METHOD OF BRAZING ALUMINUM TO STAINLESS STEEL FOR HIGH-STRESS-FATIGUE APPLICATIONS
METHOD OF BRAZING ALUMINUM TO STAINLESS STEEL FOR HIGH-STRESS-FATIGUE APPLICATIONS

By
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Prepared under contract for NASA by
Battelle Memorial Institute
Foreword

Ideally, many structures could be fabricated from a variety of metals and alloys to take advantage of the unique properties of each material. Metallurgical differences create major problems, however, when different materials are used in a structure. A variety of unfavorable reactions occur in joints between different metals. The formation of intermetallic compounds is a prime example of these troublesome metallurgical reactions. The compounds reduce the strength and ductility of the joint and, in some cases, may actually make it impossible to produce a finished joint. The Rocketdyne Division of North American Aviation, Inc., has developed for NASA a procedure for minimizing the formation of intermetallic compounds in aluminum-stainless steel joints for valve assemblies in rocket motors. The procedure can be adapted to making additional parts of combined aluminum and stainless steel, and should be adaptable to other dissimilar metal joints.

The Administrator of the National Aeronautics and Space Administration has established a Technology Utilization Program to bring rapidly to the attention of industry new technology developed by NASA. This publication is part of a series designed to provide this technical information.

George J. Howick, Director
Technology Utilization Division
National Aeronautics and Space Administration
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INTRODUCTION

Traditionally, we fabricate many structures from a single material knowing that different parts of these structures are subjected to different service conditions. In such cases, the structures' properties are a compromise of those required by the various service conditions encountered. Ideally, we should fabricate these structures from a variety of metals and alloys to take advantage of each material's unique properties. For example, high-strength steels satisfy high-stress conditions. Aluminum and copper are ideal for high electrical or heat conductivity applications. Refractory-metal alloys respond favorably to high temperatures. Stainless steels or aluminum are preferred for cryogenic temperatures.

Metallurgical differences create a major problem, however, when structures are made of more than one metal. When dissimilar metals are joined by methods using elevated temperatures, a wide variety of metallurgical reactions can and do occur. The most troublesome metallurgical problem encountered is the formation of intermetallic compounds. Continuous layers of these compounds are quite brittle, and their presence usually weakens a joint. Fabricators always try to prevent or minimize the formation of intermetallic compounds in dissimilar-metal joints. This problem has prevented industry from fully using dissimilar metals in structural design.

Aluminum and stainless steel offer an example. Aerospace manufacturers use both metals extensively because of their corrosion resistance and excellent low-temperature mechanical properties. They also use stainless steels because of their elevated-temperature properties and aluminum because of its low density. If a process for making strong, hermetically sealed joints were available, industry could capitalize on the different properties of these two metals. Many techniques for joining these materials have been tried, including welding, solid-state bonding, and brazing. Unfortunately, iron and aluminum react rapidly at relatively low temperatures to produce brittle intermetallic compounds that crack easily. The cracks provide either leak paths or reduce the strength of the joint below that required by many designs.

The Rocketdyne Division of North American Aviation, Inc. has developed for NASA a procedure for minimizing the formation of
intermetallic compounds in aluminum-stainless steel joints. They have successfully fabricated valve assemblies used in rocket motors using this procedure. The procedure can, of course, be used in making many other parts containing aluminum and stainless steel. Consequently, NASA is making this information generally available to industry.

The process uses a coating of titanium on the stainless steel to act as a diffusion barrier and minimize compound formation. The titanium layer is coated with an aluminum-silicon alloy (4043), and the joint is made by brazing the aluminum part to the coated stainless steel part. When the aluminum part is an age-hardenable aluminum alloy, it can be hardened by proper aging treatment after the brazing operation.

APPLICATIONS

Rocketdyne developed this process to produce control valve assemblies for a rocket engine and to make electrical components. Several other potential uses are:

1. Fabricating transition joints for use in piping systems containing both materials.
2. Fabricating tube-to-tube sheet joints where tubes are of one material and tube sheet of the other.
3. Fabricating extended surfaces for heat exchangers where both stainless steel and aluminum are used.
4. Applying cladding to complex shapes.

