Ceramic-Metal Bonding Research in Japan

Japanese metals laboratories are becoming materials laboratories as a result of "ceramic fever"

BY T. W. EAGAR

The Japanese call it "ceramic fever," but whatever it is, one cannot help but be impressed with the pervasiveness of research on fine ceramics in Japan. After spending one year visiting well over 50 different metals processing laboratories in Japan, it is striking to note that approximately half of these traditionally metals laboratories are now studying ceramic-metal bonding in some form. For example, at the Welding Research Institute of Osaka University, seven out of nine research divisions are working on ceramics of some form, whether it be diffusion bonding (Fig. 1), plasma spraying, brazing, or laser processing. In the Department of Welding Engineering, at least three out of eight research groups are now working on ceramics. At the Technical Research Center of Hitachi Shipbuilding, 10 out of 22 welding researchers were studying ceramic-metal bonding at the time of my visit, and those planning to begin in the next year included Nippon Kokan Steel, Sumitomo Steel and the Solid State Bonding Research Committee of the Japan Welding Society. The fever is spreading to Korea as well, with several welding laboratories there planning new programs in the next year.

In the review that follows, it should be noted that little attempt was made to visit or evaluate the ceramic-metal (C-M) research at the many traditional ceramics laboratories. Most of what follows represents new directions for researchers who traditionally have been welding metallurgists. Another factor which should be emphasized is that most of these people have only been studying C-M systems for one to three years; hence, the quantity of results does not yet match the effort level. We can expect to see a significant increase in results within the next two or three years.

Specific Research Projects

Dr. S. Kitahara of the National Research Institute for Metals (NRIM) has studied plasma spraying for nearly 20 years. Currently, he is studying mixtures of Ni-Cr-Al-Y and Y_2O_3-MgO-stabilized ZrO_2 (Ref. 1). Thicknesses of 0.1 mm (0.004 in.) are built up by varying the ceramic-to-metal ratio either in layers or continuously. The single-layer coating lasts for 400 thermal cycles from 1088° to 316°C (1990° to 600°F), while the multilayer coating lasts for 600 cycles and the continuously changed coating can withstand 1000 cycles. Currently, SiC, TiC and Si_3N_4 coatings are being tested. The effect of hot isostatic pressing on coating effectiveness and performance is also part of a cooperative program with the Kobe Steel Corporation.

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In another study at NRIM, iron-aluminum joints have been produced using an iron-oxide insert. After bonding at 1200°C (2192°F) at 3 kg/mm^2 (4267 psi) pressure, a bond strength of 11 kg/mm^2 (15,646 psi) is obtained. It is believed that this process will be useful in the manufacture of turbines and pistons.

Finally, Dr. K. Yoshihara of NRIM has shown that AISI 321 stainless steel forms a TiC surface layer when annealed at 1100 K in a vacuum for 30 min (Ref. 2). More recent studies show that this thin (50-nm) TiC coating significantly improves the bonding of Al_2O_3 or TiC to stainless steel.

Ishikawajima-Harima Heavy Industries (IHI) has been studying diffusion bonding of Si_3N_4 to steel and aluminum 6061 alloy for joints to be used in liquid-fueled rocket engines. At 580°C (1076°F), a maximum bond shear strength of 8 kg/mm^2 (11,379 psi) is typical. They have also produced Cu-Al_2O_3 bonds at 1000°C (1832°F) with 14 kg/mm^2 (19,913 psi) maximum shear strength and 8 kg/mm^2 typical. In another study of aluminum-boron composites, they found that 5051 and 5083 aluminum alloys do not form good

