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Brazing of metallic conductors onto ceramic plates in solid oxide fuel cells

Part I *Attaching a current collector*

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Furnace brazing to attach metallic plates to $LaCrO_3$ end plates in solid oxide fuel cell (SOFC) was investigated. The metallic plates act as a current collector to which a few conducting wires made of conventional heat-resisting alloys can be attached. The alloy $CrFe5Y_2O_31$ was found to be a suitable material for the current collector because its thermal expansion coefficient matches that of $LaCrO_3$ better than heat-resisting nickel- or iron-based alloys. Among various filler alloys tested, SCP6 (Cu with 18 wt% Pd) enables the best wetting of $LaCrO_3$ and $CrFe5Y_2O_31$ plates, leading to good adhesion between them. Several approaches were successfully pursued to reduce the bending of brazed $LaCrO_3$/SCP6/$CrFe5Y_2O_31$ joints. The area specific resistance of some $LaCrO_3$/SCP6/$CrFe5Y_2O_31$ joints increased slightly during annealing (1000°C in air for 2400 h) due to oxidation in the filler alloy. Nevertheless, it remained below the target limit of $0.2\ \Omega \cdot cm^2$. © *2001 Kluwer Academic Publishers*

1. Introduction

With high efficiency and low emissions, the solid oxide fuel cell (SOFC) is well suited for stationary cogeneration and primary power for a wide range of applications. The successful commercialization of this technology depends not only on its performance and stability but also on the costs for materials, manufacturing, and assembly of the SOFC unit. Conventional, commercially available materials should be used whenever possible, and manufacturing and assembling should be based on well-established processes.

We developed a two-step process to connect metallic conductors made of conventional heat-resisting alloys to ceramic end plates of SOFC stacks by the well-known process of furnace brazing. This process was developed for a planar SOFC system that is operated at high temperatures, 1000°C and above [1]. Results of our development are presented in this paper. The principal component of an SOFC is an assembly of two electrode layers (anode and cathode) with a gas-tight ceramic electrolyte in between. In planar SOFC designs, several cells are connected in series to form a stack delivering acceptable power output. Conductors connected to the end plates of the stacks enable a low-resistance connection between individual stacks in each SOFC unit, and sufficient power to be drawn from the entire SOFC unit. Usually, both end plates consist of the same material. In this case, they have to meet the following requirements: (i) corrosion resistance at the SOFC working temperature in the oxidizing cathode atmosphere (e.g., air or oxygen) and the highly reducing anode atmosphere (O_2 partial pressure of 10^{-18} bar or less) and (ii) high electrical conductivity. The same is valid for the conductors, but they will only be exposed to an air environment. Ceramic or metallic material can be used for the end plates, depending on the cell concept and the operating temperature. The perovskite lanthanum chromite ($LaCrO_3$, abbreviation LC) is the state-of-the-art ceramic material for these plates. It is often doped (e.g., with MgO, SrO, CaO, or Al_2O_3) to match the SOFC requirements better. In addition to the above-mentioned properties, this material offers compatibility and a good match of thermal expansion with other SOFC components. Compared to $LaCrO_3$, metals have some disadvantages, such as higher thermal expansion and higher oxidation rates in air. Both disadvantages become more critical with increasing temperature. Consequently, $LaCrO_3$ is considered to be the most suitable end plate material for SOFC units operating at temperatures of 1000°C or more [2].

Heat-resisting nickel alloys (e.g., Inconel 617) and ferritic stainless steels (e.g., iron alloyed with 22 wt% chromium and 5.5 wt% aluminum) are promising materials for the conductors because they are resistant to

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oxidation in air at the required temperatures [4]. However, the joining of these alloys to ceramic $LaCrO_3$ plates is problematic due to the large mismatch in thermal expansion. Between 20°C and 1000°C, the thermal expansion coefficient (α) amounts to $10.4 \times 10^{-6}/°C$ for $LaCrO_3$, but to more than $14 \times 10^{-6}/°C$ for conventional heat-resisting steels or nickel alloys [4]. Additionally, the joint has to fulfill the following requirements: (i) stability and oxidation resistance in air at temperatures of 1000°C or more and (ii) low electrical resistance at these conditions.

A two-step process was developed to connect such conductors to ceramic end plates by vacuum furnace brazing. In the first step, a metallic plate is brazed onto the ceramic plate. The metallic plate, having approximately the size of the end plate, acts as current collector and thereby compensates for the lower electrical conductivity of the $LaCrO_3$ plate (see [2, 3]). In the next step, one or a few metallic wires or strips are brazed onto the current collector. This joint area is significantly smaller than the first one, so that conventional heat-resisting nickel alloys and ferritic steels with their higher thermal expansion, compared to $LaCrO_3$, can be used. In a seperate paper in this journal, we report on such brazing of metallic wires or strips onto metallic plates used as SOFC current collectors [4].

In this paper, we present results concerning the first joining step. The goal was to determine suitable materials as current collector as well as filler alloys. Two different oxide dispersion strengthened (ODS) alloys were tried as current collector. Although their oxidation resistance is inferior to that of $LaCrO_3$, they can be used as current collector plates at 1000°C or above, as long as the resistance of the brazed assembly does not exceed a critical value. The target value for the development was an area specific resistance for the joint of less than $0.2\ \Omega \cdot cm^2$ at 1000°C in air, and this value should be maintained for at least 1000 h.

Three processes were tested to join plates made of various alloys to the $LaCrO_3$ plate.

(1) In *diffusion welding*, the surfaces of two work-pieces that fit together exactly are heated under an applied force to a temperature that enables diffusion across the work-pieces and through the interface between them. This produces a welded metallurgical bond without using a filler material [5].

