# COPPER AND SILVER MOKUME GANE

Chris Ploof
Chris Ploof Designs
Leominster, MA, USA

Stewart Grice
Hoover & Strong
Richmond, VA, USA

James Binnion
James Binnion Metal Arts
Bellingham, WA, USA



## INTRODUCTION

Mokume gane is a demanding, technical art form of great beauty. Three or more layers of nonferrous materials are stacked together into a billet, bonded using solid state or liquid phase diffusion bonding, manipulated by twisting, cutting, carving, die-striking and machining, and finally forging and/or rolling to yield wood grain patterns. This generally results in losses of up to 60% (occasionally more) from the starting weight of the billet. This incredibly large amount of waste is why many makers of mokume gane will experiment with base-metal billets, followed by copper (and copper alloys of shakudo and shibuichi) and sterling silver combinations. This allows you to have a lower price billet to develop patterns and also products. Additionally, these traditional combinations have the ability to take on a myriad of patinas and look beautiful together.

Unfortunately, the hardest combinations to bond and work tend to be these lower-cost combinations, with sterling silver and copper being high on the difficulty spectrum (just ask any long-time maker of mokume gane what they think of all precious metal vs copper and sterling silver billets). This can lead to frustration and ultimately, a lack of interest in pursuing well-bonded copper and silver mokume gane whether for practice, jewelry or hollowware applications. This paper shares best practices based on controlled firing over 30 billets of silver (sterling and fine) and copper mokume, testing the resulting materials and also examining them with metal micrography.

Beyond the problems of bonding and working these materials, they are highly susceptible to galvanic corrosion. This is something that must be discussed as it limits how they can be used for making quality jewelry.

## GALVANIC CELL

What is a galvanic cell and why is it worth mentioning when we talk about mokume? James Binnion, one of the co-authors of this paper made a blog post in 2012[1] about this reaction and how it relates to all jewelry, not just mokume. This blog is summarized with James' permission here:

"When you join two metals together in a ring you will also create something that, under the right circumstances, can destroy your work. Two metals joined together in the presence of an electrolyte create an electrolytic cell which is in essence a battery. In a ring, the electrolyte is provided by the water you constantly expose your hands to through washing, sweat, swimming, etc. One of the metals will be more electrically positive or anodic and one will be more electrically negative or cathodic. The difference between these poles is measured in volts. When exposed to the electrolyte, the anode will dissolve and supply ions to the electrolyte, just like electroplating or electroetching. The higher the voltage the greater the activity and the faster the anode will dissolve. Which metal is the anode and which is the cathode will be determined by their atomic properties but can be looked up in a chart called a galvanic series. The higher a metal is on this chart the more noble it is and the more cathodic or negative it is. You will note the precious metals are at the top of the chart and that is why you will occasionally hear them referred to as noble metals."

So, what all does this mean? If you combine silver and copper, you will have created an electrolytic cell where the silver is the cathode and the copper is the anode. The ring in this test is mokume but it will not matter how the copper and silver are bonded, soldered or riveted. Two or more metals will still create an electrolytic cell. If you place it in contact with an electrolyte then the copper will give off ions to the electrolyte and dissolve. How fast, is the next question, or at least that is what James wanted to know. There are defined standards for test solutions to simulate human sweat for testing things like colorfastness of fabric dyes and the like. Another one is used to test for nickel release in jewelry items by the EU. James researched these and picked one that seemed to be both easy to make and not too concentrated.





The decision was made to use a solution of 7.5g/l NaCl, 1.2g/l KCl, 1g/l urea, 1ml/l lactic acid with a pH of 4.57, which is one of the solutions recognized as artificial sweat.

This solution was placed into a beaker at room temperature and the ring in Figure 1 was suspended in it, hanging on a piece of nylon monofilament. The plan was to check the ring after a week, but curiosity overtook James after just one day— he took a quick peek and was very surprised to see that the ring already had visible etching (Figure 2) as evidenced by the crystal structure appearing on the copper surface.

*Figure 1: Day 0, new ring ready to be tested*

*Figure 2: Day 1, etching has already started*

The decision was then made to check back after two more days in the solution. On day three, the crystal structure of the copper was very pronounced (Figure 3).

*Figure 3: Day 3 of testing*

By day seven, the ring was severely etched, with small areas of copper completely etched away (Figure 4).

*Figure 4: Day 7, ring is deeply etched*

On day ten, the ring was more severely etched with large areas of copper missing (Figure 5). If the experiment had continued, the ring would have completely fallen apart. The decision was made to stop the experiment at this point.

*Figure 5: Day 10, ring is severely etched*

When James wrote this blog post, there was resistance from other makers, and lots of question as to what the real time frame for this would be like. Figure 6 shows a new ring made from 18k yellow gold and shakudo (a copper alloy with inclusion of 4-10% gold). Figure 7 shows a deeply etched photo of the same metal combination after approximately three years. A real-life example of the destruction caused by electrolytic etching.

*Figure 6: 18K yellow gold and shakudo ring new*





PLOOF

*Figure 7: 18K yellow gold and shakudo ring after approximately three years of wear*

What should one take away from this? Very simply, rings where copper or other base metals are a part of the mix of metals are not going to have a long lifetime. Making wedding rings out of copper/silver or gold/copper, gold/shakudo silver/shibuichi, etc. is not a good idea if you want them to truly last a lifetime. Mokume made entirely out of precious metals is expensive, however, and there are always people looking for a less expensive option. Should you choose, as a maker, to make rings incorporating these materials, you must be prepared to be honest with your customers and make sure they understand the ramifications. We choose to offer a small selection of silver and shibuichi (a copper alloy with inclusion of 5-25% silver) rings which we heavily etch. We explain to our customers that these rings will have a limited lifespan, and offer to take them back for partial trade towards all precious mokume gane rings in the future.

