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Joining ceramic to metal using a powder metallurgy method for high temperature applications

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Fecralloy was successfully joined to calcia stabilised zirconia (CSZ) using a mixture of Fe, Cr and Al powders as a brazing filler and a screen printing and powder metallurgy method. The joining process was achieved at 1000 °C for 5 h in vacuum. During the joining process the filler wetted the surfaces of the CSZ and the Fercalloy foil, and formed a Fe(Cr, Al) alloy. The joint produced using the filler of (Fe-30Cr-5Al)-0.06 (Y_2O_3) (wt.%) showed good thermal stability and good thermal cycling oxidation resistance at temperatures up to 850 °C in air, even though the joint contained some porosity. © *2001 Kluwer Academic Publishers*

1. Introduction

The use of ceramic components for structural, electrical and electronic applications is rapidly increasing, however most of these applications require joining ceramics to metals or alloys for multiple functions and at reduced cost. Due to superior properties of ceramic materials at high temperature, it is highly desirable to fabricate metal-ceramic joints, which can withstand higher temperature environments. Searching for the proper brazing materials and joining processes for the fabrication of metal-ceramic joints for high temperature applications has become a “hot topic” in recent years [1–3]. Many commercial brazing alloys, e.g. Ag-Cu-Ti alloy, have low oxidation resistance and degrade considerably at temperatures above 500 °C [4]. For high temperature application, the transient liquid phase (TLP) joining method [5, 6] and the partial transient liquid phase (PTLP) [2, 7] joining method have been developed to fabricate joints which have high melting points. Here the low melting point metal, e.g Cu, first melts and then spreads on the surface of the pieces being joined, and finally reacts with a refractory metal (Ni or Nb) in an interlayer to form a high melting point compound, which is bonded to both metal and ceramic components. These methods combine the benefit of a low joining temperature and the potential for high temperature applications. Multilayer Cu/Ni/Cu interlayers that form a thin layer of a Cu-rich transient liquid phase have been used to join Al_2O_3 to Al_2O_3 [8]. The Cu/Ni/Cu interlayer finally forms a nickel rich interlayer. However, the joint strength decreased substantially after being exposed to heat treatment in air and argon, although nickel has a high melting point. The presence of oxygen promoted the formation of a spinel at the Al_2O_3/Nickel interface, which induced cracks in Al_2O_3. To produce strong ceramic/metal interfaces for high temperature applications, it is essential to fabricate metal/ceramic joints which have good oxidation resistance at high temperature. However, little consideration has been given to improving the oxidation resistance of the joints at high temperature.

The aim of the present study is to develop a simple joining process for fabricating calcia stablised zirconia (CSZ)/Fecralloy joints which are stable in high temperature oxidising environments. The Fe-rich Fe-Cr-Al alloys have melting points above 1500 °C [9] and have high oxidation resistance at high temperature [10], therefore, they are good candidates for joint materials. The alloys contain a low melting point metal Al, so one may develop a joining technique based on the principle of the PTLP joining method where liquid aluminium reacts with Cr and Fe to form Fe-Cr-Al alloy bonded to both CSZ and Fecralloy. In this study, Fe, Cr and Al powders, and an organic binder were mixed and applied to the surface of the CSZ using a screen printing method. The organic binder holds the pieces to be joined together but vaporizes at a certain temperature. The joint was formed using the powder metallurgy method. It is both chemically and mechanically stable at high temperatures up to 850 °C in air.

2. Experimental detail

The powders in this study were aluminium powder with a purity more than 99% and a average particle size of 20 μm, chromium powder with a purity more than 99% and a particle size less than 44 μm (purity: 99+%, particle size <44 μm), iron powder (purity: 99+%, particle size <10 μm) and Y_2O_3 powder (purity: 99.99%, average particle size: 3 μm) from Aldrich Chemical Co., USA. Fecralloy foils of 0.05 mm thickness and nominal composition of Fe-22Cr-4.8Al-0.3Si-0.3Y (wt %)

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were from Goodfellow Ltd., U.K. CSZ substrates were provided by the Roll-Royce Strategic Research Centre, Derby, U.K. The powder mixtures with homogeneous and compositions given in Section 3.1, were performed by grinding in an agate mortar for 30 minutes. The Y_2O_3 powder was added to the mixture of metal powders to improve the oxidation resistance of the Fe-Cr-Al alloy [11].

