Study on the microstructure of air reactive brazing joint between Al₂O₃ ceramic and Q235 steel

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Abstract. Q235 steel /Al₂O₃ ceramics were brazed with Ag-CuO filler metal at 1050°C and held for 15min in air. When brazing Q235 steel and Al₂O₃ ceramics directly, it was found that serious oxidation occurred on the steel side during the brazing process. Although the joining was realized, a loose oxide film was formed on the surface of the base steel, which affected the mechanical properties of joints. When Q235 steel with aluminized surface was adopted to braze with Al₂O₃ ceramics, an Al₂O₃ layer formed on the surface of Q235 steel successfully avoided the oxidation of Q235 steel, and a compact and defect-free joint was obtained. The typical organization of joint was Al₂O₃/ Cu₂Al₂O₄/ CuO/ Ag/ CuO/ Cu₂Al₂O₄ / Al₂O₃/ FeAl/ FeAl₂/ Fe.

1. Introduction
Al₂O₃ ceramics have the characteristics of high strength, high temperature resistance, wear resistance, corrosion resistance and excellent insulation [1], and are widely used in the porcelain part of post insulators in the power transmission projects, so as to ensure that insulators have good electrical insulation performance and good mechanical strength. As a relatively cheap and common metal steel, Q235 steel, as the fixed part of post insulator, is generally used at the bottom of porcelain body, which is called base flange [2]. At present, for the insulation and mechanical fixation of bus bars and electrical equipment in the domestic power plants and substations, the porcelain part and metal part are usually glued with cement adhesive [3]. However, cement cementation is often difficult to ensure reliable bonding strength, and fracture often occurs during the production or use [4]. A large number of investigations have found that fracture accidents are often caused by flange adhesive cracking [5], resulting in a lot of economic losses. Therefore, aiming at the problems of low mechanical strength and unstable performance of the adhesive joint between porcelain column and flange, it is necessary to develop a convenient joining technology to realize the firm connection between Al₂O₃ ceramics and Q235 steel.

Ceramics are mainly composed of ionic bonds and covalent bonds, whereas metals are composed of metal bonds, making it difficult to bond directly between them. The coefficient of thermal expansion (CTE) between ceramic and metal is quite different and the plasticity of ceramic is poor, which will produce high thermal stress in the joint during cooling process, resulting in joint deformation and cracking. Therefore, it is a challenging task to realize the joining between ceramics and metals. At present, the main method to achieve ceramic metal connection is brazing, and active metal brazing is usually carried out in vacuum or high-purity inert gas. In recent years, researchers have introduced a new connection method in the joining area, reactive air brazing (RAB). In this method, some molten oxides that can be dissolved in precious metal solvent are used to wet the oxide
layer on the metal surface and ceramics, so that the remaining molten solder can better wet the new surface with the filler material. This bonding process does not require the use of additional cosolvent to remove the oxide film generated on the metal surface during the bonding process [6]. Compared with conventional active metal brazing, RAB has the characteristics of short process flow, low cost, good joint plasticity and oxidation resistance [7], so it has attracted the attention of researchers. At present, the commonly used metal oxide solder systems are Ag-CuO, Ag-V_2O_5 and Pt-Nb_2O_5. Among them, Ag-CuO solder system has the advantages of high plasticity and good high temperature stability. It is the most studied and used RAB solder system in the research area. Huang Xiaoke [8] successfully realized the joining between Al_2O_3 and 310S stainless steel under air using Ag-CuO solder. Wu Chengheng [9] used Ag-8mol.% CuO solder to connect 441 stainless steel with yttria stabilized zirconia (YSZ) ceramics in air. It was found that the room temperature shear strength of the joint was 32MPa. Cao et al. [10] successfully joined Al_2O_3 ceramics to YSZ ceramics using Ag-CuO solder in air. It was found that atomic bonding between CuO and ceramics was formed during brazing. Wang et al. [11] successfully welded BaZr0.1Ce0.7Y0.1Yb0.1O3-σ(BZCYYb) electrolyte to AlSi 441 on proton ceramic fuel cells (pfcfs) with Ag-CuO solder. In order to prevent oxidation corrosion of ferritic stainless steel Crofer22 during air brazing, air reactive aluminizing process was selected by Si et al. [12] to prefabricate Al_2O_3 protective layer on the surface of ferritic stainless steel Crofer22, and then Ag-2CuO solder was used to connect aluminized Crofer22 and SOFC battery (connection position: YSZ / CGO composite layer). The obtained joint was oxidized at 800 °C / 250h in air. The structure has no obvious change, which proves that the Al_2O_3 protective layer has an effective protective effect on the matrix. For RAB, there are many connections between fuel cell, Al_2O_3 and stainless steel, but the connection between Al_2O_3 and low carbon steel has not been reported.

