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Reactive brazing of ceria to an ODS ferritic stainless steel

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This research study shows that a ceria ceramic can be bonded to an ODS ferritic stainless steel (MA956) by reactive brazing using a Ag_{68}-$Cu_{27.5}$-$Ti_{4.5}$ interlayer. The ability to join these materials provides an alternative to the current ceramic interconnects used in the development of solid oxide fuel cells. Initial results show that the ceramic-metal bonds survived the bonding process irrespective of the degree of porosity within the ceria ceramic. Metallographic analyses indicate that a reaction zone formed along the ceria/braze interface, which was not only titanium rich, but also consisted of a mixture of copper oxides. When the ceramic-metal bonds were exposed to high bonding temperatures or when subjected to thermal cycling at 700°C, this reaction layer increased in thickness and had a detrimental affect on the mechanical strength of the final joints.

1. Introduction

The wide range of properties shown by engineering ceramics makes them contenders to metals for use in critical applications and in hot sections of turbine engines. However, the inherent brittleness associated with ceramic materials limits their applications particularly when intricate geometries need to be manufactured. However, for practical applications, ceramics such as Si_3N_4, SiC and Al_2O_3 have to be attached to metallic parts, which have the ability to withstand stresses or temperature gradients too great for ceramics. Extensive work has been carried to date on the joining of oxide and non-oxide ceramics to metals by diffusion bonding and brazing processes [1–4], but little is available in the literature on the joining of ceria (CeO_2) to metal alloys. Ceria has considerable potential in the fabrication of solid oxide fuel cells (SOFCs). These are devices used to convert chemical energy into electric energy and offers potential for clean, efficient and economical generation of electric power [5]. Yttria-stabilized zirconia (YSZ) is considered to be the most reliable candidate for use as the electrolyte in the solid oxide fuel cell, but YSZ requires a high operating temperature (1000°C) for optimum efficiency and high operating temperatures cause detrimental interfacial reactions, for instance at the electrode/solid electrolyte boundary, which decreases the efficiency and the stability of the cell. Although thin YSZ electrolytes are being developed to lower the operating temperature, alternatives to YSZ as the electrolyte material have also been considered [6, 7]. One such material is ceria (CeO_2), which shows potential for use as an electrolyte, cathode or anode when appropriately doped with gadolinium or praseodymium [8–10].

The scientific literature shows that until recently ceramic interconnects (i.e., bi-polar plates) consisting of doped $LaCrO_3$ have been used for joining individual fuel cell assemblies. These are not only difficult to fabricate making them expensive, but also brittle and this restrains stack design and long term integrity of the cell. Therefore, the development of an all ceria based fuel cell which functions at lower temperatures (700°C) increases the choice of metals that can be used as interconnects.

The interconnect material must possess chemical stability under oxidising and reducing environments, high electronic conductivity and coefficient of thermal expansion similar to that of the ceramic. Recent work on the oxidation behaviour of various metallic alloys [11] as interconnects has shown that a chronium rich alloy containing a dispersion of Y_2O_3 gives the best oxidation resistant behaviour. At present, a mechanically alloyed ferritic stainless steel such as MA956 has potential for use as an interconnect material because it is chromium rich and contains a Y_2O_3 dispersion giving the alloy good oxidation properties within the 500 to 900°C temperature range. However, the fabrication of ceramic to metal bonds is complicated by the fact that most conventional brazing metals (based on Ag, Cu or Ni) will not wet the ceramic surface owing to a high surface free energy. To lower this surface free energy and hence improve wettability of the ceramic surface the chemistry of the metal/ceramic interface must be changed. This is achieved by the addition of an active element (e.g., Ti) to the brazing alloy, which promotes a chemical reaction at the metal/ceramic interface. This reaction layer ensures wetting by the liquid braze metal. This paper presents a feasibility study which investigates the use

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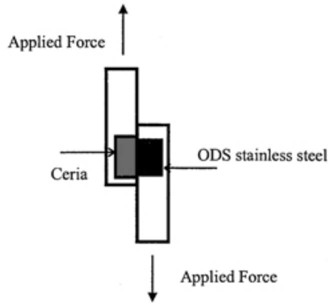

Figure 1 A schematic showing arrangement for shear testing.

of reactive metal brazing as a technique for joining ceria to MA956 an oxide dispersion strengthened (ODS) ferritic stainless steel interconnect. A ductile interlayer based on a Ag-Cu-Ti composition was used and the bonding variables optimised to produce joints. The effect of the ceramic porosity and bonding parameters on the bond microstructure and mechanical integrity were studied.

