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Effect of CeO_2 Nanoparticles on Interface of Cu/Al_2O_3 Ceramic Clad Composites

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Abstract: Cu/Al_2O_3 ceramic clad composites are widely used in electronic packaging and electrical contacts. However, the conductivity and strength of the interfacial layer are not fit for the demands. So CeO_2 nanoparticles 24.3 nm in size, coated on Al_2O_3 ceramic, promote a novel CeO_2–Cu_2O–Cu system to improve the interfacial bonded strength. Results show that the atom content of O is increased to approximately 30% with the addition of CeO_2 nanoparticles compared with the atom content without CeO_2 in the interfacial layer of Cu/Al_2O_3 ceramic clad composites. CeO_2 nanoparticles coated on the surface of Al_2O_3 ceramics can easily diffuse into the metallic Cu layer. CeO_2 nanoparticles can accelerate to form the eutectic liquid of Cu_2O–Cu as they have strong functions of storing and releasing O at an Ar pressure of 0.12 MPa. The addition of CeO_2 nanoparticles is beneficial for promoting the bonded strength of the Cu/Al_2O_3 ceramic clad composites. The bonded strength of the interface coated with nanoparticles of CeO_2 is increased to 20.8% compared with that without CeO_2; moreover, the electric conductivity on the side of metallic Cu is 95% IACS. The study is of great significance for improving properties of Cu/Al_2O_3 ceramic clad composites.

Keywords: CeO_2 nanoparticles; bonded strength; Al_2O_3 ceramic; CeO_2–Cu_2O–Cu

1. Introduction

Cu/Al_2O_3 ceramic clad composites have anti-wear, anti-corrosion, and anti-high temperature characteristics of ceramics and maintain the high conductivity and machinability of copper. They have been widely used in rail transit, electronic packaging, and electrical contacts [1,2]. Although Cu/Al_2O_3 ceramic clad composites have the advantages of a ceramic and a copper, ceramic is brittle and difficult to process. Assembly and connection structures of ceramic and metal are often used. To obtain a stable and reliable Cu/Al_2O_3 ceramic clad structure, the wettability between metals and ceramics and the formation of brittle compounds at the interface must be addressed. These problem are of great research significance [3,4].

Many researchers have carried out the research. At present, brazing and diffusion bonding are the main methods to achieve connections between ceramics and metals. Breslin et al. [5] have suggested that the key problem was the interfacial wettability between the ceramics and metals, so a method of co-continuous ceramic composites was proposed [6,7]. The surface of ceramics coated a layer of Mo–Mn could improve wettability [8]. Active metals, such as Ag, Ti, Zr and V, have been added to study effects. However, general oxygen content was lower than 1 Pa to avoid oxidizing [9–11]. Burgess et al. [12,13] have used a Cu-Cu_2O eutectic liquid system to bond Cu layers with ceramics for the first time. However, Fan Jinglian et al. [14] have discovered that wettability between Cu and Al_2O_3 was still not significantly improved when the temperature was increased from 1200 to 1400 °C.

Results [15,16] have shown that the contact angle between the molten Cu and Al_2O_3 ceramic was 158°–170° under oxygen-free conditions at 1100–1300 °C, so they were non-wetting each other. Diemer et al. [17] have found that by controlling the oxygen partial pressure (p_{O2}) and oxygen content in the copper simultaneously, contact angle could be varied between 125°and 22°. Evaluation of the Gibbs adsorption equation for the liquid/solid interface at 1300 °C suggests that adsorption of a Cu–O complex at that interface plays a key role in promoting wetting. Formation of $CuAlO_2$ and dissolution of Al_2O_3 in the melt also influence the contact angle, especially in the range of $p_{O2} > 1$ Pa. When the content of O was higher than 2 at.%, Cu began wetting the Al_2O_3. Huang [18] and Chatterjee [19] have found that the addition of oxides to metal solders could improve the wettability between Al_2O_3 ceramics and Cu layers. However, there are few reports on improving bonded strength between Cu and Al_2O_3 ceramics by the addition of rare earth oxides and reducing the bonded temperature. Thus, new methods are needed to solve these problems.

In this study, CeO_2 nanoparticles coat the interface between Al_2O_3 ceramics and Cu to form a new CeO_2–Cu_2O–Cu system to increase interfacial strength. Under a special gas pressure and temperature, the poor strengths of the ceramic/copper composites will be improved. The new phases and elements diffusing at low temperatures are studied. A new Cu/Al_2O_3 ceramic clad composite with the addition of CeO_2 is fabricated.

