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Bonding Low-density Nanoporous Metal Foams Using Sputtered Solder

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INTRODUCTION

A method has been developed for bonding low-density nanoporous metal foam components to a substrate using solder that is sputtered onto the surfaces. Metal foams have unusual properties that make them excellent choices for many applications, and as technologies for processing these materials are evolving, their use in industry is increasing dramatically. Metal foams are lightweight and have advantageous dynamic properties, which make them excellent choices for many structural applications.^[1,2] They also provide good acoustic damping, low thermal conductivity, and excellent energy absorption characteristics. Therefore, these materials are commonly used in the automotive, aerospace, construction, and biomedical industries. The synthesis of nanoporous metal foams with a cell size of less than 1 μm is an emerging technology that is expected to lead to widespread application of metal foams in micro-devices, such as sensors and actuators.^[3,4] One of the challenges to manufacturing components from metal foams is that they can be difficult to attach to other structures without degrading their properties. For example, traditional liquid adhesives cannot be used because they are absorbed into foams. The problem of bonding or joining can be particularly difficult for small-scale devices made from nanoporous foam, due to the requirement for a thin bond layer. The current study addresses this problem and develops a method of soldering a nanoporous metal foam to a substrate with a bond thickness of less than 2 μm .

There are many applications that require micro-scale metal foams precisely bonded to substrates. This study was motivated by a physics experiment that used a laser to drive a shock wave through an aluminum foil and into a copper foam, in order to determine the speed of the shock in the copper foam. To avoid disturbing the shock, the interface between the copper foam and the aluminum substrate had to be as thin as possible. There are many other applications that could benefit from the bonding technology developed in this study, such as small-scale lightweight structural members, high-strength thermal insulating layers for electronics, and micro-scale mechanical dampers, to name but a few. Each of these applications requires one or more small metal foam components precisely bonded to a substrate.

Several methods for bonding metal foam components have been developed by previous researchers.^[5] Macroscopic metal foam parts have been successfully bonded by laser welding to create T-sections and butt joints.^[6] Ultrasonic welding has been used to join aluminum sheet metal to aluminum foam for structural applications.^[7,8] These methods work well for bonding large foam components, but reducing these methods to a smaller length scale would be challenging. One method that has shown great potential for bonding layers of metal foams to substrates is a brazing process that uses a sputter-deposited interface material. Shirzadi et al.^[9] have demonstrated bonds between stainless steel foam and a stainless steel substrate using a layer of copper-titanium filler metal that is sputtered onto the interface surfaces. The foam pieces that they bonded were approximately 10 mm in diameter and 10 mm thick with a cell size of approximately 200 μm . After depositing the filler material, pressing the materials together, and heating them with an induction heater, bonds were achieved without causing significant damage to the foam.

The current study also uses a sputter-deposited interface material to bond foam to a substrate. However, in contrast to previous work, the current study examines bonding micro-scale pieces of fragile nanoporous metal foam. In this study, a method is developed to bond a thin sheet of fragile, low-density nanoporous copper foam to an aluminum foil substrate of thickness 40 μm . By sputter depositing an indium-silver alloy onto the foam and the substrate, a solder joint with a thickness of less than 2 μm was achieved.

PREPARATION OF NANOPOROUS COPPER FOAM

Material Synthesis

Several methods have been developed for synthesizing nanoporous copper foam materials.^[10-12] The nanoporous copper foams used in this study were synthesized using a filter casting method.^[12] In this method, commercially available copper nanoparticles with diameters of 10 nm to 70 nm and polystyrene spheres with a diameter of approximately 1 μm provide the building blocks for the porous monoliths.