Material combinations other than those used by Rocketdyne might also be joined successfully by this process. There is no reason other fabricators cannot use the process to join carbon steels, low-alloy steels, and high-alloy steels other than stainless to aluminum. With little or no modification, industry could use the procedure to join aluminum and nickel-base alloys. Modification of the procedure by substituting another or additional barrier layer should broaden its usefulness by increasing the types of metals that could be joined to aluminum.

The barrier layer-brazing concept applies to other metal combinations as well. A short list follows indicating other dissimilar-metal joints which have been made by techniques similar to those described:

- Beryllium—stainless steel
- Copper—stainless steel
- Copper—alloy steel
- Columbium—stainless steel
- Molybdenum—graphite
- Titanium—alloy steel.
PROBLEMS OF JOINING ALUMINUM TO IRON-BASE ALLOYS

The major problem encountered in joining iron and aluminum when heat is employed is the formation of iron-aluminum compounds. Figure 1 is an equilibrium aluminum-iron phase diagram showing the

\[\text{Figure 1.—Equilibrium phase diagram for aluminum-iron system (ref. 1).}\]
number of compounds that are possible in the system. In addition, the reaction kinetics of this system are high. Thick layers of compound can build up in relatively short times at temperatures below the melting point of aluminum. The compound layers can form during the joining operation or during service at elevated temperatures. They are quite brittle and crack under little stress when they have appreciable thickness. Consequently, joints directly between aluminum and steel have low strengths.

**DIFFUSION BARRIER**

High joint strength requires that interdiffusion of iron and aluminum across the joint interface be prevented. At North American the workmen deposit a layer of titanium on the steel part to accomplish this. They then coat the titanium with a layer of aluminum-silicon alloy to prevent oxidation of the titanium during subsequent operations. Although a titanium-aluminum compound layer forms between the two deposits, it is quite thin and does not degrade the joint properties.

The NAA fabricators use vapor deposition to coat the stainless steel with both titanium and 4043 aluminum alloy. They tried other coating methods but found them to be less effective than vapor deposition. The vapor deposition process uses two electron guns in a vacuum, one to vaporize the metal being deposited and the other to preheat the part being coated. The part is cylindrical, 2.5 inches in diameter. A 3 to 4-kV electron gun preheats the part during the vapor-deposition operation, while a 10 to 12-kV electron gun melts and evaporates the coating materials. Radiation or resistance heating would preheat the part equally well, but electron-beam heating vaporizes the material to be deposited most efficiently. This method provides high-deposition rates (which can be in pounds per hour) and high-deposition efficiency. Figure 2 shows the arrangement of the coating system; figure 3 shows details of the vaporization system.

Rocketdyne engineers found that the stainless steel components must be cleaned just before being put into the vacuum chamber for coating with titanium. Either washing or degreasing will remove dirt and films of oil and grease. Removal of soluble oils, tallow, and fats requires a hot alkaline-solution wash followed by a hot-water rinse. Grinding, filing, or wire brushing will remove scale and oxide films from stainless steel. A machining operation grinds hot cut edges to bright metals. Stainless steel brushes and cleaning tools should be used instead of carbon steel to avoid picking up bits of carbon steel in the work.

A pickling operation will also remove oxide film and scale. Table I
gives a typical pickling sequence with recommendations for solutions and times. At North American, operators clean all tooling in the vacuum chamber to free it of materials that might contaminate the part being coated. The operators wear clean gloves for handling all cleaned parts and tools.
Titanium Coating

After cleaning the parts, an operator places them in the vacuum chamber and places commercially pure titanium in the water-cooled copper crucible. Pumping reduces the chamber atmosphere to a vacuum of at least $10^{-4}$ torr. The 3 to 4 kV electron-beam gun preheats the stainless part to $1450\pm50$° F. Heating continues until a stable temperature is attained. The titanium is then melted and brought to thermal equilibrium. This produces a pool of molten titanium contained in a skull of solid titanium. When the pool of molten titanium
TABLE I.—Typical Sequence of Procedures for Pickling Series 300 Stainless Steels (ref. 2)