2. Materials and Methods

The specimens were prepared in a vacuum tube furnace (Boyun Tong company, Nanjing, China), which was vacuumed to 0.01 MPa and then filled Ar gas at a pressure of 0.12 MPa. The Cu cubes (Zhejiang wanteng metal materials firm, Ningbo, China) were 99.90 wt.% Cu. The ceramic cubes (Shenzhen beilong electronic material factory, Shenzhen, China) were 99.9 wt.% Al_2O_3. The fabrication procedures were as follows: nanoparticles of CeO_2 coated the surface of Al_2O_3 ceramics → in situ Cu_2O formed in the Cu interface in the 40 °C air → the melting of Cu and Al_2O_3 ceramic clad composites at 1300 °C for 5 min in a furnace at an Ar pressure of 0.12 MPa → a cube with the dimensions 40 × 40 × 30 mm was formed, as shown in Figure 1.

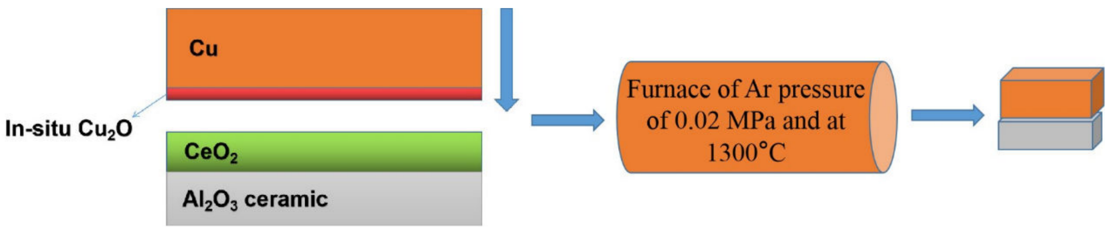

Figure 1. Sketch of experimental methods.

After preparation, the samples were etched in a solution containing 3 g of $FeCl_3$, 2 mL of HCl, and 96 mL of C_2H_5OH. Their metallurgical structures and microstructures were examined by scanning electron microscopy (SEM S-4800, Hitachi, Tokyo, Japan), and backscattered electron imaging (BSE, Hitachi, Tokyo, Japan) under a control voltage of 20 kV. The electric conductivity was measured at 60 kHz using a digital portable eddy current tester (FD-102, Xiamen xinrui instrument Ltd., Xiamen, China). The bonded strength was measured with a nanomechanical test for Nano Test 600 (Micro Mmaterials Ltd., Wrexham, UK). XRD patterns were obtained using a Bruker D8 Advance (Bruker Ltd., Karlsruhe, Germany) with Cu Kα radiation.

3. Results and Discussion

3.1. Structure and Hardness of Cu/Al_2O_3 Clad Composites

Figure 2 shows the SEM images of Cu/Al_2O_3 composites at bonded temperature of 1300 °C. When nanosized CeO_2 is not added, the metal Cu and Al_2O_3 ceramic could not form a new eutectic solution.

The wettability of the two ceramics was poor, so there are many cracks in the bonded interface at 1300 °C, as shown in Figure 2a. The measurements are taken at room temperature. However, a closely bonded interface is formed between the Cu and Al_2O_3 by addition of CeO_2 nanoparticles, as shown in Figure 2b. There are no cracks in the bonded interface at 1300 °C. The conductivity of the Al_2O_3 ceramic is 0% IACS (international annealed copper standard), whereas the conductivity of the side of metallic Cu is 95% IACS, so the conductivity of Cu in the clad composites is reserved. Figure 3 shows the bonded strengths of the interfacial layer of Cu/Al_2O_3 clad composites with CeO_2 and without CeO_2 at the bonded temperature 1300 °C. The bonded strength of Cu/Al_2O_3 interfacial layer with nanoparticles of CeO_2 is 990.3 MPa; however, that without CeO_2 is 820.1 MPa. The bonded strength of the interfacial layer coated with nanoparticles of CeO_2 increases 20.8% compared with that without CeO_2. Therefore, nanoparticles of CeO_2 can improve the bonded strength.

