Influence of the Brazing Paste Composition on the Wetting Behavior of Reactive Air Brazed Metal–Ceramic Joints

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Reactive air brazing (RAB) is a cost-effective way to produce ceramic–ceramic or ceramic–metal brazed joints in air, without applying a protective gas atmosphere or a vacuum. In addition to conventional furnace technology, the brazing with induction heating can also be used effectively. Within the scope of this study the shrinkage and wetting behavior of self-developed brazing pastes with different CuO contents and two qualities of silver powders with coarse and fine particle size are investigated by optical dilatometry on alumina (Al$_2$O$_3$, 99.7% purity). Thereby, the fine silver powder quality reveals a significant swelling effect at high temperatures, leading to an expansion of densified powder compacts caused by evolving gases. Joining tests are performed on ceramic–steel brazed joints using a muffle furnace and induction heating for short brazing cycles. The brazing seams and interfaces of the joints are investigated using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS). As a result, correlations between the brazing filler metal composition, the steel, and the brazing conditions are obtained.

1. Introduction

The brazing techniques for joining ceramic–metal components are usually performed under strictly controlled atmospheres (vacuum or argon). These processes require either complex deposition methods to metallize the ceramic component before brazing or active filler alloys in combination with costly high-vacuum atmospheres. In contrast, the reactive air brazing (RAB) was developed as a simple method without protective atmosphere during heating. The wetting of the ceramic surface by a liquid metal is performed with Ag–Cu-based brazing filler metals, in which the dissolving of oxygen by forming CuO is perquisite for RAB. In the last two decades, Weil, Hardy, and Kim investigated the wetting and sealing behaviors as well as the mechanical properties of Ag–CuO brazed ceramic–metal components. The main application of these studies was the joining of yttria stabilized zirconia (YSZ) with steel for the cell-to-frame seal in solid oxide fuel cells (SOFC). The RAB of oxygen transport membranes and alumina for gas sensors was in the focus of research in recent years.

The wetting of the ceramic is an important requirement for joining ceramic–metal components. Therefore, the wetting behavior of the Ag-based brazing filler metals in dependence of the CuO content at temperatures between 1000 and 1100 °C was investigated in almost all studies. The wetting angle of pure silver on ceramic is high (>100°) and decreases with addition of CuO. In case of YSZ, a wetting angle of 20°–30° with 8 mol% CuO was measured. The wetting angle on alumina (Al$_2$O$_3$) is higher compared with YSZ and steel and ranges between 35° and 50° for 2–8 mol% CuO. With higher content of CuO, the interface at the alumina contains brittle phases of CuAlO$_2$ together with the initiation of cracks. Phase field modeling was used to understand the Ag–Cu–O composition during melting and cooling with different contents of CuO. The molten Ag–CuO brazing filler is demixed in two liquids: the Ag-rich (L1) and Cu-rich (L2) phase. The oxygen of the atmosphere influences the solubility of the Cu, so that CuO is precipitated during cooling. The modeling gives helpful hints for the brazing process (temperature, ramps), but does not explain the formation of brittle phases or pores. These defects (cracks by brittle phases and pores) together with the oxidation of the steel influence the mechanical properties of the brazed joints. Brittle phases formed by CuO–Al$_2$O$_3$ can be suppressed using a CuO content between 4 and 8 mol%. However, the formation of pores is not finally understood. The usage of metal foils without binder instead of pastes with organic additives could be a solution to prevent the formation of pores during evaporation of the binder (<600 °C). The addition of a small amount of Al in the brazing paste was successfully used for reducing pores. The visualization of pores in the RAB joints can be done by ultrasonic testing, so that this nondestructive method opens up the possibility of...
The third reason for the decreased mechanical properties is the oxidation of the steel and thereby the initiation of cracks on the interface between brazing filler metal and steel.[21] The thickness and the morphology of the oxide layer on steel influence the mechanical properties of the brazed ceramic–metal component dramatically.[24]

