1. Introduction

Mixed ionic/electronic conducting oxygen-permeable membranes (MIEC-OPM) have been widely applied, such as oxygen separator, oxidation-reforming reactor, and solid oxide fuel cells [1–5]. Due to the high thermal expansion coefficient, low chemical stability and strength of the OPMs, the reliable sealing of OPMs with their metal support at high temperature is facing a huge challenge.

A new brazing technology named reactive air brazing (RAB) has been developed, showing a special application prospect in high temperature electrochemical devices [6,7]. In RAB, Ag-Cu (or Ag-CuO) alloys have been commonly used for brazing various OPM systems because of their excellent ductility and high-temperature oxidation resistance. The wetting behavior of Ag-Cu (or Ag–CuO) alloy on ceramic membrane has been widely reported [8–12]. Especially, our group has investigated the interfacial reaction mechanism between Ag-Cu alloy and BaCo1.7Fe0.2Nb0.1O3.6 (BCFN) ceramic membrane in the past few years [13]. However, a reliable joint requires not only good wetting ability between the alloy braze and ceramic membrane but also long-term stable operation at high temperature. In recent years, the stability of some Ag-Cu (or Ag-CuO) brazing joints under high temperature has attracted attention. J.Y. Kim et al. [14] exposed the Ag-CuO-based/Al2O3 joints to air and hydrogen, respectively, at 800°C for 100 h. The joint microstructure had no significant change in air, while the joint strength had a measurable decrease in hydrogen and was accompanied by the formation of holes. A. Kaletsch et al. [15] treated the BSCF/Ag-Cu/AISI 314 joints in air at 850°C for 500 h. The porosity at the interface between the braze and ceramic increased and the strength of the joint decreased. B. Kuhn et al. [16] found that high-temperature aging treatment at 800°C for 500 h in air had no effect on the mechanical properties of the Electrolyte/Ag-Cu/Crofer joints but aging in reducing atmosphere caused the change of microstructure and led to a reduction of the fracture energy. K. S. Weil et al. [17] tested the YSZ/Ag-Cu /Crofer joints at 750°C for 800 h in both air and hydrogen environments. The strength and microstructure of the joints in air were not degraded, but the microstructure of the joint in hydrogen was coarsened. A. Poenicke et al. [18] revealed that during annealing in air at 850°C, the bending strength of 3YSZ/Ag-Cu /Crofer joints decreased with time and the thickness of oxidation reaction layer increased. Previous studies showed that the stability of the joints under different ceramic membrane types or atmosphere conditions may be different. For each new ceramic membrane...
system, the service stability of the joint should be investigated systematically.

In this study, based on our group's previous research [13], the stability of Ag-Cu/BCFN joint under long-term high temperature in oxidizing atmosphere and low oxygen partial pressure atmosphere was evaluated from the perspective of microstructure evolution. The reasons for microstructure evolution in different atmospheres were analyzed. Potential solutions on how to improve the stability of joints were summarized and discussed, which provided a theoretical support for further optimizing the brazing sealing process and improving the sealing quality of MIEC-OPM.

2. Experimental procedures

Based on our previous study [13], Ag-6.6 mol% Cu was selected for the preparation of brazed joints. They were fabricated by vacuum induction melting and then were cut into 2 mm×2 mm×2 mm cubes by a wire-cut machine. The details of the procedure to prepare the BCFNO membrane disks have been given elsewhere [19]. The BCFNO disks were polished with waterproof sandpaper and cleaned ultrasonically with acetone and ethanol. A tubular furnace was used to prepare the samples of Ag-6.6 mol% Cu/BCFN brazed joints. The Ag-6.6 mol% Cu alloy was placed in the center of the BCFN ceramic surface. The BCFN substrate was ensured to be parallel to the ground. The heating system of the brazing process: heating to 980°C at a rate of 10°C/min and then cooling immediately with the furnace. The brazed Ag-6.6 mol% Cu/BCFN joints were put into another tube furnace for high-temperature heat treatment. They were heated to 850°C at a rate of 10°C/min and then held for 100 h, 300 h, 500 h and 1000 h, respectively. The gas used in heat treatment are air and argon. After cooling to room temperature, the samples were removed from the furnace.

