Competitive Wetting in Active Brazes

The presence of Al in the alloy enhances the spreading of Ag, while the Ag inhibits the spreading of Al

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ABSTRACT

The wetting and spreading of molten filler materials (pure Al, pure Ag, and AgAl alloys) on a Kovar™ (001) substrate was studied with molecular dynamics simulations. A suite of different simulations was used to understand the effects on spreading rates due to alloying as well as reactions with the substrate. The important conclusion is that the presence of Al in the alloy enhances the spreading of Ag, while the Ag inhibits the spreading of Al.

KEYWORDS

• Active Brazing • Wetting • Spreading • Computer Simulations
• Metals and Alloys • Molecular Dynamics

Introduction

Ceramics are highly desirable structural materials because of their excellent resistance to wear and corrosion, as well as their ability to withstand high temperatures. However, low fracture toughness and lack of ductility can limit applications, particularly when parts may be exposed to high mechanical and thermal stresses. Metals often perform better under such conditions, leading to the use of a combination of metals and ceramics to meet design goals that necessitate the formation of high-quality, strong seals.

Bonding of metals to ceramics can be accomplished through various different manufacturing processes, but active braze joints are preferred, particularly in high-temperature applications. In these cases, the ductility of the filler material can accommodate residual stresses generated during the joining of materials with different coefficients of thermal expansion (CTE). Active metal additives in the filler material (e.g., Ti, Zr, etc.) can assist with the wetting of the metals on the ceramic surface itself.

The details of the interfacial reactions between ceramics and metals remain only nominally understood. An improved understanding of these reactions can help with the choice of additives in the filler material, as well as geometric considerations for the parts themselves. A crucial component of the mechanism behind active brazing is the wetting and spreading of the filler material on the disparate metal and ceramic surfaces, and how this process changes with additives. Wetting phenomena have been the subject of a number of recent review articles, including those that focus on general wetting (Ref. 1), dissolutive (i.e., reactive) wetting (Ref. 2), and the dynamics of precursor films (Ref. 3).

A particular issue of concern with braze joints is runout (braze alloy flows out of the joint) (Ref. 4). This is a result of instabilities in the wetting and spreading of the filler material. While runout can negatively impact the cosmetics of a joint, both mechanical strength and hermeticity can also be affected through residual stresses or unfilled regions in the joint clearance, respectively. Modifications to the geometry of the joint, the chemical composition of the braze alloy, and the overall processing temperatures have been investigated as methods to reduce or eliminate runout, but have met with limited success. One of the goals of this study was to determine chemical driving forces that may lead to runout, in order to better engineer the braze alloy and the joint materials.

The present work addresses wetting and spreading as it applies to active brazing. Molecular dynamics simulations were used to study the wetting and spreading of a liquid braze filler material on Kovar™ substrates (Ref. 5). Kovar™ is a Fe-Ni-Co alloy, with other species at the sub-percent weight composition level. Kovar™ has a low CTE that allows it to be brazed to glasses and ceramics, providing hermetic seals. For the remainder of this work, the term

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Kovar™ will be used to refer to the model alloy Fe(55)Ni(28)Co(17).

While brazing to Kovar™ has been studied experimentally (Refs. 6–9), simulations of the entire braze joint are difficult to perform, due to the lack of availability of atomistic potentials that simultaneously describe both metals and ceramics. This stems, in part, from the different electronic natures of the two materials. The present study focuses on the metallic base material of the braze joint. While experiments have shown that the presence of both the ceramic and the metal are necessary for runout to occur, it has also been found that Kovar™-Kovar™ joints with Al added to the filler material can exhibit this phenomenon. The filler material itself is predominantly silver, with small amounts of Cu and Zr (Ref. 8). In the braze joint, a reduction-oxidation reaction occurs between the Zr and the ceramic (Al2O3) base material, resulting in the formation of ZrO2 at the ceramic. Elemental Al is released from the ceramic, and becomes incorporated in the molten filler material. Because it is not currently feasible to simulate this entire reaction, Al in the filler material is necessary for model runout, this work instead studied a filler material with Al already incorporated and the Zr and Cu components omitted. This approximation is justified, because Cu does not play a role, and while the Zr does, it is sufficiently well understood that it can be neglected (Ref. 1). By studying the behavior of pure metals as well as the alloy, a better understanding of the mechanisms responsible for the brazing process can be developed.

