kinsey, K. Slusarski, K. Woll, J.D. Gibbins, T.P. Weihs, *Effect of dilution on reaction properties and bonds formed using mechanically processed dilute thermite foils*, *J. Mat. Sci.*, **51**, 5738–574 (2016).
3. Alex H. Kinsey, K. Slusarski, E. Krumheuer, T.P. Weihs, *Enhanced reaction velocity and diluent homogenization in Redox Foils using arrested reactive milling thermite powder*, *J. of Mat. Sci.*, **52**, 11077–11090 (2017).

4. A. H. Kinsey, R. Behrou, J. K. Guest, and T. P. Weihs, *Critical heat dissipation length scales in fully dense thermite foils*, Combustion and Flame, **190**, 432-440, (2018).

Patent Application:

1. T. P. Weihs, A. H. Kinsey, K. A. Slusarski, K. Woll, and D. Gibbins, Reactive Composite Foils, filed on 11/30/2015 as US Application number 14/954,508.