So, with this in mind, let's take a look at what we did to create our billets, and the results we achieved.

## BILLET COMPOSITION AND FIRING METHOD

Billets were comprised of a total of 19 layers of material across two systems. We made billets of copper alloy 110 (high conductivity copper) and sterling silver, and billets of copper alloy 110 and fine silver. Billet stacking order was alternating copper and silver sheets. Dimensions of the sheets were 2.5" x 0.5" x 0.040" (63.5 mm x 19 mm x 1 mm). The decision to test both sterling silver and copper and fine silver and copper was made early on. It was done to see what differences, if any, would be found in firing.





The method used to fire the billets is what we would refer to as our "standard" practice, and was detailed in the Santa Fe Symposium's 2016 "Mokume Gane History and How-to: A Survey of Technique."[2] I've added a few details for the slight changes we have made since then, but by and large, the technique has remained the same for the past several years with a few small tweaks.

The material was thoroughly cleaned using mounted Scotch-Brite buffs on a polishing motor, making sure to thoroughly clean both sides, cutting in two directions. Care is also taken to clean all four edges of the sheet. This was followed by cleaning using Citranox and distilled water, followed by a thorough drying with lint free cloth.

Once the sheets were cleaned, they were stacked into their alternating layers of copper and silver, and the two opposing corners were tacked using a micro tig welder so the billet could be handled without danger of the layers sliding apart.

The billet was then placed between torque plates of A286 stainless steel with four holes for Inconel 718 bolts and then placed into our Bonny Doon 50-ton press and pressed until there was plastic deformation of the materials. At this point, with the press holding the stack and the torque plates together, the bolts were tightened to 90-foot pounds of torque (122 Newton-metres). After this pre-loading of the billet, it was 18.5 mm tall.

The assembly was placed in a foil bag along with charcoal, and then placed into the kiln while the kiln was at room temperature. The kiln was started and ramped as fast as possible to 1350°F (730°C), and upon completion of the firing schedule removed from the kiln and foil bag and hot-pressed to 0.59" (14.8 mm) using stop blocks to achieve a 20% reduction.

After billets had reached room temperature, they were cold-pressed in our 50t Anyang Forging Press to 12 mm, or just shy of a 20% reduction.

After the cold pressing, the layers have some uneven extrusion on the four sides of the billet (Figure 8).

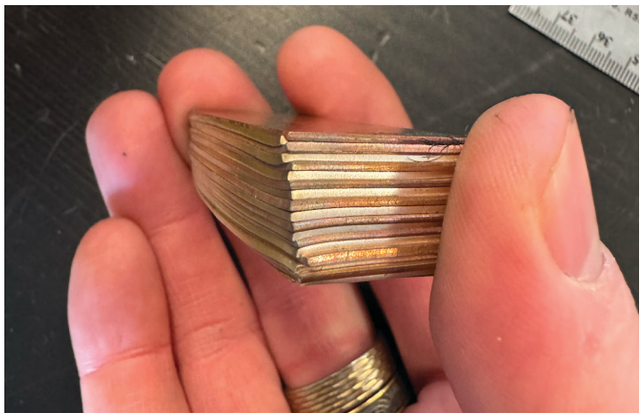

*Figure 8: Overlapping layers after pressing*

We have found it is extremely important to remove these overlapping areas so they do not act as stress risers. The four sides of the billet were trimmed back 0.080" (2 mm) past the most recessed layer of material. Then, the resulting billet was split in half lengthwise. This results in half-billets that are approximately 2.5" x 0.5" x 0.4" (65 mm x 12 mm x 10 mm). Following this step, end caps of sterling silver were soldered on to the two small faces of the billet using hard silver solder. Then the end cap was trimmed and ground to be flush with the sides of the billet. A final cold press was conducted to "square up" the materials, resulting in billets that were close to 2.6" x 0.45" x 0.45" (68 mm x 11 mm x 11 mm).

These billets were then annealed and processed in our square wire rolling mill in stages of 0.010" (0.25 mm) reductions, with kiln annealing at 1185°F (640°C) after each 0.040" (1 mm) cumulative reduction. Once billets were 0.23" x 0.23" (6 mm x 6 mm) square by running length, they were annealed a final time.

## FIRING SCHEDULES

Two billets of each combination of material (Cu 110 and fine silver and Cu 110 and sterling silver) were fired at 1350°F (732° C), for 3, 6, 9 and 12 hours respectively.

After initial bond strength testing of the billets, we decided to add a 15- and 18-hour cycle to the firing schedule of the copper and sterling silver billets for bond strength testing.





At this time, we also decided to add another six smaller billets of copper and sterling silver. These were fired, but not hot-pressed and manipulated in any way beyond solid state diffusion bonding so we could examine the diffusion zones prior to any hot or cold reductions. These billets were 1" x 0.75"x 0.75" (25.4 mm x 19 mm x 19 mm), nineteen layers and were bonded and then simply split down the center to expose the billet center for micrography.

## TESTING

In the 2009 Santa Fe Symposium paper, "Mokume Gane Billet Reductions and Their Effects on Bond Strength,"[3] we devised two tests that were based on typical reductions taken by mokume makers when making rings and also flat patterned sheet to test bond strengths.