The cross-sections of the treated joints were polished for characterization. Microstructural analysis was conducted using a scanning electron microscope (SEM, HITACHI SU-1500) equipped with energy-dispersive spectrometer (EDS). The phase composition was identified by X-ray diffraction (XRD, D8 Advance) with scanning angle ranged from 10°-90° and scanning speed of 8°/min.

3. Results and discussion

3.1. Heat treatment in air

Figure 1 shows the SEM images of the interface of Ag-6.6 mol% Cu/BCFN brazed joint after heat treatment in air for different time. From Figure 1(a), it can be seen that the interface of joint presents a very obvious stratification phenomenon before heat treatment. The interfacial reaction zone contains two phases: dark phase and gray phase. The EDS analysis results of the marked points are shown in Table 1. According to the BaO-CuO [20] and CoO-CuO [21] phase diagrams, the reaction products in the interfacial reaction layer before treatment mainly consist of Co-Cu-O (dark phase, position 1) and Ba-Co-Cu-O (gray phase, position 2). After treatment for 100 h, the stratification phenomenon disappears and the interfacial reaction zone tends to be homogeneous. The interfacial reaction products begin to appear block dispersion distribution. With the prolongation of treatment time, the block reaction products tend to aggregate and grow up to reduce their surface energy. However, the types of reaction products remain unchanged even after heat treatment for 1000 h according to the EDS results (positions 6 and 7).

Figure 2 shows the SEM images inside the alloy filler metal of Ag-6.6 mol% Cu/BCFN brazed joint after heat treatment in air for different time. Figure 2 is the EDS analysis result of the points marked in Figure 2. As shown in Figure 2(a), there are some black spots scattered in the Ag-based alloy, which are detected as copper oxide (position 1). The black substances in the alloy after heat treatment are still copper oxide (positions 2-5). According to the EDS results, the atomic ratio of copper to oxygen in the copper oxides before heat treatment is about 64:36, while the atomic ratio after heat treatment for 1000 h is about 80:20. With the extension of time for heat treatment, the copper oxides in the alloy tend to agglomerate and grow up, which is mainly related to the tendency of copper oxides to reduce their own interface energy.

To determine the phase composition of the interfacial reaction products and whether the heat treatment in air has an effect on the reaction products, the alloy braze parts of Ag-6.6 mol% Cu/BCFN joint samples before and after heat treatment were removed, and then the exposed interfacial connection micro-zone was analyzed by XRD. As shown in Figure 3, the interfacial reaction products of samples without heat treatment are the same as those after heat treatment for 300 h, mainly Ba$_2$Cu$_2$O$_5$, which is consistent with the EDS analysis results. No Co-Cu-O oxides are found in XRD analysis result, which may be due to the existence of Co-Cu-O in the form of solid solution. Compared with the standard card (PDF#89-5896, 2θ = 35.563°), the main diffraction peak of CuO in Figure 3 is slightly shifted to a large angle (2θ = 35.662°), indicating the doping of...
smaller-radius atoms. The CoO-CuO phase diagram [21] also proves that the solid solution Co-Cu–O can form at the brazing temperature (980°C). In addition, pure silver is detected at the interface, indicating that liquid alloy has entered the ceramic matrix. It is worth noting that the diffraction peak intensity of the samples after heat treatment for 300 h is increased slightly compared with that before heat treatment. Generally, the increase in the diffraction peak intensity reflects the growth of crystallite size and the decrease in lattice strain [23–25]. Meanwhile, the results in the literature showed that larger crystallite size corresponded to lower compressive strength [24] and tensile strength [26]. Therefore, in this study, the enhancement of the diffraction peak also reflects the degradation of the mechanical properties of the Ag-Cu/BCFN joints from the side.

