

Brazing Metal to Ceramic in an Oxygen-Containing Atmosphere

An alternative to the conventional vacuum brazing process was developed for joining metal to ceramic with brazing filler metals for the manufacture of solid oxide fuel cells

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Because of the different types of chemical bonding, the brazing of metals to ceramic surfaces presents various challenges. The difference in the electron configurations prevents the wetting of a liquid metal on a ceramic surface and, therefore, joining with high bond strength. For this reason, active elements like titanium or zirconium are often added to the brazing filler metal (BFM) for a vacuum brazing process. The active elements of the BFM, reacting with the ceramic surface, form a metallic/ceramic interlayer that improves the wetting behavior of the BFM on the ceramic.

The Need for Metal-Ceramic Brazements

Due to energy and CO₂ issues that are, at present, the subject of worldwide discussions, renewable energy sources and/or energy production with a favorable CO₂ balance are in greater demand than ever before. In the foreseeable future, the solid oxide fuel cell (SOFC) may play a decisive role in this field. Although a fuel cell itself does not represent an energy source, it is nevertheless capable of producing with a high efficiency electric current from a multitude of different chemical energy carriers (petroleum, natural gas, biogas, or hydrogen). The SOFC is, therefore, not only one of the options for a future energy conver-

sion, but it may, already today, contribute toward the reduction of CO₂ emissions and the saving of valuable energy resources due to its clearly higher degree of efficiency, when compared with conventional generators in combination with heat-power machines.

The centerpiece of a SOFC stack is the ceramic cell with its three functional layers: cathode, electrolyte, and anode. The ceramic cell is inserted into a metal housing made of ferritic chromium steel, which ensures the electrical contact and the gas supply of the SOFC. The working temperature of the SOFC is higher than 600°C (normally 750°–850°C), since the ceramic cell components show significant electric conductivity only from this temperature upward. To prevent a direct reaction of the working gases, the

gas compartments of the electrodes must be separated gastight from one another. This demands a gastight joint between

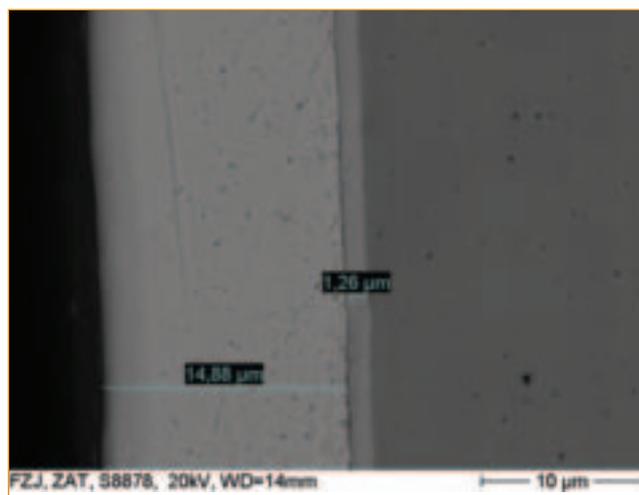


Fig. 1 — SEM image of a transverse section for the determination of the layer thickness of the PVD layers (Ag: approximately 15 µm, Zr: approximately 1.25 µm).



Fig. 2 — Schematic diagram of the PVD-layer composition.