(2) *Furnace brazing* involves the joining of an assembly by a metallurgical bond with a furnace being used to melt the filler alloy. Before brazing, the work-pieces must be assembled and secured, and the filler alloy has to be placed onto the assembly. The use of fluxes can often be avoided when either suitable protective gas atmospheres or a vacuum is applied. In cases involving no wetting of the surfaces with or without flux, the non-wetted surface has to be coated (e.g., with nickel) to obtain adequate wetting action [6, 7].

(3) *Active Brazing* can be used to join unmetallized ceramics. This procedure employs special filler materials, called active brazing alloys, which contain elements with a high affinity to oxygen, such as titanium, hafnium, and zirconium. These elements diffuse to the ceramic surface during brazing and form mixed phases with elements of the ceramic, thus promoting wetting of the ceramic [7–9].

The long-term behavior of the most promising joint was studied at 1000°C in air. This joint showed a slight bending after the brazing process, which can affect its function in the SOFC unit. We found that this bending could be decreased or avoided by changing the brazing conditions and the design of the assembly.

2. Experimental procedure

2.1. Furnace brazing parameters

For all experiments, metallic and ceramic plates of equal size were brazed together. The size of the plates was varied: 35 × 35 mm, 70 × 15 mm, and 80 × 80 mm. The surfaces of the metallic plates were cleaned and roughened prior to the brazing by grinding with conventional grinding paper and etching in HNO_3 solution. The $LaCrO_3$ plates were carefully cleaned with acetone. All joining processes were performed in a vacuum furnace, applying a vacuum of 10^{-5} mbar. The typical heating rate was 5°C/min, while the cooling rate was between 1.5 and 5°C/min. The plates were placed on top of each other. If needed, filler material in the form of a powder or foil, respectively, was placed between the plates, and steel bolts with a height of the required filler layer thickness were placed as spacers between the plates. These bolts did not melt during brazing, so that the plates were retained in the required distance. An area load was applied for all joining experiments, unless mentioned otherwise. The resulting pressure amounted to 2.5 MPa for diffusion welding and 1000 and 1600 Pa for furnace brazing and active brazing.

2.2. Materials

The filler materials used in this study are described in Table I. The titanium-containing active brazing alloys CB 2, CH 3, FeTi60, and FeTi70 can be used for brazing of ceramics. Both NiCrBSi and L-Ni 5 are high-temperature nickel-based brazing alloys, which are used for example in turbine construction. The palladium-containing alloys SCP2 and SCP6 are also classified as high-temperature brazing alloy because of their high working temperature. They are used for

TABLE I Filler alloys used for this study [9], [10]

Name	Composition, wt%	Melting range, °C
CH 3	Ag 91, Cu 6, Ti 3	<1000
Degussa CB 2	Ag, activated with 3-4% Ti Ag, activated with 10% Ti	960-970 1020-1270
Degussa L-Ni 5	Ni 71, Cr 19, Si 10, C max. 0.1	1080-1135
Degussa SCP2	Ag 58.5, Cu 31.5, Pd 10	824-852
Degussa SCP6	Cu 82, Pd 18	1080-1090
FeTi60	Ti 60, Fe 40	1085-1200
FeTi70	Ti 70, Fe 30	1085-1130
NiCrBSi	Ni 73.4, Cr 14, Si 4.6, B 3.5, Fe 4, C 0.5	950-1050

TABLE II Characteristics of the metallic and ceramic plates

Name	Manufacturer	Composition,[1] wt%	α, 10^{-6}/°C (25-1000°C)	Melting range, °C
Lanthanum chromite	Dornier GmbH, Friedrichshafen, GER	$LaCrO_3$, doped with MgO and Al_2O_3	10.3-10.5[2]	>2400 [2]
MA 956	Inco Alloys, Huntington, WV, USA	Fe bal, Cr 20, Al 4.5, Ti 0.5, Y_2O_3 0.5	14.9[1]	1482[1]
$CrFe5Y_2O_31$	Plansee, Reutte, Austria	Cr bal, Fe 5, Y_2O_3 1	11.3[1,2]	1840-60 [10]

[1] Specified by manufacturer.

[2] Measured.

brazing of metallic substrates to metals or metallized ceramics in power-electronic components such as radio and electron tubes [7, 9].

Characteristics for the employed metallic and ceramic plate materials are given in Table II. The chromium alloy $CrFe5Y_2O_31$ and the iron alloy MA 956 are both oxide dispersion strengthened alloys, which are heat-resistant in air at temperatures of 1050°C, as required. Besides their chemical composition, the main difference between them is the much lower thermal expansion coefficient of $CrFe5Y_2O_31$. This alloy was developed by Plansee (Reutte, Austria) for SOFC parts such as metallic interconnects [3].

2.3. Characterization methods

The area specific resistance (ASR, units of $\Omega \cdot cm^2$) of some brazed joints was determined by means of a four-point dc technique with platinum electrodes attached to the joint with platinum paste. A schematic for this technique is given in Fig. 1. Two identical joints of 35 × 35 mm were connected by sintering with a $LaCrO_3$-based paste. Accordingly, an average value for two joints was obtained in one experimental run. The measurements were carried out in air at temperatures ranging from 1000°C to 1040°C. Direct current of 0.25 A/cm^2 was applied. The total measured resistance was averaged in order to obtain a value characteristic for one metal/ceramic joint, and the ASR value was derived from this value.

The microstructure of some joints was studied by means of scanning electron microscopy (SEM) to evaluate the degree of wetting, and the phase composition was evaluated by energy dispersive X-ray spectroscopy (EDS). The bending of the joints was measured by means of a coordinate measuring apparatus (UPMC 850 CA from Zeiss, Germany). The given values describe the height difference between the lowest point on the joint surface, which is usually near the center, and the highest point, which is close to an edge of the joint.