New ideas are the usage of an interlayer of porous nickel for promoting the wetting angle of Ag without Cu for brazing YSZ ceramic[25] or the reinforcement with Al2O3 nanoparticles for improving the joint strength.[26]

In this study, the RAB as a cost-effective and fast method is investigated for the brazing of Al2O3 ceramic with a filler metal composition based on silver with 4 mol% CuO and 0.5 mol% Ti (Ag4CuO0.5Ti). The influence of the silver particle size on the formation of pores is investigated for the first time. The printing of pastes with the filler metal composition Ag4CuO0.5Ti was used as an industrial common method. Two different brazing techniques—conventional muffle furnace and induction brazing—are performed and compared for different types of noncorrosive steel.

2. Experimental Section

2.1. Materials and Set-up

The filler metals were prepared utilizing two different silver powders, 0–8 mol% CuO (99.7% pure by Alfa Aesar) and 0.5 mol% TiH2 (98% pure by Sigma-Aldrich). Two qualities of silver powder were used: 1) a coarse powder of Daikon and 2) a fine powder of Hereaus. The compositions of the powder mixtures are given in Table 1. The mixtures were dispersed in a solvent with polyacrylate binder for preparing printable pastes. First, the binder was dissolved and then the inorganic powders (silver, CuO, TiH2) were added to the dissolver while stirring. The paste was homogenized on the roller mill before printing. The pastes were applied on blocks of Al2O3 ceramic (99.7% pure by SIGMA–ALDRICH) with the dimensions of 18 mm × 18 mm and 10 mm height by screen-printing with a 154 mesh screen and 10 mm diameter. The steel component as cylindrical piece with 10 mm diameter and 4 mm height was placed on the dried filler metal layer with a thickness between 50 and 75 μm. The different types of steel, which were used are listed in Table 2.

2.2. Brazing Processes

The brazing experiments were conducted with two different brazing processes, induction brazing and muffle brazing. The induction brazing experiments were performed by heating the steel partner with 130 K min−1 up to a temperature of 1000 °C in air. To reduce the thermal tension in the ceramic base material, a metal casing was used and heated up together with the steel on top of the ceramic. With a conventional muffle furnace by Nabertherm, the brazing with a slower ramp of 5 K min−1 up to a temperature of 1000 °C was processed.

2.3. Analysis Methods

The specific surface of the silver powder was measured with N2 adsorption (ASAP 2010 analyzer of Micromeritics). STA 449C synchronous thermal analyzer (NETZSCH, Germany) was used for the thermogravimetric (TG) analysis with a ramp of 5 K min−1 at temperatures up to 1000 °C under synthetic air with a flow rate of 5 L h−1. The shrinkage behavior and the wetting angle were measured with optical dilatometry (Hesse Instruments) by heating up the cylindrically pressed brazing filler with 10 K min−1 at a temperature of 1000 °C. After a holding time of 10 min at 1000 °C, the wetting angle was determined by the silhouette of the molten drop by taking a picture and the angle was measured using the software ImageJ. For the investigation of the wetting behavior, the printed alumina was heated up with 5 K min−1 at T = 1000 °C and the assembly was kept at 1000 °C for a holding time of 1 min in the muffle furnace in air. Then the molten and cooled brazing filler on top of the ceramic was analyzed with scanning electron microscope (SEM) “JSM 7001F” (JEOL) and energy-dispersive X-ray spectroscopy (EDS).

For the investigation of the brazed ceramic–steel joints, the components were embedded in epoxy resin and cut for preparing the cross section. The cross section was polished with conventional wet-chemical methods. The brazing seams of the polished metal–ceramic joints were analyzed by SEM and EDS.