The powders were then mixed with a Blythe binder (John Mathew Ltd, UK) containing 50% terpineol as solvent and 50% ethyl cellulose to make the paste. The paste was then printed onto a CSZ substrate (typical size 10 mm × 30 mm) to form a thick film with a thickness of about 100–150 μm. Fecralloy foils (typical size 8.0 mm × 5.0 mm) were placed on the wet surface of the film. After this the samples were dried at 150 °C in air overnight, and then heated in a vacuum of about 5×10^{-5} torr from room temperature to 1000 °C over 1 h, being held at this temperature for 5 h before furnace cooling to room temperature.

The stability and the oxidation resistance of the joints were examined after thermal cycling experiments on joined samples. The thermal cycling was performed in air at a heating rate of 10 °C/min to 850 °C, holding for 3 h, followed by cooling to room temperature with a cooling rate of 10 °C/min. The cross sections of the joint were characterised using scanning electron microscopy (SEM) (Jeol JXA-840). The phases in the filler materials for the joints were identified using an X-ray diffraction method with a Philip PW 1140/00 powder X-ray diffractometer. The brazing filler/CSZ interface without a Fecralloy foil was also fabricated for phase analysis of the joining materials.

3. Results

3.1. Joint analysis

The presence of Cr in the brazing filler proved to be essential for fabrication of joints and improving the oxidation resistance of the joints. When the mixture of Fe and Al was used as brazing filler without Cr, there was no bonding between the filler and the CSZ substrate. Cr is an active element in brazing alloys for promoting wetting of ceramics [12]. Therefore it is assumed that the dissolution of Cr in liquid Al promotes the spreading of the liquid phase in the filler on the surface of the CSZ and promotes the bonding between the CSZ and the filler.

The compositions of the four brazing filler materials for Fabricating foil/filler/CSZ joints are (in wt. %) Fe-8Cr-4Al, Fe-15Cr-5Al, Fe-20Cr-5Al and Fe-30Cr-5Al with 0.06 wt. % of Y_2O_3. The joints of Fecralloy foil/filler/CSZ were formed after application of the brazing pastes using a screen printing technique and heat treatment at 1000 °C for 5 h in vacuum. Fig. 1 shows the microstructures of the joints with the fillers containing 8%Cr, 15%Cr, 20%Cr and 30%Cr, respectively, sandwiched between the Fecralloy (labelled as "F") and CSZ (labelled as "C"). The interlayer of the joints mainly contains a continuous matrix phase (light grey), together with another isolated phase (dark grey). The porosity of the joints increased with increasing Cr

