ABSTRACT. Sound, high strength diffusion welded joints were obtained with silver plated stainless steel, beryllium and uranium. The procedures used for preparing the substrates for plating were first characterized by using ring shear tests, which provided quantitative information on weld adhesion.

For the joining studies, a full factorial experiment with two levels and four variables \(2^4\) was run with stainless steel. Fewer experiments were run with beryllium and uranium. Best joints were obtained with welding conditions which included 1 hour at a temperature of 600°C (1112°F), pressure of 30,000 psi (207 MPa) and a plating thickness of 1 mil (0.001 in.) of silver.

Experimental Details

Specimens

Cylindrical butt specimens of the type shown in Fig. 1 were used for this work. These were plated with 0.5 or 3.0 mil (0.0005 or 0.003 in.) of silver on one face, and then two specimens were diffusion welded together using varying conditions of time, temperature, and load. Diffusion welded specimens were then machined per Fig. 2 to provide a reduced section in the joint area for tensile testing. Materials used as substrates included Type 304 stainless steel, beryllium, and unalloyed uranium.

The Type 304 stainless steel was annealed and hot-rolled; its yield strength was 43,000 psi (296 MPa) and the tensile strength 110,000 psi (758 MPa). The beryllium had a yield strength of 37,000 psi (255 MPa), and its tensile strength was 58,500 psi (403 MPa). The uranium was high purity rolled rod with a yield strength of 50,000 psi (344 MPa) and a tensile strength of 138,000 psi (951 MPa).

Most of the work was done with stainless steel, and a full factorial experiment with two levels and four variables \(2^4\) was completed with this material. When beryllium and uranium specimens were diffusion welded, one-half of each joint was a stainless steel specimen. This was done to minimize the cost of machining additional specimens, which is an expensive proposition for these metals. No precautions were taken to obtain a specified surface finish on the faces to be joined. Typically, the finish was in the
range of 8–21 μin. (0.0002–0.0005 mm), RMS, and the data showing this are included in Table 1.

**Diffusion Welding System**

A schematic of the welding fixture designed for use in an existing furnace is shown in Fig. 3. The specimens were held in vertical alignment with a close fitting tungsten carbide bushing and heat stabilizing cylinder. One half of the specimen and the bushing rested on the lower piston.

The piston provided axial vertical motion to bring the other half into contact with the stationary ram. Force for the compressive load was provided by a hydraulic ram. The specimens, alignment bushing, and heat stabilizing block were centered in an electric clam shell furnace. Temperature was controlled and monitored with two thermocouples, a time proportional controller, and strip chart recorder. The furnace in which welding was done was continually flushed with argon.

**Ring Shear Tests**

Ring shear tests were used to evaluate procedures for plating silver on stainless steel, beryllium, and uranium. For this test, a cylindrical rod was prepared with the process under study and plated to a minimum thickness of 1.5 mm (0.06 in.). The rod was machined in a manner that removed all the plated deposit except for small rings of plating of predetermined width generally 1.5 mm (0.06 in.) wide. The rod was then cut between the plated rings.

The sections of rod with the plated rings were tested by forcing the rod through a hardened steel die having a hole whose diameter was greater than that of the rod but less than that of the rod and the coating. The bond strength A (in MN/m² or psi) was determined by the formula $A = \frac{W}{\pi dt}$, where $d$ is the diameter of the rod, $t$ the width of the deposit, and $W$ the force required to cause failure in the specimen.

Figure 4 shows a ring shear test specimen and die used for testing. Additional details on ring shear testing are available.

**Table 1—Surface Roughness on Faying Surface of Cylindrical Butt Joint Specimens**

<table>
<thead>
<tr>
<th>Material</th>
<th>Surface roughness, μin., RMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type 304 stainless steel</td>
<td>9, 10, 12</td>
</tr>
<tr>
<td>Beryllium</td>
<td>12, 15, 21</td>
</tr>
<tr>
<td>Uranium</td>
<td>8, 11</td>
</tr>
</tbody>
</table>
in the literature (Ref. 7). A wealth of quantitative ring shear data is available for plating on stainless steel, beryllium and uranium. However, no data were available for silver deposited on these substrates. Therefore, these tests were run to verify that procedures that have worked for other electrodeposited coatings on these substrates worked equally well for silver.