The foam material was created by first making a liquid suspension of copper nanoparticles and polystyrene spheres in deionized water. An ultrasonication process homogenized the liquid suspension by breaking up particle agglomerates, thereby ensuring a uniform monolith. This suspension was then placed in a Teflon tube embedded in a water-absorbing medium. As the water was absorbed and the particles were deposited onto the surface of the medium, a uniform monolith consisting of 1 μm diameter polystyrene particles uniformly dispersed in a network of copper nanoparticles formed inside the tube. The monolith was then annealed at 400 °C in a mixture of 96% Ar and 4% H₂ to sinter the copper nanoparticles together. The heating process also reduced the native oxide and removed all of the polystyrene particles, replacing them with gas and leaving only an open network of sintered copper nanoparticles with a relative density of approximately 15% to 20%. Energy dispersive x-ray spectroscopy (EDS) measurements of this nanoporous copper foam material revealed that its composition was approximately 98 weight % copper and 2.3 weight % oxygen.

Diamond Turning

The result of this process was a billet of copper foam material approximately 6 mm in diameter and 2 to 3 mm thick, as shown on the left side of Figure 1. This material had a relative density of less than 20%, so it was approximately 80% air-filled void space. From this piece of material, a component had to be made with dimensions 1 mm \times 1 mm \times 30 μm . This component was created using a diamond turning process. The billet of foam was glued to a holder that was placed in the spindle of a precision lathe. Using a single point diamond cutting tool with a nose radius of 25 μm and a primary clearance angle of 6°, the material was faced flat, and the diameter was machined to 3.75 mm. The diamond turning was performed using a spindle speed of 1600 rpm. Roughing cuts were performed with a depth of cut of 5.1 μm and a feedrate of 1.9 μm per revolution. Finishing cuts were performed with a depth of cut of 1.3 μm and a feedrate of 1.3 μm per revolution. The disk of material was then parted off, and the diamond turned face was placed against a vacuum chuck in the spindle of the precision lathe. The parted surface of the foam disk was then diamond turned to create a flat surface, which reduced its thickness to approximately 0.5 mm. An image of the foam part at this stage in the process appears in the center of Figure 1. After measuring the diameter and thickness of the foam disk, its mass was measured, so that its density could be determined.



Figure 1. Copper foam material cast in the synthesis process (left), diamond turned to a disk (center), and cut into a 1×1 mm square (right)

Using a razor blade, the foam material was cut into pieces that were approximately 1 mm × 1 mm squares with a thickness of 0.5 mm, as shown on the right side of Figure 1. The two large faces of each square of foam had flat, diamond turned surfaces, but the surfaces that were cut with the razor blade were much rougher. However, the only important surface on the part was the face that would be coated with solder and bonded to the aluminum substrate. Therefore, the other surfaces were not required to be flat, and rough surfaces were acceptable. Because of the extremely fragile nature of the copper foam material, it was not possible to create freestanding components with the desired final thickness of 30 μm. Instead, the material was bonded to the aluminum substrate when it was still 0.5 mm thick, and it was later diamond turned to its final thickness of 30 μm.

BONDING PROCESS

The solder used to bond the copper foam to the aluminum substrate consisted of indium with 3 weight % silver, which is a eutectic alloy with a eutectic temperature of 144 °C. The solder was deposited on the materials using a sputtering process. In order to deposit the solder onto the copper foam, a method had to be devised to pick up and handle the fragile material. The nanoporous copper foams produced for this study were brittle and extremely fragile. The robustness of metal foams can be highly dependent on the cell size and relative density. Researchers have shown that the strength of nanoporous gold foam varies greatly with the microstructure,^[13-15] and the same is likely true for nanoporous copper foams. Nanoporous copper foams have been produced with relative densities of only a few percent, but these low-density foams are composed of small nano-scale copper particles, which makes them fragile and difficult to handle. Picking them up with a vacuum device or with tweezers posed a great risk of fracturing or chipping the edges. Therefore, to avoid the difficulties associated with handling extremely fragile materials, this initial study used a reasonably robust foam with a relative density of approximately 20%.

