



MOKUME GANE BONDS: THE EFFECTS OF QUENCHING ON BOND STRENGTHS

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INTRODUCTION

The most prevalent problem in making mokume gane is the failure of the diffusion bonds between materials. This occurs during the reduction of the billet by hot or cold forging, rolling, or during the subsequent twisting and rolling or forging the twisted mokume gane. It has been widely assumed among those who make their own mokume gane that the integrity of the initial diffusion bonds is the most important factor dictating the survival of the material through the downstream processing and patterning stages. This led to the development of the TEMTP (Thermal Expansion Mismatch Torque Plate) System,¹ “the poor man’s hot press,” as reported at the 2005 Santa Fe Symposium®. This new approach to the diffusion bonding of mokume gane utilizes a closed die system consisting of thermally mismatched torque plates, bolts, punches and a die cavity. This allows for continuous pressure to be applied to the billet during laminating that is greater than what the ‘traditional’ open torque plate system applies. The 2005 study demonstrated that the use of the TEMTP system seemed to produce stronger bonds than the open style of torque plate system. However, this study did not examine the effect of bonding time and temperature or the effect of downstream processing on bond strength.

A study was completed for the Santa Fe Symposium in 2009² that tested the effects various reduction methods have on bond strength as billets are reduced to stock sizes and types useful for the manufacture of jewelry. This paper is a follow-on to those methods of bonding and reduction, with the added variable of quenching, in an attempt to discover if quenching in water versus air cooling has any effect on the strength of the bonded materials.

EXPERIMENTAL OBJECTIVES

- To determine the effect of air cooling on bond strength
- To determine the effect of water quenching on bond strength

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We constructed a series of experiments in order to meet our objectives. Eight billets were diffusion bonded and cooled according to the experimental conditions outlined below.

- Four billets were diffusion bonded for 6 hours at 696°C (1285°F) in the TEMTP system, cooled and then reduced by rolling.
- Four billets were diffusion bonded for 1.5 hours at 696°C (1285°F) and hot pressed prior to further reduction by rolling.
- Billets were cooled by quenching in water or air cooled.
- Billets were reduced to 6.4mm and samples were cut from each for bond strength testing.

Materials Used

Billet composition was 14K palladium white gold and sterling silver and 14K red gold and sterling silver (these two metal combinations are popular choices for couples purchasing wedding rings). We thought that using 14K red gold, which should be quenched after heating, would be a good choice to show any obvious differences between water-quenched and air-cooled billets. The Vickers hardness of the three metals are fairly similar, and the bonds are easily manipulated in the studio without much risk of failure compared to some other combinations. The billets were made from 19 layers of 20-gauge sheet.

Equipment Used

- TEMTP fourth-generation system, consisting of A-286 stainless steel torque plates, Inconel 718 stainless steel die cavity, A-286 punches and Inconel 718 bolts (Figure 1)

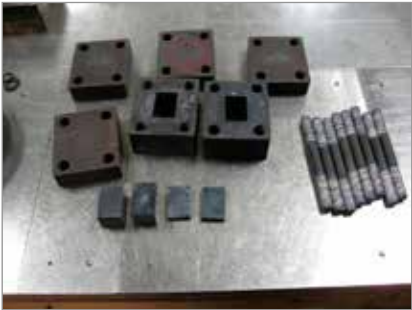


Figure 1 Fourth generation TEMTP system including Inconel bolts

- Ovens were of the small studio type, Paragon and Skutt top loading, both with digital controllers that were verified with independent thermocouple probes (Figure 2)



Figure 2 Ovens used for firing and annealing billets

- Hydraulic press was the 55-ton H-frame style used in studio metalsmith shops
- Rolling mills used were a large 6"-wide breakdown mill and a Durston powered rolling mill, over and under style
- Various hand tools common in the well-equipped studio

Billet Firing Procedure

All sheet diffusion-bonded into billets was inspected visually and vigorously cleaned prior to loading into the TEMTP. The cleaning method was an initial cut-down with 3" mounted Scotch Brite™ on a 3450rpm spindle, followed by hand scrubbing in distilled water with Simple Green® and a Scotch Brite pad. After being held under distilled water in the first of three tubs, the sheet was then removed and scrubbed with a Scotch Brite pad and Simple Green and rinsed in the same tub. The sheet was then rinsed in the second tub, inspected to make sure the water sheeted off evenly prior to being placed in the third tub of water, which contained distilled water and a pinch of citric acid. This is a very common cleaning method and its use has been documented in other papers presented here at the Santa Fe Symposium®.

