Exploring a Low Melting Temperature Silver Braze Alloy for Fuel Cell Fabrication

In the manufacture of fuel cells, particularly the solid oxide fuel cell (SOFC), the fuel cell is brazed to a surrounding metal "cassette" frame to form the subassembly using a silver/copper or silver/vanadium braze. Unfortunately, brazing filler metals used for this process have a liquidus temperature substantially higher than the melting point of pure silver, and this restricted the use of some fuel cell materials.

Delphi Technologies, Inc., Troy, Mich., disclosed a brazing alloy comprised of silver and silicon at a silver/silicon ratio between 95/5 and 99/1, preferably around 97/3, and this is to be used instead of the conventional silver/copper braze (Ref. 1).

The brazing procedure includes two steps: 1) brazing of one fuel cell element to the cassette frame at the temperature below 962°C (1764°F) using a first Ag-Si filler metal, and then, 2) brazing another fuel cell element at the temperature below that of the first step, using an eutectic Ag-3Si filler metal that has the melting point of 835°C (1535°F).

The Ag-3Ru eutectic alloy, which has a melting point of 920°C (1688°F), can also be used as the brazing filler metal at the first step of the process.

Looking at Lightweight Lead-Free Sn-Cu-Al-Ag Solder Compositions with High Soldering Temperature

Matsushita Electric Industrial Co. invented and tested a new lead-free solder containing 25 wt-% copper, 1 wt-% aluminum, and tin in the balance, or 3.5 wt-% copper, 1.5 wt-% aluminum, 5 wt-% silver, and tin in the balance (Ref. 2). The first composition has a specific gravity of 7.48 g/cm^3 and a soldering temperature of ≥300°C (572°F), while the second composition has a specific gravity of 7.63 g/cm^3 and a soldering temperature of ≥ 330°C (626°F).

Alternatively, the solder may comprise 20 wt-% of the Sn-0.7Cu eutectic alloy mixed with 70 wt-% of Ag-30Al alloy and 10 wt-% of the Bi-35In eutectic alloy. This composition has a specific gravity of 8.11 g/cm^3 and a soldering temperature of ≥ 450°C (842°F).

All new solders have a specific gravity significantly lower than that of the conventional Pb-5Sn solder, which is 11.15 g/cm^3.

Examining GMA Brazing of Galvanized Steel Sheet Joints for the Automotive Industry

The gas metal arc (GMA) brazing process is extensively studied in Europe to provide a cost-effective technology of joining thin Zn-coated steel sheets. Two articles that were published last winter, almost simultaneously, showed the whole specter of process parameters and the brazing filler metals compatible to galvanized carbon steel used in the automotive industry. The brazing filler metals are silicon bronze (Cu-3Si), tin bronze (Cu-6Sn), and aluminum bronze (Cu-8Al).

The first paper (Ref. 3) discusses the effects of shielding atmospheres (argon and mixtures of argon with H_2, N_2, O_2, and CO_2) on the quality of joints and gives guidelines on the selection of parameters of GMA brazing in the short-arc range and with a pulsed arc. Also, recommendations for different joint designs, particularly butt joints, flange joints, lap joints, and edge joint types, can be found here. The second paper (Ref. 4) is focused on tensile strength and corrosion resistance of joints brazed with different shielding gases or different process parameters, but in the same atmosphere.

The process temperature is only slightly above the boiling point of zinc coating; therefore, brazing avoids a developed porosity in the joints that often occurs after arc welding of galvanized steel. A certain degree of internal porosity is still noticed in brazing joints, but it is not critical for mechanical properties (Ref. 3). Sometimes, transverse cracks may arise in the brazed joints due to a mismatch in thermal expansion coefficients between steel and bronze filler metal. In order to avoid cracks in the joints of thicker sheets, the brazing is to be carried out by linking short (< 50 mm) joints in a sequence. The average strength of brazed joints was reached 330 N/mm^2 (47 ksi) at the steel sheet thickness of 1 mm (0.04 in.). A macrostructure of the joint of a rear wing of a passenger car demonstrates the quality of the process (Ref. 4).