These tests involve taking annealed stock and processing it to failure with none of the annealing steps during reduction that would typically be taken. This allows us to see relative strength of material with the only variables being the billet composition and firing times. We decide to use these tests again for these materials.

The 0.23" x 0.23" (6 mm x 6 mm) square stock from above was end trimmed to remove the silver plates soldered on before rolling into square stock, and then cut into 1" (25.4 mm) long pieces for testing.

The first test was supposed to be rolling with the layers perpendicular to the flat rolling mill rolls, but the instructions were misread by my research assistant and the material was rolled with the layers parallel to the rolls. Results are included here, despite this not being the test we aimed for, as there was some correlation to the other tests that we conducted. We then did a second round of testing and rolled the material properly with the layers perpendicular to the press rolls.

The third test was to press the samples in 5-ton increments to failure. The samples were placed between two parallel plates with the layers perpendicular to the plates. After we discussed the results of our testing, we found a need to add a few more series of tests.

We decided to conduct a twist test, as this is a very common processing method of square wire stock when making rings. We rolled our 0.23" x 0.23" (6 mm x 6 mm) stock to 0.19" x 0.19" (4.8 mm x 4.8 mm), which is a dimension we commonly start

with when making twisted rings, and then gripped one end 0.2" (5 mm) in the vise with the layers parallel to the jaws and gripped the other end with Vise-Grip locking pliers 0.2" (5 mm) and twisted 180 degrees counter-clockwise, followed by a return to the starting position. This was considered one cycle. We had previously used a similar test to this in the 2014 Santa Fe Symposium paper "Mokume Gane Bonds: The Effects of Quenching on Bond Strengths."[4]

We also added two bend tests, one with layers parallel to the vise jaws, and a second with layers perpendicular to the vise jaws. The samples were clamped 0.2" (5 mm) into the vise on one end, and clamped with Vise-Grip locking pliers 0.2" (5 mm) on the other end. The sample was bent to the left (+90 degrees), then bent back to straight (0 degrees), then bent to the right (-90 degrees) then back to 0 degrees etc. This was repeated until diffusion bond failure or fatigue failure was noted, in 10's of degrees, meaning if the piece failed after three bends, it would be a 270-degree failure.



## RESULTS

First, the fine silver and copper billets. This combination was only tested by pressing with layers perpendicular to the press platens and also rolling with layers parallel to the flat rolls of the press.

At best, we can safely say the bonds were weaker than the bonds between the sterling silver and copper billets. Figure 9 shows the results of rolling the fine silver and copper billets from 25.4 mm x 6 mm x 6 mm with 0.2 mm reductions per pass through the rolling mill flat rolls, with the layers parallel to the faces of the rolls. The 3-hour billet failed with just one pass through the rolling mill, with the rest of the material lasting longer in line with the duration of the firing cycles.



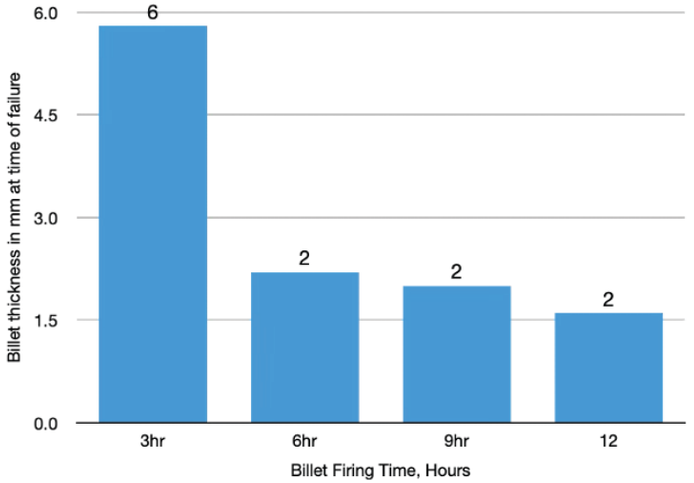


*Figure 9: Fine silver parallel roll test*

Press testing showed similar weaknesses, with Figure 10 showing the failure of the 3-, 6- and 9-hour billets occurring at 5 tons with the exception of the 12-hour billet which failed at 10 tons. It is worth noting that the actual size of the physical failure did get smaller as the firing time increased, but nonetheless, all exhibited failures when pressed to 5 tons except for the 12-hour billet.



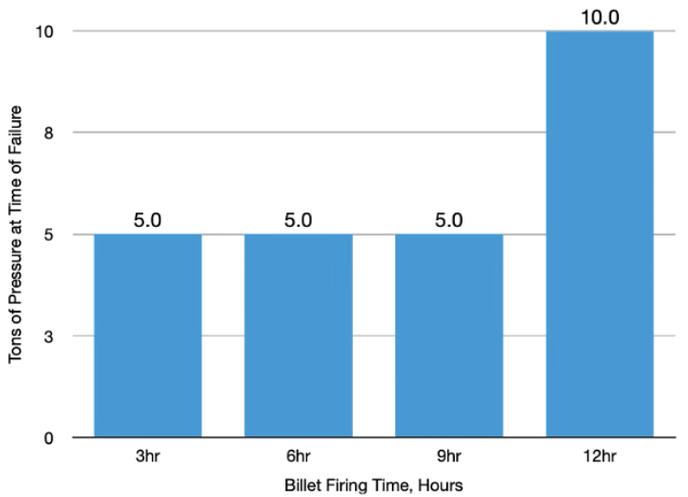


*Figure 10: Fine silver press test*

The fine silver and copper billets were all significantly weaker than the sterling silver and copper billets, but it is absolutely worth noting that the longer 12-hour firing time did survive longer than the shorter times in our test of the fine silver and copper.