### 3.2. Heat treatment in argon

Figure 4 shows the SEM images of the interface of Ag-6.6 mol% Cu/BCFN brazed joint after heat treatment in argon for different times. Similar to the results of heat treatment in air, the stratification phenomenon at the interface also disappears after heat treatment in argon. However, serious holes appear at the joint interface after heat treatment in argon for 100 h. When the heat treatment time reaches 300 h, the number of holes at the interface increases and many cracks appear. The formation of holes may be related to the decomposition of some reaction products, which needs to be further characterized. After 500 h, the interface morphology changes more greatly. The dark phase and gray phase can hardly be distinguished in the whole interfacial reaction zone. From Figure 4(e), it can be seen that the dark phase (position 8) is distributed in strips. The EDS analysis results of the marked points are shown in Table 3. According to Table 3, the dark phases (positions 3, 5 and 8) after heat treatment in argon are still Co-Cu-O. It is noteworthy that there are some Co (rich)-Cu-O phases (position 4 and 7) with much higher cobalt content than other Co-Cu-O dark

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**Table 1.** EDS results of the marked points in Figure 1 (at. %).

| Position | 1   | 2   | 3   | 4   | 5   | 6   | 7   |
|----------|-----|-----|-----|-----|-----|-----|-----|
| Ba       | /   | 6.81| /   | /   | /   | 6.92| 1.52|
| Co       | 6.27| 5.75| 3.17| 4.73| 2.50| 5.08| 2.83|
| Cu       | 56.15| 62.29| 63.72| 65.15| 79.47| 68.66| 77.26|
| O        | 37.58| 25.15| 33.11| 30.12| 18.03| 19.34| 18.39|

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**Figure 1.** SEM micrographs of the interface of Ag-6.6 mol% Cu/BCFN joint after heat treatment at 850°C in air for different time: (a) 0 h; (b) 100 h; (c) 300 h; (d) 500 h; (e) 1000 h.
phases at the junction of Ag-Cu alloy and interfacial reaction zone. This can be explained by the fact that the BCFN matrix decomposed under low oxygen partial pressure and then part of Co precipitated from the matrix to participate in the interfacial reaction.

Figure 5 shows the SEM images inside the alloy filler metal of Ag-6.6 mol% Cu/BCFN brazed joint after heat treatment in argon for different times. The EDS analysis results of the marked points are shown in Table 4. It can be seen that the change law inside the alloy after heat treatment in argon is the same as that in air. The copper oxides in the alloy also agglomerate and grow up. However, compared with heat treatment in air (Table 2), the oxygen content in copper oxides is relatively low, which may be due to the decomposition of copper oxides under low oxygen partial pressure.

The phase composition of the interfacial connection micro-zone of Ag-6.6 mol% Cu/BCFN joint samples after heat treatment for 300 h in argon was analyzed by XRD in the same way as before. As shown in Figure 6, the interfacial products before heat treatment are mainly Ba₂Cu₃O₅ and some CuO, while the products after heat treatment are BCFN matrix, Ag and Cu₂₁O. This indicates that the interfacial reaction products (Ba₂Cu₃O₅)
CuO is studied basically facial the 15

Figure 714 after obviously, decomposed Table (a) Figure 4.

![SEM micrographs of the interface of Ag-6.6 mol% Cu/BCFN joint after heat treatment at 850°C in argon for different time: (a) 0 h; (b) 100 h; (c) 300 h; (d) 500 h; (e) 1000 h.](image)

Table 3. EDS results of the marked points in Figure 4 (at. %).

| Position | 1 | 2   | 3   | 4   | 5   | 6   | 7   | 8   |
|----------|---|-----|-----|-----|-----|-----|-----|-----|
| Ba       | / | 0.68| /   | /   | /   | /   | /   | /   |
| Co       | 6.45| 3.34| 3.06| 71.10| 2.08| 2.15| 70.86| 1.02|
| Cu       | 55.83| 62.77| 83.75| 7.51| 87.25| 83.86| 6.18| 82.76|
| O        | 37.72| 25.21| 13.19| 21.39| 10.67| 13.99| 22.96| 16.22|

decomposed under low oxygen partial pressure, which is the reason for the formation of holes. In addition, the CuO in the reaction zone is also decomposed into Cu$_{2+1}$ O. Similarly, the diffraction peak intensity of the samples after heat treatment in argon for 300 h increases more obviously, which indicates that the mechanical properties of the joints are more seriously degraded.

