

Brazing Ceramic Oxides to Metals at Low Temperatures

Titanium vapor deposited on the ceramic surface was demonstrated to produce sound low-temperature, metal-to-ceramic brazements

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ABSTRACT. A metal-to-ceramic brazing process, termed active substrate process, was developed for joining partially stabilized zirconia to nodular cast iron for advanced-design diesel engines. By vapor depositing titanium on the ceramic to a thickness of 0.3 to 1.0 μm and using a 60Ag-30Cu-10Sn braze filler metal, this process enables joining in a single brazing operation at a temperature sufficiently low (735°C/1355°F) as not to impair the properties of the ceramic or nodular iron. Demonstration pieces of 2-cm (0.8-in.) diameter were fabricated exhibiting composite interfaces of excellent braze quality and shear strength. Dilatometry was used on the joint component materials to assess thermal strain on the ceramic, and a titanium metal transition piece was used to reduce stress.

The composition and structure of the ceramic-metal bond zone in the zirconia-to-nodular iron joints were analyzed by electron probe microanalysis and x-ray diffraction. The microstructure of the brazed zirconia surface was shown to consist sequentially of ZrO_2 , oxygen-impooverished ZrO_2 , TiO , a $\text{Ti}_x\text{Cu}_y\text{Sn}_z$ intermetallic, and a two-phase filler metal deposit. Brazing behavior, in terms of limitations on braze temperature and thickness of the vapor-deposited titanium coating, was rationalized by depicting the role of TiO in preventing wetting and $\text{Ti}_x\text{Cu}_y\text{Sn}_z$ intermetallic in abetting it.

Introduction

The preparation of strong and reliable ceramic joints is becoming an increasingly important technological problem. For instance, many advanced designs for automotive engines have requirements for high-strength joints of ceramic to

ceramic and ceramic to metal. One such problem studied at Oak Ridge National Laboratory is joining partially stabilized zirconia (PSZ) to nodular cast iron (NCI) for an advanced diesel engine design. A relatively low brazing temperature was desired for these joints because the properties of the zirconia and nodular cast iron are developed by controlled heat treatments, and high brazing temperatures would erase the effects of prior heat treatments, thereby rendering the joint components unsuitable for the intended application. A low brazing temperature and the desired mechanical properties were attained with a process termed "active substrate brazing," which is described in this paper.

A major impediment to successfully brazing ceramics with metallic alloys is the well-documented observation that liquid metals generally do not wet ceramic substrates unless special provisions are made. Three methods have been detailed in the literature for promoting wetting of ceramics and preparing ceramic-to-ceramic and ceramic-to-metal joints, *i.e.*, the molybdenum-manganese process (Refs. 1-3), the active filler metal process (Refs. 4-6), and the active hydride process (Ref. 7). The molybdenum-manganese process uses a Mo-Mn paint initially applied to the ceramic surface, which after sintering and brazing

results in a mixture of refractory metal dispersed in a glass in the bond zone. Although this process has proven successful for applications requiring leak-tight seals, joints produced by it generally have low strength. Also, since the process relies on a preliminary high-temperature sintering treatment in wet hydrogen to reduce and coalesce the paint, the zirconia-base material stands to be seriously damaged. The active filler metal process relies on alloying of the filler metal with key active elements (*e.g.*, titanium and zirconium) known to promote wetting of ceramic surfaces. Braze joints with high strength can be produced with the active filler metal process, although the alloying required may significantly compromise the ductility and toughness of the filler metal, and typically imposes the restriction of using high brazing temperatures. Recent alloy development efforts have, however, significantly reduced brazing temperatures for active brazing alloys (Refs. 6, 8, 9). The active hydride process involves applying a metal hydride, such as titanium or zirconium hydride, to ceramic surfaces prior to brazing. As the braze assembly is heated, the metal hydride decomposes, evolving hydrogen and leaving a metal (*e.g.*, titanium) residue on the ceramic. Although this method enables brazing at relatively low temperatures (as low as a nonactive filler metal will allow), joints prepared by this process are plagued with lack of ductility and low strength (Ref. 6).

In the active substrate process (Refs. 10-12), a material that promotes wetting by the braze filler metal is vapor coated onto the surface of the ceramic in a preliminary treatment designed to optimize surface reactivity and adhesion. Thus, flexibility is available for selecting filler metals that are compatible with the required processing constraints or joint properties (*e.g.*, low brazing temperature, high-strength stable joint, oxidation resistance, etc.). The essential features are illustrated in Fig. 1 for joining partially

KEY WORDS

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Active Substrate
Substrate Process
Zirconia/Cast Iron
Titanium Vapor
Ti Vapor Deposit
Ti Metal Transition
Stress Reduction
Thermal Strain

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Metal-to-ceramic brazing can be accomplished by first applying a metallic layer onto the ceramic surface or by brazing directly to the unmodified ceramic (oxide) surface. Several metallization methods have been proven to work effectively; however, this article is limited to the two metallization methods most commonly used (Refs. 1, 2). A controlled expansion alloy often used when brazing to ceramics. All of the brazed samples shown in Table 1, as well as those shown in the subsequent tables (Tables 2-4) passed a helium mass spectrometer leak detection test (leak rate $< 2.0 \times 10^{-9}$ atm-cc/s) prior to being tensile tested. The part brazed in two stages (the first stage involving brazing of the copper with 1.4571 and the second stage, at a lower temperature, the brazing of this pre-stage with the metallized ceramic) reached a leakage rate $< 10^{-10}$ mbar \cdot l/s for He in the tightness test. From the deformation of the copper by around 1 mm per side lengthways in the joint zone, it can be seen that the mechanical stresses imposed there during cooling from the brazing temperature have been sufficiently reduced by plastic flow.

11: Basic types of ceramic-metal joints FRIALIT®-DEGUSSIT® Oxide Ceramics - Joining oxide ceramics. flat brazing with compensation ring. 7. This paper reviews a new, low-temperature process for soldering and brazing ceramics to metals that is based on the use of reactive multilayer foils as a local heat source. The reactive foils range in thickness from 40 μ m to 100 μ m and contain many nanoscale layers that alternate between materials with large heats of mixing, such as Al and Ni. This paper draws on earlier work to review the bonding process and its application to a variety of ceramic-metal systems. Predictions of thermal profiles during bonding and the resulting residual stresses are described and compared with results for conventional soldering or brazing processes.