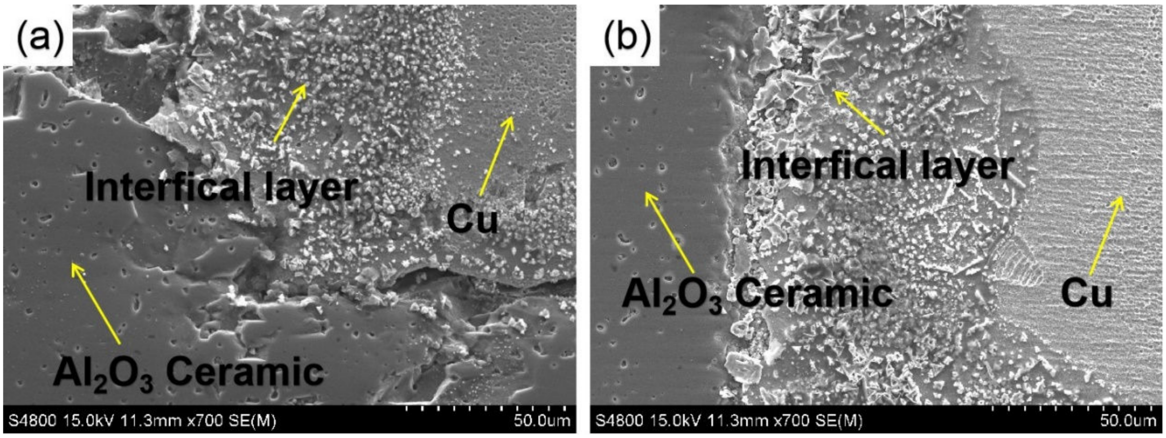

Figure 2. SEM images of Cu/Al_2O_3 composites at bonded temperature 1300 °C: (**a**) without CeO_2 and (**b**) with CeO_2.

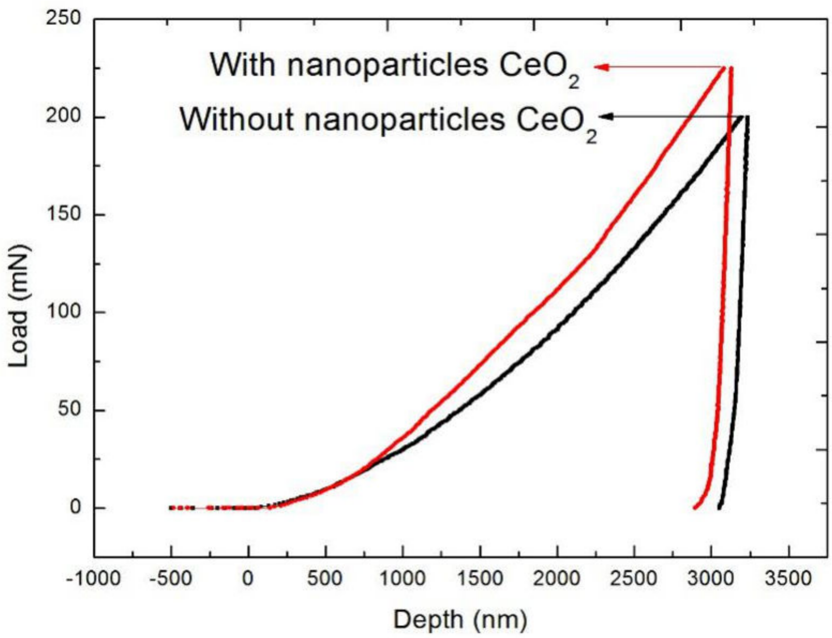

Figure 3. Bonded strength of interfacial layer.

3.2. EDS of Interface

The element distributions of the interfaces of the composite materials are presented in this section. Figure 4 shows the energy-dispersive X-ray spectroscopy (EDS) of the Cu/Al_2O_3 interface without

CeO_2. In the range of 0–40 μm, the contents of Al and O are high, whereas the content of Cu is the lowest, which indicate that 40 μm is the dividing line of the interface of the clad composites. However, in the range of 40–150 μm, the content of Cu is the highest, and a small amount of Al and O can diffuse to the copper layer.