3.3. Thickness variation and solid-state diffusion

Figure 7 shows the thickness variation of the interfacial reaction layer of Ag-6.6 mol% Cu/BCFN brazed joint with the heat treatment time. In air, the thickness of interfacial reaction layer increases slightly with the extension of heat treatment time in the first 500 h, but it remains basically unchanged after 500 h. A. Kaletsch et al. [15] studied the effect of long-term static treatment on the interface structure of air reactive brazing BSCF/AISI 314 and found that the reaction layer between filler metal and ceramic was thickened during static treatment at 850°C in air, which was similar to our experimental results. However, the thickness of the reaction layer decreases slightly after heat treatment in argon.

The change in thickness is mainly related to the behavior of solid-state diffusion. According to Fick's second law, the diffusion component diffuses from high concentration to low concentration. Within the first 500 h of heat treatment in air, the copper oxides at the interface were sufficient. Under the action of the concentration gradient, the copper oxides gradually diffused and continued to participate in interfacial reaction to generate more reaction products. Meanwhile, the porous structure of the BCFN matrix also provided a fast channel for solid-state diffusion, resulting in thickening of the reaction layer. After 500 h, the copper oxides were exhausted and the interfacial reaction did not occur, so the thickness of the interfacial reaction layer was basically unchanged. However, after heat treatment in argon, part of the reaction products decomposed and then the holes formed in the original position. The interfacial reaction layer may shrink to the
position of the hole, resulting in a slight decrease in thickness.

Table 4. EDS results of the marked points in Figure 5 (at. %).

| Position | 1  | 2  | 3  | 4  | 5  |
|----------|----|----|----|----|----|
| O        | 36.20 | 11.56 | 12.17 | 11.98 | 11.25 |
| Cu       | 63.80 | 88.44 | 87.83 | 88.02 | 88.75 |

Figure 5. SEM micrographs inside the alloy filler metal of the Ag-6.6 mol% Cu/BCFN joint after heat treatment at 850°C in argon for different time: (a) 0 h; (b) 100 h; (c) 300 h; (d) 500 h; (e) 1000 h.

Figure 6. XRD patterns of Ag-6.6 mol% Cu/BCFN interface before and after heat treatment in argon at 850°C.

3.4. Summary of microstructure evolution and optimization scheme

The microstructure evolution of the Ag-6.6 mol% Cu/BCFN joints can be described by Figure 8. During the brazing process, an interfacial reaction occurred between the copper oxides in the Ag-Cu braze and the BCFN matrix. The interfacial reaction zone showed a layered structure, as
shown in Figure 8(a). The interfacial reaction products were Ba$_2$Cu$_2$O$_5$ (purple block) and Co-Cu-O (blue block). Meanwhile, some Ag (red block) and copper oxides (yellow block) entered the interfacial reaction zone. After heat treatment in air, the interfacial products were still Ba$_2$Cu$_2$O$_5$ (purple block) and Co-Cu-O (blue block), but they tended to agglomerate and grow up. As the interfacial reaction continued, the layered structure disappeared and the reaction layer gradually thickened. After 500 h, the interfacial reaction stopped due to the depletion of copper oxides in the reaction zone and the microstructure remained basically unchanged, as shown in Figure 8(b). However, in argon, with the extension of the heat treatment time, the interfacial product Ba$_2$Cu$_2$O$_5$ gradually decomposed due to the low oxygen partial pressure and left holes in the original position. Only Co-Cu-O phase (blue stripe), pure silver (red block) and some Cu$_2$O$_2$O$_5$ oxides (yellow block) remained at the interfacial reaction layer. Meanwhile, due to the precipitation of cobalt from the BCFN matrix, a cobalt-rich phase (orange block) was formed at the junction of Ag-Cu alloy and interfacial reaction zone. The interfacial reaction layer shrank to the position of the holes, resulting in a slight reduction in thickness, as shown in Figure 8(c).