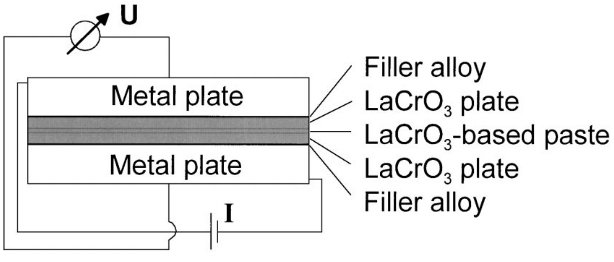

Figure 1 Schematic of the four-point dc technique for resistance measurements.

3. Results and discussion

3.1. Brazing of a metallic plate to the end plate

Table III summarizes the experiments performed to braze metallic plates to $LaCrO_3$ plates. Initial experiments to join $LaCrO_3$ plates to MA 956 or $CrFe5Y_2O_31$ plates, respectively, by diffusion welding were not successful. No adhesion was obtained, even when the ceramic surface was metallized prior to the brazing with gold using physical vapor deposition (PVD). Coating the $CrFe5Y_2O_31$ plate with a filler of $CrFe5Y_2O_31$ powder led to a remarkable progress, since it increased the sintering activity of the metal surface. Further changes included increasing the brazing temperature to 1300°C and extending the brazing time to 12 h. Due to these changes, a diffusion bond between $LaCrO_3$ and $CrFe5Y_2O_31$ was achieved, but the bond was not ideal. A further disadvantage was the long time required for the high-temperature treatment in vacuum.

A NiCrBSi filler alloy was used for furnace brazing of MA 956 to $LaCrO_3$. This filler alloy wetted the MA 956 surface well, but the $LaCrO_3$ surface only partially. Additionally, the high mismatch between the thermal expansion coefficients of MA 956 and doped $LaCrO_3$ (see Table II) caused spalling and breaking of the ceramic plate during cooling after brazing. The same was observed in a few experiments to join $LaCrO_3$ to plates consisting of Inconel 617, which is a nickel-based alloy with an even higher thermal expansion coefficient ($\alpha = 16.6 \times 10^{-6}$/°C between 20°C and 1000°C). For these reasons, no further experiments with nickel- or iron-based alloys having similar thermal expansion coefficients were carried out. All subsequent experiments used $CrFe5Y_2O_31$ as material for the metallic plate.

Furnace brazing experiments with nickel-based filler alloys (NiCrBSi, and L-Ni 5) revealed a good wetting of the $CrFe5Y_2O_31$ surface, but only poor wetting of the $LaCrO_3$ surface. Consequently, poor adhesion was observed: the plates could easily be separated. A previous metallization of the ceramic surface by coating it with nickel or a chromium/nickel alloy did not improve the adhesion. The same was observed when the ceramic surface was coated with titanium by PVD to promote the wetting mechanisms of active brazing.

Various titanium-containing iron or silver alloys, designed for active brazing, were tested for brazing the

TABLE III Experiments to join the LaCrO$_3$ plate to a metallic sheet (vac. = vacuum, PVD = physical vapor deposition)

Process	Metal Plate	Treatment	Filler	Joining Conditions	Result
Diffusion welding	MA 956			1000°C, vac., 10 h	No adhesion
Diffusion welding	MA 956	Ceramic Au-coated (PVD)		1000°C, vac., 10 h	No adhesion
Diffusion welding	CrFe5Y$_2$O$_3$1			1000°C, vac., 10 h	No adhesion
Diffusion welding	CrFe5Y$_2$O$_3$1		CrFe5Y$_2$O$_3$1	1300°C, vac., 12 h	Poor adhesion
Furnace brazing	MA 956		NiCrBSi	1050°C, vac., 10 h	Adhesion, but spallation
Furnace brazing	MA 956	Load-free brazing	NiCrBSi	1050°C, vac., 16 h	Adhes., ceramic broken
Furnace brazing	CrFe5Y$_2$O$_3$1	Load-free brazing	NiCrBSi	1050°C, vac., 0.5 h	Poor adhesion
Furnace brazing	CrFe5Y$_2$O$_3$1		NiCrBSi	1050°C, vac., 0.5 h	Poor adhesion
Furnace brazing	CrFe5Y$_2$O$_3$1	Ceramic CrNi-coated (PVD)	NiCrBSi	1200°C, vac., 1 h	Poor adhesion
Active brazing	CrFe5Y$_2$O$_3$1	Ceramic Ti-coated (PVD)	NiCrBSi	1200°C, vac., 1 h	Poor adhesion
Furnace brazing	CrFe5Y$_2$O$_3$1		L-Ni 5	1190°C, vac., 2 h	Poor adhesion
Furnace brazing	CrFe5Y$_2$O$_3$1	Ceramic Ni-coated (PVD)	L-Ni 5	1190°C, vac., 2 h	Poor adhesion
Active brazing	CrFe5Y$_2$O$_3$1	Ceramic Ti-coated (powder)	L-Ni 5	1300°C, Ar, 0.5 h	Poor adhesion
Active brazing	CrFe5Y$_2$O$_3$1	Ceramic Ti-coated (PVD)	L-Ni 5	1200°C, vac., 1 h	Poor adhesion
Active brazing	CrFe5Y$_2$O$_3$1		CH 3	1000°C, vac., 0.5 h	Adhesion
Active brazing	CrFe5Y$_2$O$_3$1		CB 2 + 3-4% Ti	1000°C, vac., 0.5 h	Adhesion, but cracks
Active brazing	CrFe5Y$_2$O$_3$1		CB 2 + 10% Ti	1200°C, vac., 1 h	Adhesion, but spallation
Active brazing	CrFe5Y$_2$O$_3$1	Load-free brazing	FeTi60	1250°C, vac., 2 h	Poor adhesion
Active brazing	CrFe5Y$_2$O$_3$1		FeTi70	1300°C, vac. 1 h	Poor adhesion
Furnace brazing	CrFe5Y$_2$O$_3$1		SCP2	900°C, vac., 3 h	Adhesion
Furnace brazing	CrFe5Y$_2$O$_3$1		SCP6	1140°C, vac., 10 min	Good adhesion

