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Vacuum heat-treatment of MgO-densified silicon nitride ceramics and their compatibility with molten aluminium and copper

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Abstract

Silicon nitride with 3% MgO powder mix was compacted with cold isostatic pressing followed by uniaxial pressing. Pressureless sintering of the compacted silicon nitride (Si_3N_4) crucibles was at 1600 °C for 30 min in the carbon furnace. The densities achieved after this process are 3140 kg/m^3. One of these crucibles was vacuum heat treated at 1575 °C for 5 h to remove grain boundary glass. Both this crucible and the as-sintered crucibles were used for melting aluminium and copper by heating in, air atmospheres to 700 °C and 1100 °C, respectively. Vacuum heat-treated glass free ceramic crucible was successfully used for the molten aluminium and copper handling. On the other hand, the chemical bond occurred for as sintered Si_3N_4 crucible. No adherence was observed after examining of interface between Al and the heat-treated ceramic crucible with SEM and EDX analysis.

Keywords: Silicon nitride ceramics; Vacuum heat treatment; Crucible; Molten metal handling

1. Introduction

Silicon nitride (Si_3N_4) ceramics have been investigated since 1970s for structural applications because of their high fracture toughness, oxidation resistance, thermal stability, low coefficient of thermal expansion [1–3]. It is essential to achieve high densification to obtain these properties for Si_3N_4 ceramics. It is impossible to sinter Si_3N_4 ceramics for full density without using sintering additives because of strong covalent bond and low decomposition temperature (1800 °C). When the oxide additive MgO is mixed with Si_3N_4 powders, the liquid phase takes place due to the eutectic reaction of MgO, surface silica and silicon nitride during sintering. As a result of the eutectic reaction, liquid grain boundary glass Mg–Si–O–N forms between the Si_3N_4 grains. Therefore, the liquid phase sintering mechanism which is provided by sintering additives is essential for Si_3N_4 densification [2–5].

The corrosion of ceramics by liquid metals, such as aluminium, copper alloys and cast iron, is a matter of increasing interest for casting processes. Despite the great interest in using Si_3N_4 materials, their corrosion resistance has not been studied extensively so far, particularly under industrial conditions [6–9]. The environments were chosen to approach industrial conditions by avoiding an inert atmosphere commonly found in earlier scientific experiments [6–9].

The emphasis of much of the research carried out on nitrogen ceramics has been the preparation of more refractory materials with good mechanical properties for high temperature use. An important application is in the field of molten metal handling but previous work has shown that this is limited by the residual glassy phase in the sample which readily reacts with slag on the surface of the molten metal, resulting in degradation of the ceramic. Thus, the reaction which bonded silicon nitride with its 20% of porosity (but glass-free), is an excellent container material for molten aluminium. One of the challenges of attempt to remove glassy-phase from pressureless sintered nitrogen ceramics is therefore to produce high density (and therefore high strength) materials suitable for carrying liquid metals at high temperatures.

In this work, the research focused upon the feasibility of melting, aluminium (melting point 660 °C) and copper (melting point 1089 °C) in vacuum heat treated silicon nitride crucible.

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2. Experimental methods

In the present work, silicon nitride containing 3 w/o of MgO was used as the composition for making the refractory crucible. In order to prepare crucibles, the mixed powder was introduced into a steel die fitted with a plunger capable of pressing out a cylindrical crucible when uniaxial pressure was applied (see Fig. 1). A pressure of 250 MPa was applied, and maximum densities of 60% of theoretical were obtained in this way after isostatic pressing. Fig. 1 gives details of the procedure used for making the crucible. Crucibles, which were sintered to high (>95%) densities as described in Demir, were pressureless sintered [10], and then vacuum heat treatment was carried out in the vacuum furnace to remove grain-boundary glass (Fig. 2).

Aluminium and cupper metal were melted separately inside the both as sintered and vacuum heat-treated silicon nitride crucible. On heating to high temperature, the metal melts and comes into contact with the material, which can then be examined for evidence of attack from the molten metal. In order to examine reaction between molten metal and the crucible SEM, the image analysis and EDX elemental analysis were carried out.

3. Results and discussion

3.1. Melting aluminium

After pressureless sintering of silicon nitride crucibles at 1600 °C for 30 min in the carbon furnace, 3140 kg/m^3 density was achieved. As a result of liquid phase sintering, approximately 10% Mg–Si–O–N glass left within the silicon nitride grain boundaries. This glass could react with aluminium or cupper if the as sintered Si_3N_4 ceramic is used for molten metal handling. In this study, grain boundary glass was removed under vacuum heat treatment so that the melt was not able to react with the ceramic crucible. Therefore one of these crucibles was vacuum heat treated at 1575 °C for 5 h for grain boundary glass removal. During heat-treatment, Mg within the glass was volatilised and come off from surface of the Si_3N_4 ceramic crucible. The remaining glass either crystallized as SiO_2N phase or remained amorphous.

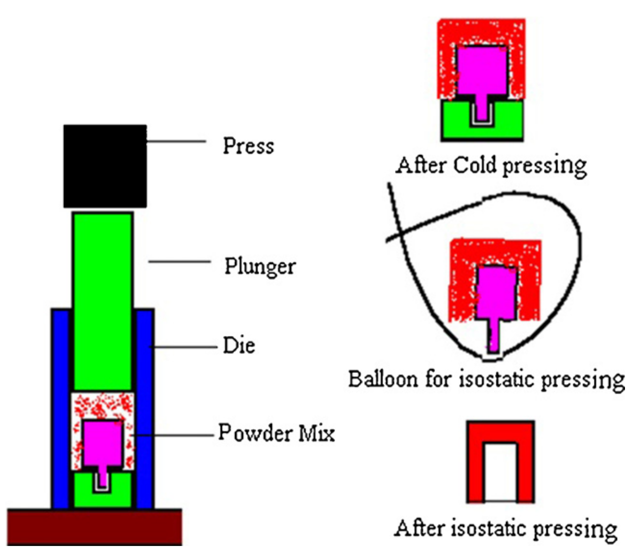

Fig. 1. Green crucible preparation by uniaxial and cold isostatic pressing.