Stacking Order and Firing Sequence

All billets consisted of 19 alternating layers of equal thicknesses of the 14K Pd white and .925 silver, with the .925 silver as the outermost layers. The 14K red-gold billets were built in the same fashion.

The two firing sequences were used to represent extremes. The longer method was designed to allow for greater diffusion zones, while it was hoped the shorter firing time would keep the diffusion zones narrower.

The first four billets were fired in the TEMTP system. Billets 5-8 were fired in an open system: torque plates but no die cavity. We used boron nitride on the faces of the torque plates, the punches and all screw threads to prevent unwanted bonding. The torque plates were then pre-loaded to 50 tons using the H-frame press and

the bolts were tightened evenly in a diagonal pattern using a torque wrench to 90 foot-pounds. The system was placed into a 321 stainless steel foil bag and was loaded with about one cup of activated filter charcoal. The charcoal is used to create a reducing atmosphere in the stainless steel bag. The charcoal was baked for one hour prior to being placed in the system to remove any possible moisture. The top of the bag was then sealed, and the whole system was placed into a preheated kiln. This method of diffusion bonding utilizing the stainless wrap and charcoal is common in the small shop for those who bond their own mokume. The firing sequence was 696°C (1285°F) for 6 hours for billets 1-4, and 696°C for 1.5 hours for billets 5-8.

Upon completion of the firing sequence, one of two cooling actions was taken. For the air-cooled billets, the kiln was turned off and opened to speed cooling. The billet was left in the foil bag system and TEMTP assembly to cool overnight to room temperature. Billets 3, 4, 7 and 8 were fired and air cooled. From here forward, these billets will carry the suffix of “A” for air cooled. After cooling to room temperature, the TEMTP system was disassembled and the billet removed. As seen in the photos, the pressure generated within the die cavity caused by the mismatch in thermal properties caused “finning” of the top layers, i.e., actual extrusion beyond the punch (Figure 3).



Figure 3 Billet with extrusion beyond the punch

The second cooling action was a water quench. Billets 1, 2, 5 and 6 were fired and quenched in this manner. From here forward, these billets will carry the suffix of “Q” for water quenched. Upon completion of the firing sequence, the water quenched were immediately removed from the kiln, the foil bag was quickly removed, and then the whole TEMTP system was quenched in 40 gallons of tap water. The TEMTP system was removed when cooled and disassembled.

Table 1 Billet composition, cooling and firing method

Billet #	Cooling Method	Materials	Firing Method	Firing Time, Hours
1Q	water quench	14K PdW/.925	TEMTP	6
2Q	water quench	14K R/.925	TEMTP	6
3A	air cool	14K PdW/.925	TEMTP	6
4A	air cool	14K R/.925	TEMTP	6
5Q	water quench	14K PdW/.925	open system	1.5
6Q	water quench	14K R/.925	open system	1.5
7A	air cool	14K PdW/.925	open system	1.5
8A	air cool	14K R/.925	open system	1.5

Billets 5-8 were initially processed by hot pressing, followed by rolling to 6.4mm. Billets 1-4 were removed and went directly to cold rolling. After every 1mm of reduction, the billets were re-annealed. We typically accomplish more reduction between anneals, but we felt deliberately underworking the materials would help compound issues caused by either the air cooling or the water quenching.

Reducing and annealing were achieved with a large breakdown rolling mill adjusted in .05mm increments, and electric kiln annealing at 677°C (1250°F) for fifteen minutes. Additionally, the billets were wrapped in 321 foil with small amounts of flux coating the billets. Upon removal from the kiln, the billets were immediately removed from the foil and either set on the anvil to cool or quenched.

Bond Strength Testing and Results

After reduction to 6.4mm, samples were taken from each of the billets for testing to failure. The methods used were initially for the 2009 Santa Fe Symposium paper, "Mokume Gane Billet Reductions and Their Effects on Bond Strength."² These methods, consisting of both a rolling and pressing test, had previously proven to be tests that easily illustrated the differences between materials fired using different methods.

We cut billets with a slitting saw on a horizontal mill to 6.4mm x 6.4mm square, and then the long axis corners were broken slightly to 45 degrees. The samples were rolled in the square wire grooves of the rolling mill to 6.15mm x 6.15mm to be certain they were of equal cross section from sample to sample. The last step, to make sure we were testing apples to apples, was to trim the samples to a uniform test length of 22mm. All samples were annealed and either air cooled or quenched.