3. Results and Discussion

Using two different types of silver powders in the filler metal, the influence on the shrinkage, the wetting, and the formation of a pore-free brazing seam was investigated. The first powder consisted of coarser particles with spherical shape and a low

Table 1. Composition of silver-based filler metals.

| Filler metal | Ag [mol%] | CuO [mol%] | TiH2 [mol%] |
|-------------|-----------|------------|-------------|
| Ag0.5Ti     | 99.5      | –          | 0.5         |
| Ag2CuO0.5Ti | 97.5      | 2          | 0.5         |
| Ag4CuO0.5Ti | 95.5      | 4          | 0.5         |
| Ag8CuO0.5Ti | 91.5      | 8          | 0.5         |

Table 2. Types and composition of steel.

| Steel       | Behavior                      | Cr   | Ni   | Mo   | Mn   | Ti   | La | Si | Cu   | Al   |
|-------------|-------------------------------|------|------|------|------|------|----|----|------|------|
| X2CrNiMo    | Austenitic, noncorrosive     | 16–18| 10–14| 2–3  | 0–2  | –    | –  | –  | 0–0.75| –    |
| X1CrTiAl5Mo | Ferritic, low thermal expansion coefficient | 20–24| –    | 0.3–0.8| 0.03–0.2| 0.04–0.2| 0.05| 0–0.5| 0.0–0.5| 0–0.5|
| X10Cr18Ni10 | Ferritic, noncorrosive       | 17–19| –    | 0–1.0 | –    | –   | 0.7–1.4 | –  | 0.7–1.2 |
specific surface of 0.49 m² g⁻¹ (Figure 1). In the following text, this powder is named as “coarse silver powder”.

In comparison, the second powder contains a large amount of fine particles and has a higher specific surface of 1.82 m² g⁻¹ (named as fine powder). Utilizing the fine powder, different filler metal compositions in the range of 0 and 8 mol% CuO with addition of 0.5 mol% TiH₂ were prepared (Table 1). It could be observed that the wetting angle of the molten mixtures on Al₂O₃ ceramic at T = 1000°C extremely decreases with the addition of CuO (Figure 2).

In comparison to the data of Chen et al.[13] the tendency of the reduced wetting angle with increasing CuO content is shown too. But the value with 4 mol% CuO in our experiment with fine silver powder is lower. The cause of the difference between the values could be the roughness of the ceramic surface, the particle size of the used silver powder, or the standard deviation estimated with 1–3.

The wetting angle of the AgₓCuO0.5Ti filler metal with 4 ≤ x ≤ 8 mol% CuO is comparable, so that in the following experiments the composition was fixed at a value of 4 mol% CuO. With this composition, two different mixtures were prepared, one with the fine and one with the coarse silver powder. The shrinkage of the filler metal with the coarse silver powder started at a comparably high temperature of 750°C and finished with the melting at T = 940°C (Figure 3a).

The filler metal containing fine silver powder behaves differently. It shows a low-temperature shrinkage starting at a temperature of 260°C and an expansion above 600°C. A possible explanation for this expansion is the low-temperature shrinkage that is related to an enclosing of gas species in this early stage of sintering. These gas species were detected with TG measurements in connection with mass spectroscopy between 170 and 280°C, so that the degassing of the binder overlaps with the densification during sintering of the brazing paste with fine Ag powder (Figure 3b). The outgassing at higher temperature results in a swelling effect, leading to an expansion of the sintered specimen with enclosed porosity. During the brazing process, such a behavior could lead to the formation of pores in the brazing seam.

For the wetting of oxide ceramics, the presence of CuO plays an important role (as shown earlier). The reason for this wetting behavior is the formation of two liquids above 960°C: the Ag-rich (L₁) and Cu-rich (L₂) phase. Although L₁ is wetting the steel component, the oxide ceramic has a higher
attractiveness to the L2 phase. To evaluate the wetting behavior of the different pastes (coarse and fine silver powder) and liquid phases (L1 and L2), wetting tests were conducted with printed alumina samples without a steel joining partner. Taking a look on the ceramic surface after wetting with the filler metal Ag4Cu0.5Ti, the ceramics was not covered by a continuous layer of metal (Figure 4). The silver formed some melting beads and was surrounded by a CuO-rich phase. With the coarse silver powder, this CuO-rich phase was more homogeneous and separated compared to the filler metal with fine silver powder. In the last case, the separation of CuO was obvious. Probably, the partial oxidation of the fine silver powder with high specific surface can be a reason for the differences in solubility of CuO.