Silver Plating Solution

Plating was done in a 10 liter (10.6 quarts) silver cyanide plating solution of the formulation shown in Table 2. Agitation was kept constant with an electric stirrer. No proprietary additive was used, since compounds of this type which are used to brighten deposits and refine the grain structure also increase the impurity content of the coatings. Table 3 shows that a deposit produced in a solution with an additive had nearly twice as much carbon as a deposit produced in an additive-free solution.

Factorial Experiment with Stainless Steel

A two level, four variable factorial (2^4) experiment was run with stainless steel specimens. This was done to get a better understanding of the key variables which influence the joining process. Moreover, this type of design strategy has been shown to be a powerful tool for understanding plating processes and provides considerable information in return for a minimum of experimentation (Ref. 6).

Stainless steel was chosen for this work since, as mentioned earlier, these specimens were the least expensive to fabricate. In every experiment, each variable can have one of two states (high +, or low −). The four variables included in this study and the limits chosen were: time — 1 hour (h) and 4 h; temperature — 300 and 600°C (572 and 1112°F); welding pressure—10,000 and 30,000 psi (68.9 and 206.8 MPa); and plating thickness—1 mil and 6 mil (0.001 and 0.006 in.).

Plating variables were not included as part of this investigation. Operating conditions such as plating current density, temperature, solution flow, and solution composition were kept constant.

Results

Ring Shear Tests

The cleaning/activating procedures that were evaluated are those that have proved successful for preparing stainless steel, beryllium and uranium for plating with other metals such as copper or nickel. Ring shear test results are included in Table 4. The procedures providing the best results are those that were used for specimens for the diffusion welding studies. Complete details on these procedures are provided in the Appendix. For all three substrates, the best procedures resulted either in failure of the silver deposit or a combination of failure in the substrate and the silver.

With stainless steel, the key step in the activation procedure is anodic treatment in sulfuric acid followed by a Wood’s nickel strike; this has been well documented in previous literature (Ref. 9). With this technique, an adherent thin deposit of nickel is applied to the stainless steel, and this serves as a base for subsequent coating.

For good adhesion to beryllium, it is absolutely essential to apply an adherent immersion zinc deposit (this is called a “zincate treatment”) before electrodepositing the primary metal of interest (Ref. 10). Our data show that zincate treatment time is critical, with the strongest bonds obtained with a 60 second immersion. These good results with beryllium are of particular significance.

### Table 2—Silver Plating Solution Formulation

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver cyanide</td>
<td>40</td>
</tr>
<tr>
<td>Potassium cyanide</td>
<td>60</td>
</tr>
<tr>
<td>Potassium carbonate</td>
<td>15</td>
</tr>
<tr>
<td>Free cyanide</td>
<td>41</td>
</tr>
<tr>
<td>Temperature</td>
<td>21–27°C (70–81°F)</td>
</tr>
<tr>
<td>Current density</td>
<td>54–161 A/m² (5–15 A/ft²)</td>
</tr>
</tbody>
</table>

### Table 3—Impurity Content of Silver Deposits

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>8</td>
</tr>
<tr>
<td>Lead</td>
<td>1</td>
</tr>
<tr>
<td>Magnesium</td>
<td>2</td>
</tr>
<tr>
<td>Nickel</td>
<td>3</td>
</tr>
<tr>
<td>Iron</td>
<td>10</td>
</tr>
<tr>
<td>Oxygen</td>
<td>30</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>4</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>11</td>
</tr>
<tr>
<td>Carbon</td>
<td>60</td>
</tr>
<tr>
<td>Sulfur</td>
<td>9</td>
</tr>
</tbody>
</table>

### Table 4—Ring Shear Test Results

<table>
<thead>
<tr>
<th>Procedure</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Best procedures for stainless steel</td>
<td>Failure of silver deposit or combination of failure in the substrate and the silver.</td>
</tr>
<tr>
<td>Best procedures for beryllium</td>
<td>Failure of silver deposit or combination of failure in the substrate and the silver.</td>
</tr>
<tr>
<td>Best procedures for uranium</td>
<td>Failure of silver deposit or combination of failure in the substrate and the silver.</td>
</tr>
</tbody>
</table>

---

*Deposits were plated at 108 A/m² (10 A/ft²).