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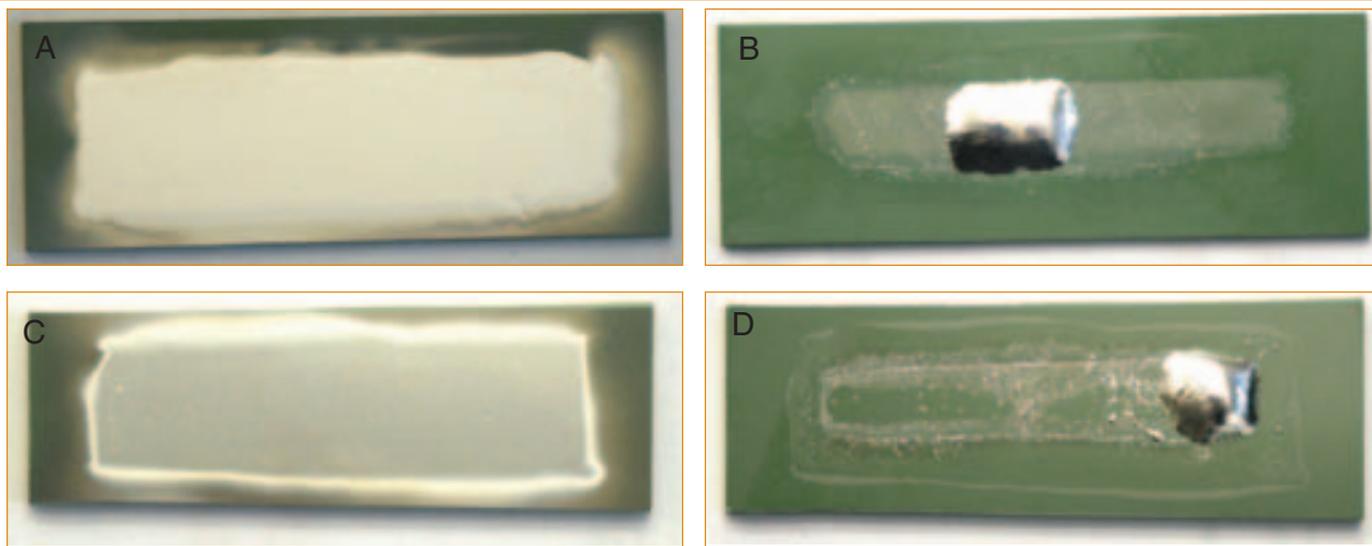


Fig. 3 — Wetting tests (sessile drop) on the 8YSZ-electrolyte of a SOFC half cell. A — Specimen with Ti as the active element before the brazing process; B — specimen with Ti as the active element after the brazing process; C — specimen with Zr as the active element before the brazing process; D — specimen with Zr as the active element after the brazing process.

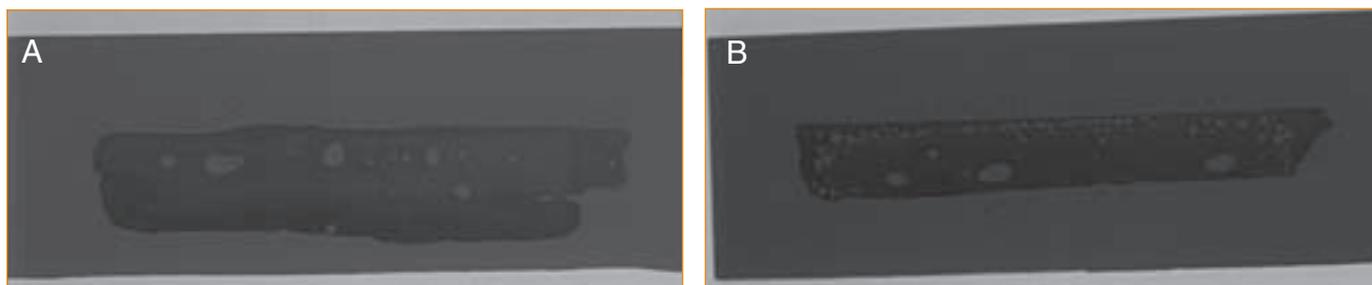


Fig. 4 — X-ray microscope radiographs of the joints of cell/Crofer 22 APU. A — Joint with Ti as the active element; B — joint with Zr as the active element.

the electrolyte and the ferritic chromium steel. Under operating conditions, the joint must be maintained gastight for several thousands of hours under reducing and oxidizing atmosphere. The joint must also be resistant to stresses that are caused by the different temperature-strain behaviors of the joining members.

Beside glass ceramics (so-called glass brazes) and high-temperature stable compressible seals (e.g., on the basis of mica), high-temperature brazing is a promising joining method for application in the field of SOFCs.

The high working temperature of 750°–850°C, the oxidizing and reducing working gases, and the material properties of the SOFC strongly restrict the selection of suitable brazing materials for a ceramic/metal joint.