Both types of pastes were used for brazing ceramic–steel joints at $T = 1000 \, ^\circ\mathrm{C}$ in air with fast induction and furnace heating. Independent of the heating method, the mixture with coarse silver powder forms a well-filled brazing seam, whereas the filler metal with fine silver is interrupted by cavities (Figure 5 and 6). The ineffective wetting of a closed brazing seam in case of using fine silver seems to be correlated with expansion behavior of this mixture during heating.

Comparing the fast induction brazing with slow brazing in a furnace, the formation of an oxide layer on the steel is the main difference. The interfacial reaction on the ceramic side is driven by the composition of the filler metal, whereas the oxide layer in the steel is formed with external oxygen of the air. In Figure 5, an example for the reaction layers between the filler

![Figure 3](image_url)  
**Figure 3.** a) Shrinkage behavior of two dried brazing pastes (Ag4CuO0.5Ti) made of two different silver powders as function of the temperature and b) thermal gravimetry of the fine Ag powder and dried paste of this powder (Ag4CuO0.5Ti) with detected molecules by mass spectroscopy.

![Figure 4](image_url)  
**Figure 4.** Wetting of the filler metal on the Al2O3 ceramic after heating ($T = 1000 \, ^\circ\mathrm{C}$ in air). The ceramic was printed with Ag4CuTi0.5 paste containing a) coarse silver powder and b) fine silver powder.
metal and both components is given. The silver of the filler metal improves the wettability on the steel and the amounts of CuO and Ti interact with the Al$_2$O$_3$ ceramic. Therefore, the oxide layer on steel contains elements of the steel alloy (Fe, Cr, Mn, Ni, Mo, and Si). These oxide layers are brittle, so that the cracks can be found in this part of the brazing seams (Figure 5b). Thus, the failure of the brazed joints is mainly located in the oxide layer at the interface of filler metal and steel, where additionally also smaller pores were observed (Figure 5 and 6). The large cracks in the oxide layers seem to be formed during cooling by thermal stress, because the embedding material fills the cracks before preparation of the cross sections. Therefore, the components seem to be held together more by mechanical interlocking rather than by brazing. The impact of the porosity on cracking in the oxide layer cannot be differed from the effect of thermal stresses, because after preparation of the cross sections, the cracks dominate the visual impression.

Figure 5. SEM pictures of the cross section of the brazed component made of steel X2CrNiMo17–12–2, filler metal Ag4Cu0.5, and Al$_2$O$_3$ ceramic. a–c) Induction brazed with coarse silver-based filler metal and d–f) furnace brazed with coarse silver-based filler metal (left: overview of the brazing seam; middle: interface between steel and filler metal; right: interface between filler metal and ceramic).

Figure 6. SEM pictures of the cross section of the brazed component made of steel X2CrNiMo17–12–2, filler metal Ag4Cu0.5, and Al$_2$O$_3$ ceramic. a–c) Induction brazed with fine silver-based filler metal and d–f) furnace brazed with fine silver-based filler metal (left: overview of the brazing seam; middle: interface between steel and filler metal; right: interface between filler metal and ceramic).
Table 3. Thickness of the oxide layer between the brazing seam and the steel after brazing at $T = 1000\,^\circ C$ in air in dependence of the brazing method.

| Steel               | Thickness of the oxide layer [μm] |
|---------------------|-----------------------------------|
|                     | Induction brazing (130 K min$^{-1}$) | Furnace brazing (5 K min$^{-1}$) |
| X2CrNiMo 17-12-2 (1.4404) | 2.9 ± 1.5                          | 7.0 ± 2.0                        |
| X1CrTiLa22 (1.4760)   | 3.6 ± 2.0                          | –                               |
| X10CrAlSi18 (1.4742)  | 2.0 ± 1.0                          | 2.0 ± 1.0                        |

In comparison, the interfacial layer on the ceramic side is formed of the elements Cu, Ti, Al, and O, so that a phase formation to a spinel CuAl$_2$O$_4$ or pseudobrookite Al$_2$TiO$_5$ structure can be assumed (Figure 5f). Regardless of the reaction on the interfaces, the filler metal is dotted with CuO segregations as a result of the insolubility of Ag and CuO.