LaCrO$_3$/CrFe5Y$_2$O$_3$1 assembly. The Ag-based alloys CB 2 and CH 3 wetted the ceramic surface. However, their melting point is too low to enable a long-term use of the brazed joints at 1000°C. An SEM observation of the joint brazed with CB 2 revealed a titanium-rich reaction layer (3 μm thickness) on the ceramic surface, and a similar but thinner reaction layer on the metallic surface. Accordingly, the wetting mechanism typical for active brazing occurred. Long cracks parallel to the ceramic surface were found in the thicker reaction layer. That may result from the high brittleness of this Ti-rich layer, which causes crack initiation and propagation during cooling after brazing.

In another experiment, the filler CB 2 was alloyed with 10 wt% titanium. Thereby, the melting point of the alloy was increased in such a manner that the brazed joints offer a long-term stability at 1000°C. We chose a low brazing temperature of 1200°C for this filler in order to avoid an excessive loss of silver by evaporation during brazing, which can occur due to the high vapor pressure of silver [9]. The brazing temperature is lower than the liquidus temperature of the filler [10]. However, titanium will migrate to the surfaces to be joined, as shown before. The titanium amount present in the filler will continuously decrease, and thereby lower the liquidus temperature. Accordingly, the entire filler layer will eventually be molten. The brazing experiments showed that this alloy does wet the ceramic surface to a certain extent. However, the bond was so brittle that spallation occurred during the preparation of the joint for metallographic examination. It was concluded that the AgTi active brazing alloys are not suitable for the present joining problem, since (i) AgTi alloys with a titanium amount between 3 and 4 wt% wet the ceramic surface, but their melting temperature is lower than the required operating temperature for the joint, and (ii) AgTi alloys with a higher titanium amount of 10 wt%, offering a sufficient high melting point, lead to the formation of a brittle bond. The iron-containing filler alloys FeTi60 and FeTi70, which are designed for active brazing, were also not suitable since they do not wet the LaCrO$_3$ surface well.

The palladium-containing alloys SCP2 and SCP6 enable wetting of the surfaces to be joined. However, the joint brazed with SCP2 showed only a partial wetting of the LaCrO$_3$ and cracks in the filler alloy close to the ceramic surface. Furthermore, its melting point is too low to enable the long-term use of brazed joints at 1000°C.

In contrast, the filler alloy SCP6 showed good wetting of the materials to be joined. As can be seen in Fig. 2, complete wetting action took place on the LaCrO$_3$ surface, while the CrFe5Y$_2$O$_3$1 surface deteriorated during the brazing process. The filler alloy seems to have dissolved the metallic material along grain boundaries, leading to the complete pull-out of some CrFe5Y$_2$O$_3$1 grains. The spherical shape of these grains (found close to the CrFe5Y$_2$O$_3$1 surface) indicates that their dissolution had already begun. The light-gray spots present in the filler alloy contain approximately 94.2 wt% Cr and 5 wt% Fe, but only 0.5 wt% Cu and 0.3 wt% Pd, as we observed by means of EDS. The filler layer itself contains less than 1.5 wt% each of Cr and Fe. Accordingly, the dissolved material was almost completely re-precipitated. We assume that this happened during cooling after brazing as a result of a decreasing solubility for Cr and Fe in the liquid and solid filler alloy. This decreased solubility was inferred from binary phase diagrams [10].

Of all filler materials tested, SCP6 was the most suitable for our joining task. Accordingly, further experiments focused on the characterization of the LaCrO$_3$/CrFe5Y$_2$O$_3$1 joints brazed with SCP6.

3.2. Long-term behavior of the joint

The area specific resistance of several LaCrO$_3$/CrFe5Y$_2$O$_3$1 joints was determined at temperatures