Due to the vacuum incompatibility of various cell components (e.g., the perovskite structure of the cathode), the

vacuum active brazing method is not applicable for the conventional joining of ceramic-metal joints. A brazing process in normal atmosphere with conventional, noble metal-based vacuum solders (e.g., Ag-based solder) is also not applicable due to the high oxidation tendency of the active elements, such as Ti or Zr, that are used for the vacuum solders. Active elements support wetting of the metal-based solder material on the ceramic. If the active elements are dispensed with, the metal solder (metallic atomic bond) is no longer capable of sufficiently wetting the ceramic (covalent bond). The active elements in the solder system are, moreover, reacting with the ceramic and form an intermetallic phase that supports the wetting behavior.

One alternative is reactive air brazing with copper-oxide-bearing silver-based BFM (AgCuO). Previous examinations have shown that this joining method still

requires further optimization and development (Refs. 4, 7).

For this reason, this article introduces a novel method that serves as an alternative to the conventional vacuum brazing process. In this method, the classical active elements Ti and Zr are protected against premature oxidation through the air oxygen during the furnace process. For this purpose, active elements were, by means of plasma vapor deposition (PVD) methods, precipitated on the electrolyte surface and coated via a further PVD process with the silver brazing filler metal. This protects the active element from premature oxidation and allows the active element during the brazing process right to the melting of the solder base material a wetting-promoting reaction with the ceramic surface. This method allows us to dispense with additional flux and also with a reduced or inert furnace atmosphere.

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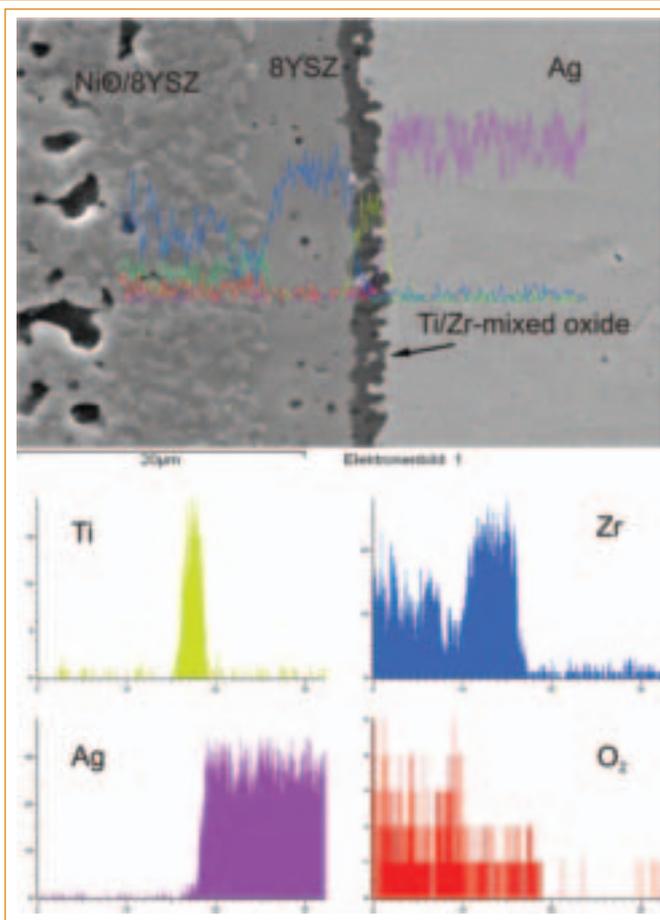


Fig. 5 — SEM micrograph of the transverse section of the joining zone Ag/8YSZ with Ti as the active element.