This is because, traditionally, a copper strike has been used after the zincate step and this is followed by the deposit of adherent nickel, for example, as an intermediary coating before plating. The process we prefer for unalloyed uranium consists of etching in a ferric chloride reaction products in nitric acid before plating. The process we prefer for unalloyed uranium consists of etching in a solution containing 1400 grams/liter ferric chloride (Ref. 12).

Poor bond strengths were obtained when silver was plated over uranium samples that had been etched and this is consistent with past experience with copper and electroless nickel deposits (Ref. 13). Good bond strengths are obtainable when etched uranium is plated with nickel. For this reason, a nickel deposit was used as an intermediary coating before silver plating, and this provided good adherence, e.g., a bond strength of 18,300 psi (126.2 MPa).

**Diffusion Welding—Stainless Steel**

The factorial experiment conducted with silver-plated stainless steel specimens is detailed in Table 5 along with the results. Good bonds were obtained using a variety of conditions with the mean strength being 47,800 psi (329.6 MPa). Table 6 summarizes the analysis of variance (ANOVA) data for the 2^5 factorial experiment with diffusion welded stainless steel specimens. Time was a non-significant variable. On the other hand, thickness, pressure and temperature were significant as were the interactions of temperature with pressure and temperature with thickness. Plots of joint strength v. time, pressure, or thickness, included in Fig. 5 help to visually explain the analysis. It is to be noted that:

1. Temperature was significant when diffusion welding pressure was 10,000 psi (68.9 MPa); it was nonsignificant when the pressure was 30,000 psi (206.8 MPa)—Fig. 5A.
2. Temperature was significant for 6 mil (0.006 in.) thick silver coating, but it was nonsignificant for 1 mil (0.001 in.) thick coatings—Fig. 5B.
3. Pressure was significant at 300°C (572°F) but was nonsignificant at 600°C (1112°F)—Fig. 5C.
4. Pressure was significant for 6 mil (0.006 in.) thick silver coatings but was nonsignificant for 1 mil (0.001 in.) thick coatings—Fig. 5D.
5. Thickness was significant at 10,000 psi (68.9 MPa) but was nonsignificant at 30,000 psi (206.8 MPa)—Fig. 5E.
6. Thickness was significant at 300°C.
but was nonsignificant at 600°C—Fig. 5F.
7. Time was nonsignificant—Fig. 5G.

Scanning electron photomicrographs of some fractured joints are shown in Figs. 6 and 7. With strengths greater than 40,000 psi (275.8 MPa), the ruptured surfaces showed well developed ductile dimples. In these cases silver-to-silver joint separation occurred by void coalescence—Fig. 6. With poor welds, e.g., specimens at low temperature (300°C or 572°F) and low pressure (10,000 psi or 68.9 MPa), incomplete contact is clearly visible—Figure 7. The ridges exhibited joining, but the valleys were not welded. In addition, other areas did not make contact during welding.

Figures 8 (0.5 mil or 0.0005 in. silver) and 9 (3.0 mil or 0.003 in. silver) of
as-plated specimens show how the deposit follows the machining marks of the stainless steel. Cells are built up that are similar to the ductile dimples found on ruptured surfaces.

**Beryllium**

Good welds were obtained with beryllium joined to stainless steel using a variety of conditions—Table 7. The mean weld strength was 34,300 psi (236.5 MPa) excluding two sets of specimens that exhibited very low strengths—3200 and 2500 (22 and 17 MPa) and 14,900 and 2200 psi (103 and 15.2 MPa) due most likely to the low temperature used for joining these specimens.

Failure typically occurred in the beryllium-
um, and it is important to point out that no special precautions were taken during tensile testing to assure proper alignment of the samples. These results were very encouraging inasmuch as they verified that the procedures used for electroplating silver on the beryllium produce weld strengths that are at least as strong as the base metal beryllium substrate and not degraded by heating.

The data of Table 7 were averaged for each variable and plotted along with data obtained for similar conditions with stainless steel and uranium joints. Inspection of these curves (Figs. 10-12) reveals a number of significant findings.