This led us to focus exclusively on the sterling silver and copper billets.

The sterling silver and copper billets were subjected to the same tests as the fine silver and copper, and we decided to add the 15-hour and 18-hour firing cycles to these as well. We did not test the 15- and 18-hour billets with the incorrect parallel layer rolling test.

The sterling silver and copper parallel (incorrect) roll test showed an increase in strength over the fine silver and copper parallel roll test. The copper and sterling silver were stronger, but interesting to note, even the weaker fine silver and copper exhibited greater strength with the higher firing times of 9 and 12 hours. The reason we included these incorrect tests is that they do seem to correlate with our other results, shown below, for the 3-, 6-, 9- and 12-hour sterling silver and copper billets. Figures 11, 12 and 13 show the results of the rolling tests and press tests of the sterling silver and copper billets.

So, this was our first “Houston, we have a problem” moment. Every sterling and copper billet survived the press test intact to the limits of our 50-ton Bonny Doon Press. It was apparent that while the rolling tests did provide some results, they were not conclusive. After seeing that the longer firing times of both the fine silver and copper and sterling silver and copper billets seemed to lead to stronger material, I was quite surprised to note that the 15-hour and 18-hour billets seems to have a decrease in strength (Figure 12). This is why we added the previously detailed twisting and bend tests. We were hunting for results, and we found some.

Figures 14, 15 and 16 detail the results of our bending and two twisting tests.