Two samples from each billet were rolled with bonded layers perpendicular to the rolling mill rolls without any further annealing steps. Billet 1Q exhibited a lamination failure at 2.7mm. No other billets had exhibited any lamination failure at 1.5mm, and we made the decision to trim off the leading edge in our plate

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shear. We were worried that the leading edge, which had become folded over, was impeding any failures. After trimming, the remaining 15 samples were rolled. At 0.25mm in thickness, there was much ‘feathering’ on the silver layers on the sides, but NO other failures of the lamination. We stopped rolling at this point. The samples are pictured in Figure 4.

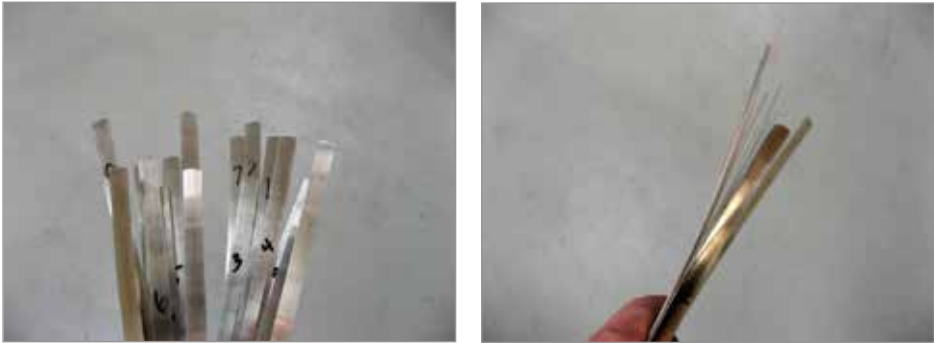


Figure 4 Rolled samples

The second series of tests used the 50-ton hydraulic press. The 6.15mm x 6.15mm samples were placed on the platens, with layers perpendicular to the platens, and then pressed in five-ton increments. Two samples from each of the eight billets were tested this way. Results are shown in Figure 5, with the water-quenched material in gray and the air-cooled material in red.

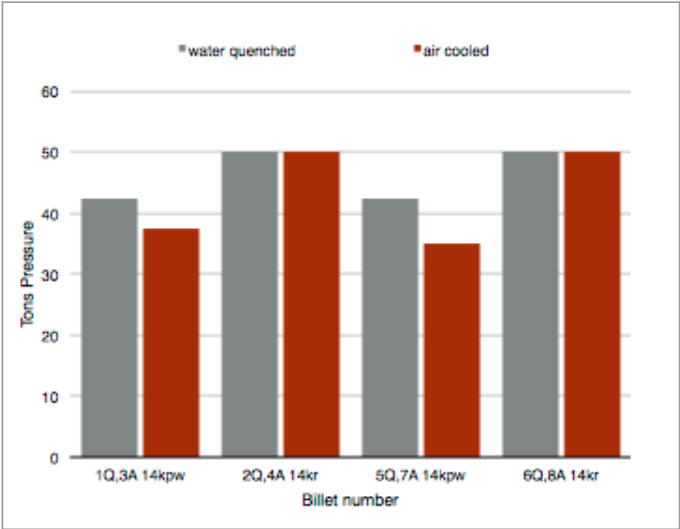


Figure 5 Billets tested to failure, in tons

The first remarkable result was the fact that the 14K red-gold and silver billets (all the even numbered billets in Figure 5) did not exhibit failures. The 14K palladium white-gold and silver billets (odd numbers in Figure 5) didn't fare as well. The quenched billets seemed slightly stronger than the air-cooled materials, and nearly equal results were realized regardless of the firing time. At this point, with little in the way of results, a third test was devised.

Rolling mokume gane in the square wire rolls of the mill has always been a process that seems to invite failure of the leading or trailing edge. When making rings, these small failures at the very end of the square wire are irrelevant, but we decided this would be a good way to test if there was a difference between the air-cooled and water-quenched materials.

One sample from each billet was rolled in the square wire rolls of the mill, with large reductions of 0.25mm per pass taken in the attempt to encourage failure prior to running out of square wire steps. Additionally, after each pass the material was rotated 90° so we could be certain stresses were applied both parallel and perpendicular to the layers. When material is properly bonded but overworked, these failures have been observed to occur most often at the trailing edge. Figure 6 shows our results. Gray bars are for the water-quenched materials, red bars for the air-cooled materials.