2. Experimental procedure

Ceria discs with the dimensions 5 × 18 mm were produced using a pressure of 6.6 MPa. Each disk was sintered in nitrogen gas (flow rate 0.33 m^3/sec) at 1600°C for 2 h. Ceramic specimen densities were measured by using the mercury displacement technique in order to determine the approximate % porosity before the bonding process [12]. Oxide dispersion strengthened ferritic stainless steel with a composition in wt% of Fe-bal., Cr-20.0, Al-4.5, Ti-0.35 Y_2O_3-0.52 was used as the metallic interconnect. The steel was bonded in the recrystallized condition (grain size 400–600 μm in length) in the form of discs with dimensions 5 × 18 mm, which were prepared to give flat surfaces. The ceramic and steel specimens were ground to a 400 grit surface finish then cleaned using acetone and dried. Reactive brazing foil of thickness 20 μm based on Ag-68 Cu 27.5 Ti-4.5 (composition in wt%) was used for bonding the ceria to the steel.

Reactive metal brazing was carried out in a resistance furnace and the joining process involved heating in air up to 600°C using a heating rate of 10°C/min followed by a faster heating rate of 30°C/min up to the bonding temperature of 900°C in a nitrogen atmosphere (flow rate 0.33 m^3/sec) for 5 min. The first step of the process encouraged the absorption of oxygen in to the ceria ceramic and the second step involving a nitrogen atmosphere prevented further oxidation of ceria. The presence of oxygen in the ceramic can be expected to encourage chemical bonding across the ceria/braze interface through the reaction of activate elements such as Ti within the braze, which has a high affinity for oxygen.

The ceramic-metal bonds were shear tested to failure using a crosshead speed of 1 mm/min as shown by the schematic in Fig. 1. The test gave a load/elongation graph from which the values of shear strength and plastic deformation were derived. Two ceramic-metal bonds were tested per condition and plastic deformation of the joints was measured from the yielding point to the fracture point. The integrity of the ceramic-metal bonds was further assessed by subjecting the joints to a thermal cycle. This involved heating up to 700°C in air and holding at this temperature from 2 to 10 hrs. These thermally cycled joints were allowed to cool to room temperature before shear testing using a crosshead speed of 1 mm/min.

3. Results and discussion

Although a number of stack configurations for SOFC systems are under consideration, an important requirement of any joining process employed to connect the various cell assemblies will be the ability to successfully bond ceria consisting of varying % porosity. This is because the ceria will require a certain level of porosity to provide a high surface area for the absorption of fuel gases (e.g., O_2 and H_2) passing over the electrode surfaces. However, the ceria will also be used in the dense state (i.e., with low porosity) when used as the electrolyte. Therefore, it was important to study the