Previous studies have investigated the dynamics of wetting in metal systems (Refs. 10, 11) with a stronger focus on spreading rates, and comparisons to molecular kinetic theory (Ref. 12). Some earlier work compared the results of reactive to nonreactive systems in the case of Ag on Cu (Refs. 13, 14), and a CuAg alloy on Cu (Ref. 14). The latter simulations are closest in spirit to the present work, except for the presence of the substrate material in the liquid drop. The system studied here is inherently more complex (with two components in the filler material, and three in the substrate) leading to an interplay between the elements and results that are challenging to interpret in the context of wetting theory. Therefore, no attempt to study the details of the spreading rates or contact angles was made, and instead this work focused on the effects of substrate interactions and competitive wetting of the braze filler components.

**Simulation Details**

Large-scale molecular dynamics (MD) simulations were used to model the spreading of liquid filler material on a Kovar™ substrate. The LAMMPS simulation code was used with a timestep of 1 fs and a velocity Verlet integration scheme. All simulations were performed at the experimentally used brazing temperature of 1250 K, which is maintained through the use of a Langevin thermostat.

The embedded atom method (EAM) was used, which is related to second moment tight binding theory, and approximates the electron density through the use of an “embedding” term. The EAM is particularly well suited for atomistic simulations of metals, and many potentials exist that have accurately predicted mechanical and structural properties. The EAM potentials were developed by Zhou et al. (Ref. 15), using a normalization procedure that allows for the mixing of multiple components in the simulation. Given the complexity of the current system (Fe, Ni, Co, Ag, and Al), the availability of atomic potentials is quite limited. These specific potentials were fit to shear moduli, elastic anisotropy ratios, and sublimation energies with approximate fits to vacancy formation energies (Ref. 16). While this specific multicomponent alloy potential does not appear to have been previously studied, the potential database used to create it has successfully predicted enthalpies of solution (Ref. 15), which can be used to fit alloy po-
tentials. While a potential specifically created for this alloy would likely provide more quantitative results, it is expected that the alloy interactions generated with this method are acceptable approximations.

The Kovar™ substrate was created from an initial block of pure, single crystal FCC Fe, with the (001) face exposed. Atoms in the substrate were randomly replaced with Ni and Co to form the desired composition. This substrate was then equilibrated at the brazing temperature. Calculated density profiles of the various components demonstrate that the species are thoroughly mixed. Initial simulations held the atoms in the substrate fixed (i.e., forces on the atoms are calculated and then discarded). This allows for study of the wetting of the separate components without the complication of chemical reactions between the filler material and the substrate. Results of wetting simulations with a mobile (i.e., reactive) substrate are presented second, since they are best understood in the context of the results of the initial nonreactive simulations.

The liquid metal was created from an equilibrated bulk sample, in which pure FCC metal was melted and held at the braze temperature of 1250 K. This procedure was duplicated for pure Ag and pure Al samples. Creating the alloy began with the pure Ag sample, followed by random substitution of 15 at.-% of the Ag atoms with Al atoms, and a final re-equilibration. Calculated atomic density profiles show that the Al is well incorporated in the Ag.

The wetting simulations were designed to mimic sessile drop experiments, with one caveat. While full 3D simulations, in which a hemispherical drop of liquid metal was allowed to spread on the substrate, have been performed, it was determined that it was feasible to increase the simulation size without affecting relative spreading rates by instead moving to a quasi-2D simulation. In this geometry, an infinite half-cylinder of liquid spreads on a substrate that can now be much larger in the direction of spreading. The substrate is 56.2 nm in the spreading direction (x), 5.4 nm thick (y), and 5.1 nm perpendicular to the spreading direction (z). The liquid drop initially had a 15-nm radius, and a 5.4-nm thickness to match the substrate. A snapshot of the initial state of the simulation is shown in Fig. 1.

The half cylinder of molten alloy was allowed to spread dynamically on the substrate, in most cases, until the liquid had fully wet the Kovar™. In order to analyze the dynamics of spreading, histograms of the liquid atoms as a function of height through the simulation box were calculated. The bins were 4 Å thick, and for each bin, the radius that contains 95% of the atoms in that bin was found, and plotted as a function of simulation time. In this geometry, the radius refers to a linear distance from the middle of the half-cylinder in the direction of spreading.

Figure 2 shows examples of the binned data for pure Al on fixed Kovar™ for the drop (A) at the beginning of the simulation and (B) after almost 9 ns of simulation time. The profile in Fig. 2A shows the initial curved profile of the drop as can also be seen in Fig. 1, while Fig. 2B shows the drop has spread with a precursor foot that formed near the Kovar™ substrate.