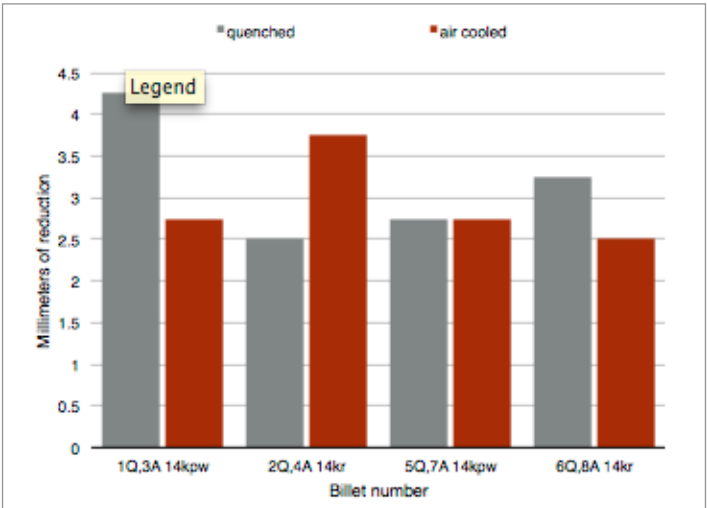


Figure 6 Billet testing using square wire rolling

Here, the strongest materials were a 14K red-gold sample that was quenched and one that was air cooled. Close behind were the short-fired 14K palladium white-gold samples, both water quenched and air cooled, and the long-fired air-cooled. The long-fired 14K red-gold air-cooled sample and the 14K palladium white-gold sample failed soonest. These results didn't corroborate the results from the pressing test in the second series of tests.

When in doubt, continue testing!

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We made the decision to add a fourth test. Paul Nordt’s paper, “Creating Special Jewelry Materials by Hot Deformation Bonding,”³ presented at the 2013 Santa Fe Symposium®, mentions a twisting test used to gauge relative strengths of the bonded materials produced for that paper. Paul was gracious enough to share his testing steps, which follow.

The remaining eight annealed 6.15mm x 6.15mm samples were prepared for testing using Paul’s methodology by cold pressing, annealing and then rolling to final dimensions of 7mm x 2mm x 100mm. The samples were then annealed. All annealings were followed by the water quench or air cooling, depending on the billet. 10mm of one end was clamped into a vice, and then 10mm at the other end was gripped with a pair of vice grips.

Paul’s test called for a full 360° of rotation, followed by a return to the starting point. Each one of these is a cycle count of one. At the first sign of delamination, we recorded the number of twists. Then we continued twisting until the material sheared completely. Figure 7 illustrates our results.

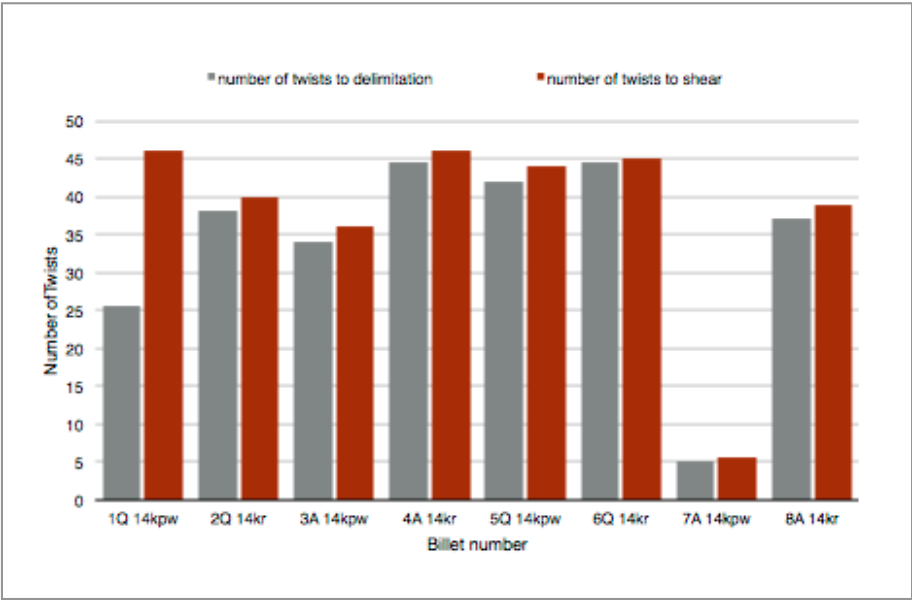


Figure 7 Twist test results

The twist test yielded one anomalous result: the air-cooled, short-fired 14K palladium white-gold and silver sample failed much sooner than the others. This was followed by the long-fired, water-quenched 14K palladium white-gold and silver sample. Regardless of material, cooling method and firing time performed similarly.