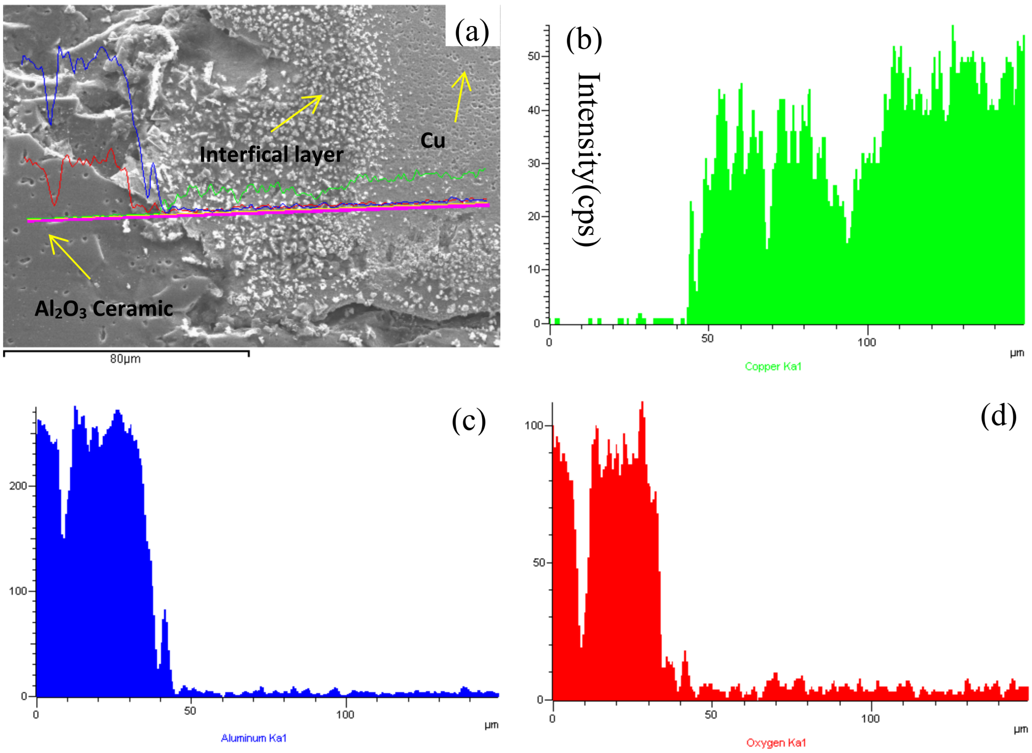

Figure 4. Energy-dispersive X-ray spectroscopy (EDS) of Cu/Al_2O_3 ceramic interface without CeO_2: (**a**) interface, (**b**) Cu, (**c**) Al, (**d**) O.

On the bonding surface coated with nanoparticles of CeO_2, the contents of these elements are different from that without CeO_2, as shown in Figure 5. In the range of 0–40 μm, the contents of Al and O are higher than Cu, whereas the content of Cu is the lowest in all. This indicates that 40 μm is the dividing line of the interface for the clad composites. The content of O is significantly increased to 30% with addition of CeO_2 compared with that without $CeO_{2.}$, which indicate that CeO_2 could raise the content of O in the interface. The atom content of O tested by EDS is 15.4% when CeO_2 nanoparticles are not coated in the surface of Al_2O_3 ceramic; however, the atom content of O is increased to 20.4% when CeO_2 nanoparticles are coated. Again, the results prove that the atom content of O is 30% higher compared with that without $CeO_{2.}$

Moreover, the content of Ce arises from the range of 0–150 μm due to the addition of CeO_2. Figure 5b shows that the CeO_2 coated on the surface of the alumina ceramics can easily diffuse into the metallic Cu layer, but not to the Al_2O_3 ceramics. O and Cu easily form a eutectic liquid of Cu_2O–Cu under certain conditions [12,13], so CeO_2 can accelerate to form the eutectic liquid of Cu_2O–Cu by storing or releasing O at Ar pressure of 0.12 MPa. However, in the range of 40–150 μm, the content of Cu is the highest, and the contents of O and Al are reduced. The eutectic liquid of Cu_2O–Cu is the key factor in improving the wettabilities of the Cu and Al_2O_3 layers.