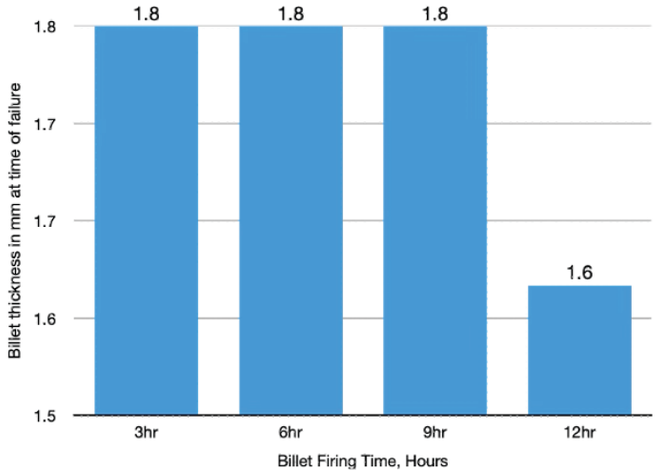


*Figure 11: Sterling silver parallet roll test*

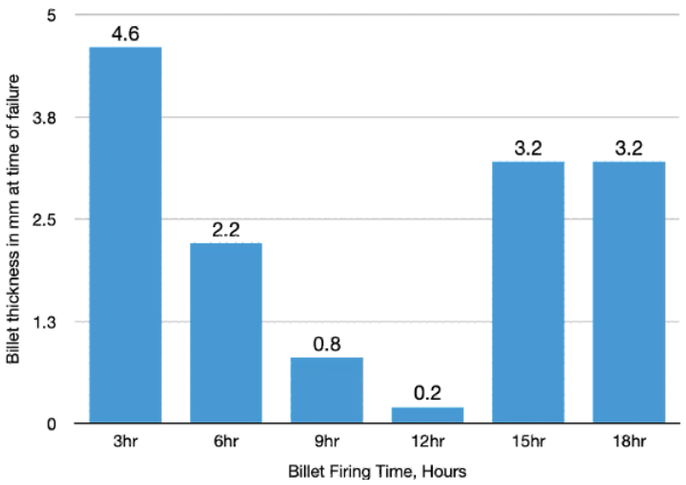


*Figure 12: Sterling silver perpendicular roll test*

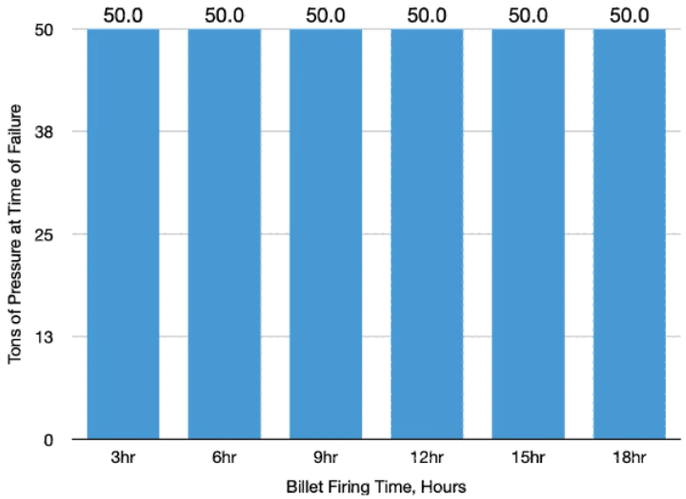


*Figure 13: Sterling silver press test*

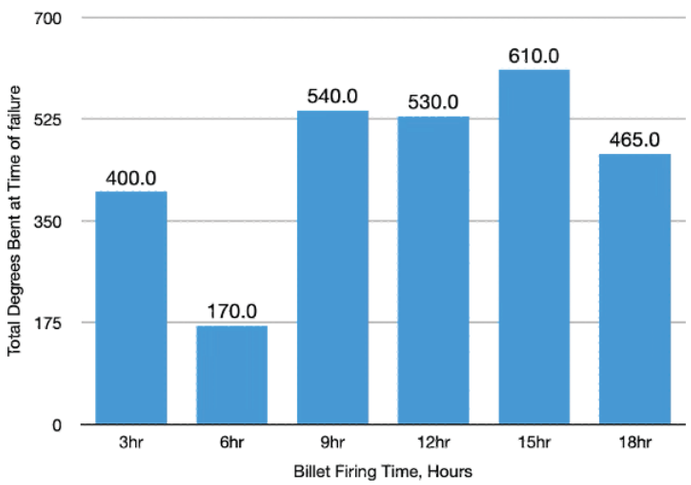


*Figure 14: Sterling silver parallel bend test*

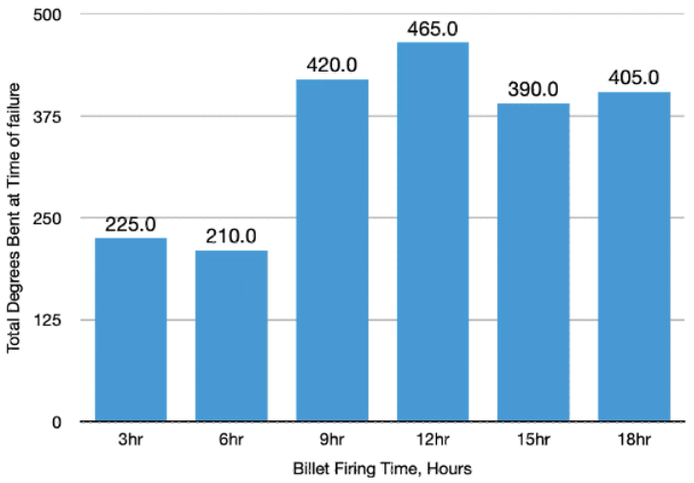


*Figure 15: Sterling silver perpendicular bend test*

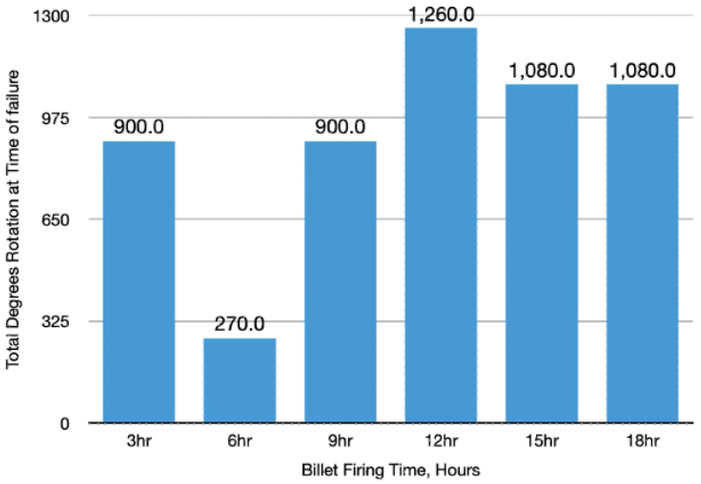


*Figure 16: Sterling silver twist test*

These additional tests gave us some more data, but there are a few important things to note. In our small shop environment, it is really difficult to tell if the failures we are seeing are initiated by bond or material failure. I'm not sure that matters, because across all of the tests including the fine silver and copper billets, we do seem to be seeing increased material strength at longer firing times, to a point.

The final results we have to share is the metallography conducted by Stewart.

We took a look at some of the failures. To the naked eye, the failures appeared to be directly between the layers, making me wonder if we had possibly contaminated the billet in some way during the bonding process. Stewart took a look, and discovered that the failures were actually in the diffusion zone, and always occurred on the silver side. Not unexpected, metallurgically, but it was good to be able to confirm this. Figures 17, 18 and 19 are all of the same piece of 3-hour bonded material.

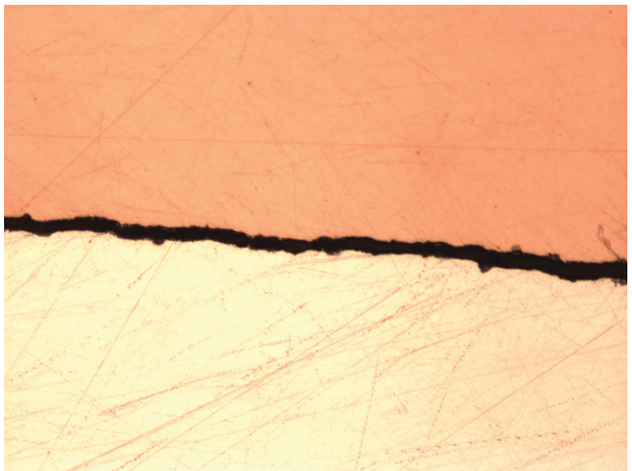

*Figure 17: 3-hour billet unetched, failure appears to be between the copper and sterling silver, magnification x100*



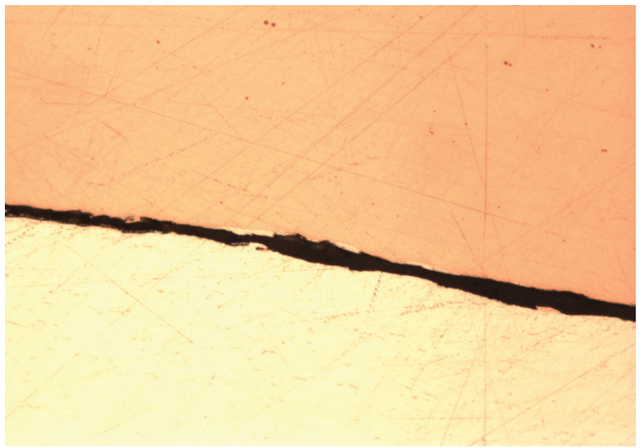

*Figure 18: Second unetched view showing what appears to be silver and copper on opposing sides, magnification x100*