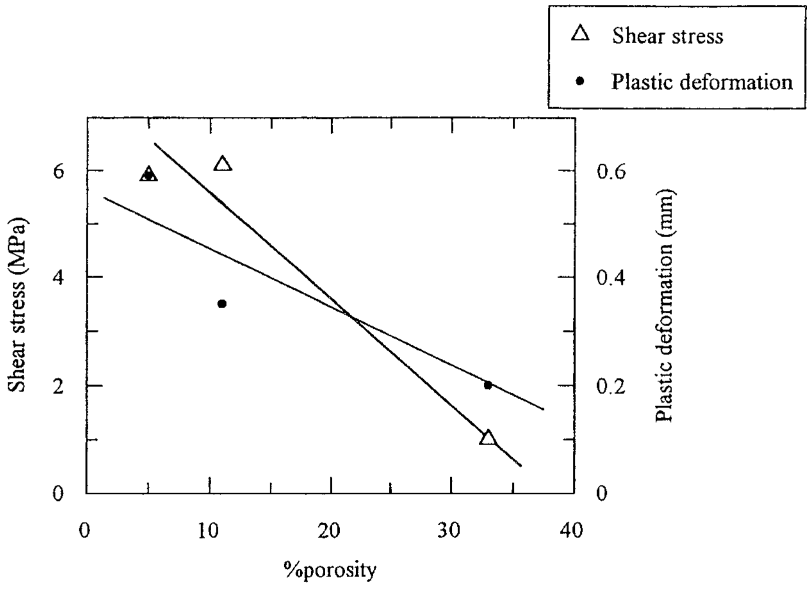

Figure 2 Variation in shear stress and plastic deformation as a function of porosity in the ceria ceramic.