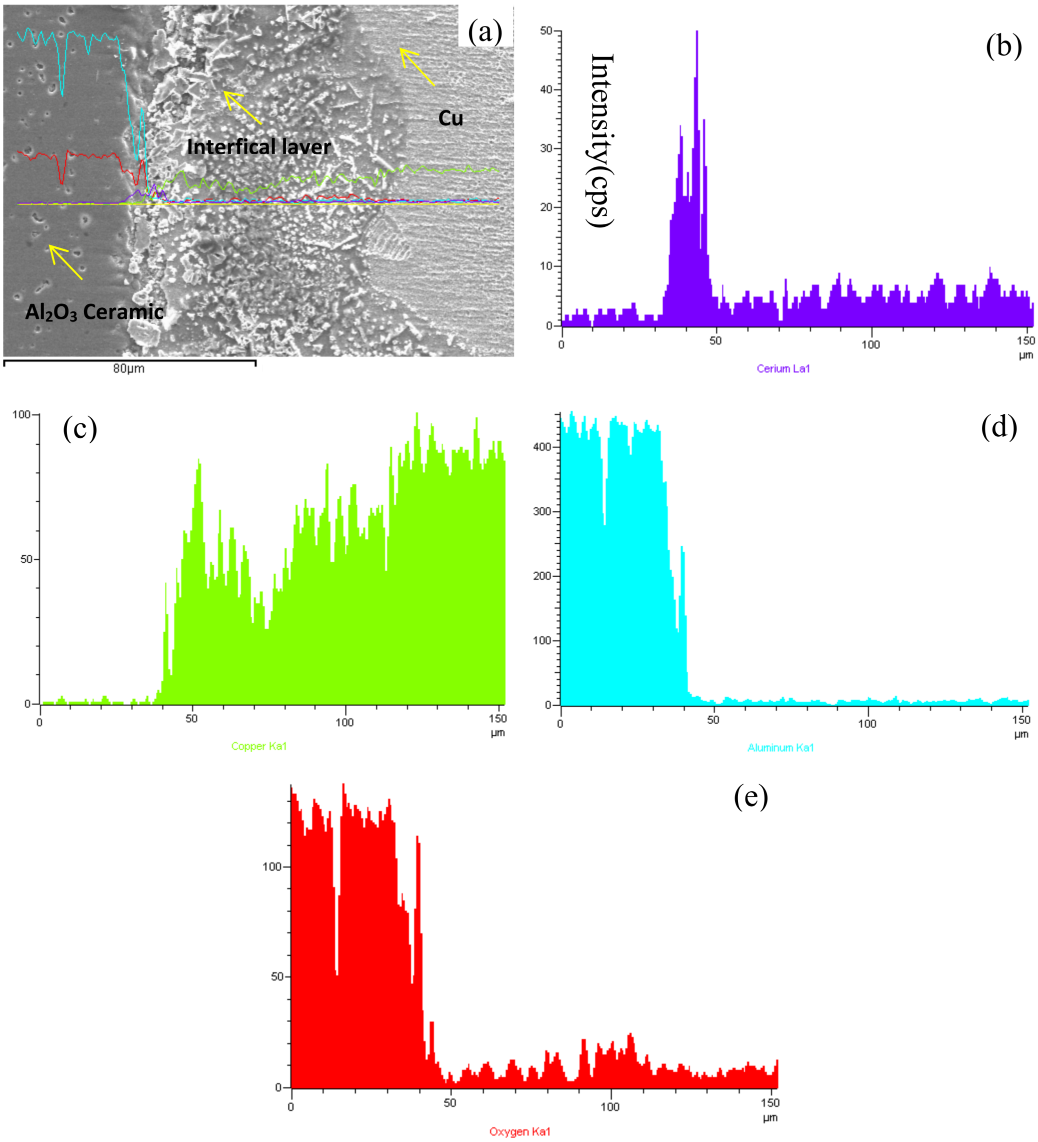

Figure 5. EDS of interface coated with CeO_2: (**a**) interface, (**b**) Ce, (**c**) Cu, (**d**) Al, (**e**) O.

3.3. Mechanisms Discussion

Figure 6 shows the XRD patterns of the nanoparticles of CeO_2, the size of which are 24.3 nm for 28.5°according to the Peak Search Report of XRD. Thus, rare earth oxide coated on the surface of Al_2O_3 ceramics is CeO_2. Figure 7 shows the SEM image of CeO_2. Due to the presence of nanoparticles of CeO_2, elements are active and easily diffused into the layers, which is beneficial for reducing the bonding temperature. Figure 8 shows the BSE images of the interface at bonded temperatures of 1300 and 1500 °C. At 1500 °C, Al and Cu easily diffuse into each other to form the compound of $CuAlO_2$. Which is beneficial to the improvement of wettability [8]. At 1300 °C, the diffusion rates of the elements are decreased and oxidation cannot occur in time; however, the interface coated with CeO_2 shows that Al and Cu can diffuse into each other quickly in 5 min. Consequently, slags and cracks cannot form at low temperatures. The results show that the addition of nanoparticles CeO_2 is beneficial for reducing the bonding temperature.