Results – Fixed Substrate

Spreading simulations were performed for pure Al on a fixed Kovar™ substrate. Density profiles for each atomic type are shown in Fig. 3 after ~9 ns of spreading. These density profiles demonstrate that the Kovar™ was reasonably well mixed during the simulation. The liquid Al profile shows a density peak near the surface (corresponding to the first layer of Al on the substrate) with an approximate width of 4 Å, indicating the proper bin size for analysis of the spreading dynamics.

Figure 4 shows the “drop” radius as a function of time for pure Al spreading on fixed Kovar™ for the lowest three nonzero bins. The bin from -4 to 0 Å has been calculated, and indicates no interdiffusion (note that the top of the Kovar™ substrate is at approximately 0 Å), as there are no Al atoms in this bin. This is expected for simulations in which reactions with the substrate are forbidden. In the figure, the first bin from 0 to 4 Å shows the formation of a precursor foot that quickly spreads and covers the entire substrate by approximately \( t = 3 \) ns. Above this layer, from 4 to 8 Å, there is some indication that a second foot forms and spreads but fails to cover the substrate. The dynamics of the two bins above 8 Å, 8 to 12 Å, and 12 to 16 Å (not shown) are similar, indicating that this is the spreading behavior of the bulk drop (i.e., not associated with a precursor foot).

The spreading of a pure Ag drop on the same fixed Kovar™ substrate is substantially different, as shown in Fig. 5. While a precursor foot does extend before the spreading of the main...
drop, the motion of this foot is slower by a factor of approximately 10 as compared to the pure Al, and barely covers the substrate after 30 ns of simulation time. The height of the foot, however, is similar to that in Al. The next two 4 Å layers from 8 to 12 Å and 12 to 16 Å (not shown) show the spreading of the main drop.

Next, the wetting and spreading of a binary alloy with the composition 85Ag-15Al (at.-%) was examined. The behavior of each individual component of the alloy was assessed, and the results were found to be nonintuitive when compared to the pure metals. Figure 6 shows the spreading of the precursor foot region as a function of time for four different simulations: 1) pure Al, 2) pure Ag, 3) Al in the 15Al-85Ag alloy, and 4) Ag in the 15Al-85Ag alloy. These simulations demonstrate that the presence of Ag in the alloy greatly inhibits the spreading of Al, which spreads at a rate close to the pure Ag. These results also show some enhancement of the spreading of Ag in the alloy (as compared to the pure metal) due to the presence of the Al. Also shown for comparison is the spreading of the bulk drop region for the two different components in the alloy. This demonstrates that there is indeed a precursor foot in the alloy, the leading edge of which is composed more of Ag than of Al. Nevertheless, the percentage of Al in the foot is higher than one would expect from the alloy concentrations.

Figure 7 shows the spreading of the bulk of the drop for both components in the alloy as well as the pure Al and Ag systems. From this figure, again it is clear that the presence of Ag inhibits the spreading of Al, although in the case of the bulk drop, it is only in the initial stage of spreading (less than 1-ns simulation time) that the pure Al spreads more quickly. After this time, the rate of spreading is similar to all other species shown.

The disproportionate amount of aluminum at the Kovar™ substrate is clear from the ratio of the number of Al atoms to Ag atoms as a function of height above the substrate. Shown in Figure 8 are the bulk drop spreading of Al in the alloy (solid line), and Ag in the alloy (dotted line). The bin representing the bulk drop is taken from 8 to 12 Å above the surface.

A calculation was made of the surface tension, $\gamma$, of both of the pure metals and the alloy through the mechanical definition of the surface stress (Ref. 17). The calculated values of $\gamma$ are incorrect, including the ordering, for both metals [$\gamma$(Ag) = 725 mN/m and $\gamma$(Al) 874 mN/m] compared to experiment [$\gamma$(Ag) = 917 mN/m and $\gamma$(Al) = 814 mN/m (Ref. 18)]. The difficulty in predicting surface tensions with EAM has been documented previously (Ref. 19), and is not unexpected. While the incorrect ordering, however, could lead to anomalous behavior of the two metals in the alloy, the ratio of $\gamma$(Ag)/$\gamma$(Al) is close to 1.0 in both cases (0.83 for simulations and 1.1 for ex-
experiments), and thus these effects should be weak.

