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Bonding of silicon nitride using preceramic polymer and germanium powders for potential fuel cell applications

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A new method for bonding blocks of Si₃N₄ has been developed that produces bonds whose maximum service temperature is equal to the temperature used during the bonding process. In the present paper a system consisting of blocks of Si₃N₄ coated with a preceramic film containing a fine dispersion of silicon and a thin layer of germanium powder has been investigated to determine the effect of the thickness of the germanium film. The maximum service temperature is not determined by the melting point of the germanium since the germanium forms a higher melting point solid solution with the silicon in the film. Control of the thickness of the germanium film is found to be critical as a thicker layers results in lower strength bonds owing to differences in thermal expansion, and the maximum service temperature is lower owing to the lower liquidus temperature of the leaner Ge–Si solid solution. This technique has potential applications in fuel cells as a result of the small differences in thermal expansion coefficients and firing shrinkage in fuel cell materials, thus allowing successful fabrication and joining of monolithic solid oxide fuel cells (MSOFCs) with few defects.

Keywords: Ceramic fibres, Crystal growth, Firing temperature, Insulating wool, Shrinkage

Introduction

As methods of bonding silicon nitride for service at high temperatures, diffusion sintering and brazing methods are proposed. Diffusion sintering involves heating materials under pressure at high temperature. Such high temperature can be a cause of deterioration in bonded materials. In brazing, heat resistance cannot be expected above the melting point of the metal used for bonding.1–3 Iseki et al. investigated bonding of silicon carbide blocks using germanium powder. When heated, the germanium reacts with free silicon in the silicon carbide to form a solid solution between Si and Ge. This results in bonds which can be maintained up to 1323 K despite the fact that germanium has a melting point of only 1210 K.

Shaltz et al. developed a partially transient liquid phase (PTLP) method of joining two high melting point components using a trilayer film consisting of a high melting point material sandwiched between two low melting point materials. Specifically, SiC and Si₃N₄ were joined using a number of metal films. This technique is simpler than Iseki et al.’s, but it does require the use of the silicon dispersed phase. This demonstrates that bonding using low melting point materials need not result in a low melting point bond.

The present work embraces both Iseki et al.’s and Shaltz et al.’s approaches to obtaining high temperature bonds using relatively low melting point materials. It employs germanium powder and polyureasilazane (Si₁₀N₁₀C₁₄H₅₂), which is widely used to sinter SiC–Si₃N₄ composites, to form strong, heat resistant bonds between Si₃N₄ components. In conventional high pressure sintering processes employing a nitrogen atmosphere, the polyureasilazane reacts to form a Si₃N₄–SiC nanocomposite that helps form the bond between the powders. In the process described below the germanium also plays a role in bonding when it reacts with free silicon in the ceramic, and silicon dispersed in the polyureasilazane provides a source of free silicon. As in previous work, this allows for higher service temperatures than were used in the bonding process. Potential applications in fuel cells include the chemical reactor/heat exchanger in a MEMS device, consisting of suspended tubes of low stress silicon nitride with integrated slabs of silicon, attached to a silicon substrate for hydrogen production, with a potential joining application of silicon nitride components.

Experimental procedure

The experimental procedure consisted of forming the silicon dispersed polyureasilazane film on a block of Si₃N₄, evaluating the wetting of germanium on the...
Si$_3$N$_4$, then bonding two blocks of Si$_3$N$_4$. Four point bend testing and examination of the surfaces and cross-sections of the film followed.

**Film formation**

The silicon dispersion was produced using an agate mortar and pestle. It was put into a 10 cm high cylinder with acetone for sedimentation. After 25 min, silicon particles less than 5 $\mu$m in size were still dispersed (as per Stokes’s Law) while particles larger than 5 $\mu$m settled to the bottom. The top clear layer was then warmed and stirred to evaporate part of the acetone in order to adjust the concentration to 0.05 g Si per millilitre of suspension. After letting the suspension set again for approximately 25 min, particles larger than 25 $\mu$m settled to the bottom. This was confirmed using SEM, as shown in Fig. 1. The sediment at the bottom of the cylinder was discarded and the liquid kept. The liquid contained a suspension of fine silicon particles smaller than 25 $\mu$m.

Polyureasilazane (Tonen, Tokyo, Japan) was dissolved in the acetone–silicon mixture (1.0 g acetone–silicon, 2.0 g polyureasilazane). One face of a 10 mm cube of Si$_3$N$_4$ (Nippon Fine Ceramics, Japan) was briefly dipped in the solution, and then spun at 8000 rev min$^{-1}$ for 1 min to remove excess solution. It was then heated at 210°C for 5 min to remove the residual acetone, with insignificant Si–O bond incorporation from the intake of oxygen in the air, and then fired at 1200°C in a purified nitrogen atmosphere (oxygen and water were removed using a copper catalyst, silica gel and phosphor pentoxide) for 60 min. X-ray diffraction confirmed that the resulting film was amorphous. Only silicon peaks were observed.

**Measurement of wetting**

A small particle of germanium (approximately 1 mm$^3$) was put on the film side of a Si$_3$N$_4$ block and heated to 1150°C under a vacuum of 0.6 Pa. A microscope equipped with a measuring reticule was used to measure the contact angle.