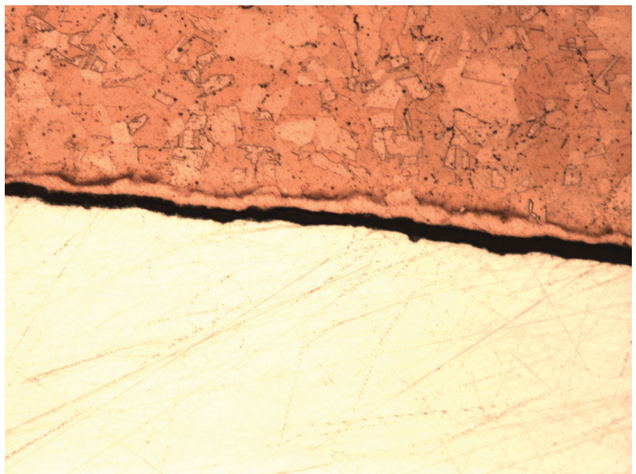

*Figure 19: Failure on the sterling side of the diffusion zone, magnification x100*

Etching the sample (Figure 19) highlights that the failure was on the sterling side of the diffusion zone.

It is worth mentioning here that when diffusion bonding, a phenomenon known as Kirkendall porosity or voiding can occur.[5] Kirkendall stated that the interface between two solids can distort due to the mechanism of diffusion being from vacancy exchange

rather than direct atomic exchange. If the atoms of metal A diffuse faster into metal B than B to A, there will be distortion at the interface, which can lead to the formation of voids or porosity. This is important with mokume gane because if small voids occur at the interface of two layers, this will decrease the strength of the diffusion bond and potentially lead to premature billet failure. For all of the samples tested in this study, even at x1000 magnification, no voids were identified. Analysis at higher magnification may reveal voids, but we did not have the analytical capabilities to do this.

Finally, we examined the billets we had fired and not reduced in any way. We were curious about diffusion zone size as a function of time. The longer the billet sat in the kiln would obviously seem to suggest that the diffusion would increase with this time, and our test findings did seem to indicate that stronger material resulted from longer diffusion times. Stewart first examined a prepared but unetched sample (Figure 20). Unlike when we have previously looked at gold-to-silver mokume gane billets, there is no indication of diffusion across the faces of the materials in these samples. It looks as though one material abruptly ends and the other begins. We'd typically expect to see maybe a "paler" copper layer or pinker silver layer where there had been some diffusion, but we don't see this at all.

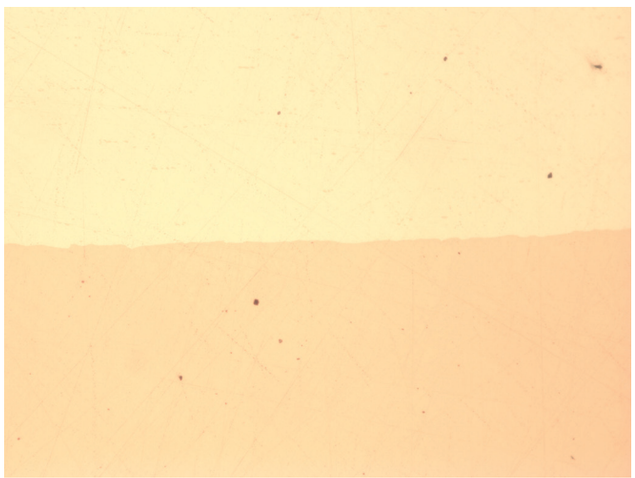

*Figure 20: 12-hour billet, unetched, looks like no diffusion across faces, magnification x 200*



Without access to equipment such as a scanning electron microscope (SEM) for EDX analysis, the concentration of silver and copper in the diffusion zone could not be determined. For this study, all analysis is qualitative in nature— visual examination of the microsections under magnification for color changes both before and after etching.

When the samples are etched in a dilute solution of 50/50 chromic/sulfuric acid, it's a very different story to that seen in the unetched samples. The grain structure of the copper becomes very visible, but the diffusion zone itself was still very pink in color. We noticed that it did not etch as much as the copper layer, possibly suggesting movement of silver atoms into the copper layer making the etchant less effective?

Diffusion of one metal into another is affected by various factors such as atomic size, temperature, unit cell configuration, and structure. A general rule is a metal of smaller atomic size will diffuse into that of a larger atomic size at a greater rate. Since the atomic radius of silver is 0.175 nanometers and copper is 0.157 nanometers, it may be reasonable to assume that copper should diffuse more into silver than silver into copper. If we also look at published data[6] for the diffusion coefficients of each metal close to our firing temperature:

| | |
|---|---|
| Diffusion coefficient of silver into copper | $4.37 \times 10^{-11}$ cm²/s |
| Diffusion coefficient of copper into silver | $8.30 \times 10^{-11}$ cm²/s |

This also suggests that copper will diffuse at a greater rate into silver than silver into copper. However, our rudimentary qualitative analysis shows the opposite. Maybe we expected more of a reaction from the etching process to be visible on the sterling side if a significant amount of copper was moving into the sterling? This may be a possibility; however, we must take into consideration that the sterling silver layer will be two-phase in these samples, and the dilute etching solution did not show this copper-rich phase.