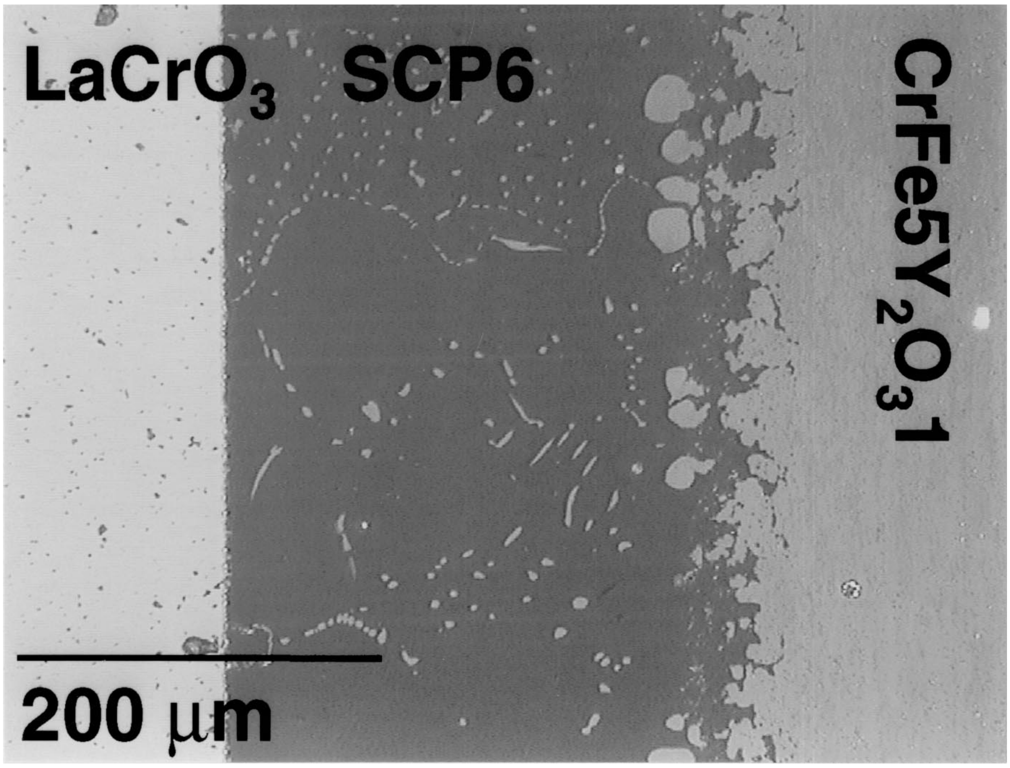

Figure 2 Cross section (light-optical micrograph) of $LaCrO_3/CrFe5Y_2O_31$ joint after brazing in vacuum at 1140°C for 10 min, using SCP6 as filler alloy.

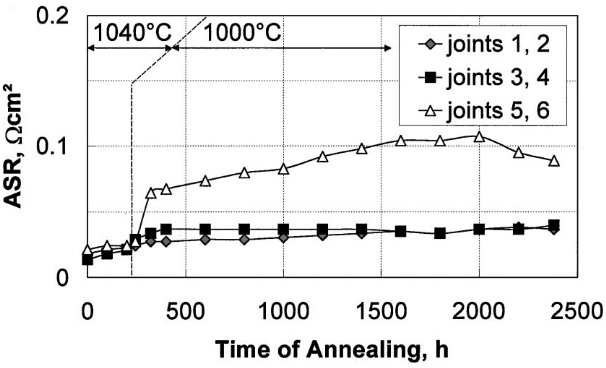

Figure 3 Area specific resistance (ASR) for $LaCrO_3/CrFe5Y_2O_31$ joints (35 × 35 mm) brazed with SCP6. Measured in air at 0.25 A/cm^2.

ranging from 1000 to 1040°C in air for >2400 h (Fig. 3). The joints were brazed at 1140°C in vacuum, and SCP6 foil of 50 μm thickness was used as filler. We characterized six brazed joints, which had been connected by sintered $LaCrO_3$-based paste to three samples. Accordingly, each curve given in Fig. 3 represents the average value of two joints. Initially, all joints show a similar resistance of 0.025 to 0.03 $\Omega \cdot cm^2$ at 1040°C, while this resistance is slightly increasing with time. After 280 h, the joints were cooled down to room temperature and then heated up to 1000°C in order to study the influence of a thermal cycle. Two joints (no 5, and 6) show an increased ASR value in the range of 0.06 to 0.11 $\Omega \cdot cm^2$ after this thermal cycle. Partial damage of the $LaCrO_3$ connection layer between the two joints caused the increase. No damage in the SCP6 filler layers of these joints, however, was visually observed. Even after 2400 h at such high temperatures, the ASR values of all joints are still lower by a factor of two than the specified target value of 0.2 $\Omega \cdot cm^2$.

The oxidation behavior of the filler alloy was studied on a $LaCrO_3/CrFe5Y_2O_31$ joint having a 200 μm thick SCP6 filler layer, which was annealed at 1000°C in air for 1000 h. The filler alloy was partially oxidized after annealing. This oxidation was especially observed at the outer surfaces on the sides of the joint. Three different oxide phases are shown in Fig. 4. Their composition was determined by EDS. A (palladium/copper) oxide was formed that contains roughly 46 at.% Pd, 32 at.% O, 19 at.% Cu, 1.5 at.% Fe, and 1.5 at.% Cr. Furthermore, Cu_2O and $CuCrO_2$ were formed. The former contained 0.9 at.% Fe, the latter 1.6 at.% Fe. In the Cr_2O_3-Cu_2O-CuO system according to Jacob *et al.* [11], these phases coexist for a CuO_x amount higher than approximately 67 mol%, but only at temperatures between approximately 1025 and 1125°C. The transformation to CuO and $CuCr_2O_4$ due to the oxidation of Cu^+ to Cu^{2+} did not occur in the present system. This may be a consequence of the fast cooling after the annealing. The Cu_2O was mainly found in the center of the filler layer, while layers of $CuCrO_2$ were formed at the interfaces to $CrFe5Y_2O_31$ and $LaCrO_3$. The $CuCrO_2$ layer at the metal interface is much thicker than that at the ceramic interface, and it contains a higher amount of fine pores. Based on these observations, we assume that chromium diffusion from the plates into the filler layer transforms the Cu_2O to $CuCrO_2$. Accordingly, the chromium content dropped by approximately 2 at.% in the $LaCrO_3$ surface. It did not drop at the $CrFe5Y_2O_31$ surface but increased to roughly 97 to 98 wt%. That can be explained by a higher diffusion of Fe into the filler layer, leading to an enrichment of chromium at