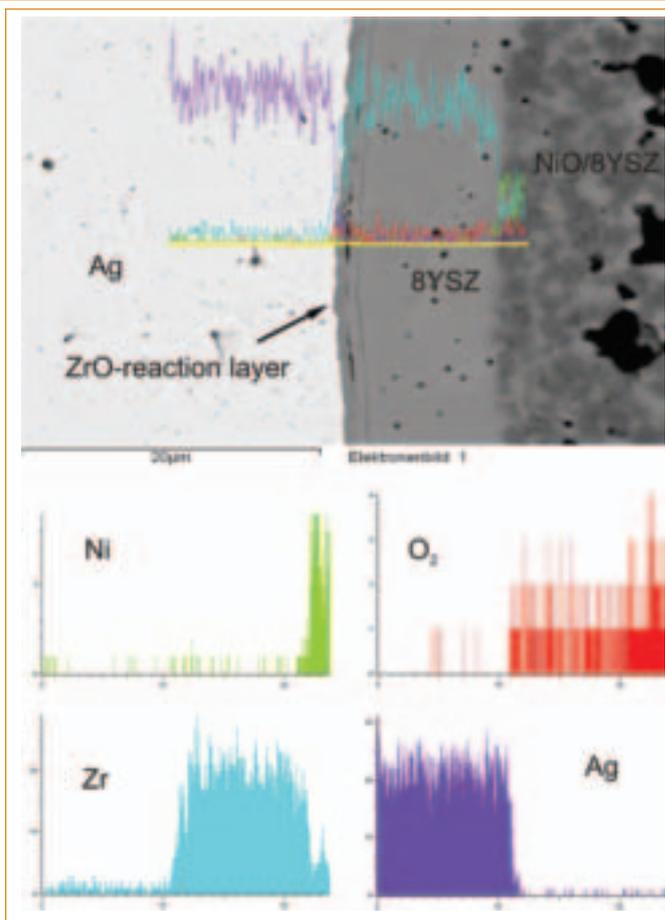


Fig. 6 — SEM image of a transverse section of the joining zone Ag/8YSZ with Zr as the active element.

Experimental Procedure

The joining and brazing experiments were carried out on SOFC cells without cathode-functional layers (so-called half cell, 8YSZ electrolyte and anode, made by the IEF-1 at FZJ (Ref. 1)). The metal joining partner was the ferritic chromium steel Crofer 22 APU (Ref. 2), which was developed for application with SOFCs. The noble metal silver was used as the brazing filler metal. A melting point of 962°C, and resistance to oxidizing and also in reducing atmosphere make silver highly suitable for application in SOFCs.

Zirconium (Zr) and titanium (Ti) were used as the active elements. These elements were precipitated by means of the PVD method onto the ceramic electrolyte of the SOFC half cell via a template (layer thickness approximately 1 μm, Fig. 1). In order to protect the active element against the air oxygen in the fur-

nace atmosphere, a further PVD process was carried out where the active element received a gastight silver coating (coating thickness approximately 15 μm) — Fig. 2.

A silver foil (99.99% Ag, thickness: 100 μm) was, in addition to the BFM, used for the wetting and joining tests. Before brazing took place, all parts were cleaned using alcohol. The joining and wetting tests were made in a KS-80 muffle furnace from Linn Co. A brazing temperature of 1000°C, which was kept constant for 10 min, was selected as the temperature program. The temperature ramp was 3 k/min during heating and 5 k/min during cooling.

Subsequent to the joining process, the specimens were irradiated using microfocus X-ray equipment and then examined via metallographic sections in the scanning electron microscope. The wetting angles were determined via metallographic transverse sections.

Results and Discussions

Ti as the Active Element

Figure 3A shows the results from the wetting tests on brazing specimens. By means of the wetting angle BFM/8YSZ, the brazing specimens show if the surface tension due to the reaction of the active elements with the 8YSZ decrease and thus support the wetting process. It was, moreover, planned to examine whether the BFM was wetting exclusively within the required joining zone (the region where the active element was applied). Wetting outside the coated joining zone is, with regard to the subsequent application in the SOFC and due to the design-induced requirements that demand a joint with contour accuracy, not desired.