Figures 21-25 are of the remaining etched samples and show the width of the diffusion zones. The zones continue to increase up to the 12-hour firing, but past that (15-hour and 18-hour), there seems to be little increase of the diffusion zone size. Average diffusion zone widths were calculated by measuring each sample in six random places along the zone and averaging the results, which are shown in Table 1.

*Table 1: Diffusion zone width vs firing time.*

| Firing time | Width of diffusion zone |
|---|---|
| 3hrs | 0.025mm |
| 6hrs | 0.035mm |
| 9hrs | 0.050mm |
| 12hrs | 0.060mm |
| 15hrs | 0.065mm |
| 18hrs | 0.070mm |

Interesting to also note, there seems to be little increase in copper grain size across all of the samples, even though we have a significant time at temperature difference between them. It is also worth noting that the samples were very difficult to etch. If you etch with a sufficiently strong solution and long enough time for the silver grain structure to be visible, the copper layer, being a base metal, is completely eaten away and you can't really make any sense of the microsections where the two metals join.

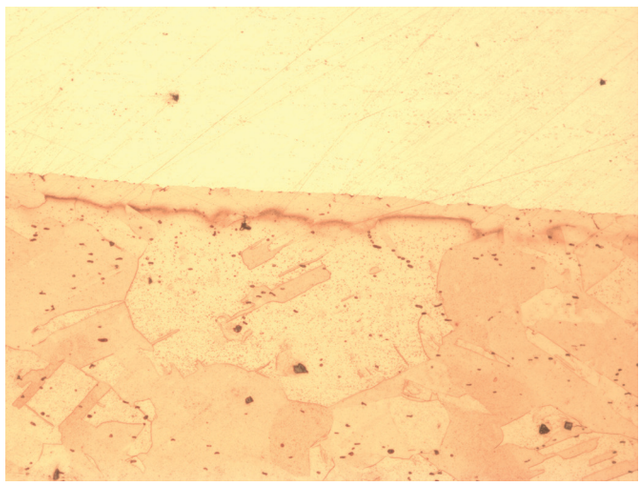

*Figure 21: 3-hour billet diffusion zone, etched, magnification x200*



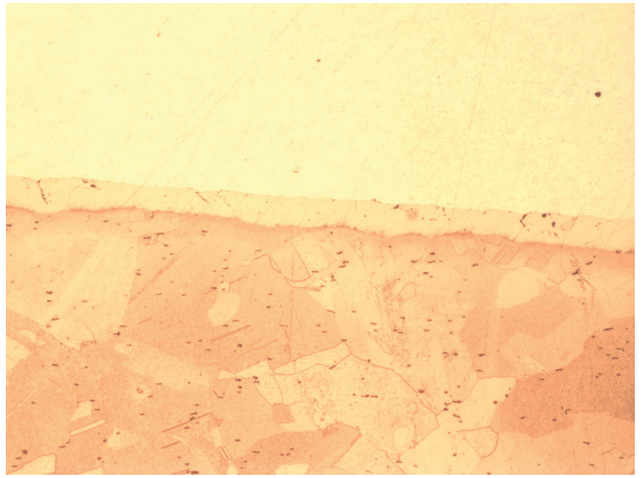

*Figure 22: 6-hour billet diffusion zone, etched, magnification x200*

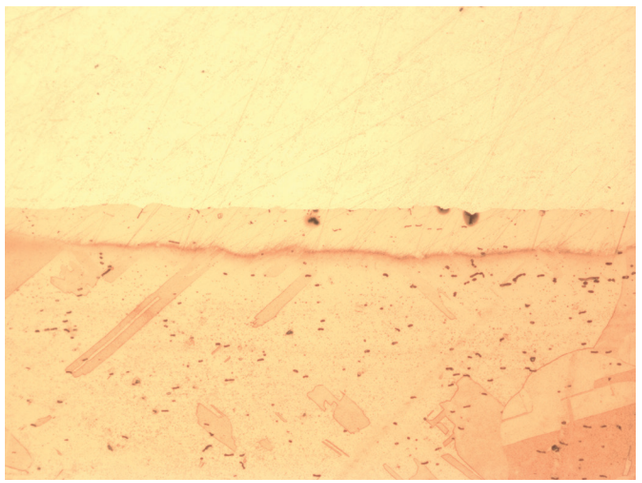

*Figure 23: 9-hour billet diffusion zone, etched, magnification x200*

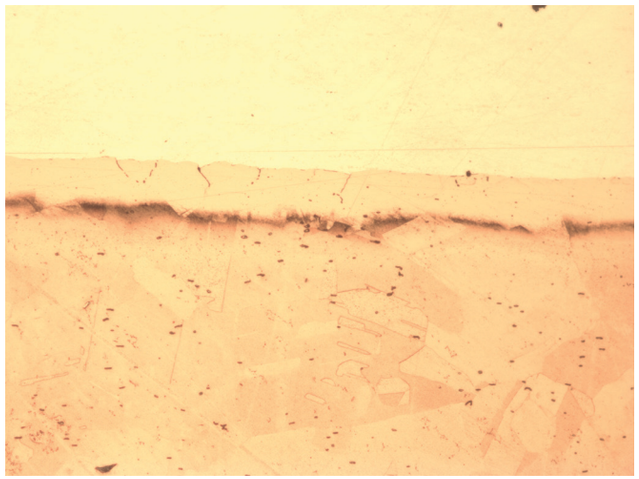

*Figure 24: 12-hour billet diffusion zone, etched, magnification x200*

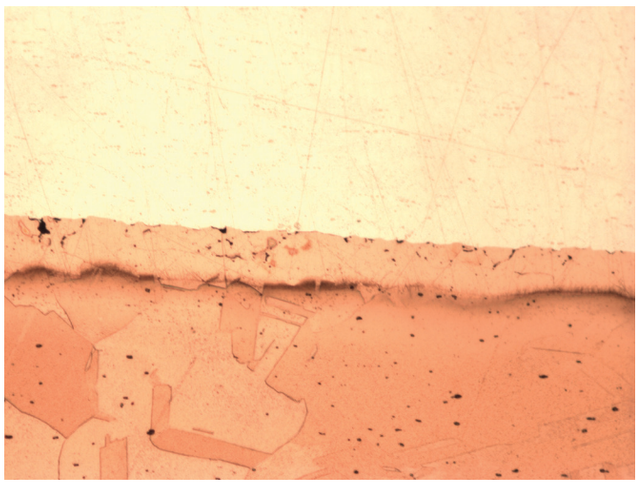

*Figure 25 – 15-hour billet diffusion zone, etched, magnification x200*





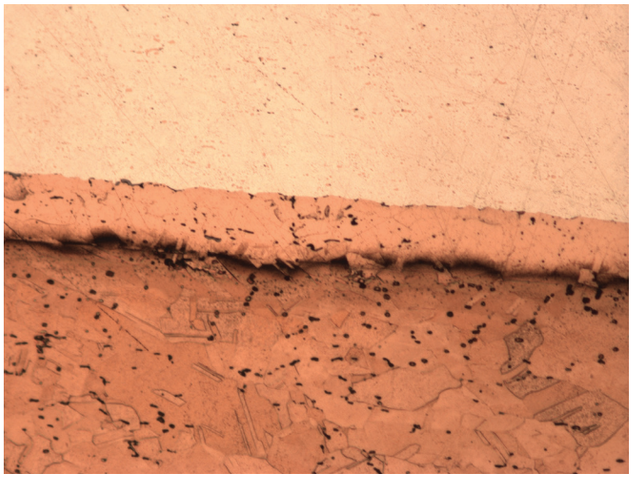

*Figure 26 – 18-hour billet diffusion zone, etched, magnification x200*

## CONCLUSION

So, what did we learn? Anecdotally, James and I had been seeing that an increase in strength seemed to come from a longer firing time. The research does confirm this.

Longer firing times, to a point, make a stronger bond. The metallography conducted on the samples that were not reduced show that the diffusion zone is wider, up to 12 hours. Looking at the test results of our samples, this is correlated by the stronger materials. It seems that there is little to gain from firing past 12 hours, and in fact the tested samples seemed to indicate this, with all but one not surviving as far into our testing.

I can say that in our shop, moving forward, we will be using the 12-hour firing cycle for our billets.