For both, the induction and furnace brazing, the joining of steel and Al$_2$O$_3$ ceramic is possible with filler metal composition of Ag4CuO0.5Ti. The main difference between the two brazing methods is the thickness of the oxide layer on the steel component, which is influenced by the brazing time. With slow furnace brazing, the oxide layer of the austenitic steel X2CrNiMo 17-12-2 is between 1.5 and 4 times thicker compared with the fast induction brazing (Table 3, Figure 7). Changing the steel component to a ferritic steel such as X1CrTiLa22 or X10CrAlSi18, the oxide layer is thinner for both brazing techniques. With the austenitic steel X2CrNiMo 17-12-2 and the ferritic steel X10CrAlSi18, the formed oxide layer on the steel side indicates porosity, whereas the steel X1CrTiLa22 forms a dense oxide layer. The mechanism of pore formation seems to be related to oxide formation, but has not been fully understood. With this limiting of the oxidation, the cracks on the steel X1CrTiLa22 can be prevented and a tight and dense brazing seam is formed.

Comparing the silver powders, the sintering of the fine silver powder overlaps with the debinding and the swelling effect of the filler metal seems to be a result of enclosed binder (as discussed earlier). In this case, the brazing seam contains larger pores, which, for example, is shown in Figure 6a with an interrupted contact of the filler metal on the steel interface as well as on the interface of the ceramic. In conclusion, the coarser silver powder shows a homogenous sintering and melting followed by a more complete filling of the brazing seam. But other parameters such as differences in the thickness of the printed braze, the flowing and wetting of the filler, and the heating in local areas by the different processes could also influence the behavior. Therefore, the influence of the particle size and shape of the silver powder seems to be significant, but is not understand completely.

4. Conclusion

The influence of the specific surface of the silver powder on the formation of a dense and tight brazing seam without cavities and pores for brazing Al$_2$O$_3$ ceramic–steel components in air was investigated. The optimized composition of Ag4CuO0.5Ti with 4 mol% CuO and 0.5 mol% TiH$_2$ as filler metal was prepared with two types of silver powder: a fine and a coarse, spherical powder. The shrinkage of the fine silver powder quality revealed a significant swelling effect caused by gas formation at high temperatures before melting. This leads to a brazing seam interrupted by cavities and larger pores. With the coarse silver powder, the filling of the brazing seam is more complete. The particle size and shape of the silver seem to influence the wetting behavior and the filling of the brazing seam, but the impact of other effects such as the thickness of the brazing layer, the flowing of the filler, local heating, and heating rates cannot be excluded.

After brazing, on both interfaces (filler/steel and filler/ceramic), reaction layers are formed. Although on the ceramic side mixed oxides of Cu–Ti–Al–O are detectable, the formation of brittle oxides on the steel is caused by the oxidation during brazing in air. The thermal stress due to the different thermal expansion of the materials results in cracks in the brittle oxide layers on the steel side. The brazing methods influence the thickness of the oxide layer, so that the layer thickness is higher with the slow furnace brazing compared with fast inductive heating. For both techniques, RAB Al$_2$O$_3$ ceramic–steel components can be obtained with noncorrosive, austenitic steel such as X10CrAlSi18.

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Figure 7. SEM pictures of the brazing seam of the induction-brazed component made of different types of steel, filler metal Ag4CuO0.5 with fine silver powder, and Al$_2$O$_3$ ceramic; a) X2CrNiMo 17-12-2, b) X1CrTiLa22, and c) X10CrAlSi18 steel.
Conflict of Interest

The authors declare no conflict of interest.

Keywords

ceramic–metal joints, reactive air brazing, silver-copper oxide metal fillers

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