A zone with brownish discoloration was observed on the electrolyte surface of the specimen that was coated with Ti. The

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discoloring on the electrolyte surface suggests that a reaction between the electrolyte material and the titanium had occurred. The dark discoloration of 8YSZ is a sign for the removal of oxygen due to the Ti from the crystal lattice of the 8YSZ, which has a strongly reducing effect (Ref. 3). The position and size of the reaction zone complied with the original, titanium-coated area on the electrolyte surface. The silver was wetting within the reaction zone with a wetting angle of approximately 35–40 deg. Compared with pure silver, which has, on the electrolyte surface, a wetting angle of approximately 73 deg in air (Ref. 4), this stands for a significant improvement in the wetting behavior.

Figure 4A depicts the radiograph of a joint between the cell, which had been prepared with the PVD method and/or electrolyte surface, and a ferritic steel sheet made of Crofer 22 APU.

The braze filler material distribution was mainly observed in the region of the originally applied active element Ti. In places, the braze filler material ran over the zone, which was originally coated with Ti. The reason for the running of the braze filler material off the joining zone is the slight tilt of the joining weight due to missing braces in the joint clearance during the brazing process, which caused the pressing of some of the brazing filler material out of the joining zone. The cause of the defects (pores) in the joint is the oxygen that is released during the solidification process. In molten form, silver is capable of dissolving an approximately 40-fold quantity of oxygen more than it would do in a solid state (Ref. 5). Due to the fact that the brazing process is carried out in an oxygen-containing atmosphere, the superfluous oxygen is released during the silver solidification and gas pores that are filled with oxygen may develop in the joint.

Figure 5 shows the transverse section of the joining zone solder/8YSZ, recorded with a scanning electron micrograph (SEM). The titanium applied via the PVD method has developed a Ti/Zr mixed oxide with the 8YSZ surface of the cell, whereas the Zr concentration in the reactive layer is continuously decreasing with the increasing distance to the 8YSZ surface. Comparable mixed oxides develop if titanium-containing solder materials are applied in a vacuum brazing process on 8YSZ (Ref. 6). The connection of the reactive layer on the 8YSZ surface is, with the exception of a few silver-containing inclusions, complete. The silver solder

also shows a good connection to the Ti/Zr mixed oxide.

Zr as the Active Element

A discoloration of the electrolyte surface (removal of oxygen off the crystal lattice) was observed on the specimen that was coated with Zr (Fig. 3D), mainly in the edge region of the coated region. The silver primarily wet within the reactive zone. The wetting angle was approximately 45–50 deg, which points to a slightly improved wetting behavior, in comparison to pure silver on the electrolyte surface (wetting angle approximately 73 deg).

Figure 4B shows the X-ray radiograph of a joint between the electrolyte surface that was prepared using the PVD method and a Crofer 22 APU sheet. The silver

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wet the Zr-coated specimen mainly in the region of the Zr coating — Fig. 4B. A slight spreading of the solder over the coated zone was observed at the ends. Due to the solubility differences of oxygen in the molten silver and the silver solid body, gas pores developed in the joint.

The SEM image of the metallographic transverse section shows an end-to-end uniform ZrO-containing reactive layer on the 8YSZ surface of the cell — Fig. 6. Few and far between, pore formation within the ZrO reactive layer was observed. The connection to the 8YSZ surface was consistently good. The silver also showed good, uniform connection to the ZrO reactive layer.

Conclusions

The tests showed that the sealing of the active element with the solder base material — in this case pure silver — may protect the active element during the furnace process in normal atmosphere from premature oxidation with the air oxygen. The active element reacts during the furnace process with the ceramic surface and forms a comparable reactive layer with the ceramic surface, as in the vacuum fur-

nace process with a comparable vacuum solder material. Due to the reactive layers that develop during the furnace process, the wetting behavior of the metal solder material, and/or in this case the pure silver, was significantly improved.

In the future, it is planned to test the leak tightness on respective leakage test specimens that will be produced using the method specified here. These initial tests show that, using this method, leaktight joints are produced, but the quality and/or contour accuracy of the joint is not yet convincing. In this regard, further tests about the optimization of the process parameters are required.

It is, moreover, scheduled to carry out tests with regard to the strength of the joints by means of the fourpoint bending fracture test (method in accordance with Charalabides).♦

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