CONCLUSION AND RECOMMENDATION

The conclusion made in the studio is that quench method and bonding time do not affect the billet strength as much as had previously been believed. Results for different material combinations may affect this conclusion. A standardized test should be developed to test the strength of multi-layer, diffusion-bonded materials.

FURTHER ANALYSIS

Stewart Grice, Mill Products Director of Hoover and Strong, was enlisted to provide a further analysis of the data set in case anything was missed. He offered the following analysis of the results as recorded.

Second Test Data Analysis: Press Test

Table 2 Billet firing characterization

14K PdW/Sterling			14K Red/Sterling		
1Q	TEMTP	Quench	2Q	TEMTP	Quench
3A	TEMTP	Air cool	4A	TEMTP	Air cool
5Q	Open	Quench	6Q	Open	Quench
7A	Open	Air cool	8A	Open	Air cool

A further analysis of the press test, where wire stock 6.15mm x 6.15mm x 22mm was placed in a press with layers perpendicular to the platens, then pressed in five-ton increments, follows. All results are the average of two tests. Force noted in tons is when failure/de-lamination occurred.

Table 3 Press test results of materials

14K PdW/Sterling		14K Red/Sterling	
Billet #	Tons of force to failure/de-lamination	Billet #	Tons of force to failure/de-lamination
1Q	42.5 tons	2Q	50 tons
3A	37.5 tons	4A	50 tons
5Q	42.5 tons	6Q	50 tons
7A	35 tons	8A	50 tons

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For the 14K Red/Sterling billets, all performed very well with full deformation up to a 50-ton load, resulting in no failures or de-lamination. For 14K PdW/Sterling, there was no noticeable difference between TEMTP firing and open firing; however, both methods show some change between quench and air cooling. It is common when firing mokume gane billets to slow cool after an overnight firing, so the air-cooled numbers will be the baseline data. With respect to this, quenching gave a 13% increase in deformation before failure for the TEMTP billet and a 21% increase for open-fired billets.

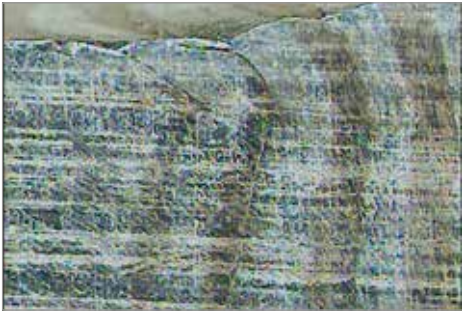


Figure 8 De-lamination in sample 7A



Figure 9 14K Red/Sterling billet: no de-lamination

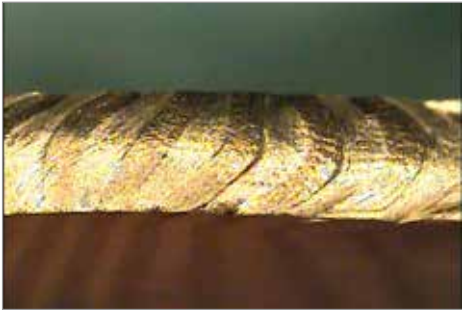


Figure 10 14K PdW/Sterling billet: de-lamination

Does this suggest a better bond between the 14K Red/Sterling compared to the 14K PdW/Sterling? Possibly yes. It must also be considered that the 14K PdW alloy itself will be more prone to failure if overworked. This alloy has some order/disorder and precipitation reactions within the system and so is more ductile and malleable when quenched after a heat treatment. The quenched alloy typically has a hardness number of 125 HV whereas when air cooled, depending on the rate of cooling, it can have a hardness number over 200 HV. Since sterling silver has an annealed hardness of no greater than 75 HV, this will deform the most out of the two materials. This mis-match in hardness between the two alloys may lead to a higher risk of de-lamination i.e., the bond faces will have a greater potential to pull apart since the sterling silver will want to deform at a much greater rate than the 14K PdW.