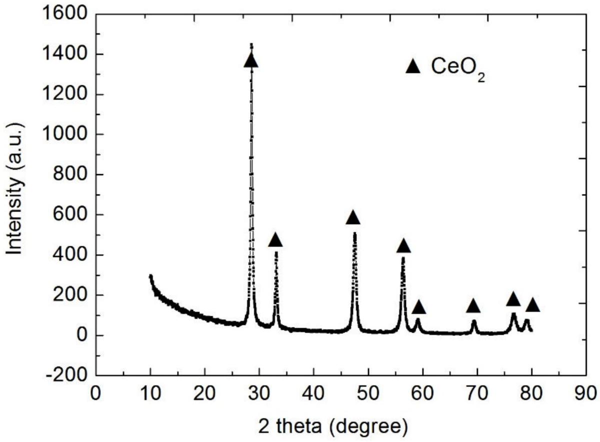

Figure 6. XRD patterns of CeO_2.

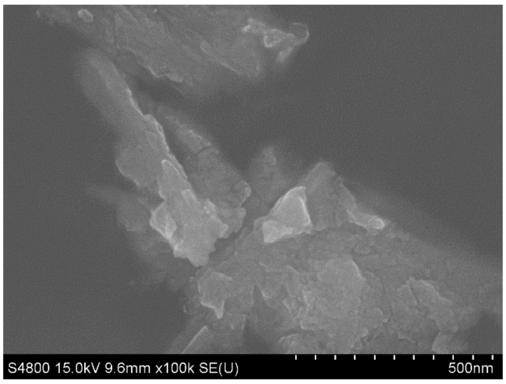

Figure 7. SEM image of CeO_2 nanoparticles.

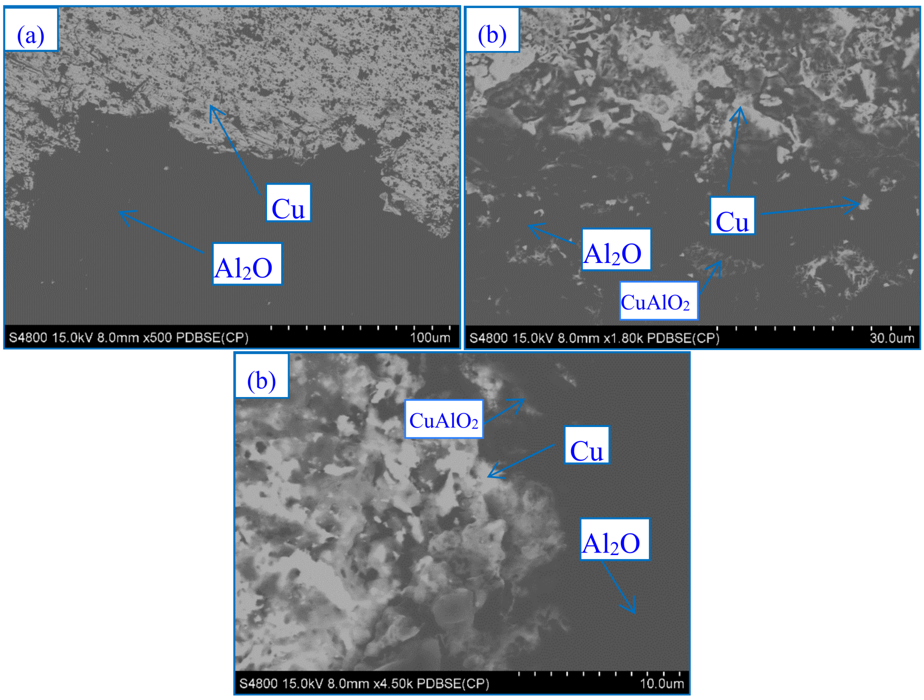

Figure 8. Backscattered electron imaging (BSE) images at samples' bonded temperatures: (**a**) without CeO_2 at bonded temperature 1300 °C, (**b**) without CeO_2 at bonded temperature 1500 °C, and (**c**) with CeO_2 at bonded temperature 1300 °C.