In this paper, aluminized Q235 steel and Al_2O_3 ceramic were joined by air reactive brazing with Ag-CuO solder. The microstructure of aluminized Q235 steel / Al_2O_3 joint was analyzed by scanning electron microscope (SEM) and energy dispersive X-Ray spectroscopy (EDS).

2. Materials and methods
The materials used in this paper are conventional commercial materials, in which the purity of Al_2O_3 ceramics is 95wt.%. Ag powder (purity > 99.9wt.%) and CuO powder (purity > 99.9wt.%) used in this research were purchased from Shanghai McLean Biochemical Technology Co., Ltd., and the average particle size is 10μm. Q235 steel was cut by wire cutting machine before testing for 4mm×4mm×4mm microstructure sample and 10mm×5mm×4mm mechanical sample. Before brazing, 600 #, 800 #, 1000 # water sandpapers were used to polish the surface of the cut samples, and then 600 #, 1000 # metallographic sandpapers were used to polish the surface to be bright without scratches. Finally, it was immersed in acetone solution for ultrasonic cleaning for 3 min to remove surface impurities. Al_2O_3 ceramics were cut into 4mm×4mm×4mm, then ground with 800# diamond grinding disc. Finally, the samples were put into acetone solution for ultrasonic cleaning for 3min.

Using electronic balance with an accuracy of 0.0001g, 20g of Ag powder and CuO powder were weighed, separately. Then the powder was put into a planetary ball mill for 8h with an appropriate amount of ethanol solution, to obtain uniformly mixed brazing powder with different proportions. The obtained solder is pressed into a sheet shape by a powder tablet press.

The aluminizing treatment of Q235 steel was performed under the process of holding at 900 °C for 30min under vacuum, so that an Al protective layer could be formed on the surface of the Q235 steel. The weld was observed and analyzed by SEM equipped with EDS.

3. Results and discussions
3.1. air reactive brazing of Al_2O_3 and Q235 steel
Figure 1 is the microstructure diagram on both sides of the joint obtained by air reaction brazing of Q235 steel and Al_2O_3 at 1010 °C for 15min. As can be seen from the backscattering diagram on one side of Q235 steel in Figure 1 (a), it can be divided into two parts (I and II) from the middle of solder
area to the Q235 steel side. Part I is relatively loose, while Part II and brazing interface are dense and free of defects. The interfaces of region I and region II are tortuous, and a reaction layer was formed. On the ceramic side of figure (b), there is a light gray discontinuous interface reaction layer at the interface. Most of the braze are bright white phases, and some gray particle phases exist in the bright white phases.

![Figure 1. interface structure of 1050°C/15min Q235 steel /Ag-12mol%CuO/Al2O3 joint.](image)

(a) interface structure of Q235 steel side; (b) interface structure of Al2O3 side

In order to determine the composition of each phase in the weld, EDS was carried out for different phases in the joint, and the element distribution results are shown in Table 1. It can be inferred from the energy spectrum analysis results (Table 1) that the sparse area I in Figure 1 (a) has high contents of Fe and O, so it is inferred as FeO formed by the oxidation of Fe in Q235 steel and the corrosion of Q235 steel by CuO in the solder during brazing. There is a small amount of bright white B in region I, the energy spectrum results show that the content of Ag element is high, so it is speculated to be Ag based solid solution, which indicates that Ag has obvious penetration into the oxide layer during brazing. Point C in area II is CuO. Bright white D in the weld is Ag based solid solution, in which a small amount of gray particle phase E is CuO. On the Al2O3 ceramic side of the joint in Figure 1 (b), light gray F and black G are speculated to be CuO and CuAl2O4 formed by the reaction of CuO with Al2O3, respectively. In the summary, the typical interface structure of the joint is Al2O3 / CuAl2O4 / CuO / Ag / Cu / CuO / FeO / Fe. From the above analysis, it can be seen that Q235 steel matrix is seriously oxidized during brazing, and loose oxide film is formed on the surface. Then the mechanical properties of the joint are deteriorated.

![Table 1. EDS analysis result of each point of Q235/Al2O3 joint in Figure1(at.%)](image)

| Point | Ag  | Cu  | O   | Fe  | Al  | Possible phase     |
|-------|-----|-----|-----|-----|-----|--------------------|
| A     | 0.32| 11.93| 45.12| 41.95| -   | FeO                |
| B     | 47.08| 31.01| 19.71| 2.2  | -   | Ag                 |
| C     | 1.16| 83.08| 15.76| -    | -   | CuO                |
| D     | 95.16| 3.06| 1.78 | -    | -   | Ag                 |
| E     | 5.36| 46.39| 48.25| -    | -   | CuO                |
| F     | 8.62| 40.76| 46.05| -    | 4.57| CuO                |
| G     | 3.73| 24.28| 31.98| -    | 40.01| CuAl2O4           |