These results would suggest the mis-match in hardness is having an effect since, regardless of firing cycle, the quenched billets are capable of resisting failure to a higher load than the air-cooled ones. However, it must be noted that all things are relative. The 14K PdW/Sterling combination is generally known by mokume gane users as a robust combination and these results, while showing that this combination is inferior to the 14K Red/Sterling combination, are by no means cause for concern. Maybe a less user-friendly pairing would show up a larger gap in properties.

Conclusions to draw from this test are that you can process the 14K Red/Sterling combination any way you like—it performs just fine. With the 14K PdW/Sterling combination, you have to be a little more careful to allow for the 14K PdW drawbacks, and quenching should give a greater resistance to de-lamination.

Third Test Data analysis: Square Rolling Test

Table 4 Square rolling results of materials

14K PDW/Sterling		14K Red/Sterling	
Billet #	Size in mm ² at time of failure	Billet #	Size in mm ² at time of failure
1Q	4.3	2Q	2.6
3A	2.8	4A	3.8
5Q	2.8	6Q	3.2
7A	2.8	8A	2.6

There do not seem to be any conclusions to draw from the data in Table 4.

Fourth Test Data: Paul's Test

Table 5 Twists to de-lamination and total failure

14K PDW/Sterling			14K Red/Sterling		
Billet #	Twists to de-lamination	Twists to total failiure	Billet #	Twists to de-lamination	Twists to total failiure
1Q	26	46	2Q	38	40
3A	34	36	4A	45	46
5Q	42	44	6Q	45	47
7A	5	6	8A	36	39

Once again, as far as a correlation of results is concerned between TEMTP and open firing or quenched and air cooled, there appears to be none. The results for the 14K PdW/Sterling open-fired and air-cooled tests are low, but this must be looked at with some suspicion and may be an anomalous result since it is so far from anything else tested. In general, the results show good resistance to de-lamination; 20, 30 and 40 twists until failure is a significant number without any intermediate anneals.

What can be concluded from these results is that, again, the 14K Red/Sterling combination is more robust than the 14K PdW/Sterling. The number of turns before de-lamination is greater for the former, and the number between initial de-lamination and final failure is very small. The 14K PdW/Sterling samples de-laminated easier. Figures 11 and 12 are typical failures for each type, showing that the 14K PdW/Sterling combination exhibited more de-lamination at the failure than the 14K Red/Sterling, which has little or no de-lamination visible. Again, this is a relative view, suggesting the 14K PdW alloy is the reason, and in no way suggests that this combination is not good for general mokume gane use.



Figure 11 14K PdW/Sterling failure

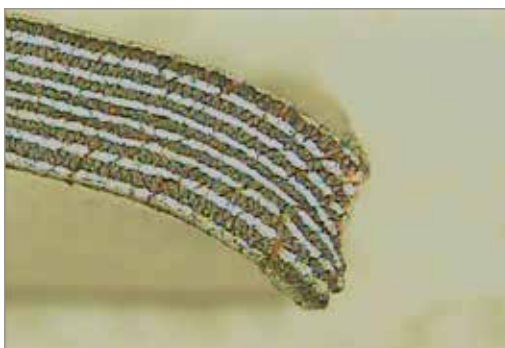


Figure 12 14K Red/Sterling failure

CONCLUSIONS AND RECOMMENDATIONS

Sometimes, when we go looking for a problem, we don't find one. That seems to be the case for this paper. However, we were able to conclude the following:

- The overall conclusion is that the strength of the billet is more dependent upon the combination of metals chosen rather than the processing route.
- In some cases, the faster cooling by water quenching will be acceptable and save time.
- Air cooling is always acceptable, even with the inclusion of 14K red gold in the billet.

REFERENCES

1. James Binnion, Andrew Nyce, Stewart Grice, "Designing, Building and Testing a Thermal Expansion Mismatch Torque Plate (TEMTP) System for Diffusion Bonding Mokume Gane Gillets: 'The Poor Man's Hot Press,'" *The Santa Fe Symposium on Jewelry Manufacturing Technology 2005*, ed. Eddie Bell (Albuquerque: Met-Chem Press, 2005): 65-101.
2. Chris Ploof, Stewart Grice, 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 Press, 2009): 325-342.
3. Paul W. Nordt III, H.G. Simpson, Jr., W. Clark Hill, "Creating Special Jewelry Materials by Hot-Deformation Bonding," *The Santa Fe Symposium on Jewelry Manufacturing Technology 2013*, ed. E. Bell and J. Haldeman (Albuquerque: Met-Chem Press, 2013): 289-318.