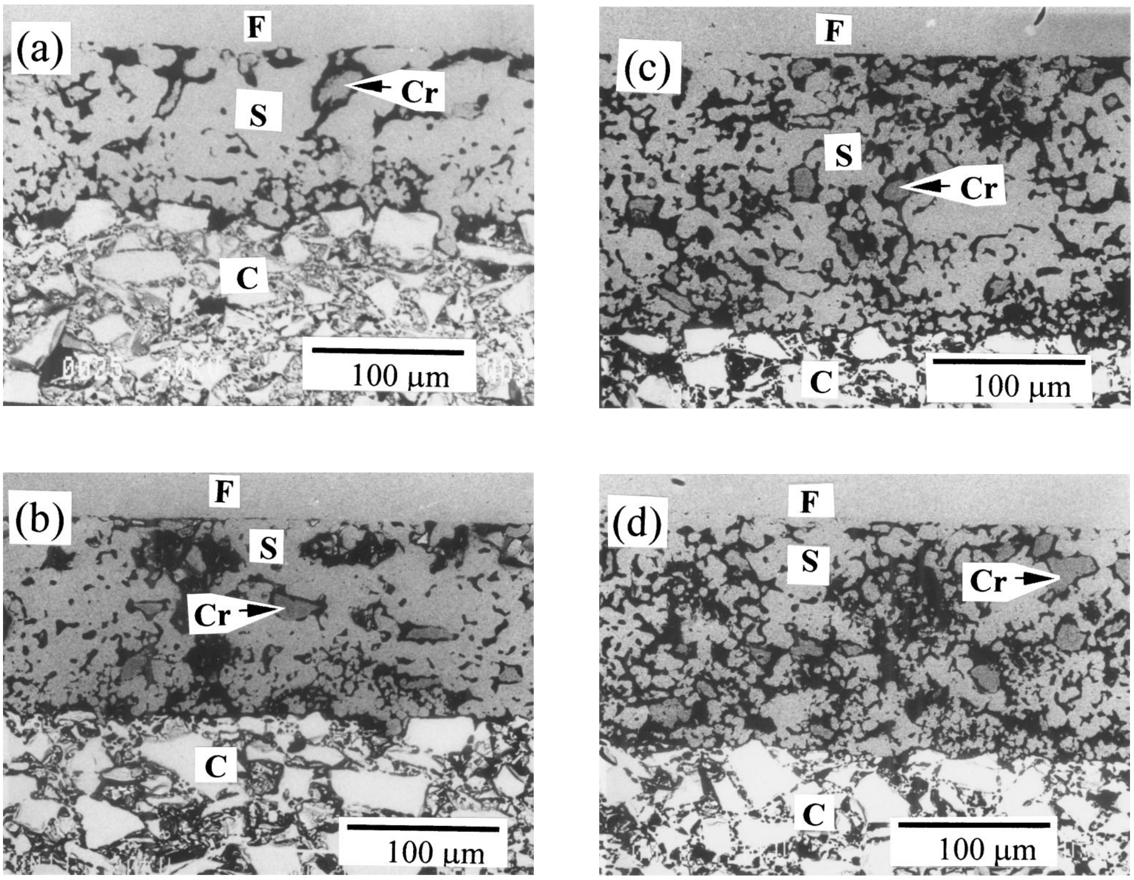

Figure 1 SEM image of cross-sections of the Fecralloy foil/filler/CSZ joints with the fillers containing: (a) 8%Cr, (b) 15%Cr, (c) 20%Cr and (d) 30%Cr. "F" for Fecralloy foil; "S" for the solid solution Fe(Cr, Al); "Cr" for the pure Cr and "C" for CSZ substrate.

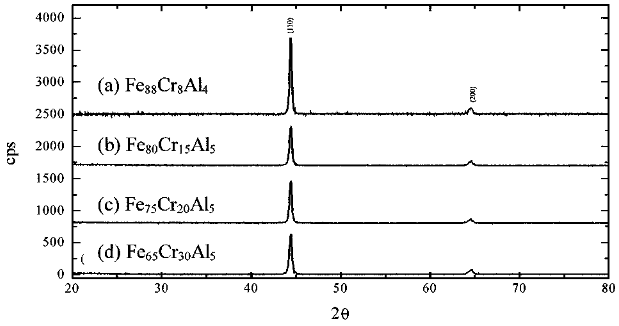

Figure 2 X-ray diffraction patterns from the surface of the filler/CSZ thick films using the fillers containing (a) 8%Cr, (b) 15%Cr, (c) 20%Cr and (d) 30%Cr.