To deposit solder on one of the faces of this small, fragile component, a special gripper was fabricated. The gripper was similar to a set of tweezers that held the foam between a flexible stainless steel reed and a rigid arm by lightly pinching two of the razor-cut surfaces, leaving the diamond turned surface exposed. The gripper was used to pick up the 1 mm foam

square, hold it upside down in the sputtering system during deposition, move it to the assembly area, and place it during assembly.

The gripper was mounted in the sputtering system along with the 40 μm thick aluminum foil that would be bonded to the foam. The surfaces of the foam and aluminum were ion milled for 2 min at 500 eV to remove the oxide layers. A layer of titanium was then deposited on both surfaces to promote adhesion. Initially, 10 nm of titanium was deposited, followed by an additional 10 nm of titanium that was cosputtered with indium-silver solder alloy. Next, approximately 0.7 μm of the indium-silver solder alloy was deposited. Photographs of a foam square in the gripper before and after deposition of the solder appear in Figure 2.

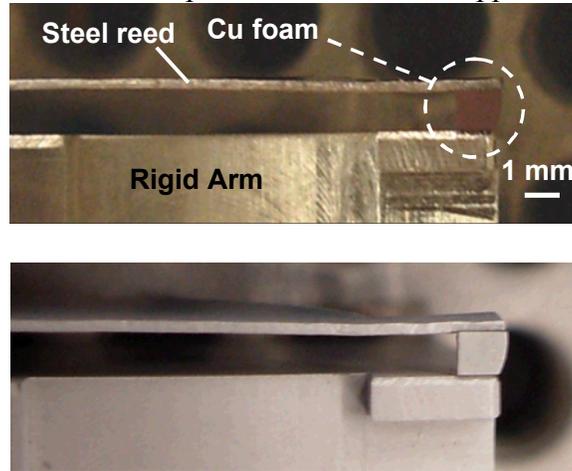


Figure 2. Copper foam sample held in the gripper before (top) and after (bottom) coating it with solder

The coated aluminum foil and the gripper containing the coated foam were removed from the sputtering system and placed into an assembly fixture with the coated surfaces facing each other. Because the aluminum foil was only 40 μm thick, it had a tendency to warp. Therefore, the assembly fixture included a vacuum chuck that held the aluminum foil flat during assembly and bonding. The gripper containing the foam was placed on a three-axis stage that allowed the operator to move it with respect to the aluminum foil with a resolution of a few μm . With the aid of a microscope, the copper foam square was placed on top of the foil and then released from the gripper. A schematic illustration of the parts assembled together for the bonding process appears in Figure 3.

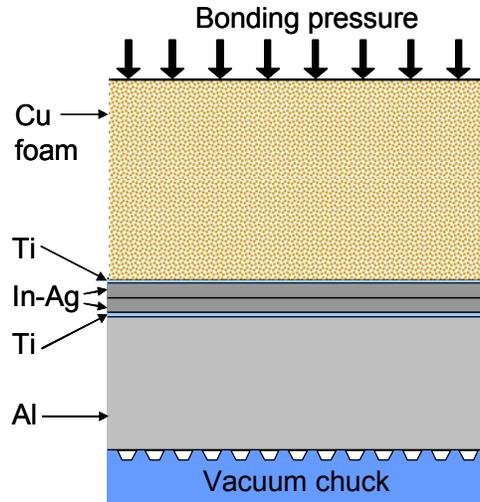


Figure 3. Assembled components

The assembly fixture used a weighted arm to press the components together. A steel ball of diameter 1.6 mm at the end of the arm was carefully aligned over the square of copper foam using a microscope that viewed the parts from the side. The force exerted by the ball onto the foam had to be large enough to create a strong bond, but small enough to avoid damaging the foam at the bonded interface. The yield strength of the foam was measured using indentation tests. The yield strength of foams with a large proportion of voids is known to be approximately equal to the hardness,^[16,17] which was approximately 5 to 6 MPa for this 20% dense foam. After gently lowering the ball onto the foam, the ball exerted a compressive force of 0.3 N between the components. This load corresponded to an average pressure of approximately 300 kPa at the interface surface, which was approximately 6% of the yield strength of the foam. Therefore, although this load resulted in an indentation mark on the surface of the foam, it did not damage the material at the interface. The assembly fixture was then placed into an oven set to 180 °C to heat the parts and melt the solder. Using a thermocouple embedded in the assembly fixture for temperature feedback, the parts were heated to a temperature of 156 °C, at which point they were removed from the oven so they could cool back to room temperature.