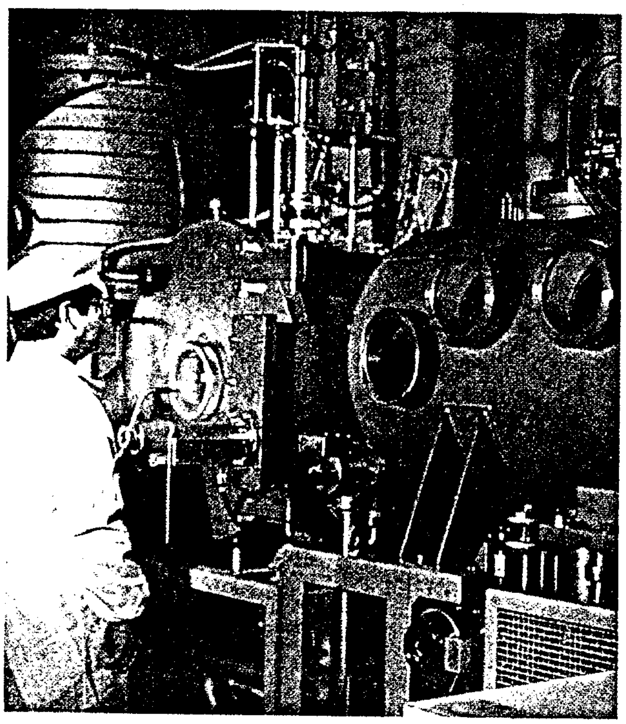

Fig. 1 — Sophisticated diffusion bonding equipment is being used to accurately join newly developed materials not easily joined by conventional means

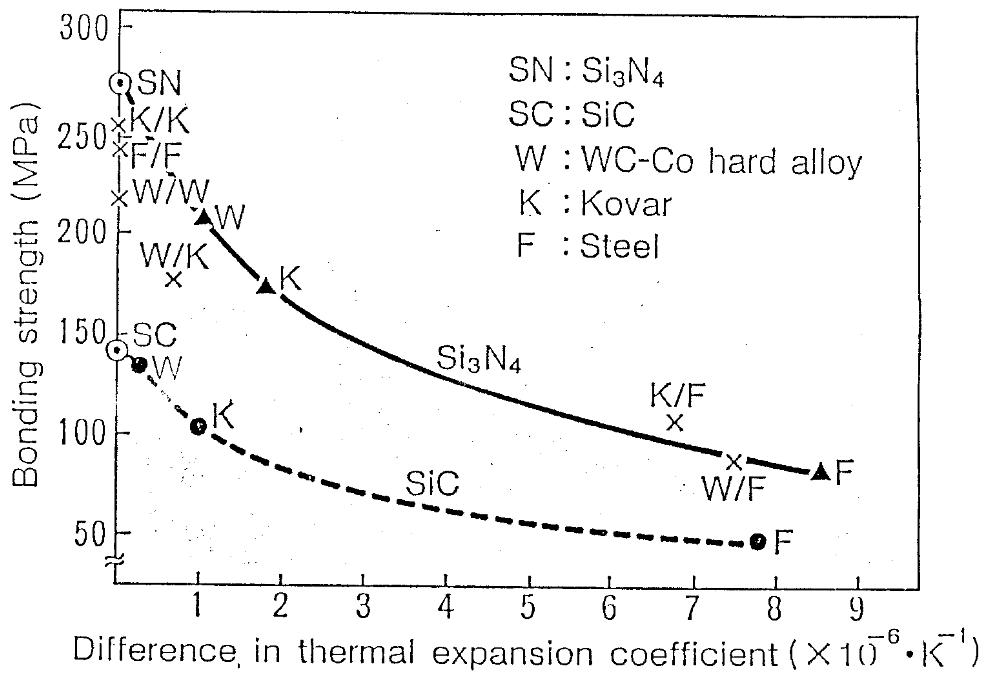

Fig. 2 — Strengths of specimens joined with an Al-Si clad metal, plotted as a function of the difference in the thermal expansion coefficients (temperature — 883 K, pressure — 9.8 MPa, time — 1.8 ks, interlayer thickness — 0.6 mm)

bonds, while 6061 alloy does form a bond. IHI plans to braze Si_3N_4 to itself using aluminum-based filler metals.

Hitachi Shipbuilding has developed bonding of Si_3N_4, SiC and sialon to Cr-Mo steel, Kovar and WC-6Co by using an aluminum-10, silicon alloy clad sheet with a pure aluminum core. The best bonds were formed when the Al-10Si alloy clad layer was molten, but the pure aluminum core of the composite brazing sheet was still solid. Strengths of 43 ksi (30 kg/mm^2) were obtained for sialon, 35 ksi (25 kg/mm^2) for Si_3N_4 and 20 ksi (14 kg/mm^2) for SiC, when bonded to Kovar or WC-6Co. As shown in Fig. 2, the strength was strongly influenced by the differential coefficient of thermal expansion of the two materials being joined.