The optimal gas mixture for GMA brazing with the Cu-3Si filler metal is Ar+2.5% CO_2, which provides good joint formation, lower heat input, and the best corrosion resistance. The corrosion resistance clearly depends on the heat input during the brazing; this means that the process parameters and gas mixture, which are characterized by lower heat input, result in better corrosion resistance (Ref. 4).

Residual stresses in the joints depend on many factors such as the clearance between steel sheets to be brazed, the standoff dimensions, direction of brazing, and prefixing of sheets by arc brazed spots. Prefixing is not recommended (Ref. 4).

Coating Spray Process Developed for the Deposition of Cu-Sn-P-Ni Brazing Filler Metal

A wire arc spray coating process and a new wire for the application of Cu-Sn-P-Ni brazing filler metal has been developed through the combined efforts of Luvata (formerly Outokumpu Copper), Mill Masters, Inc., and Praxair Surface Technologies, Inc. The new process is an alternative to the use of paste or braze foil in the CuproBraze® process.

The process involves the application of a braze filler material during the on-line manufacture of automotive heat exchanger tubes. The tubes are subsequently assembled with mating components and brazed with the manifold in the manufacture of automotive heat exchangers. The new brazing alloy was developed by a Praxair Surface Technologies subsidiary, TAFA, Inc., Concord, N.H. The material 15T3 is a proprietary Praxair and TAFA alloy. Testing of the arc wire process has shown that significantly less material may be needed than that needed for the paste process.

The effectiveness of the process was demonstrated in the presentation of Y. L. Shabtay (Luvata) at the 3rd Int. Brazing & Soldering Conference held April 23–26, 2006, in San Antonio, Tex. (Ref. 6).

Investigating Brazing Repair of Gas Turbine Parts without Removing All Cracks

A new technology for repairing a gas turbine stator vane has been disclosed by Kabushiki Kaisha Toshiba, Tokyo, Japan. The method includes the following: (a) grinding the oxidized layer and the cracks formed at surface portion so that a part of cracks remains; (b) filling a powder mixture of an equivalent material and a brazing filler metal into a ground place, whereby said equivalent material has a chemical composition close to the base metal; (c) heating and melting the brazing filler metal under a pressurized inert gas atmosphere; and (d) performing brazing by diffusing the melt into the cracks. Thus, the novelty is brazing under a high gas pressure of 95–200 MPa (ksi).

The solution heat treatment (HIP) and aging heat treatment are carried out after the brazing at a temperature lower than a temperature at which said base material is partially molten, or lower than a temperature at which a cell structure formed of eutectic carbides collapses (Ref. 7).

For example, the stator vane made of the superalloy FSX-414 was repaired by brazing with a mixture of IN939 (which is the equivalent material powder) and the brazing powder having a composition of Cr 13.1, Co 20, B 2.6, Si 4.0, C 0.002 wt-%, and Ni in the balance.

Brazing was performed at 1150°C (2100°F) and the inert gas pressure 95–115 MPa (14–17 ksi). The postbrazing HIP heat treatment was made at 1170°C (2138°F) and gas pressure 100 MPa (ksi).

Silicon Package Invented for Piezoelectric Device in Low-Production-Volume Application

A hermetic package for electronic components made of metallic silicon has been invented by P. Ferreiro and K. Martin, Erie, Pa. (Ref. 8). The base member is mounted atop a glass pedestal with the lower end fastened to a source of vacuum. The quartz crystal resonator is attached to the base member by brazing with a gold-indium eutectic at 495°C. The same technique is then employed to attach a silicon spacer ring.

Once assembly of the surface-mountable electronic component is completed, the source of vacuum is activated and typically maintained for one week to pull a vacuum in the range of between 10^{-6} and 10^{-10} torr to remove all potential pollutants from the cavity between hollowed portions of design.