Based on the above analysis and discussion, it can be concluded that the microstructure of the Ag-6.6 mol% Cu/BCFN joint is unstable when it is served at high temperature, especially under a low oxygen partial pressure atmosphere. The evolution of the microstructure generally affects the mechanical properties and air tightness. The microstructure evolution of the joint in both atmospheres is closely related to the interfacial products formed during brazing. Excessive original interfacial products are detrimental to the stability of the joint. Therefore, controlling the amount of the original interfacial product, such as appropriately reducing the copper content in the Ag-Cu braze, is the key to improve the long-term high-temperature stability of the joint.

4. Conclusion

In this work, the Ag-6.6 mol% Cu/BCFN brazed joints were heat treated at 850°C in air and argon for a long time. After heat treatment in air, the copper oxides in the interfacial reaction layer diffused along the pores to BCFN matrix and continued to participate in the reaction until they were exhausted, causing the thickness of the reaction layer to increase first and then remain unchanged. The interfacial products were Ba$_2$Cu$_2$O$_5$ and Co-Cu-O (solid solution), which are consistent with those before heat treatment. With the prolongation of heat treatment time, the copper oxides in the alloy tended to agglomerate and grow up, which is mainly related to the tendency of copper oxides to reduce their own interface energy. After heat treatment in argon, the interfacial product Ba$_2$Cu$_2$O$_5$ decomposed seriously under low oxygen partial pressure, leaving holes in the interfacial reaction layer. Part of Co precipitated from the BCFN matrix and participated in the reaction to form a cobalt-rich phase at the junction of the Ag-Cu alloy and the interfacial reaction zone. The microstructure evolution of copper oxides in the alloy after heat treatment in argon is similar to that after heat treatment in air. The CuO in the interfacial reaction zone is also decomposed into Cu$_2$O$_2$O$_5$.

From the perspective of microstructure evolution, the Ag-6.6 mol% Cu/BCFN brazed joint cannot remain stable after long-time working at high temperature, especially the formation of holes at the joint interface under low oxygen partial pressure is a severe challenge to its sealing performance. To obtain more reliable joints, the amount of interfacial products formed during brazing must be strictly controlled.
Disclosure statement