content, which shows it is more difficult to form a continuous matrix phase with increasing Cr content in the filler due to its higher melting point. Energy dispersive X-ray (EDX) microanalysis indicates the continuous solid solution (labelled as "S") is a Fe-Cr-Al alloy and the second phase (dark grey regions) is pure Cr (labelled as "Cr"). The compositions of the continuous solid solution are Fe-6.2Cr-3.1Al, Fe-10.6Cr-4.2Al, Fe-15.5Cr-4.3Al and Fe-24.9Cr-3.4Al (wt. %), formed from the starting materials containing 8%Cr, 15%Cr, 20%Cr and 30%Cr, respectively. The Cr content in the solid solution is lower than that in the starting materials since some Cr did not react during the joining process. X-ray diffraction analysis also confirms that the matrix alloy is a single phase. The diffraction patterns for the fillers used in this investigation, shown in Fig. 2, consist of those of the continuous solid solution Fe(Cr, Al) and the Cr phases. It is difficult to identify the diffraction pattern of the Cr phase because it is overlapped by that of the solid solution Fe(Cr, Al). According to the phase diagram of Fe-Cr-Al ternary system [9], the equilibrium phase for the alloys with the compositions of all the fillers used for this investigation at 1000 °C should be a single phase, continuous solid solution Fe(Cr, Al). This indicates that the small amount of Cr in the interlayer can be dissolved to form the homogenous solid solution Fe(Cr, Al) completely by fabricating joints at a higher temperature or sintering for a longer period.

From the SEM observation (Fig. 1) there is no reaction layer found between the Fecralloy foil and the filler, or between the filler and the CSZ substrate. However, there is no clear boundary between the Fecralloy foil and the solid solution Fe(Cr, Al) in the filler layer because they have the same crystal structure and very similar lattice parameters. A solid solution Fe(Cr, Al) was formed on the foil. For the interface between the filler and the CSZ substrate, the solid solution Fe(Cr, Al) partially penetrates into the pore structure of the CSZ substrate to form a mechanical interlock. Although no mechanical testing of the joints was carried out due to the poor mechanical properties of the porous CSZ substrate used, it is evident that the bonding strength exceeds the strength of the CSZ substrate since the failure of the joints mainly occurred inside the substrate. It is reasonable to believe that the strength of the joints is sufficient for electrical contact applications.

3.2. Thermal stability and oxidation resistance

In order to examine the stability and oxidation resistance of the joints at high temperature, the joined samples were examined after thermal cycling in air. Thermal cycling was carried out at a heating rate of 10 °C/min to 850 °C, held for 3 h, and then cooled to room temperature with a cooling rate of 10 °C/min. Most of the joints with the filler containing 8%Cr were broken after 2 thermal cycles. Cracks were found in the CSZ substrate (Fig. 3). The filler between the foil and CSZ substrate was largely oxidised. It seems that the stress in the interface between the filler and the CSZ substrate was mainly generated due to oxidation and is the main cause for generating cracks in the CSZ substrate.

The joints with the filler containing 15%Cr were much more stable during thermal cycling than the joints with the filler containing 8%Cr because of their improved oxidation resistance. Unlike the joint with the filler containing 8%Cr, the joint with the filler containing 15%Cr was only partly oxidised after 10 thermal cycles. Fig. 4a shows the X-ray diffraction pattern from the oxidised surface of the filler containing 15%Cr after 10 thermal cycles and indicates that the dominant phase in the filler is the solid solution Fe(Cr, Al), together with a small amount of $Cr_{1.3}Fe_{0.7}O_3$ and $FeO{\cdot}Cr_2O_3$. Spallation of oxide scales occurred at the surface of

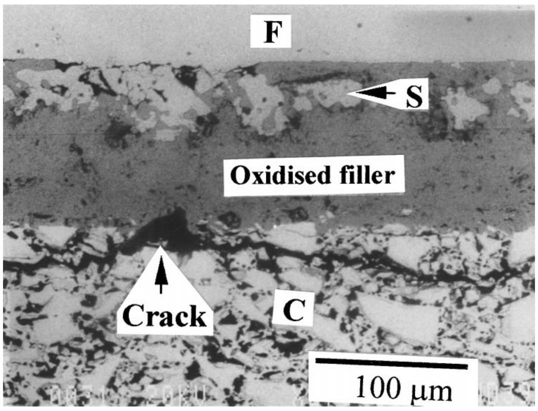

Figure 3 SEM micrograph of cross-section for Fecralloy foil/filler/CSZ joint with the filler containing 8%Cr after 2 thermal cycles to 850 °C in air. "F" for Fecralloy foil; "S" for the solid solution Fe(Cr, Al); and "C" for CSZ substrate.