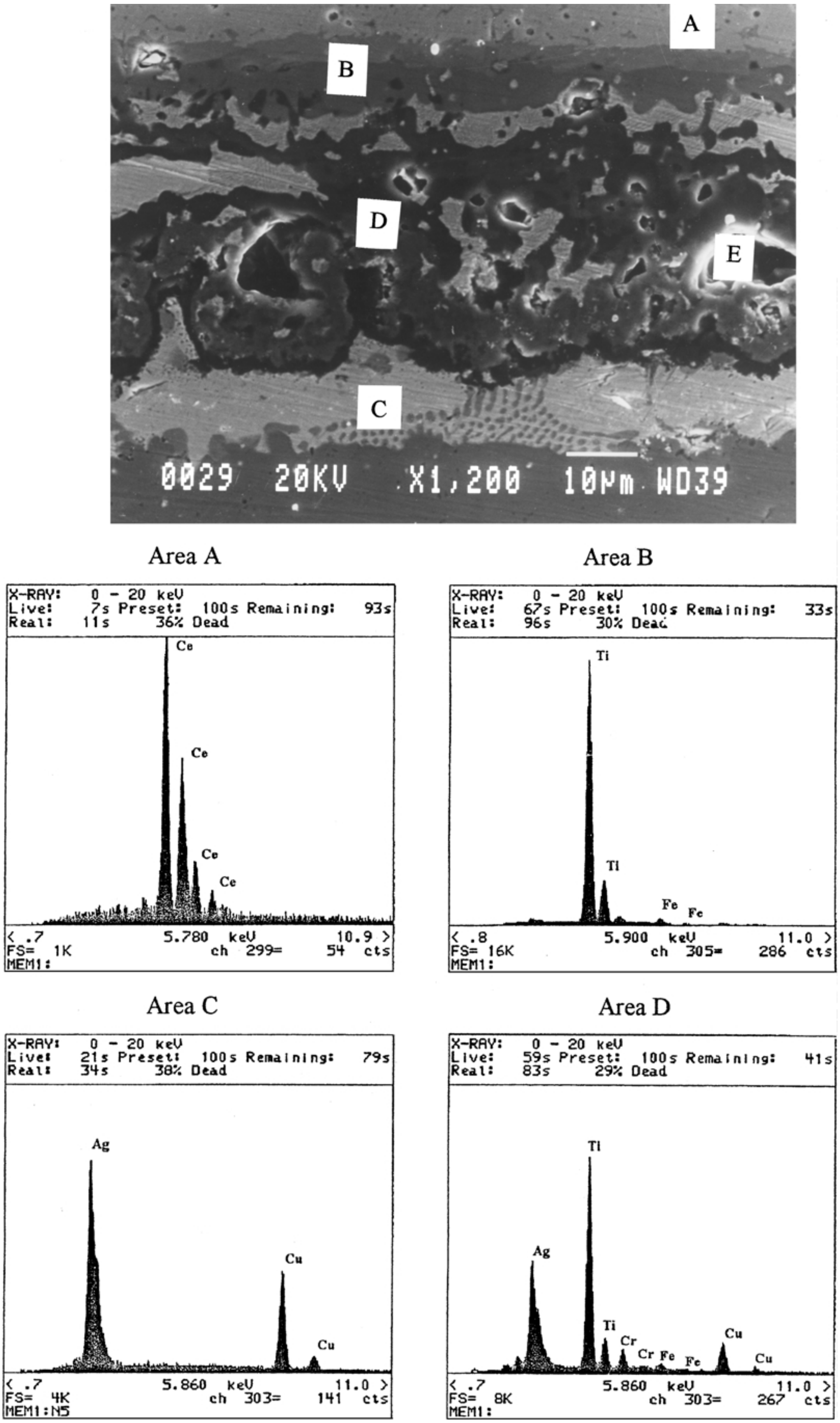

Figure 3 Scanning electron micrograph of the ceria/braze/steel bond made at 900°C for 5 min: A-ceria; B-reaction layer; C-lamellar eutectic phase; D-dark phase at centre of braze; E-pore.

effect of different % porosity (5%, 11%, and 33%) on the mechanical integrity of the ceramic-metal joints, and the results obtained are shown in Fig. 2. Bonds made at 900°C, for a hold time of 5 min produced shear stress values, which showed a gradual decrease in shear stress value from about 6 MPa to 1MPa with an increase in ceria porosity. The plastic deformation of the bonds indicated a similar decrease in bond ductility as the level of porosity increased and these observations can be explained by studying the microstructural developments at the bond interfaces.

A cross-section through the ceramic-metal joint region is shown in Fig. 3. Energy dispersive spectroscopy (EDS) was used to analyse the different phases seen within the braze microstructure and the spectrum taken from the ceria/braze interface shows strong peaks for Ti. This analysis corresponds to an irregular but continuous reaction layer along the interface (area B). The formation of a titanium reaction layer most probably oxides of titanium (e.g., TiO/TiO_2) is consistent with thermodynamic data which shows that titanium has a high affinity for oxygen [13]. This reaction layer can be expected to contribute to the strength of the joint through chemical bonding. Other phases present within the braze included a layered Ag-Cu eutectic (area C), and dark regions (area D) which were found to be rich in Ag and Ti with Cr and Fe also in solid solution having diffused into the braze from the steel side. Pores seen within the braze (region E) were found mainly near the ceria side and their formation can be attributed to the movement of liquid braze into the ceramic.

This flow of braze material into the ceria is shown in Fig. 4. This would provide mechanical bonding in addition to the chemical bonding resulting from a titanium rich reaction zone at the ceria/braze interface. From EDS analysis of the ceria pores it was clear that copper and not silver had diffused into the ceria. This can be explained by Gibbs free energy of formation of copper oxide (CuO) showing the strong affinity of copper for oxygen (-127 kJ/mol^{-1}), which can be expected to further enhance chemical bonding across the ceramic/metal interface. These results were consistent with some earlier research by Greenhunt (1998) on sessile drop experiments using pure copper on alumina surfaces. The work also showed that on solidification copper oxide dendrites penetrating the alumina surface provided bonding to the ceramic [14].

By examining the fracture surfaces of bonds subjected to a shear test, it was possible to determine the influence of ceria porosity on crack propagation within the bond. Fig. 5 shows the fracture surface for a bond made with ceria containing 5% porosity. The failure appears to have occurred along the ceria/braze interface in particular at the titanium reaction layer because the fracture revealed a needle like morphology, which was titanium rich. When the porosity of ceria increased to 11%, the fracture was seen to propagate through the ceria ceramic and parallel to the ceria/braze interface. However, the ceria failed catastrophically on shear testing when the porosity of the ceramic was increased to 33%. These observations are summarised schematically in Fig. 6, and show that as the amount of porosity in ceria decreased failure occurred preferentially along the ceramic/braze interface.