1. Temperature had the most significant influence and was consistently important for each of the three metals.
2. Time was insignificant in all cases.
3. Thickness and load were relatively insignificant for both beryllium and uranium but were significant for stainless steel. However, it is important to note that the weakest joints obtained with stainless steel regardless of thickness or load, were still stronger than the best joints obtained with both beryllium and uranium under similar diffusion welding conditions.
With beryllium, strong silver-silver joints could not be examined, since the specimens broke entirely in the beryllium. Two specimens welded at low temperature — 300°C (572°F) for 1 and 4 h welding time at 30,000 psi (206.8 MPa) — did not show the good silver-silver joint typical of that seen on stainless steel. Figure 13 shows a region of beryllium fracture and silver-silver rupture typical of these specimens. Use of high temperature (600°C, i.e., 1112°F) during welding resulted in complete failure in the beryllium.

Uranium

Regardless of the pretreatment process, good joints were obtained with uranium under a variety of welding conditions — Table 8. Thickness, load, and time were insignificant, but temperature was very important as it was with beryllium and uranium. This is shown in Fig. 10 and Table 8. The weakest joints were always those that included a low welding temperature (300°C or 572°F) as part of the joining process.

In general, the diffusion welds were stronger if no etch was used, or if the

<table>
<thead>
<tr>
<th>Pretreatment</th>
<th>Time (1 hr)</th>
<th>Temperature (300°C)</th>
<th>Bonding pressure (30,000 psi)</th>
<th>Silver plating thickness (1 mil)</th>
<th>Failure load, psi</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeCl₃ etch</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>12,700</td>
</tr>
<tr>
<td>Plus 0.5 mil</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>36,300</td>
</tr>
<tr>
<td>Electroplated Ni then</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>40,000</td>
</tr>
<tr>
<td>electroplated Ag</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>36,300</td>
</tr>
<tr>
<td>FeCl₃ Etch</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>44,500</td>
</tr>
<tr>
<td>plus 0.25 mil</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>35,400</td>
</tr>
<tr>
<td>Electroplated Ni then</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>47,300</td>
</tr>
<tr>
<td>electroplated Ag</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>35,400</td>
</tr>
<tr>
<td>FeCl₃ Electroplated Ag</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>23,600</td>
</tr>
<tr>
<td>Electroplated Ag</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>26,400</td>
</tr>
<tr>
<td>No FeCl₃ etch</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>28,200</td>
</tr>
<tr>
<td>Electroplated Ag</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>39,100</td>
</tr>
<tr>
<td></td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>33,600</td>
</tr>
<tr>
<td></td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>33,900</td>
</tr>
</tbody>
</table>

Fig. 12 — Influence of welding variables on joint strength for stainless steel

Fig. 13 — Beryllium specimen showing fracture in beryllium (left) and silver (right). Welding conditions were 1 h, 300°C (572°F), 30,000 psi (206.8 MPa), and 6 mil (0.006 in.) of silver. The joint failed at 23,000 psi (158.6 MPa).

Table 8 — Diffusion Welding Results for Uranium Joined to Stainless Steel
etch was used and followed by a thin coating of nickel. The fact that good welds were obtained when no etch was used is of particular interest and is an example of a situation where the pressure and heat used for diffusion welding overcame the deficiencies encountered with less than optimum plating adhesion. Similar improvements in joint strength have been obtained with diffusion welded titanium and zirconium substrates even though less than optimum plating procedures had been used to provide the bonding layer (Ref. 14). Although good joints were obtained with no etch prior to plating, it is recommended that uranium parts for solid state welding be etched prior to plating. This is suggested because without the etch there is no adhesion between the coating and uranium, and deposits could easily be damaged prior to welding.

Recommendations

For optimum diffusion welding results it is recommended that stainless steel, beryllium and uranium be cleaned, activated and plated with silver using the processes described in the Appendix. For the diffusion welding operation, the use of high temperature, high pressure, and low thickness—e.g., 600°C (1112°F), 30,000 psi (206.8 MPa) and 1 mil (0.001 in.)—is suggested. If the parts are of a complex configuration, a thicker silver plating can be used without noticeably degrading weld strength. Since time was shown to be insignificant for all three materials, 1 h would be quite adequate to facilitate joining.

Summary

Stainless steel, beryllium and uranium were diffusion welded with the aid of electroplated silver. Sound, strong joints were obtained with 1/2 in. (12.7 mm) diameter cylindrical butt specimens under a variety of diffusion welding conditions. The procedures used for preparing the substrates for plating were first characterized by using ring shear tests which provided quantitative information on adhesion.

For the diffusion welding studies, a full factorial experiment with two levels and four variables (24) was run with stainless steel. Fewer experiments were done with beryllium and uranium.