It would be interesting, I think, to test liquid phase diffusion bonding vs solid state, or possibly a hybrid firing of both methods. One could use the solid-state method to fire a billet, and, after cooling, firing it again using the liquid phase method. The difficulty with liquid phase bonds is typically they are done with a torch and heat control is critical– larger billets are difficult to make this way. It would be interesting to see if there is some form of kiln or other device with extremely accurate and tight temperature control to test this, but I have not found anything like this that is at a price point I can afford to try. Until then, 12 hours in our kiln it is!!

We also learned that galvanic corrosion is a very real issue, and makers should consider this when using copper and silver or copper alloys and silver in mokume gane jewelry. Copper, copper alloys and silver mokume gane is not suitable when used for rings even when lined in another material (your neighboring fingers will still make contact), and great care should be taken when using it for other types of jewelry. Skin and sweat contact should be avoided wherever possible.

## REFERENCES


1. James Binnion, "Why you don't want a copper and silver mokume gane ring.", https://mokume-gane.com/2015/07/06/why-you-dont-want-a-copper-and-silver-mokume-gane-ring/
2. Chris Ploof and Stewart Grice, "Mokume Gane History and How-to: A Survey of Technique," *The Santa Fe Symposium on Jewelry Manufacturing Technology 2016*, ed. Eddie Bell, Janet Haldeman and Jessica Cast (Albuquerque: Met-Chem Research, 2016): 409-430.
3. Chris Ploof, Stewart Grice and Andrew Nyce, "Mokume Gane Billet Reductions and Their Effects on Bond Strength," *The Santa Fe Symposium on Jewelry Manufacturing Technology 2009*, ed. Eddie Bell (Albuquerque: Met-Chem Research, 2009): 325-342.
4. Chris Ploof and Stewart Grice, "Mokume Gane Bonds: The Effects of Quenching on Bond Strengths," *The Santa Fe Symposium on Jewelry Manufacturing Technology 2014*, ed. Eddie Bell and Janet Haldeman (Albuquerque: Met-Chem Research, 2014): 389-402.
5. Paul W. Nordt III, H.G. Simpson Jr, W.C. Hill, "Creating Special Jewelry Materials by Hot Deformation Bonding", *The Santa Fe Symposium on Jewelry Manufacturing Technology 2013*, ed. Eddie Bell and Janet Haldeman (Albuquerque: Met-Chem Research, 2013): 289-317.
6. Daniel B. Butrymowicz, John R. Manning, Michael E. Read, "Diffusion in Copper and Copper Alloys Part II: Copper-Silver and Copper-Gold Systems", J. Phys. Chem. Ref Data, Vol.3, No. 2, 1974.






PLOOF