Any increase in bonding temperature or hold time would be expected to affect the diffusion kinetics of any chemical reactions at the ceramic/braze interface. In order to study the growth behaviour of the interfacial reaction layer and its affect on the integrity of the ceramic-metal bonds, reaction layer thickness measurements at a bonding temperature of 900°C as a function of bonding time were carried out and the results are shown in Fig. 7. Furthermore, the growth of the reaction layer on the shear strength of the joints was assessed by subjecting the bonds to a thermal cycle by heating up to 700°C in air followed by a slow cool to

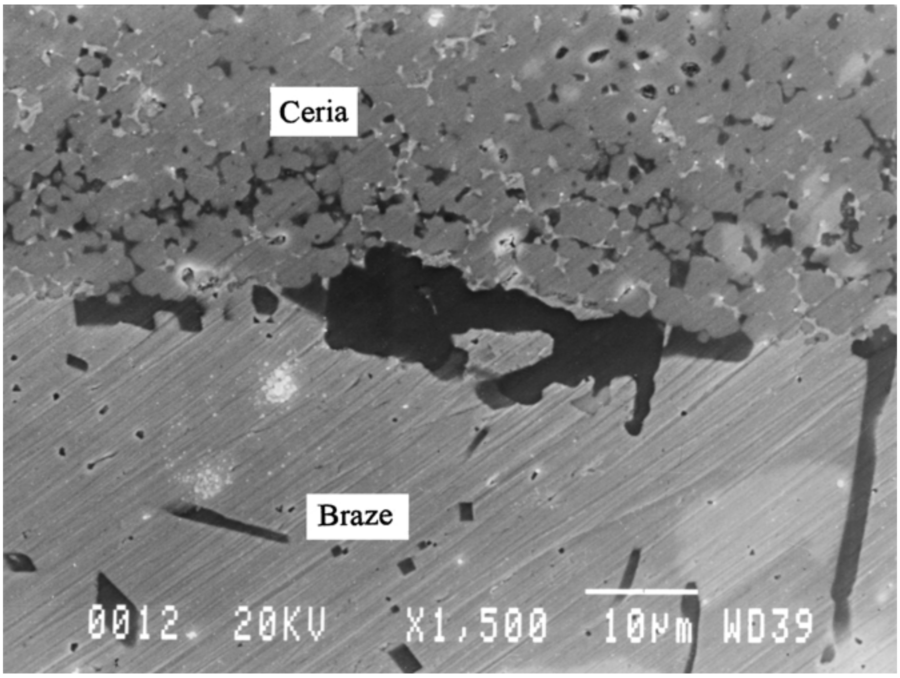

Figure 4 Scanning electron micrograph showing ceria/braze interface with 11% porosity within the ceria. Bond made at 900°C for 5 min.

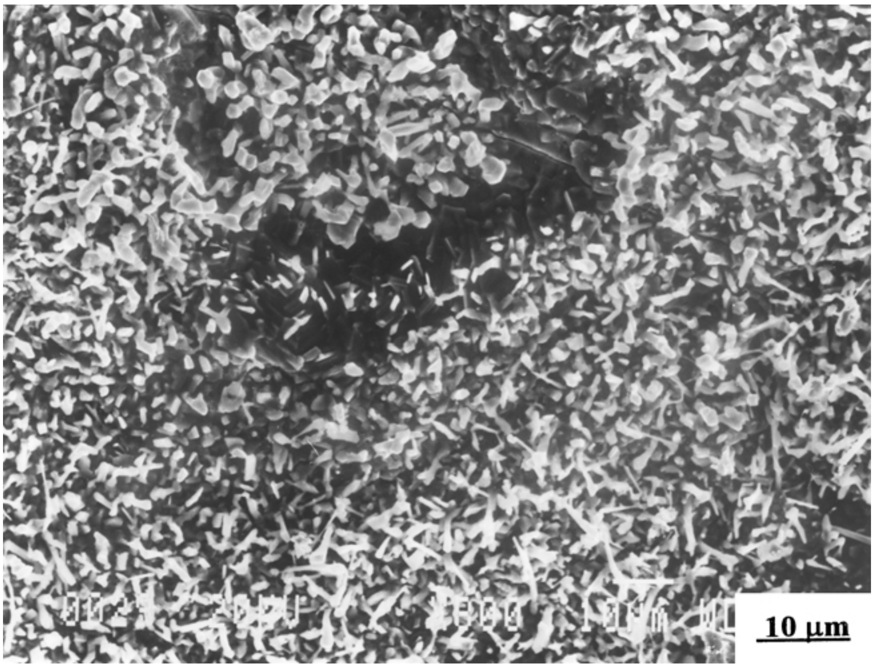

Figure 5 Scanning electron micrograph showing the fracture surface of a bond made with ceria (5% porosity) at 900°C for 5 min.