To understand the effects of surface tension on wetting and spreading, it is necessary to be able to calculate the liquid/solid interfacial tension. While methods do exist for calculating this in simple systems (Ref. 20), extending these methods to species like metals, that are characterized by collective interactions, is challenging. Because of this difficulty, it was decided to calculate force-separation curves for the various liquids approaching the Kovar™ substrate. For these simulations, a slab of liquid metal (either pure Al, pure Ag, or the Al15-Ag85 alloy), infinite in the x-y plane but with thickness ~ 3 nm in the z dimension, was equilibrated. The slab was then brought into contact with a Kovar™ substrate at a fixed velocity of 2 m/s, and the force on the liquid was measured as a function of separation.

Figure 9 shows approach curves for pure Al (solid lines), pure Ag (dashed lines), and the Al15-Ag85 alloy (dotted lines). The zero of separation is arbitrary, and serves as a reference point. Figure 9 shows clearly that the Al has a much stronger adhesive interaction with the substrate. This point can be seen both in the earlier start of adhesive forces, as well as the larger magnitude of the adhesion. Stronger adhesion leads to the preferential movement of the Al to the substrate, which enhances the movement of Ag. While this adhesion is an atomistic phenomenon, it likely implies a strong tendency for the Al to alloy with the constituents of the Kovar™, forming the experimentally observed aluminides (Ref. 4).

Results – Mobile Substrate

The wetting and spreading of the Al, Ag, and 15Al-85Ag alloy on mobile Kovar™ (i.e., in which reactions with the substrate are allowed) follow a similar pattern as on the fixed substrate. In Fig. 10, binned data are shown for pure Al spreading on the mobile substrate. Nevertheless, when compared to Fig. 4, which shows the wetting and spreading of pure Al on the fixed substrate, several differences are immediately apparent. On the mobile substrate a line was included that indicates the spreading of Al below the surface of the substrate, from –4 to 0 Å. These data indicate that the Al reacts with the substrate near the initial location of the drop, but does not spread significantly beyond the initial reaction zone. The next two higher bins, from 0 to 4 Å and from 4 to 8 Å, have spreading behavior nearly identical to each other, reaching the edge of the substrate in less than 15 ns. When compared to the highest bin shown, it can be inferred that the two intermediate bins show some advanced spreading of a rather thick precursor foot above the reaction zone.

The spreading behavior of the pure Ag on the mobile substrate, shown in Fig. 11, is qualitatively similar with the notable exception of the bin from 0 to 4 Å, which spreads only slightly more quickly than the subsurface bin. This implies that the Ag reacts strongly with the substrate throughout these first two layers, and only above this (i.e., from 4 to 8 Å) can a foot begin to spread. This interpretation is further validated through analysis of the spreading of the separate components in the 15Al-85Ag alloy, shown in Fig. 12. Both below (–4 to 0 Å) and at (0 to 4 Å) the surface, Al and Ag show similar dynamics. It is only in the next higher layer that the foot dynamics are revealed, where it is clear that Ag in the alloy spreads significantly faster than Al in the alloy, and comparison to Fig. 11 shows that Ag in the alloy spreads faster than the pure Ag alone.

The changes in spreading rates in the alloy as compared to the pure components can only be ascribed to the competitive wetting of the two constituents. In Fig. 13, a comparison is made between the spreading of the precursor feet in the pure metals and the separated components of the alloy. For the reasons discussed above, the bin used to describe the foot is from 4 to 8 Å. While in the case of pure metals, Al spreads somewhat faster than Ag, competitive wetting in the alloy leads to significantly different behavior. The Al in the alloy spreads much more slowly than either of the pure metals, or the
Ag in the alloy, while the Ag in the alloy spreads at the rate of pure Al. These results suggest that it is possible to control the speed at which certain components of an alloy spread by tailoring the composition of that alloy. Wetting can also be affected by pretreating the faying surface with a coating that changes spreading behaviors.

To investigate this concept, two cases were studied, the first was an alloy with a higher Al content, namely 30Al-70Ag, and the second by prewetting the surface with a monolayer of pure Al. The results of the spreading of the 30Al-70Ag alloy are also shown in Fig. 13, where it is clear the increase of the Al content has essentially no effect on the spreading of the Ag, but results in faster spreading of the Al itself. As the percentage of Al in the filler material increases, so should the rate of spreading of the Al, approaching that of the pure metal.