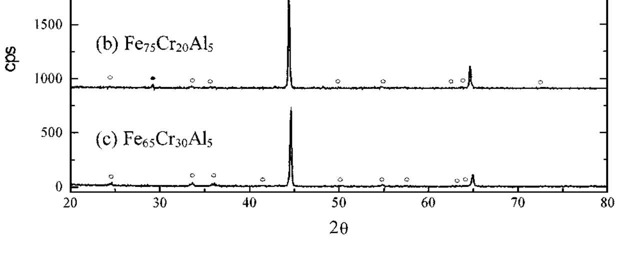

Figure 4 X-ray diffraction patterns from the surface of the filler/CSZ thick films using the fillers containing (a) 15%Cr, (b) 20%Cr and (c) 30%Cr after 10 thermal cycling to 850 °C in air: "o" for $Cr_{1.3}Fe_{0.7}O_3$ phase; "∗" for $FeO{\cdot}Cr_2O_3$ and "•" for $FeCr_2O_4$.

the filler after 10 thermal cycles. There is no spallation occurring at the surface of the joints with the filler containing 20%Cr or 30%Cr after 10 thermal cycles. Adherent and dense scales on the surface of the film were formed during thermal cycling and these protected the filler against oxidation, and thus protected the joints from failure. Fig. 4b and c show the X-ray diffraction patterns of the surface layer of the filler which was bonded to the CSZ where the fillers contain 20%Cr and 30%Cr respectively. The phases $Cr_{1.3}Fe_{0.7}O_3$ and $FeCr_2O_4$ were found in the oxide scale formed at the surface of the filler containing 20%Cr, while only a single phase, $Cr_{1.3}Fe_{0.7}O_3$, was formed at the surface of the filler containing 30%Cr.

Buckling of the scale was found on the surface of the filler/CSZ thick film with the filler containing 20%Cr after 10 thermal cycles, while that with the filler containing 30%Cr remained flat. Therefore, the joint with the filler containing 30%Cr shows the best thermal stability and best oxidation resistance among the samples fabricated for this investigation.

Fig. 5 shows the cross-section of the scale formed at the surface of the filler/CSZ joints with the filler containing 30%Cr after 10 thermal cycles. A uniform layer of about 10 μm thickness was formed at the surface of the filler. Although the filler/CSZ joint forms a network microstructure with some porosity, no internal oxidation was found in the joint. The interface between the scale and the filler remained unchanged during thermal cycling to 850 °C. EDX analysis confirmed that this scale is a single phase containing Fe, Cr and Al (Fig. 6) and indicated that the atomic ratio of Fe : Cr : Al in this phase is 32.1 : 48.1 : 19.8. According to the phase diagram of the Al-Cr-Fe-O system [13], a single sesquioxide phase $(Cr, Fe, Al)_2O_3$ at 1250 °C is formed in air from the mixture of Cr_2O_3, Fe_2O_3 and Al_2O_3 when the content of Cr_2O_3 is above 30 mol.%. This scale protects the filler and the joints, although it is slightly thicker than that formed at the surface of the Fecralloy foil at the same oxidation condition (about 8 μm). Experimental results also showed that thermal cycling of these joints didn't change the microstructure of the joints. No interaction between the filler and CSZ was detected during thermal cycling, so the joints are chemically stable during thermal cycling. Thermal cycling of the joint with the filler containing 30%Cr to 1000 °C showed that the joint was still firm, but significant buckling of oxide scales on the surface of the filler occurred. No further study was made on the effect on joints of thermal cycling up to 1000 °C.