Once the package is hermetic to the desired degree, the glass pedestal is melted to seal the device.

Silver-Based Ag-Cu-Pd-Ge-Co/Mn Filler Metals Effective for Brazing Difficult-to-Wet Stainless Steels

Umicore AG&Co. KG, Hanau, Germany, tested new silver-based brazing filler metals that are effective for joining difficult-to-wet stainless steels, which comprise such components as W, Ti, V, Cr, etc. (Ref. 9). Combined alloying of silver-copper-palladium alloys with germanium and cobalt or manganese resulted in improved thermal stability and vacuum tightness of brazed joints made from the above-mentioned stainless steels. The melting range of new brazing filler metals is between 800° and 940°C.

For instance, the brazing filler metal Ag-3Cu-2Pd-2Ge-0.3Co has the melting range of 870°–930°C (1600°–1706°F), the filler metal Ag-8Cu-5Pd-2Ge-0.3Co has the melting range of 800°–900°C (1472°–1652°F), and the filler metal Ag-8Cu-3Pd-2Ge-2Mn has the melting range of 800°–890°C (1472°–1634°F).

These alloys exhibit fair levels of plasticity and strength in the annealed state. The alloy Ag-3Cu-2Pd-2Ge-0.3Co has the yield strength 83 N/mm^2 (12 ksi), tensile strength 180 N/mm^2 (26 ksi), and elongation 11%.

The filler metal Ag-8Cu-3Pd-2Ge-2Mn has the yield strength 200 N/mm^2 (29 ksi), tensile strength 242 N/mm^2 (35 ksi), and elongation 8%.

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A Look at Recent Growth in Amorphous Brazing Foil Applications

In recent years, growing attention toward energy conservation and the elimination of atmospheric pollution has spurred substantial growth in amorphous Metglas Brazing Foil (MBF) applications.

MBF technology, which started about 30 years ago in the aerospace industry, has been widely used in the production of plate heat exchangers that are important parts of fuel cells, heat pumps, and exhaust systems for both gas and diesel internal combustion engines. Most of these applications are associated with the production of thin-walled, three-dimensional, multichanneled, and lightweight structures. These structures, with mostly honeycomb cross-section geometry, require a low erosiveness of the filler metals used combined with a high strength and corrosion/oxidation resistance.

Brazing foil is produced with a consistently thin, even thickness, and is very convenient for preplacement across the total joint cross-section of the structure; thus, it provides an ultimately low and measured erosion of a thin base metal during brazing operations. At the same time, the resulting joints are strong and can withstand many years of service under hard environmental conditions.

New, fast growing, and very large volume applications are evolving in the automotive industry. In addition to joining more efficient metal catalytic substrates, which are now replacing ceramic substrates in automotive exhaust systems, the industry is also utilizing production of exhaust gas recirculators and particulate filters. These devices clean the exhaust gases of diesel engines and, simultaneously, preheat or cool the incoming air to the diesel cylinders, thus increasing overall engine efficiency.

Today, diesel engines are gaining in popularity vs. gasoline-based auto engines in Europe and the United States. Metglas amorphous alloys, which contain a high chromium concentration, have all been tested and are used successfully in the production of these devices. Millions of cars and trucks with various gasoline and diesel engines are running throughout the world containing brazed parts made with amorphous foil.

Another success was achieved recently in the "delicate" brazing of fragile and very lightweight metallic foams used in diesel particulates filters. No catastrophic foam dissolution has occurred, whereas the integrity and joint strength are sufficient to form a unique integral structure combining the enclosing thick frames and foams. These filters are the newest step in environmental improvement.

As expected, the efforts to improve environmental protection and energy savings in both the power-generation and automotive industries have also begun to spread into the stationary and ship engine manufacturing segments. As a result, a vast increase in foil production — that today is measured in hundreds of tons — is expected in the near future due to the introduction of new environmental protection milestones coming soon in both developed countries and emerging countries such as China, India, and elsewhere.

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