Al_2O_3 and Cu usually do not wet each other. The contact angle between the molten Cu and Al_2O_3 ceramic is 158°–170° under oxygen-free conditions at 1100–1300 °C [15,16]. Thus, the Cu and Al_2O_3 are completely non-wetting when the Cu is molten. To achieve excellent properties of Cu/Al_2O_3 clad composite, it is necessary to improve the wettability between them. A small amount of O could reduce the wetting angle between Cu and Al_2O_3 [17]. When the content of O is higher than 2 at.%, Cu begins wetting the Al_2O_3. Moreover, Cu and Cu_2O could form a eutectic liquid [20]. However, CuO is easily formed at this temperature, so its formation must be strictly prevented. Therefore, reducing the content of O to prevent the formation of CuO and promoting the formation of Cu–Cu_2O are the key factors. In this study, CeO_2 can react with copper to form Cu_2O instead of CuO, promoting the formation of the Cu–Cu_2O eutectic solution. Yang, Y.M. [21] declared that in CeO_2 crystal structure Ce^{+4} was easily converted to Ce^{+3}, or vice versa, which makes the nanoparticles of CeO_2 have strong functions of storing and releasing oxygen, as shown in chemical Equation (1). Chemical Equation (2) shows that Cu_2O can be formed under the condition of trace oxygen content. The chemical equations are as follows:

$$CeO_2 \leftrightarrow CeO_{2(1-X)} + xO_2 \ (0 \leq x \leq 0.25) \tag{1}$$

$$Cu{+}O_2 \rightarrow Cu_2O \tag{2}$$

The reduction of CeO_2 to Ce_2O_3 has been reported in the high temperature sintering of fine CeO_2 particles by [22,23]. The authors in reference [24] have also proved the conclusion by High Resolution Transmission Electron Microscopy (HRTEM) imaging and Fast Fourier Transformation (FFT) diffraction. Thus, nanoparticles of CeO_2 can improve the bonded strength, as CeO_2 nanoparticles have strong functions of oxygen storage and release and, thus, the addition of CeO_2 nanoparticles play an important role for a novel system of CeO_2–Cu_2O–Cu at an Ar pressure of 0.12 MPa.

The authors in [17] reported that, due to the mutual diffusion and redistribution of chemicals in the melting process, these oxides react with Al_2O_3 under certain conditions to form $CuAlO_2$, which is beneficial to the improvement of wettability [8]. The corresponding Gibbs free energies (ΔG^0) [25] are as follows:

$$2Cu_2O + O_2 \rightarrow 4CuO \qquad \Delta G^0 = -62354 + 44.89\ T \tag{3}$$

$$2Cu_2O + O_2 \rightarrow 4CuO \qquad \Delta G^0 = -62354 + 44.89\ T \tag{4}$$

Equations (3) and (4) show that the Gibbs free energies of the above reactions are negative at 1300 °C, so $CeO_{2(1-X)}$ can absorb a small amount of O_2 to prevent CuO formation, and $CuAlO_2$ can also be formed spontaneously.

The reaction temperature of 1300 °C is 65 °C higher than the melting point of Cu_2O (1235 °C). Thus, Cu_2O reacts rapidly with Al_2O_3 to form compounds of $CuAlO_2$ at the interface in only 5 min. The formation of these low melting point copper oxides and interfacial compounds ($CuAlO_2$) is beneficial for the liquid phase copper wetting of the alumina ceramic (melting point of CuO is 1200 °C). Under certain conditions, CeO_2 is decomposed at 1000 °C and easily diffuses to the Cu layer, accelerating the formation of the CeO_2–Cu_2O–Cu eutectic, as shown in Figure 9. Figure 10 shows the SEM images and EDS of the interface. A strong structure, which is the key to strengthening the bonding interface, is formed due to the triangular type of the Cu_2O, and Y type of CeO_2 and $CuAlO_2$.