In another study, Hitachi obtained bond strengths up to 100 kg/mm^2 (142,233 psi) when bonding WC-6Co to tool steel using a Permalloy insert. This maximum strength was obtained with an optimum Permalloy thickness of 0.25 mm (0.01 in.).

For use as a fusion reactor or MHD first wall material (Fig. 3), Hitachi has bonded SiC-BeO ceramics, which have high electrical resistivity, to stainless steel, copper or aluminum substrates using a copper-carbon composite interlayer. They use the aluminum-silicon braze discussed previously. Unfortunately, this limits the effective "use" temperature of the product. By varying the copper-to-carbon ratio in the interlayer, they can vary the coefficient of thermal expansion between 6 and 10×10^{-6} per °C. Several of these joints have been tested in coal-fired MHD channels with reportedly excellent ability to withstand heat (Ref. 3).

Finally, Hitachi has developed molecular-beam epitaxy systems fabricated out of aluminum, which are capable of low-temperature baking to obtain ultrahigh vacuum. The interior surfaces of the system have a proprietary alumina coating (presumably anodized), while the flange joints are coated with CrN (presumably by plasma deposition). Hitachi claims that this new system will considerably reduce the cycle time for ultrahigh vacuum processing equipment.

At Osaka University, Dr. A. Nishimura is bonding Si_3N_4 to tungsten using an amorphous 80Cu-Cr-Co brazing alloy. Professor F. Matsuda is studying boronizing of gold and refractory metals, and Dr. I. Miyamoto is laser beam welding mullite and alumina. Professor A. Matsunawa is forming TiN coatings on titanium by laser surface heating in a nitrogen atmosphere. Professor Y. Arata, director of the Welding Research Institute and the only recent engineer to be awarded the Japan Science Prize, has a large program in C-M bonding. He has studied the formation of the TiO_2 interlayer in Cu-Al_2O_3 joints when using Cu-Ti brazing alloys (Ref. 4). In similar work on Si_3N_4 and SiC, titanium silicides were found to form (Ref. 5). The Si_3N_4 joints had strength of over 17 kg/mm^2 (24,180 psi), but the SiC joints were less than one-quarter of this value. Additional studies of alumina-Kovar joints have produced strengths of 15 kg/mm^2 (21,335 psi) (Ref. 6).

Professor A. Omori, also of Osaka University, is studying the corrosion behavior of stainless steel with plasma-sprayed layers of ZrO_2, Al_2O_3 or TiO_2-Al_2O_3. A recent addition to his laboratory is vacuum-spraying equipment, with which he is studying bonding of SiC, Si_3N_4 and WC-Co on metal substrates. He has found that TiO_2 decomposes to Ti_3O_5 and WC to W_2C during plasma spraying. In a related study, Professor Inoue is laser remelting these plasma-sprayed coatings in order to reduce their porosity and improve their corrosion performance.

Professor Enjoh of Osaka University is studying diffusion bonding of Al_2O_3 and ZrO_2 to steel, and Al_2O_3 to itself. He is also brazing Al_2O_3 to steel using Cu-Ti alloys. In simple tension tests, the fracture is in the ceramic. When bonding ZrO_2 with the Cu-Ti alloy, the Ti aggressively attacks the ceramic. An attempt was made using the Cu-Zr brazing alloy, but suboxides of zirconia formed with resultant poor properties. Professor Enjoh has also made excellent Cu-Al_2O_3 joints by oxidizing the copper before diffusion bonding. Presently, they are studying Fe-Cu-Al_2O_3 composites in hope of reducing the interfacial stresses. A maximum strength of 3 to 4 kg/mm^2 (4267 to 5689 psi) is obtained when using a 2-mm-thick (0.08-in.) Cu interlayer.

At Hitachi Shipbuilding, they are studying plasma spraying, brazing, adhesive bonding, and thermal spraying of ceramics. They are presently producing a 90-mm-diameter (3.5 in.) ceramic-capped diesel piston. Next year, they expect to expand this to 120 mm (4.7 in.) and in two years to 400-mm-diameter (15.7-in.) pistons. Hitachi Shipbuilding uses interlayers to reduce the stress between the ceramic and the steel. They produce their own ceramics and are actively working on the machining of ceramics and plasma spraying for furnace coatings and turbine blades. Composite coatings of continuously graded compositions which are up to several millimeters in thickness are also being developed.