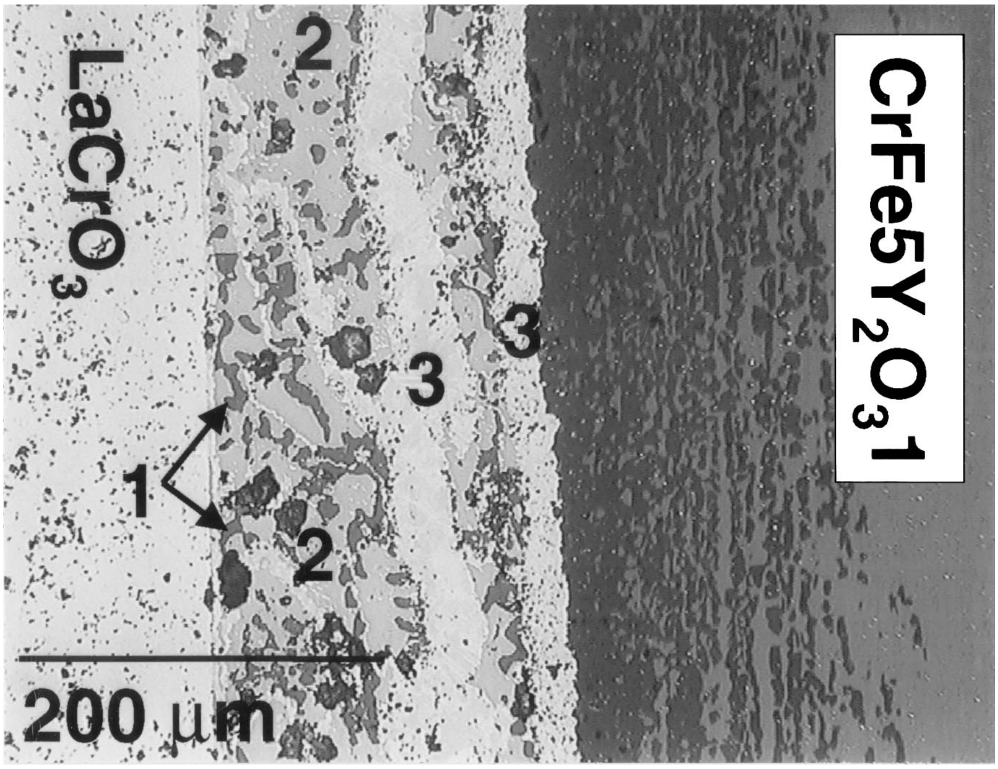

Figure 4 Cross-section (light-optical micrograph) of $LaCrO_3$/SCP6/$CrFe5Y_2O_31$ joint near the surface. Sample was brazed as before (see Fig. 2) and annealed (1000°C in air for 1000 h): 1 = (palladium/copper) oxide, 2 = Cu_2O, and 3 = $CuCrO_2$.

the $CrFe5Y_2O_31$ surface. Owing to a preparation effect, the $CrFe5Y_2O_31$ surface in Fig. 4 seems to consist of two phases. A single-phase composition, however, was observed by EDS.

Although oxidation of the filler alloy occurs, it seems to be a very slow process. Hence, the resistance of the joints increased only slightly with annealing time. Further investigations are required to prove this hypothesis. We assume that oxygen diffusion is the rate-limiting step. The oxygen has to diffuse from the outer surface at the sides of the joints through the already formed oxides to the metallic filler material.

3.3. Bending of the joint

The $LaCrO_3$/SCP6/$CrFe5Y_2O_31$ joint was slightly bent after furnace brazing. It showed a concave curvature (Fig. 5), assuming that the $LaCrO_3$ plate is located on top of the $CrFe5Y_2O_31$ plate. The bending can lead to structural damage of the end plate or a deteriorating electrical contact to the SOFC stack during SOFC operation. The bending is caused by two mechanisms.

First, the materials to be joined exhibit a slight mismatch in their thermal expansion, shown in Fig. 6. The mismatch amounts to 0.09% in the range of 25°C to 1000°C. A crystallographic transformation from orthorhombic to rhombohedral at 75°C adds to the mismatch. Accordingly, the metallic plate contracts more during cooling after brazing than the ceramic plate. Bending of the joint results, since both plates are strongly connected.

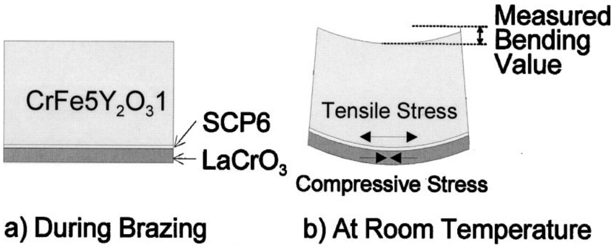

Figure 5 Schematic illustrating bending of the ceramic/metal joint.

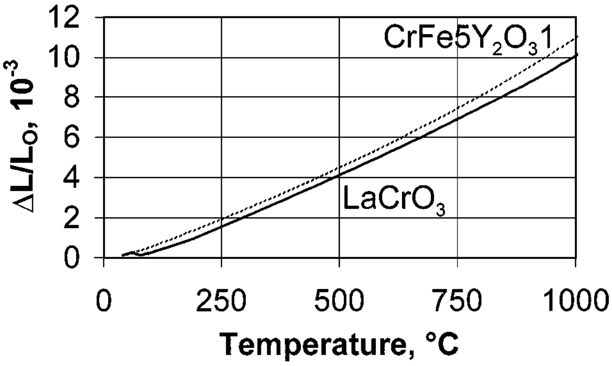

Figure 6 Relative linear expansion between 25°C and 1000°C for $LaCrO_3$ and $CrFe5Y_2O_31$.

Second, the bending is enlarged due to expansion of lanthanum chromite under a reductive atmosphere, which is related to loss of some oxygen and the simultaneous reduction from Cr^{4+} to Cr^{3+} to maintain electroneutrality [12, 13]. We observed that the lanthanum chromite plates employed for our study plate expanded by 0.2% during a complete brazing step under vacuum (heating, brazing at 1140°C for 10 min, cooling) that lasted 15.25 h.

Several means to decrease the joint bending for the given materials were tested. The results are given in

TABLE IV Bending of initial materials and joints 70 × 15 mm in size

Joint No	Thickness CrFe5Y$_2$O$_3$1 plate, mm	Thickness SCP6 filler, μm	Thickness LaCrO$_3$ plate, mm	Bending, μm
1	3.5			3-7
2	0.4			42-45
3			0.42	≈60
4	3.5	50		20-100[1]
5	0.4	50		560-680[1]
6		50	0.42	≈1790[1]
7	3.5	50	0.42	64
8	0.4	50	0.42	918
9	3.5	100	0.42	98

[1] Plate not homogeneously coated with the filler alloy.