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

[1] Sunarso J, Baumann S, Serra JM, et al. Mixed ionic-electronic conducting (MIEC) ceramic-based membranes for oxygen separation. J Membr Sci. 2008;320:13–41.
[2] Geffroy P-M, Fouletier J, Richet N, et al. Rational selection of MIEC materials in energy production processes. Chem Eng Sci. 2013;87:408–433.
[3] Wei YY, Yang WS, Caro J, et al. Dense ceramic oxygen permeable membranes and catalytic membrane reactors. Chem Eng J. 2013;220:185–203.
[4] Dong XL, Jin WQ. Mixed conducting ceramic membranes for high efficiency power generation with CO2 capture. Curr. Opin. Chem. Eng. 2012;1(2):163–170.
[5] Engels S, Markus T, Modigell M, et al. Oxygen permeation and stability investigations on MIEC membrane materials under operating conditions for power plant processes. J Membr Sci. 2011;370(1–2):58–69.
[6] Wei KS, Kim JY, Hardy JS. Reactive air brazing: a novel method of sealing SOFCs and other solid-state electrochemical devices. Electrochem. Solid-State Lett. 2005;8(2):A133–A136.
[7] Kim JY, Hardy JS, Wei KS. Silver-copper oxide based reactive air braze for joining yttria-stabilized zirconia. J Mater Res. 2005;20(3):636–643.
[8] Kim JY, Hardy JS, Wei KS. Effects of CuO content on the wetting behavior and mechanical properties of a Ag-CuO braze for ceramic joining. J Am Ceram Soc. 2005;88(9):2521–2527.
[9] Wei KS, Kim JY, Hardy JS. Interfacial analysis of (La0.6Sr0.4)(Co0.5Fe0.5)O3-δ substrates wetted by Ag-CuO. J Mater Sci. 2005;40(9–10):2341–2348.
[10] Bobzin K, Schlafer T, Kopp N. Thermochemistry of brazing ceramics and metals in air. Int J Mater Res. 2011;102(8):972–976.
[11] Joshi VV, Meier A, Darrell J, et al. Trends in wetting behavior for Ag-CuO braze alloys on Ba0.7Sr0.3CoO0.8 Fe0.8O3-δ at elevated temperatures in air. J Mater Sci. 2013;48(20):7153–7161.
[12] Raju K, Muksin YDH. Reactive air brazing of GDC-LSCF ceramics using Ag-10wt% CuO paste for oxygen transport membrane applications. Ceram Int. 2016;42(14):16392–16395.
[13] Zhang YW, Zhang LL, Guo W, et al. Interfacial reaction and microstructural evolution of Ag-Cu braze on BaCo0.7Fe0.3Nb3/4O3-δ at high temperature in air. Ceram Int. 2017;43(1):810–819.
[14] Kim JY, Hardy JS, Weil KS. High-temperature tolerance of the silver-copper oxide braze in reducing and oxidizing atmospheres. J Mater Res. 2006;21(6):1434–1442.
[15] Kaletsch A, Pfaff ED, Broeckmann C. Effect of aging on microstructure and mechanical strength of reactive air brazed BSCF/AlSi 314-joints. Adv Eng Mater. 2014;16(12):1430–1436.
[16] Kuhn B, Wessel E, Malzbender J, et al. Effect of isothermal aging on the mechanical performance of brazed ceramic/metal joints for planar SOFC-stacks. Int J Hydrogen Energy. 2010;35(17):9158–9165.
[17] Weil KS, Coyle CA, Darsell JT, et al. Effects of thermal cycling and thermal aging on the hermeticity and strength of silver-copper oxide air-brazed seals. J Power Sources. 2005;152:97–104.
[18] Poenickie A, Arnold S, Schilm J, et al. Mechanical properties of reactive air brazed ceramic-metal joints for SOFC. In: Gourley R, Walker C, editors. Proceedings of the 5th International Brazing and Soldering Conference (IBSC); 2012; Dresden, Germany.
[19] Zhang YW, Li Q, Shen PJ, et al. Hydrogen amplification of coke oven gas by reforming of methane in a ceramic membrane reactor. Int J Hydrogen Energy. 2008;33(13):3311–3319.
[20] Lindermer TB, Specht ED. The BaO-CuO-Cu2O system solid-liquid equilibria and thermodynamics of BaCu2O and BaCuO2. Physica C. 1995;255(1–2):81–94.
[21] Zabdyr LA, Fabrichnaya OB. Phase equilibria in the cobalt oxide-copper oxide system. J. Phase Equilb. 2002;23(2):149–155.
[22] Kim JY, Hardy JS, Weil KS. Dual-atmosphere tolerance of Ag-CuO-based air braze. Int J Hydrogen Energy. 2007;32(16):3655–3663.
[23] Abd-Elwahed MS, Wajih A, Najjar IMR. Correlation between micro/nano-structure, mechanical and tribological properties of copper-zirconia nanocomposites. Ceram Int. 2020;46(1):56–65.
[24] Eltaher MA, Wajih A, Melaabari A, et al. Effect of Al2O3 particles on mechanical and tribological properties of Al-Mg dual-matrix nanocomposites. Ceram Int. 2020;46(5):5779–5787.
[25] Sadouna AM, Meselhy AF, Deabs AW. Improved strength and ductility of friction stir tailor-welded blanks of base metal AA2024 reinforced with interlayer strip of AA7075. Results Phys. 2020;16:102911.
[26] Zhou L, Chen SY, Wei MW, et al. Microstructure and properties of 24CrNiMoY alloy steel prepared by direct laser deposited under different preheating temperatures. Mater Charact. 2019;158:109931.