The four variables included in the study were: time—1 and 4h; temperature—300 and 600°C (572 and 1112°F); bonding pressure—10,000 and 30,000 psi (68.9 and 206.8 MPa); and silver plating thickness—1 and 6 mil (0.001 and 0.006 in.). With stainless steel the mean joint strength was 47,800 psi (329.6 MPa). Time was a nonsignificant variable, while thickness, pressure and temperature were significant as were the interactions of temperature with pressure and temperature with thickness.

Although full factorial experiments were not run with beryllium and uranium, enough data were obtained to reveal that time was insignificant for these materials. On the other hand, temperature was very significant, and thickness and load were relatively insignificant. For joining of these materials the use of 1 h at 600°C (1112°F) and 30,000 psi (206.8 MPa) is suggested. The optimum plating thickness would be 1 mil (0.001 in.) of silver.

Acknowledgments

The work described in this paper was sponsored by the Mechanical Engineering Department at LLNL, and we are thankful for the support. We would like to acknowledge W. W. Feng, who heads the M.E. Research Program, for help and assistance throughout the program, W. D. Ludemann for many technical discussions and for providing scanning electron microscopy support, and R. W. Mersing for providing the analysis of the factorial experiment with stainless steel.

The work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract W-7405-ENG-48.

References


Appendix

A. Procedure for Cleaning, Activating and Plating Silver on Type 304 Stainless Steel

1. Degrease.
2. Electroclean in Oakite 195 at 70°C, (158°F) cathodic 1½ min; then anodic 30 s.
3. Water rinse.
4. Immerse 10% (wgt) sulfuric acid for 3 min.
5. Anodic activate in 70% (wgt) sulfuric acid for 3 min at 538 A/m² (50 A/ft²).
7. Immerse in 2% (vol) hydrochloric acid for 30 s.
8. Wood’s nickel strike for 5 min at 538 A/m² (50 A/ft²). Composition of Wood’s nickel strike: nickel chloride—240 g/L; hydrochloric acid—125 ml/L; Temperature—25°C (77°F).
10. Immerse in potassium cyanide, 10 g/l for 1 min.
11. Silver strike for 1 min. at 108 A/m² (10 A/ft²). Composition of silver strike: silver cyanide—7.4 g/L; potassium cyanide—75 g/L; temperature—25°C (77°F); anodes—stainless steel.
12. Silver plate to final thickness at 54 A/m² (5 A/ft²). Composition of silver plating solution: silver cyanide—40 g/L; potassium cyanide—60 g/L; potassium carbonate—45 g/L; temperature—25°C (77°F); agitation—stirring rod.

B. Procedure for Cleaning, Activating and Plating Silver on Beryllium

1. Degrease.
2. Scrub with pumice.
3. Water rinse.
4. Etch in 20 parts water, 20 parts nitric acid, 1 part hydrofluoric acid for 5 min, 23°C (73°F).
5. Rinse.
6. Zincate in solution containing sulfuric acid 25 ml/L, potassium fluoride 15 g/l, zinc oxide 30 g/L, 1 min, 27°C (81°F).
7. Water rinse.
8. Strip zincate in 50% nitric acid.
12. Silver strike—see stainless steel procedure (appendix A) for details.
13. Silver plate—see stainless steel procedure (appendix A) for details.
C. Procedure for Cleaning, Activating and Plating Silver on Unalloyed Uranium

1. Degrease.
2. Immerse in nitric acid (50% vol.) for 3 min.
3. Water rinse.
4. Scrub with pumice.
5. Water rinse.
6. Immerse in nitric acid (50% vol.) for 3 min.
7. Water rinse.
8. Scrub with pumice.
10. Immerse in nitric acid (50% vol.) for 3 min.
12. Etch in 1400 g/L ferric chloride, 32°C (90°F), 5 min.
14. Immerse in nitric acid (50% vol.) for 3 min.
15. Water rinse.
16. Plate with ~0.25 mil in nickel sulfamate solution, 215 A/m² (20 A/ft²), 55°C (131°F).
17. Water rinse.
18. Immerse in sulfuric acid (10% wgt) for 1 min.
20. Immerse in potassium cyanide, 10 g/L for 1 min.
21. Silver strike—see stainless steel procedures (appendix A) for details.
22. Silver plate—see stainless steel procedure (appendix A) for details.