3.2. air reactive brazing of aluminized Al2O3 and Q235 steel

Figure 2 shows the backscattered electron phase of the joint obtained by air reactive brazing of aluminized Q235 steel and Al2O3 with Ag-12mol% CuO at 1050 °C for 15min. As shown in Figure 2 (a), Ag-CuO solder is closely combined with aluminized Q235 steel and Al2O3 ceramics, and the joint has no obvious defects such as cracks and holes. Figure 2 (b) shows the micro morphology of the
braze/ Al₂O₃ ceramic interface. It can be seen that a discontinuous reaction layer is formed at the Al₂O₃ ceramic side interface, and there are two phases A and B with different contrasts. There are a large area of bright white C and a small amount of gray phase D in the brazing seam. Figure 2 (c) shows the micro morphology of the braze/ aluminized Q235 steel interface. It can be seen that the interface on one side of Q235 steel is divided into three different regions I, II and III. From the locally enlarging areas of I and II (Figure 2 (c)), it can be seen that in area I, there are bright white C, light gray phase E and dark gray phase F. There is discontinuous black phase H between the interface of region I and region II, and light gray phase G exists in region II.

In order to determine the composition of each phase in the joint, EDS was carried out for the phases with different contrasts in the joint. The results are shown in Table 2. On the side of Al₂O₃ ceramics, the structure is relatively simple. According to the EDS analysis and the discussion in the previous section, discontinuous gray phase A is CuO phase, while black phase B is CuAl₂O₄ phase formed by the reaction between CuO and Al₂O₃. CuAl₂O₄ is also the key for the Ag-CuO solder to wet Al₂O₃ ceramics. In the middle area of the weld, there are a large area of bright white phase C and a small amount of granular gray phase D. C only contains Ag, so it is an Ag matrix, whereas the contents of Cu and O in D are almost the same, so it is referred as CuO left in the Ag matrix without participating in the interfacial reaction. According to the analysis of Ag CuO phase diagram in Figure 3[13], silver and copper oxide will form non fused silver rich liquid phase L1 and copper oxide rich liquid phase L2 at 1050 ℃, which are mutually exclusive. According to the principle of minimum thermodynamic energy, CuO will preferentially migrate to the base metal interface and react with Al₂O₃ to reduce the total energy of the system. Therefore, CuO in silver based brazing alloy migrates to the joint interface, increasing the CuO concentration at the interface. The increase of CuO concentration at the interface further accelerates the reaction between CuO and Al₂O₃ ceramic base metal. However, because the copper oxide rich liquid phase L2 is in a large amount of silver rich liquid phase L1, when the temperature decreases from 1050 ℃ to 969 ℃, part of the copper oxide liquid phase has no time to flow from the silver rich liquid phase to the interface, so this part of the copper oxide rich liquid phase L2 will rapidly solidify into CuO solid, surrounded by silver rich liquid phase L1, and the silver rich liquid phase L1 will gradually solidify as the temperature continues to decrease. Finally, the light gray phase CuO in Figure 2 (b) is formed. In Figure 2 (c), the main
elements of E in Area III on one side of Q235 steel are Fe and Al, and the ratio of the two elements is 1:2. Therefore, it is FeAl\textsubscript{2} formed by the reaction between Al foil and Fe element in the steel during the aluminized process. The content of Fe and Al in the large area of gray phase H in area II in Figure 2 (d) is roughly 1:1, which is speculated to be the FeAl compound formed by the diffusion of Fe in steel and the reaction with Al coating during welding. The black phase I at the interface of region I and region II is speculated to be Al\textsubscript{2}O\textsubscript{3}. This shows that Al\textsubscript{2}O\textsubscript{3} produced by Al coating prepared on the surface of Q235 steel during air reaction brazing can well protect the steel matrix from air oxidation and CuO corrosion in solder. The light gray phase F and dark gray phase G in area I in Figure 2 (d) are the same as the phase on the side of Al\textsubscript{2}O\textsubscript{3} ceramic joint, which are CuO and CuAl\textsubscript{2}O\textsubscript{4}, respectively. This is because Al is easily oxidized to form Al\textsubscript{2}O\textsubscript{3} under air, and the melting point of Al\textsubscript{2}O\textsubscript{3} is 2054 °C. Therefore, during air reactive brazing, the surface of aluminized Q235 steel always maintains the solid film state of Al\textsubscript{2}O\textsubscript{3}. Although the internal Al foil has been melted, it is still wrapped in Al\textsubscript{2}O\textsubscript{3}, and only a small part can flow out. When Al\textsubscript{2}O\textsubscript{3} on the surface reacts with CuO and is consumed, the internal liquid phase Al will continuously flow out and convert into Al\textsubscript{2}O\textsubscript{3}, so that a layer of Al\textsubscript{2}O\textsubscript{3} film is always maintained on the surface of Q235 steel. Therefore, after brazing, the interface structure of Q235 steel side is the same as that of Al\textsubscript{2}O\textsubscript{3} ceramic side. The typical structure of the interface is Al\textsubscript{2}O\textsubscript{3} / CuAl\textsubscript{2}O\textsubscript{4} / CuO / Ag / CuO / CuAl\textsubscript{2}O\textsubscript{4} / Al\textsubscript{2}O\textsubscript{3} / FeAl / FeAl\textsubscript{2} / Fe.