Tables IV and V. The joints were brazed at 1140°C for 10 min in vacuum (10^{-5} mbar) unless indicated otherwise. The effect of various factors on joint bending are discussed below.

3.3.1. Ratio of the plate thickness

The ratio of the thickness of the ceramic and metallic plates affects the bending of the joint. The plate thickness influences the stiffness of the plates, and the stiffness of the plates influences the bending. Bending is maximized for both plates having the same thickness, and it decreases when one plate, preferably the stiffer one, is much thicker than the other one. As a consequence, the bending of joint no 7 in Table IV, having a CrFe5Y$_2$O$_3$1 plate which is much thicker than the ceramic plate, is significantly lower than that of joint no 8, having ceramic and metallic plates of the same thickness. According to this observation and the need for a low electrical resistance, the joint should be manufactured with a thin LaCrO$_3$ plate and a very thick CrFe5Y$_2$O$_3$1 plate. On the other hand, a LaCrO$_3$ plate having a thickness of less than approximately 0.4 mm may not withstand stresses that occur during SOFC manufacturing or operation.

3.3.2. Braze thickness

The SCP6 braze has a significantly higher thermal expansion coefficient (18.9×10^{-6}/°C, [14]) than the plate materials. Bending occurred in the metallic and ceramic strips that had been coated with SCP6 to study the wetting behavior (joints 4–6 in Table IV). Furthermore, the LaCrO$_3$/CrFe5Y$_2$O$_3$1 joint brazed with 100 μm SCP6 is significantly more bent than the one brazed with only 50 μm SCP6 (compare joints 7 and 9 in Table IV). The thickness of the braze layer should, therefore, be kept low but should not fall below approximately 50 μm in order to enable a complete wetting of the surfaces to be joined.

3.3.3. Brazing time

The time under vacuum, which includes the brazing time as well as the heating and cooling periods, determines the amount of expansion for LaCrO$_3$ as a consequence of its dimensional changes in this environment. That is in agreement with the results for joints 11 and 12, given in Table V. Decrease of the time under vacuum by a factor of two for joint 11 caused the bending to decrease from 360 to 304 μm. The brazing time was reduced by increasing the cooling rate from 1.7°C/min to 5°C/min, while the heating rate amounted to 5°C/min. However, both joints show almost the same amount of bending, approximately 260 μm, after annealing in air at 1000°C for 48 h (Table V). The annealing revoked the LaCrO$_3$ expansion, and the remaining bending is only caused by the mismatch in thermal expansion.

3.3.4. Symmetric joint design

An attempt was made to avoid bending of the ceramic/metal joint by designing a symmetric joint. Two LaCrO$_3$ plates having the same size were brazed onto both sides of the CrFe5Y$_2$O$_3$1 plate. Such a joint, no 13 in Table V, bent by approximately 100 μm after brazing. This comparatively low value is more likely caused by the inhomogeneous thickness of the joint, especially the CrFe5Y$_2$O$_3$1 plate, which had a deviation in thickness of about 100 μm. Consequently, annealing in air does not lower this bending value (Table V). The symmetric design effectively suppresses bending due to the LaCrO$_3$ expansion as well as the mismatch in thermal expansion. However, it is an expensive solution since twice as much interconnect and filler material is needed.

3.3.5. Segmentation of the metallic plate

Both mechanisms causing the bending of the joint (mismatch of thermal expansion between materials and volumetric expansion of the LaCrO$_3$) determine the bend radius. The amount of bending is also determined by the area and maximum diameter of the brazed LaCrO$_3$/CrFe5Y$_2$O$_3$1 interface. The smaller these values are, the less the joint will be bent. On the other hand, the LaCrO$_3$ plate should be almost completely connected with CrFe5Y$_2$O$_3$1 current collector

TABLE V Bending of initial materials and joints 80 × 80 mm in size

Joint No	Materials	Time under vacuum, h	Bending after Brazing, μm	Bending after Annealing, μm
10	CrFe5Y$_2$O$_3$1		≈100 (for the initial material)	
11	CrFe5Y$_2$O$_3$1/SCP6/LC	7.6	304	254
12	CrFe5Y$_2$O$_3$1/SCP6/LC	15.25	360	268
13	LC/SCP6/CrFe5Y$_2$O$_3$1/SCP6/LC	7.6	103	97
14	CrFe5Y$_2$O$_3$1/SCP6/LC, CrFe5Y$_2$O$_3$1-plate segmented	15.25	177	

thickness: CrFe5Y$_2$O$_3$1, 3.5 mm; LaCrO$_3$, 0.4 mm; and SCP6, 50 μm.

plate(s) to ensure a low-resistance current transport through the joint. In order to overcome this contradiction, it is beneficial to realize a given size for the $LaCrO_3$/$CrFe5Y_2O_31$ interface by brazing several small $CrFe5Y_2O_31$ segments onto the $LaCrO_3$ plate as opposed to only one $CrFe5Y_2O_31$ plate, assuming that the segments are homogeneously distributed on the $LaCrO_3$ surface. Nine $CrFe5Y_2O_31$ segments with a size of 25 × 25 mm were brazed onto a $LaCrO_3$ plate having a size of 80 × 80 mm in order to produce such a segmented joint. The area of the $LaCrO_3$/$CrFe5Y_2O_31$ interface was thereby reduced from 6400 mm^2 to 5625 mm^2. That decreased the bending after brazing from 360 μm to 177 μm (compare joints 12 and 14 in Table V). Disadvantages of this solution are: (i) a segmented joint is more complicated to produce, and (ii) conducting wires have to be attached to all segments in order to draw power from them under SOFC operating conditions.