After cooling to a temperature of 25 °C, the weighted arm was lifted from the foam, and the bonded components were removed from the assembly fixture. An indentation mark from the steel ball was evident on the surface of the foam, but the deformed foam material was machined away in the next step. The assembly was mounted on a precision lathe by placing the uncoated surface of the aluminum foil against a flat vacuum chuck on the spindle. The vacuum chuck held the part off-axis, a distance of 100 mm from the axis of rotation of the spindle. Using a spindle speed of 1600 rpm, the copper foam was flycut from a thickness of about 0.5 mm to a thickness of 30 μm using the diamond tool. The completed part was then removed from the precision lathe.

INTERFACE CHARACTERIZATION

Several of the completed assemblies were examined to characterize the bonded interface. After initially attempting to examine the interface by potting one of the assemblies in a resin, sectioning it with a saw, and then polishing it, it was discovered that the foam was not strong enough to withstand a polishing process. The mechanical forces from the polishing process

created surface damage that made it impossible to see the interface between the copper foam and the aluminum substrate. Therefore, the parts had to be sectioned using a more precise method.

One of the parts was placed in a Focused Ion Beam (FIB) system, which machined a $100 \times 100 \mu\text{m}$ section through the $40 \mu\text{m}$ thick aluminum foil and into the copper foam using a 30 keV Ga focused ion beam. After rough machining the section with a current of 20 nA , a final side-wall polish of the cross-section was performed using a current of 7 nA . It was very important that the machining be performed from the aluminum side of the part. Parts that were machined from the copper foam side contained artifacts created by secondary sputtering from the ion beam. As the foam was being bombarded with ions, some of the ions passed directly through the porous copper foam and struck the underlying aluminum substrate. A portion of the substrate material was ablated by the ions and then redeposited back up into the copper foam. The result of this ablation and redeposition was a gap between the copper foam and the aluminum substrate with a thickness of several μm , which made it impossible to characterize the bonded interface. However, by turning the sample over and machining from the back side so that the ions machined first through the full-density aluminum substrate and then into the porous copper foam, there were no noticeable issues with artifacts created by secondary sputtering or redeposition.

The surface that was cross-sectioned and polished with the FIB was examined with a scanning electron microscope (SEM). An image of the interface appears in Figure 4. The $40 \mu\text{m}$ thick aluminum substrate appears in the bottom portion of the image. The nanoporous copper foam appears in the top portion of the image, which clearly shows the sub- μm pores in the material. The indium-silver solder alloy is evident between the foam and the substrate, and the two layers of solder that had been deposited on the individual components appear to have melted together to form a single layer. As shown in the image, the indium-silver solder layer had a thickness of approximately $1.5 \mu\text{m}$ and did not wick into the foam to any significant extent. The diamond turned surface of the copper foam appears to be seated flush against the aluminum substrate, and there are no voids in the foam at the interface larger than a few μm . Furthermore, there is no evidence that the foam was compacted or suffered any other type of damage from the pressure applied during the bonding process.