The effects of pretreating the surface by creating a Kovar™ substrate with a monolayer of Al already pre-wet on the surface were investigated. This substrate was created by starting from the simulations of pure Al spreading on the fixed substrate. When the Al had fully spread on that substrate, a monolayer of Al atoms was removed from the top of the fixed Kovar™, and added to the top of a mobile Kovar™ substrate. This simulation was then equilibrated before the half-cylinder of 15Al-85Ag alloy was placed on top and allowed to spread. In Fig. 14, the results of the Ag component of the alloy spreading on the monolayer are shown, and compared to the spreading of Ag in the same alloy on the mobile surface without the pre-wet layer. The presence of the monolayer makes the identification of the correct bin for the foot slightly more difficult, as the bin from 4 to 8 Å shows some irregularities. Therefore, the data from the next higher bin have also been included. It is clear, especially in comparison to the data without the pre-wet layer, that an existing coating of Al causes the Ag in the alloy to spread significantly faster than over an untreated substrate. While this effect has been seen previously and ascribed to lubrication of the substrate by the precursor film (Ref. 3), the present work seems to point at a different explanation that is addressed in the next section.

Discussion

The results presented here show the Al liberated from the oxidation-reduction reaction at the ceramic surface quickly moves through the braze filler material to the Kovar™ surface. This effect seems to be mostly due to a higher affinity of the Al for the Kovar™ (as compared to the Ag that forms the bulk of the filler material), although surface energy effects cannot be completely ruled out at the present time. Experiments found that Al has a lower surface energy than Ag, and thus would be expected to preferentially coat a surface. In our simulations, however, the situation is reversed. The calculations presented here find that the Al has a slightly higher surface energy than Ag, and would tend to allow the Ag to cover the surface. In both simulations and experiments, however, the surface energies are close to each other, implying that this effect would not be very strong. Experiments can be strongly affected by oxidation, which can alter the surface energies, but these calculations indicate that other factors dominate the spreading.

Regardless of the cause, the presence of Al at the Kovar™ surface in all cases enhances the rate of spreading of the Ag, and it is likely that this is the source of the instability leading to runout. This could be ascribed to a lubrication effect, as discussed elsewhere (Ref. 3), but this does not appear to be the case in our simulations. Additional simulations in which a thin monolayer stripe of Al is present on the Kovar™ surface along the wetting direction were performed. This stripe was 1 nm in width (i.e., perpendicular to the spreading direction) along the entire length of the substrate. With the 15Al-85Ag alloy on top of this prepared substrate, there is no enhancement of the Ag spreading rate over the system in which the
Elemental Al is liberated from the material and the substrate are supplied. It is proposed that this competitive effect, if it exists in this system, is not a strong effect. Note that the diffusivity of Al on the Kovar substrate necessitates that these “stripe” simulations be performed with a fixed substrate (and stripe) to maintain the structure of the pre-wet Al stripe.

In previous simulation work, it has been found that spreading is enhanced in reactive systems (Refs. 13, 14). While the present simulations show a slight enhancement of the spreading of Ag on a mobile substrate compared to the fixed substrate (not shown here), this is for the pure metal only. The Ag component of the 15Al-85Ag alloy, on the other hand, shows essentially no difference in spreading behavior on the two substrates. Similarly, the Al in the alloy spreads at nearly identical rates on the fixed and mobile substrates. The pure Al, in contrast, shows a significant decrease in spreading on the mobile substrate compared to the fixed. These results imply that the changes in spreading rates between reactive and nonreactive systems is strongly dependent on the specific elements, and more work will need to be performed to understand these results.

Conclusions

In this work, the wetting and spreading of pure Al and Ag on a (001) Kovar substrate was studied, as well as the spreading of two different Al–Ag alloys, with the goal of understanding the cause of filler material runout in active brazes. The results presented show that while in the case of pure metals Al spreads more quickly than Ag, the multicomponent interactions in the alloy lead to nonintuitive results. On both frozen substrates (in which interactions between the filler material and the substrate are suppressed) and mobile substrates (in which all interactions are allowed to proceed), the presence of Al in the alloy leads to faster spreading of the Ag. It is proposed that this competitive effect is the mechanism behind runout. Elemental Al is liberated from the Al$_2$O$_3$ during the brazing process, and quickly migrates through the braze alloy to the Kovar surface. The presence of Al at the Kovar surface results in faster spreading of the Ag in the braze alloy, leading to potential runout.

While these results are atomistic in nature, what is clear is that there exists one aspect of the wetting and spreading that is atomistic in nature (the precursor foot), and one that is more macroscopic (the spreading of the bulk drop on top of this precursor foot), and thus representative of experiments. The differences in spreading rates, both in the precursor foot as well as in the bulk drop, should accurately reflect the spreading seen experimentally, within the accuracy of the potentials used.

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References

5. Kovar is a registered trademark of Carpenter Technology Corp., Wyomissing, Pa.