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Solution</th>
<th>Immersion Time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Composition (%) by volume</td>
<td>Operating Temperature (°F)</td>
</tr>
<tr>
<td>Sulfuric acid dip</td>
<td>15 to 25 H₂SO₄</td>
<td>160 to 180</td>
</tr>
<tr>
<td>Water rinse</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitric-hydrofluoric acid dip</td>
<td>5 to 12 HNO₃; 2 to 4 HF</td>
<td>Ambient</td>
</tr>
<tr>
<td>Water rinse</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Caustic-permanganate dip</td>
<td>18 to 20 NaOH; 4 to 6 KMnO₄</td>
<td>Ambient</td>
</tr>
<tr>
<td>Water rinse</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfuric acid dip</td>
<td>15 to 25 H₂SO₄</td>
<td>160 to 180</td>
</tr>
<tr>
<td>Water rinse</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitric acid dip</td>
<td>10 to 30 HNO₃</td>
<td>120 to 180</td>
</tr>
<tr>
<td>Water rinse (dip)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Acid solutions are not inhibited.
- Shorter times are for lower-alloy steels; longer times are for more highly alloyed types, such as 309, 310, 316, 317, and 318.
- Sodium chloride (up to 5% by weight) may be added.
- Dip or pressure spray.
- Sometimes used to loosen scale.
- Percent by weight.
- Boiling water may be used to facilitate drying.

has stabilized, an operator moves the vapor barrier aside and titanium vapor deposits on the stainless-steel part. Deposition continues until the titanium layer reaches the desired thickness—as thin as possible but still thick enough to prevent reaction between the aluminum and iron.

After satisfactory deposition, the operator shuts off both electron-beam guns and the part cools in a vacuum. This prevents oxidation of the freshly deposited titanium. Cooling is quite slow. For parts adaptable to their use, water-cooled fixtures would speed up cooling.

**Aluminum Coating**

Obtaining a good braze joint between the titanium-coated stainless steel part and an aluminum part requires that the titanium be vapor coated with aluminum. North American's experience indicates that
the aluminum-silicon alloy 4043 is a good secondary coating material. The fabricators deposit this alloy in the same way that they deposit the titanium. However, they fill the copper crucible with zirconium to \( \frac{3}{4} \) to \( \frac{1}{4} \) inch from the top before adding the aluminum alloy. The zirconium controls the evaporation rate of the 4043 aluminum alloy. Aluminum alloy is added as wire and fed into the crucible at the rate required to maintain a pool during the deposition procedure.

The vacuum used is again \( 10^{-4} \) torr. After obtaining this vacuum, Rocketdyne preheats the titanium coated stainless steel part to 1450\( ^\circ \) F, cools it to 1100\( ^\circ \) F, and stabilizes it there. An operator turns on the vaporizing gun and moves the vapor barrier aside. Heating continues until the coating reaches the desired thickness. Coatings of 0.040 to 0.060 inch are adequate, although thicker coatings have been deposited. When the desired thickness is obtained, the operator shuts off the electron-beam guns and the part cools in vacuum. Aluminum-coated parts may be machined after coating to obtain the needed clearances for brazing. However, the operator must take care not to machine through the vapor deposits.

**Brazing**

North American's experience shows that dip brazing can produce excellent joints between the titanium-aluminum vapor-coated stainless steel parts and aluminum alloy parts. Dip brazing is an excellent way of heating and fluxing aluminum joints simultaneously. You can dip braze as follows. Dip the assembled parts into a molten brazing flux held at the brazing temperature. Then apply heat to all of the parts of the assembly at the same time. Use flux to force air out of the joints. The uniform temperatures and fast heating obtained in this manner minimize temperature gradients. This makes it possible to join close tolerance parts and assemblies of thin materials.

Normally, you can use standard proprietary aluminum brazing fluxes for dip brazing. In selecting filler metal, North American found that BAlSi-4 (11 to 13 percent silicon) produced good joints. This alloy has a liquidous temperature of 1080\( ^\circ \) F and a brazing range of 1080\( ^\circ \) to 1120\( ^\circ \) F. When brazing a large number of parts, add flux as you go. A small amount of flux (about \( \frac{1}{2} \) oz per sq ft of part surface) leaves the bath each time a part is brazed. As with coating, be sure all parts are clean before brazing.

Vapor or solvent cleaning will remove oil and grease. Dirt can be removed by washing in hot water. Heat-treated alloys may require a chemical treatment; a common one is a 5-percent sodium hydroxide dip at 140\( ^\circ \) F followed by a cold water rinse, dipping in 50-percent nitric acid at room temperature, and another cold water rinse.
It is equally important to clean the fixtures, if they are used, and to take every precaution not to contaminate the parts during assembly. Fixtures must be designed to preserve proper clearances in the joints during brazing.