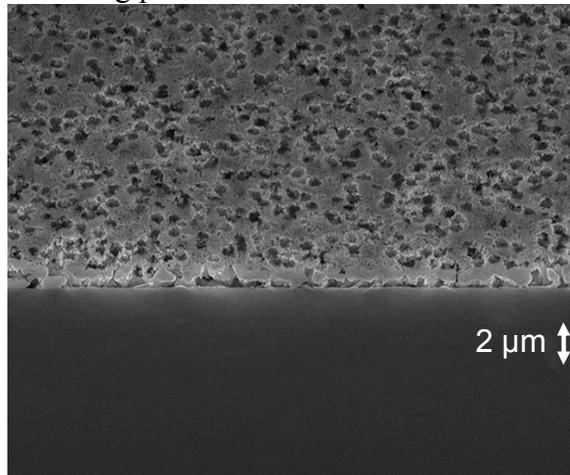


Figure 4. Bonded interface between the nanoporous copper foam and the aluminum substrate

This method can create relatively robust bonded interfaces that are stronger than the foam material. The actual strength of the bond is a function of several factors, including the pressure applied when melting the solder, the oven temperature, and the composition of the atmosphere.

Any oxidation of the indium solder that occurs after removing the parts from the sputtering system also has a large impact on the bond strength. In this case, when the bonded samples were stressed, failure usually occurred within the nanoporous copper foam rather than at the interface.

DISCUSSION

The process developed in this study successfully bonded the foam to the substrate while preserving the advantageous properties of the nanoporous foam material. Unlike a bonding process that uses a liquid adhesive that can be absorbed into the foam, the sputter-deposited solder acted only on the surface of the foam and created an interface layer with a thickness of 1.5 μm . Therefore, almost all of the foam material maintained its porosity. The fact that the molten solder did not wick into the copper foam may have been related to the oxide on the surfaces of the copper linkages that made up the foam. Because copper oxidizes readily, all surfaces exposed to the atmosphere would be expected to form an oxide layer to which a solder would not adhere. It is for this reason that the copper foam was ion milled prior to depositing the titanium adhesion layer and the indium-silver solder. Because the ion milling and titanium deposition acted only on the surface material in the line of sight of the sputtering system, only these surfaces of the copper linkages were receptive to the molten solder. The linkages just below the surface of the foam maintained their surface oxide, which may have prevented the molten solder from being drawn into the foam. The bonding process also did not compact or otherwise densify the foam material, so it maintained its low-density, porous properties.

This bonding process could be used with other types of foam materials for a variety of applications. However, solders must be selected to be compatible with the materials. Likewise, appropriate fluxes, adhesion layers, or ion milling processes must be carefully selected. For example, this study used an indium-based solder with a relatively low eutectic temperature in order to minimize thermal stress, because the thermal expansion coefficient of aluminum is 50% larger than that of copper. In addition, a titanium adhesion layer was used, because it is well known to promote adhesion to aluminum. This bonding process is applicable to components of varying shapes and sizes. One of the difficulties in the current study was handling extremely small, fragile foam components, and special hardware had to be developed to move them between the different stages of the bonding process. Larger pieces would be easier to handle and could be joined to form complex structures. Bonding dissimilar materials can be complicated by differences in their coefficients of thermal expansion, which can lead to thermal stress during the bonding process. Therefore, careful attention must be given to the material properties, the component size and geometry, and the melting temperature of the solder.

CONCLUSIONS

A method has been developed for bonding low-density nanoporous metal foam to a substrate with a bond thickness of a few μm . In the bonding process, a sputtering system was used to deposit a sub- μm layer of indium-silver solder onto the surface of a nanoporous copper foam and on the surface of an aluminum substrate. After assembling the components together, they were heated to melt the solder and bond them together. The resulting interface contained a layer of indium-silver solder with a thickness of approximately 1.5 μm . Analysis with a scanning electron microscope indicated that the copper foam was seated flush against the aluminum substrate, and there were no voids in the foam at the interface larger than a few μm . Furthermore, there was no evidence that the foam was compacted or suffered any other type of damage during the bonding process. Therefore, this bonding process allowed the foam to be

joined to a substrate while maintaining its advantageous nanoporous properties. This process could be used to bond other types of foam materials of varying shapes and sizes.