4. Conclusions

The following conclusions were reached from this work:

1. The feasibility of joining metallic plates to $LaCrO_3$ end plates by vacuum furnace brazing was successfully demonstrated. The metallic plate acts as a current collector to which conducting wires made of conventional heat-resisting alloys can easily be attached [4]. Therefore, current collectors made from these conventional alloys will allow low-resistance connections required between individual SOFC stacks and sufficient power to be drawn from the SOFC.

2. The alloy $CrFe5Y_2O_31$ is a suitable material for the current collector plate. Its thermal expansion matches that of $LaCrO_3$ better than nickel- or iron-based heat-resisting alloys, such as MA 956. Hence, brazed $LaCrO_3$/$CrFe5Y_2O_31$ joints showed good adhesion and were free of cracks or spallation.

3. Such $LaCrO_3$/$CrFe5Y_2O_31$ joints can be brazed with filler of the palladium-containing copper alloy SCP6. This filler showed a much better wetting of the metallic and the ceramic surface than all other tested alloys, including high-temperature nickel-based brazing alloys, titanium-containing active brazing alloys on a nickel base or with a high iron content, and a palladium-containing silver alloy. Furnace brazing with SCP6 filler led to a much better adhesion between $LaCrO_3$ and $CrFe5Y_2O_31$ than diffusion welding without filler alloy.

4. After long-term annealing in air at 1000°C, the SCP6 filler of $LaCrO_3$/SCP6/$CrFe5Y_2O_31$ joints was partially oxidized. However, oxidation seems to occur slowly. Accordingly, the area specific resistance of most of the tested $LaCrO_3$/SCP6/$CrFe5Y_2O_31$ joints increased only slightly during long-term annealing. Even after 2400 h at 1000°C, the ASR values of all tested joints were two times lower than the defined target value of $0.2\ \Omega \cdot cm^2$.

5. The $LaCrO_3$/SCP6/$CrFe5Y_2O_31$ joint was initially slightly bent after furnace brazing. This bending results from a slight mismatch in the thermal expansion between $LaCrO_3$ and $CrFe5Y_2O_31$, and from expansion of $LaCrO_3$ in reducing environments (due to the loss of oxygen and the simultaneous reduction from $Cr^{4+}$to Cr^{3+}). Successful approaches to decrease the bending include reducing the braze thickness, shortening the brazing time under high vacuum, designing a symmetric $LaCrO_3$/$CrFe5Y_2O_31$/$LaCrO_3$ joint, brazing segments of $CrFe5Y_2O_31$ onto the $LaCrO_3$ plate, and using a $LaCrO_3$ plate that is significantly thinner than the $CrFe5Y_2O_31$ plate. The amount of permissible joint bending determines which of these approaches would be applied for a specific SOFC design.

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References

1. D. STOLTEN, R. SPAEH and R. SCHAMM, in Proc. 5th Int. Symp. on SOFC, edited by U. Stimming, S. C. Singhal, H. Tagawa and W. Lehnert, Proceedings Vol. 97-40 (Electrochemical Society, Inc., Pennington, NJ, USA, 1997) p. 88.
2. N. Q. MINH, *J. Amer. Ceram. Soc.* **76**(3) (1993) 563.
3. W. KOECK, H.-P. MARTINEZ, H. GREINER and M. JANOUSEK, in Proc. 4th Int. Symp. on SOFC, edited by M. Dokiya, O. Yamamoto, H. Tagawa and S. C. Singhal, Proceedings Vol. 95-1 (Electrochemical Society, Inc., Pennington, NJ, USA, 1995) p. 841.
4. R. WILKENHOENER, H. P. BUCHKREMER, D. STOEVER, D. STOLTEN and A. KOCH, "Brazing of Metallic Conductors onto Ceramic Plates in Solid Oxide Fuel Cells, Part 2: Attaching Conducting Wires," this journal.
5. in "Ullmann's Encyclopedia of Industrial Chemistry, Vol. A 28," edited by B. Elvers and S. Hawkins (VCH Verlagsgesellschaft mbH, Weinheim, Germany, 1996) p. 219.
6. in "Metals Handbook, 9th ed., Vol. 6: Welding, Brazing, and Soldering" (American Society of Metals, Metals Park, Ohio, USA, 1983) p. 929.
7. in "Ullmann's Encyclopedia of Industrial Chemistry, Vol. A 24," edited by B. Elvers, S. Hawkins, *et al.* (VCH Verlagsgesellschaft mbH, Weinheim, Germany, 1993) p. 427.
8. E. LUGSCHEIDER, H. KRAPPITZ and M. BORETIUS, *Tech. Mitt.* **80** (1987) H. 4, 231, in German.
9. in "Lieferprogramm Loettechnik" (Degussa AG, Geschaeftsbereich Edelmetalle, Arbeitsgebiet Loettechnik, Hanau, Germany, 1994) p. 12, 14, 15, in German.
10. in "Binary Alloy Phase Diagrams," 2nd ed., Vols. 1 and 2, edited by T. B. Massalski *et al.* (ASM International, Materials Park, OH, USA, 1990 and 1992).
11. K. T. JACOB, G. M. KALE and G. N. K. IYENGAR, *J. Mater. Sci.* **21**(8) (1986) 2753.
12. T. ARMSTRONG, J. W. STEVENSON and L. R. PEDERSON, In Proc. 2nd European Solid Oxide Fuel Cell Forum, Oslo, Norway, May 6–10, 1996 (published by Ulf Bossel, Oberrohrdorf, Switzerland, 1996) p. 521.
13. K. MORI, H. MIYAMOTO, K. TAKENOBU and T. MATSUDAIRA, see [12] p. 541.
14. in "Degussa Information, Datenblatt fuer CuPd18 (SCP 6)" (Degussa AG, Geschaeftsbereich Edelmetalle, Arbeitsgebiet Loettechnik, Hanau, Germany, 1996), in German.

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