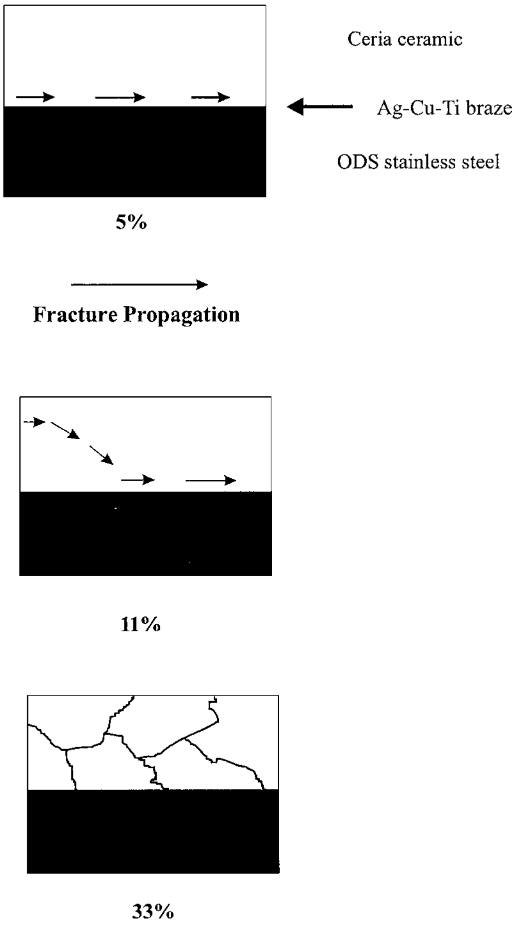

Figure 6 Schematic showing effect of % porosity on crack propagation at the bond.

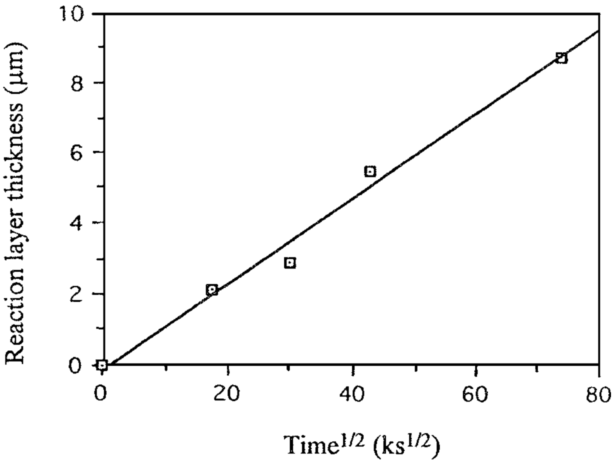

Figure 7 Reaction layer thickness as a function of time at a temperature of 900°C.

room temperature (see Fig. 8.) In these experiments the ceramic-metal bonds were made using a ceria with 5% porosity content. As expected, the thickness of this layer was seen to increase with bonding time and hold time during the thermal cycle. The growth mechanism is considered to be diffusion controlled and the kinetics of this layer have been studied using the familiar equation:

$$x = kD^{1/2}t \tag{1}$$

where x is the reaction layer thickness, D is the diffusion coefficient, k is a constant and t is the hold time.