**Bonding**

Spreading germanium powder on the silicon dispersed polyureasilazane film of one block and placing a second coated Si$_3$N$_4$ block on top with the film coated sides in contact with each other bonded two film coated blocks of Si$_3$N$_4$. The assembly was heated at 1150°C for 240 min under a vacuum of 0.6 Pa and a clamping pressure of 13 MPa.

**Four point bend testing**

The four point bend samples were bars 2 mm high by 2 mm wide by 20 mm long and were obtained from the centre sections of the bonded block assemblies. The bond was located at mid length and was oriented parallel to the direction of loading. Two samples were tested, one having been processed using a 1 mm thick layer of germanium powder and the other using a 0.5 mm thick layer. In one set of tests a load of 75 kPa was applied to both samples while they were heated and the temperature at which they failed was noted. In the second set of tests both samples were tested at room temperature and the fracture strengths recorded.

**Results and discussion**

**Wetting measurements**

Wetting between silicon nitride and germanium is essential for good bonding. Figure 2 shows the results of wetting measurements of the Ge–Si solid solution conducted on uncoated Si$_3$N$_4$ at 1150°C, where increasing the concentration of silicon lowers the contact angle. This effect is pronounced at 10 wt-%Si. Figure 3 shows the results of similar measurements made for the case where the Ge–Si solid solution is placed on the film coated Si$_3$N$_4$. As before, the contact angle decreased over time, but this time the decrease was greater. The film, which contains amorphous silicon carbide and amorphous silicon nitride, is effective at increasing the
wettability. In both cases, however, the contact angle decreased to less than 90°, so conditions for good bonding can be met with and without the film. However, the film improved wettability and should therefore result in better bonds.

**SEM imaging of bond regions**

Figure 4 shows SEM (SEI) and X-ray dot map images of cross-sections of bonded Si₃N₄ blocks where a 1 mm thick layer of germanium powder was spread on the polyureasilazane coated blocks. These images show that the bond region is about 50 µm thick, that the concentration of silicon in this region is relatively low and that the concentration of germanium is high. The bond region itself consists of three layers where the germanium rich layer in the centre is from the original powder and the top and bottom layers are from the polyureasilazane film. The top film layer is difficult to see in the SEI image while the bottom layer is barely visible in the silicon dot map (Fig. 4).

Figure 5 shows similar images for the case where only a 0.5 mm thick layer of germanium powder was used. The bond region is thinner, the layer of germanium is thinner and the polyureasilazane film cannot be seen in either the SEI image or the X-ray dot maps. In addition, the concentration of silicon is nearly uniform. The silicon poor region seen in Fig. 4 is almost undetectable in Fig. 5.

**Four point bend testing**

The four point bend tests were conducted at constant load while the temperature was steadily increased. The temperature at which the bonds failed was noted and is shown in Fig. 6a. The results show that the bond created using the thinner (0.5 mm) layer of germanium held to a higher temperature. The sample with the thicker germanium layer (1 mm) failed at about the melting point of germanium (bond failed at 950 °C, germanium melts at 937 °C). Apparently melting occurred in the thicker layer of germanium seen in Fig. 4, consisting probably of germanium that did not enter solution with the silicon. The phase diagram in Fig. 7 illustrates the problem. During the bonding process, which took place at 1150 °C, both liquid and solid phases would exist unless sufficient time was allowed for the germanium to diffuse away from the bond surface and into the Si₃N₄. As it cooled, the concentration of germanium in the
Both cases fracture occurred at Ge–Si/(Si₃N₄ from preceramic polymer), (Si₃N₄ from preceramic polymer)/(Si₃N₄ block), inside the Ge–Si layer, and inside the Si₃N₄ from preceramic polymer. Iseki et al.⁵,⁷ found that the strength in the bonds in reaction bonded Si₃N₄ containing germanium and free silicon decreased as the thickness of the Ge–Si solid solution layer increased. This was attributed to stresses caused by differences in thermal expansion. The results in the present work, where the bond with the thinner Ge–Si layer was stronger, are consistent with Iseki et al.’s findings.

Conclusions

A new method for bonding blocks of Si₃N₄ has been developed. The process involves coating these blocks with a polyureasilazane film containing a fine dispersion of silicon. This film is coated with a thin layer of pure germanium powder fractured at 40 MPa while the sample with the 0.5 mm layer fractured at 75 MPa. In both cases fracture occurred at Ge–Si/(Si₃N₄ from preceramic polymer), (Si₃N₄ from preceramic polymer)/(Si₃N₄ block), inside the Ge–Si layer, and inside the Si₃N₄ from preceramic polymer. Iseki et al.⁵,⁷ found that the strength in the bonds in reaction bonded Si₃N₄ containing germanium and free silicon decreased as the thickness of the Ge–Si solid solution layer increased. This was attributed to stresses caused by differences in thermal expansion. The results in the present work, where the bond with the thinner Ge–Si layer was stronger, are consistent with Iseki et al.’s findings.

The bonding technique described in the present paper can be effectively used in such systems. The bonds are intact to temperatures above 1000 °C, and the small mismatch in coefficients of thermal expansion reduces the likelihood of failure due to internally generated stresses and should tolerate many heating and cooling cycles, thereby extending the service life of the components.

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