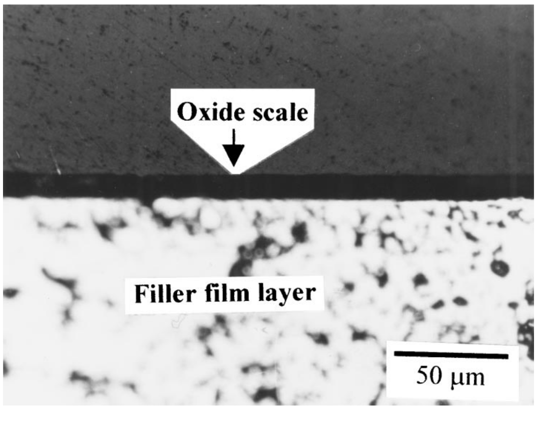

Figure 5 Optical micrograph of cross section for the scale formed on at the surface of the filler containing 30%Cr after 10 thermal cycling to 850 °C in air.

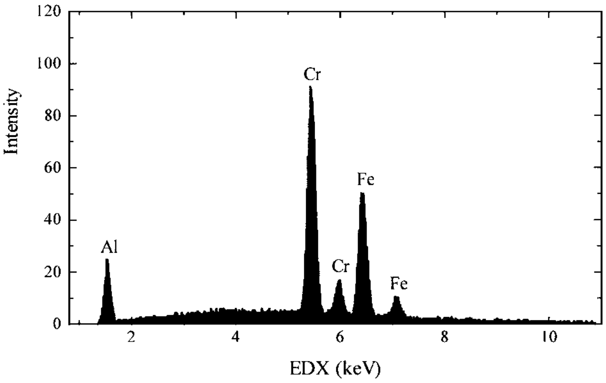

Figure 6 EDX pattern for the phase in the scale formed at the surface of the filler containing 30%Cr after 10 thermal cycling to 850 °C in air.

4. Discussion

In our previous study [14], nickel and aluminium powders were used for joining CSZ to Fecralloy using a screen printing method and a reaction forming process. The reaction between nickel and aluminium was carefully controlled to produce ceramic/metal joints containing NiAl and Ni_3Al, which show not only high temperature stability, but also high oxidation resistance in air. However, the main problem with these joints is the brittleness and stiffness of the nickel aluminides, which leads to crack formation in the joints during thermal cycling.

The Fe(Cr, Al) alloy is much more ductile than nickel aluminides. The coefficient of thermal expansion (CTE) of the dense CSZ is $\alpha_{CSZ} = 10.7 \times 10^{-6}\ K^{-1}$ [15]. The CTE for the Fecralloy is about $12 \times 10^{-6}\ K^{-1}$ [16]. Thus the CTE difference between the Fecralloy and CSZ substrate is not very large. In addition, the porous structure of the Fe(Cr, Al) alloy in the joint reduces its elastic modulus and enhances the crack resistance of the joint. The damage to the joints is mainly caused by their oxidation. The high stability of the joint containing 30%Cr at high temperature is mainly due to high oxidation resistance of the alloy containing 30%Cr.

One potential application for this method is to fabricate metal/ceramic joints for electrical applications, e.g. in the construction of solid oxide fuel cells and chemical sensors at high temperature. In these applications, joints forming chromium oxide scales from oxidation are preferred to joints forming alumina scales since the electrical resistance of chromia is significantly higher than that of alumina. In addition, the screen printing method is also suitable for fabrication of multilayer structures which are widely used for production of electronic devices. Therefore, this method has a great potential in fabrication of electrical and electronic devices.

5. Conclusion

Fecralloy foil has been successfully joined to calcia stabilised zirconia (CSZ) using mixtures of Fe, Cr and Al powders as brazing filler which were applied to the surface of the CSZ using screen printing and then sintering at 1000 °C for 5 h in vacuum. It has been shown that the metal powders in the brazing filler react to form a Fe-Cr-Al continuous solid solution and this bonds to both CSZ and Fercalloy during the joining process. No interaction has been found between the brazing filler and the Fecralloy or CSZ. The joint with the composition of (Fe-30Cr-5Al)-0.06 (Y_2O_3) (wt.%) showed good thermal stability and good thermal cycling oxidation resistance at 850 °C in air.

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