It is suggested that although titanium initially segregates to the ceria/braze interface to form titanium oxides, further growth of the reaction layer is complex and will also involve the diffusion of copper to the interface to form copper oxides. Therefore, the chemical reactions expected at the ceramic/braze interface will be:

$$CeO_2 + Ti \rightarrow TiO_2 + Ce$$

and

$$CeO_2 + 4Cu \rightarrow 2Cu_2O + Ce \tag{2}$$

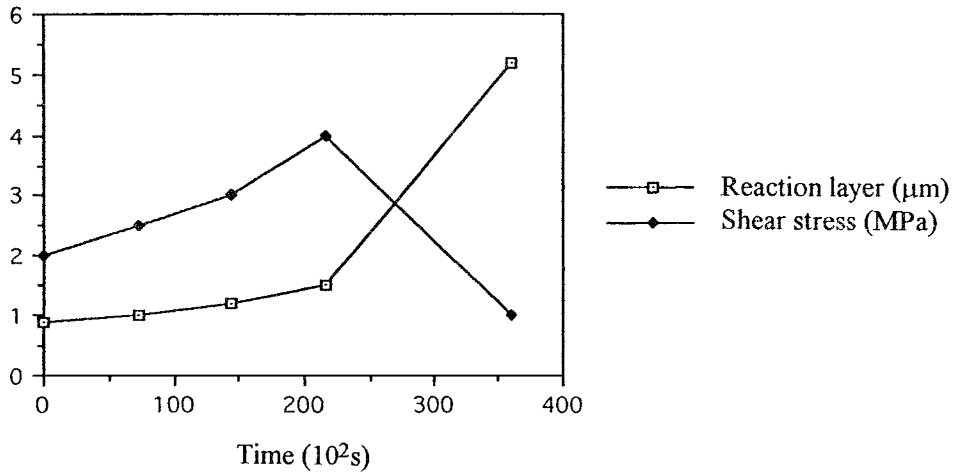

Figure 8 Plot showing the effect of thermal cycling at 700°C on mechanical strength and reaction layer growth at the bond.

However, unlike other ceramic-metal bonded systems where for instance, when joining Si_3N_4 to a steel [15] using $Ag_{68.8}$-$Cu_{26.7}$-$Ti_{4.5}$ braze, results in the rejection of free Si into the braze. Such a rejection of cerium (Ce) was not observed.

The results in Fig. 8 show that the ceramic-metal bonds show a gradual increase in shear stress to a value of 4 MPa with increasing hold time at 700°C. However, the strength of the bonds decreased significantly above an exposure time of 6 hrs. Interfacial reaction layer thickness measurements indicated that bonds held at 700°C in air showed a gradual increase in reaction layer thickness, which reaches a critical value (1.5 μm) at an exposure time of 6 hrs. Above this critical thickness further growth in the reaction layer reduces the strength of the joint. These results indicate that although the formation of a reaction layer is responsible for providing chemical bonding and improved wetting characteristics for brazing, the subsequent exposure of the joints to service conditions will have a detrimental affect on the long term mechanical strength of the joint assembly. The results suggest that the $Ag_{68.8}$-$Cu_{26.7}$-$Ti_{4.5}$ interlayer used in this study is capable of fabricating joints between the ceria ceramic and ODS steel, however, a lower Ti content will reduce the extent of reaction layer produced at the ceramic/metal interface and improve the mechanical integrity of the joints.

4. Conclusions

This feasibility study shows that reactive metal brazing using a commercially available Ag_{68}-$Cu_{27.5}$-$Ti_{4.5}$ interlayer can be used as a technique for joining ceria to MA956 an ODS ferritic stainless steel. The results show that an interfacial reaction layer forms at the ceria/braze interface and is a mixture of titanium and copper oxides, which will provide chemical bonding across the ceria/braze interface. Some capillary flow of copper into the ceria ceramic surface will also provide some mechanical bonding and this is influenced by the % porosity present within the ceria ceramic. However, a short bonding time is necessary to prevent excessive growth of this reaction layer and low porosity within the ceria in order not to compromise the strength of the ceramic. The thermal cycling results showed that when the joint was exposed to 700°C in air the reaction layer increased in thickness and this had a detrimental affect on the mechanical integrity of the final joint.

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