After proper cleaning, assemble the parts in the fixture and preplace the filler metal at the joints. Then, preheat the fixtured assembly to 1000° to 1050° F, transfer it to the brazing pot, and completely immerse it in the molten flux. Leave the assembly in the molten flux long enough to assure that the braze metal is molten. Then, remove it from the bath and suspend it over the bath for a short time to allow molten flux to drain back into the bath and to allow the braze metal to freeze. When sufficient time has elapsed to be certain the braze metal has solidified, you may quench the assembly.

Brazed aluminum assemblies must always be cleaned after brazing. If not removed, the brazing fluxes accelerate corrosion. You can clean after brazing by first washing the assembly in hot (180° to 212° F) agitated water. Scrubbing will help to remove flux. Take particular care with any assembly with design details that may trap flux. After washing, remove the last remaining flux by chemical cleaning. Thick parts can be treated by a 5-minute immersion in cold, ½-percent hydrofluoric acid. This treatment attacks the aluminum and should not be used for thin parts. For thin parts, use solutions containing 5 percent phosphoric acid plus 2 percent chromium trioxide at 180° F. You can also use cold, 10 to 15 percent nitric acid solutions with thin parts if you are careful to limit the effects of chloride pickup from the flux.

If the aluminum parts of the assembly are made from a heat-treatable aluminum alloy you can use the brazing operation as a solution heat treatment. Aging at the proper temperature after brazing will then produce maximum properties in the aluminum.

JOINT PROPERTIES

The Rocketdyne Division of North American Aviation, Inc., used the system described to make aluminum-to-stainless steel joints in fabricating J-2 engine control valves and electrical components. They developed the proper procedures by making and testing a number of joints between stainless steel and aluminum. These joints were made from 304L stainless tubing with an outside diameter of 2½ inches and inside diameter of 2 inches. Their engineers coated the stainless steel tubes with titanium and 4043 aluminum and brazed them into a 6061-aluminum valve prototype. After brazing, they welded end caps of 6061 aluminum and 304L stainless to the ends of the assemblies so that they could be pressurized.
Figure 4.—Cross-section of vapor-deposited, brazed joints between 6061-T6 aluminum and 347 stainless steel. (a) 347 stainless steel, (b) vapor-deposited titanium, (c) vapor-deposited 4043 aluminum, (d) brazed joint—13% Si and 87% Al alloy, (e) 6061-T6 aluminum.
Figure 4 is a photomicrograph of a brazed joint cross section, showing all of the layers in the joint. The effectiveness of the vapor deposited titanium in preventing reaction between the steel and the aluminum is clearly evident.

North American ran a series of sequential laboratory tests on the brazed assemblies. These were:

1. Exposure to salt spray atmosphere for 50 hours (per MIL-E-5272).
2. Thermal cycling 50 times from room temperature to $-327^\circ$ F.
3. Vibration of 40-g input for 30 minutes at resonant frequency.
4. Hydrostatic test to determine shear strength of dissimilar-metal joint.

After each of the first three steps, helium mass spectrographic leak tests were run. The results of these tests showed that the leak rate for the joints was less than $1 \times 10^{-7}$ cc of helium per second both before and after the first three test exposures described above. Hydrostatic tests showed that separation of the joints did not occur at a shear stress of 4000 psi. Continuation of the hydrostatic tests showed that the shear strength of joints in the as-quenched from brazing temperature condition was 6000 to 7000 psi. In one test assembly, separation occurred at the vapor-deposit interface at a stress of 6000 psi. In five other test assemblies, failure occurred in the braze metal. When the 6061 aluminum used in the joints was heat-treated to the T651 condition after brazing, the shear strength of the joint was over 7000 psi. Failure occurred away from the joint area in these heat-treated test assemblies.

REFERENCES

"The aeronautical and space activities of the United States shall be conducted so as to contribute . . . to the expansion of human knowledge of phenomena in the atmosphere and space. The Administration shall provide for the widest practicable and appropriate dissemination of information concerning its activities and the results thereof."

—National Aeronautics and Space Act of 1958

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