Kawasaki Heavy Industries is weaving SiC-C fibers with aluminum 6061 foil to produce fiber-reinforced metal cylinders. These are diffusion bonded at 575°C (1067°F) and 200 kg/mm^2 (284,466 psi) pressure. They expect to apply this product during production in the near future. In addition, studies with a new vacuum plasma-spraying unit have begun.

Mitsubishi Heavy Industries (MHI) has the world's largest diffusion-bonding unit capable of handling 10,000 tons (9072 t) and parts of 2.5- × 3.5-m (8.2- × 11.5-ft) size. They are studying diffusion bonding of Al_2O_3 and Si_3N_4 to metals in the laboratory. Brazing and adhesive-bonding studies are also in progress. MHI has extensive surface-coating equipment and is studying ion plating of TiN, BN, Si_3N_4, TiC, SiC, Al_2O_3 and TiO_2. Mitsubishi has made a very large investment in these surface modification laboratory facilities.

At the Tokyo Institute of Technology, Professor I. Iseki has studied bonding of SiC for many years. In one study, germanium was used as a braze alloy (Ref. 7), and bending strengths in excess of 20 kg/mm^2 (28,447 psi) were obtained. In a more recent study, he has shown that Al_4C_3 forms at the interface of SiC and aluminum joints (Ref. 8) and that this compound is hygroscopic, which causes long-term degradation of the joint (Ref. 9). Other studies include joining of SiC by reaction sintering (Refs. 10, 11) and brazing of SiC using Ag-Cu-Ti filler metals (Ref. 12). Reaction sintering can produce joint strengths of 40 kg/mm^2 (56,893 psi), while brazing produces joints of only 5 kg/mm^2 (7112 psi).

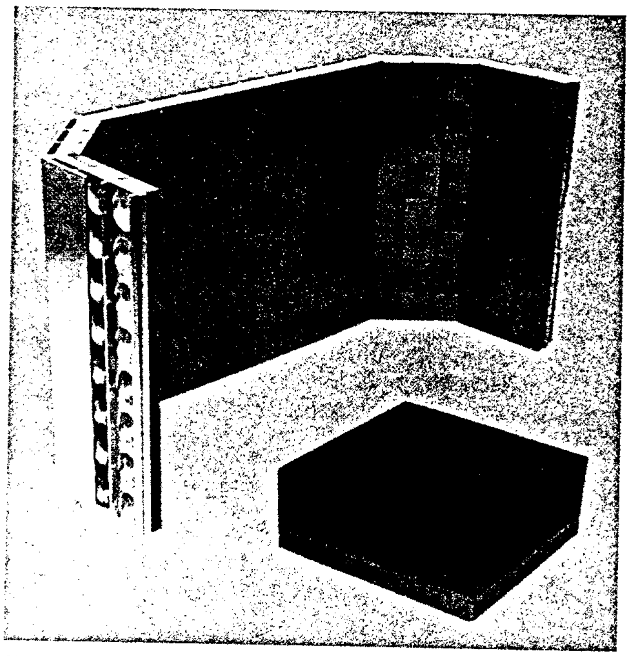

Fig. 3 — This scale model of a heat-resistant wall for a nuclear reactor shows a structure of metal on one side and a ceramic material on the other, joined together by brazing

The Mechanical Engineering Laboratory at Tsukuba is involved with a special project where engineers are studying C-M bonding, but no details are available. The Ship Research Institute has studied plasma spraying of Al_2O_3 for diesel engines, and Toshiba is studying thermal spraying of ceramics. Professor Kiuchi of the University of Tokyo has made cermet pipes by blending iron, iron oxide, and alumina powders, and hot rolling the mixture on the surface of steel plates. The plate is later rolled into a pipe with the cermet on the interior surface. Indeed, nearly every month some laboratory reports a new ceramic-metal bonding technique in the popular press in Japan.

Conclusions

Much of the increase in ceramic-metal bonding research in Japan can be attributed to the Japanese group structure. If someone else is studying something, that is justification for others to study it. Most of the research cited in this article does not have a specific goal or application; it is merely an attempt by metallurgists in Japan to join the ceramic fever. Certainly, one result will be a large increase in technical papers in this area within the next few years, but it also portends a decrease in the metals research papers over the same period. The traditional Japanese metals laboratories are becoming materials laboratories. This same trend is obvious in the United States, but not to the extent that it is visible in Japan.

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