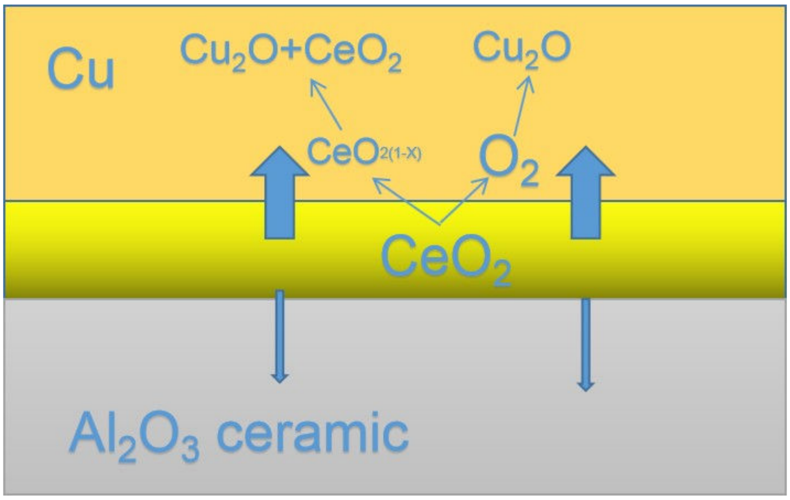

Figure 9. Mechanism of Cu-Cu_2O-CeO_2 eutectic liquid formation at bonded temperature 1300 °C.

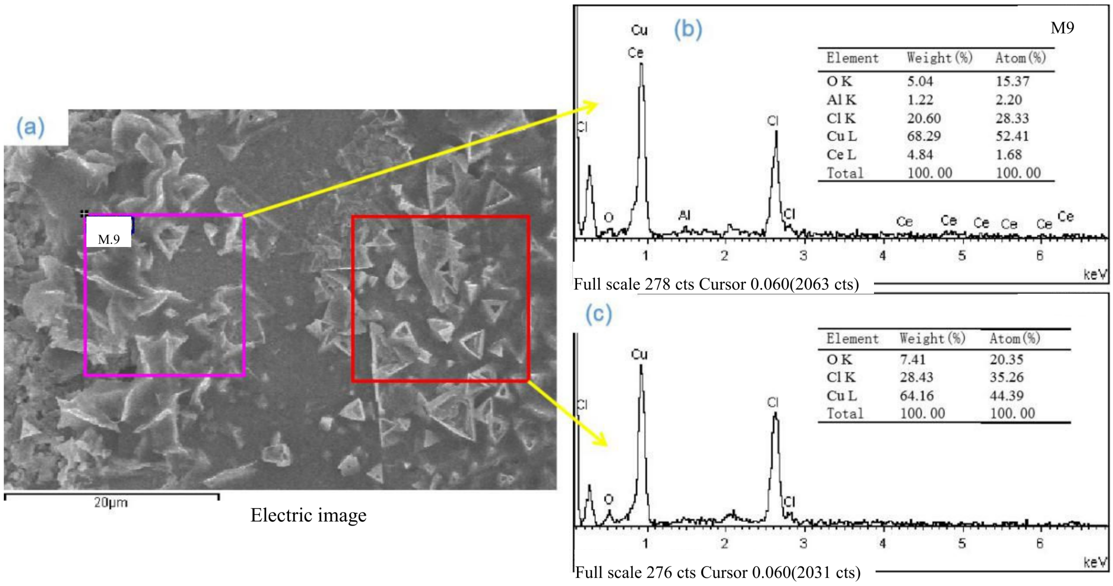

Figure 10. SEM images and EDS of interface (Cl is the etched residuum): (**a**) SEM, (**b**) ceramic side, (**c**) Cu side.

4. Conclusions

(1) The atom content of O is increased to approximately 30% with addition of CeO_2 nanoparticles 24.3 nm in size compared with the atom content without CeO_2 nanoparticles in the interfacial layer of the Cu/Al_2O_3 ceramic clad composites, so the addition of CeO_2 could raise the atom content of O;

(2) CeO_2 nanoparticles coated on the surface of the Al_2O_3 ceramics can easily diffuse into the metallic Cu layer, but they do not in Al_2O_3 ceramics. CeO_2 nanoparticles can accelerate to form the eutectic liquid of Cu_2O–Cu, as they have strong functions of storing and releasing O at an Ar pressure of 0.12 MPa;

(3) The addition of CeO_2 nanoparticles is beneficial for promoting the bonded strength of Cu/Al_2O_3 ceramic clad composites. The bonded strength of the interface coated with nanoparticles of CeO_2 is 20.8% higher than that without CeO_2; however, the electric conductivity of metallic Cu is 95% IACS.

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