By comparing Figure 1 and Figure 2, it can be found that vacuum aluminizing on Q235 steel in advance can successfully avoid the oxidation of Q235 steel and the formation of loose oxide layer during brazing. When joining aluminized Q235 steel, it can be seen that CuO in the solder preferentially polymerize to the Q235 steel side, which is different from more segregation of CuO on
Al₂O₃ side during direct joining. CuO will react with Al₂O₃ coating to form a large amount of CuAl₂O₄ when joining aluminized Q235 to Al₂O₃ ceramic, and only a small amount of CuO phase and CuAl₂O₄ are left on the Al₂O₃ side.

4. Conclusion
(1) When Ag-12mol% CuO is used to braze Al₂O₃ and Q235 steel in air at 1050 °C for 15min, Q235 steel will oxidize and produce loose oxide film during brazing. The typical microstructure of the joint is Al₂O₃ / CuAl₂O₄ / CuO / Ag / CuO / FeO / Fe.
(2) When Ag-12mol% CuO is used to connect Al₂O₃ and aluminized Q235 steel at 1050 °C for 15min, the oxidation of Q235 steel can be successfully avoided. CuO in the solder will react with Al₂O₃ on both sides to form CuAl₂O₄ phase. Mechanical interlock is formed at the interface on both sides and the generation of FeO is avoided. The typical structure of the joint is Al₂O₃ / CuAl₂O₄ / CuO / Ag / CuO / CuAl₂O₄ / Al₂O₃ / FeAl / FeAl₂ / Fe.

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References
[1] Liu J.H, sun K.N., Tian Y.S. (2005) Direct brazing of multiphase Al₂O₃ based ceramics / steel in atmosphere. Hot working process, 04: 29-30.
[2] Zhong L.M., Bai Y.P., Wang P.Y. (2019) Study on failure causes and detection methods of DC UHV post insulators. Shanxi electric power, 03: 63-68.
[3] Gao B., Yan Z.H., Tan C., et al. (2019) Study on mechanical properties of 35kV pillar porcelain insulators. Electric porcelain arrester, 06: 251-256.
[4] Liu Z.M., Bi W.W., Chen X.S., et al. (2020) Structural optimization design of metal accessories of pillar porcelain insulators. Electric porcelain arrester, 04: 228-232.
[5] Wei X.W. Study on mechanical properties of post insulators. (2015) Beijing: North China Electric Power University
[6] Weil K.S., Kim J.Y., Hardy J.S. (2005) Reactive air brazing: a novel method of sealing SOFCs and other solid-state electrochemical devices. Electrochemical and Solid-State Letters, 8(2): 133-136.
[7] Wang Z.Q., Cao J., Si X.Q., et al. (2018) Review of ceramic air reactive brazing. Precision forming engineering, 010 (001): 1-9.
[8] Huang X.K. (2018) Study on Microstructure and properties of reactive air brazed joint between Al₂O₃ ceramics and 310S stainless steel. Wuhan: Wuhan University of technology.
[9] Wu C.Z. (2019) Study on thermal shock resistance of 441 stainless steel and YSZ ceramic air reactive brazed joint. Harbin: Harbin Institute of technology.
[10] Cao J., Si X., Li W., et al. (2017) Reactive air brazing of YSZ-electrolyte and Al₂O₃-substrate for gas sensor sealing: Interfacial microstructure and mechanical properties. International Journal of Hydrogen Energy, 42(15):10683-10694.
[11] Wang X.Y., Si X.Q., Li C., et al. (2021) Joining the BaZr0.1Ce0.7Y0.1Yb0.1O3-σ Electrolyte to AISI 441 Interconnect for Protonic Ceramic Fuel Cell Applications: Interfacial Microstructure and Long-Term Stability.. ACS Applied Energy Materials, 4(7):7346-7354.
[12] Si X.Q., Cao J., Ritucci I., et al. (2019) Enhancing the long-term stability of Ag based seals for solid oxide fuel/electrolysis applications by simple interconnect aluminization[J]. International Journal of Hydrogen Energy, 44(5):3063-3074.
[13] Huang J. (2015) Study on reactive brazing process of alumina ceramics in air furnace. Hangzhou: Zhejiang University of technology