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REFERENCES

- [1] K. Ito, H. Kobayashi, "Production and Fabrication Technology Development of Aluminum Useful for Automobile Lightweighting," *Adv. Eng. Mater.* **2006**, *8*, 828-835.
- [2] R. Neugebauer, T. Hipke, "Machine Tools with Metal Foams," *Adv. Eng. Mater.* **2006**, *8*, 858-863.
- [3] J. Erlebacher, M. J. Aziz, A. Karma, N. Dimitrov, K. Sieradzki, "Evolution of Nanoporosity in Dealloying," *Nature* **2001**, *410*, 450-453.
- [4] J. Weissmüller, R. N. Viswanath, D. Kramer, P. Zimmer, R. Würschum, H. Gleiter, "Charge-Induced Reversible Strain in a Metal," *Science* **2003**, *300*, 312-315.
- [5] T. Bernard, H. W. Bergmann, C. Haberling, H. G. Haldenwanger, "Joining Technologies for Al-Foam-Al-Sheet Compound Structures," *Adv. Eng. Mater.* **2002**, *4*, 798-802.
- [6] H. Haferkamp, J. Bunte, D. Herzog, A. Ostendorf, "Laser Based Welding of Cellular Aluminium," *Sci. Technol. Weld. Joining* **2004**, *9*, 65-71.
- [7] C. Born, H. Kuckert, G. Wagner, D. Eifler, "Ultrasonic Torsion Welding of Sheet Metals to Cellular Metallic Materials," *Adv. Eng. Mater.* **2003**, *5*, 779-786.
- [8] C. Born, G. Wagner, D. Eifler, "Ultrasonically Welded Aluminium Foams/Sheet Metal – Joints," *Adv. Eng. Mater.* **2006**, *8*, 816-820.
- [9] A. Shirzadi, M. Kocak, E. Wallach, "Joining Stainless Steel Metal Foams," *Sci. Technol. Weld. Joining* **2004**, *9*, 277-279.
- [10] H. C. Shin, J. Dong, M. Liu, "Nanoporous Structures Prepared by an Electrochemical Deposition Process," *Adv. Mater.* **2003**, *15*, 1610-1614.
- [11] J. R. Hayes, A. M. Hodge, J. Biener, A. V. Hamza, K. Sieradzki, "Monolithic Nanoporous Copper by Dealloying Mn-Cu," *J. Mater. Res.* **2006**, *21*, 2611-2616.
- [12] J. R. Hayes, G. W. Nyce, J. D. Kuntz, J. H. Satcher, A. V. Hamza, "Synthesis of Bi-modal Nanoporous Cu, CuO and Cu₂O Monoliths with Tailored Porosity," *Nanotechnology* **2007**, *18*, 275602.
- [13] A. M. Hodge, J. R. Hayes, J. A. Caro, J. Biener, A. V. Hamza, "Characterization and Mechanical Behavior of Nanoporous Gold," *Adv. Eng. Mater.* **2006**, *8*, 853-857.
- [14] A. M. Hodge, J. Biener, J. R. Hayes, P. M. Bythrow, C. A. Volkert, A. V. Hamza, "Scaling Equation for Yield Strength of Nanoporous Open-cell Foams," *Acta Mater.* **2007**, *55*, 1343-1349.
- [15] J. Biener, A. M. Hodge, A. V. Hamza, "Microscopic Failure Behavior of Nanoporous Gold," *Appl. Phys. Lett.* **2005**, *87*, 121908.

- [16] M. C. Shaw, T. Sata, "The Plastic Behavior of Cellular Materials," *Int. J. Mech. Sci.* **1966**, 8, 469-478.
- [17] M. Wilsea, K. L. Johnson, M. F. Ashby, "Indentation of Foamed Plastics," *Int. J. Mech. Sci.* **1975**, 17, 457-460.