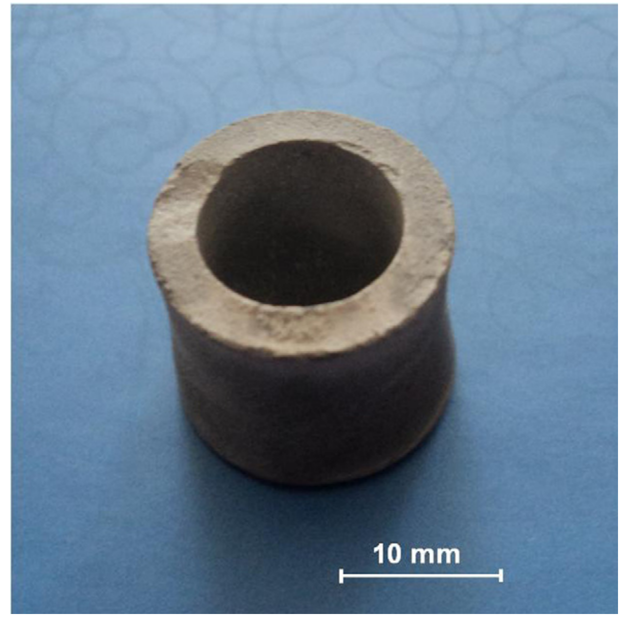

Fig. 2. Vacuum heat-treated S_3N_4 crucible after pressureless sintering.

After grain boundary glass removal, both heat-treated crucible and the as-sintered crucibles were used for melting aluminium by heating air atmospheres to 700 °C for aluminium and 1100 °C for copper. The results for the air and nitrogen-melted samples were very similar, and only the results in air were presented. Fig. 3 shows the interface between the as-sintered silicon nitride crucible (left side of picture) and the melted aluminium (right side of picture). There is an interfacial region of variable thickness consisting of a mix of lighter and darker regions. The darker regions are mainly aluminium-rich and the lighter regions are believed from careful X-ray mapping to be spinel, $MgAl_2O_4$. These results point to the interface being oxygen-rich, and forming from the oxygen rich outer surface always observed after sintering and also the melting was carried out in air. The Al and Si EDX traces shown in Fig. 4 are consistent with this; the Mg trace is unusual in showing such sharp peaks, which probably correspond to localized regions of $MgAl_2O_4$. It is well-known that Mg element is a volatile species within the Mg–Si–O–N grain boundary glass at high temperatures. Therefore, Mg diffuses to the surface of silicon nitride during oxidation.

It was observed that the aluminium slug came out of the crucible quite easily on tapping. The absence of a chemical bond can be understood partly because of the large thermal mismatch, and also because of the dissimilarity in bonding across the $Si_3N_4/MgAl_2O_4$ interface. This was also the situation for the crucible which had been vacuum heat-treated. In fact, in this case the sample was already loose on cooling to room temperature. Fig. 5 shows a typical interface between the silicon nitride crucible (left hand side) and the more ragged aluminium on the right hand side. EDX analysis shows that the white layer on the surface of Si_3N_4 is silicon rich, and is

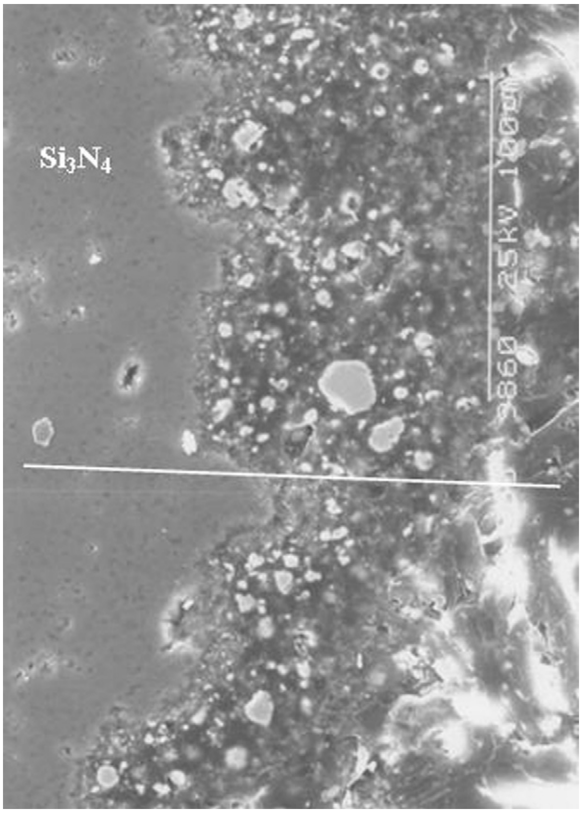

Fig. 3. Si_3N_4/Al interface for Al melted at 700 °C in air in a pressureless sintered silicon nitride crucible.

believed to be the residue of the silicon carbide layer originally present on the silicon nitride crucible after vacuum heat treatment. EDX analyses taken across Fig. 5 are plotted in Fig. 6 for each element. The EDX plots reveal that aluminium was not wetted the Si_3N_4 crucible surface by molten aluminium. The break between the Si_3N_4 and aluminium is clearly apparent from the EDX traces (Fig. 6) which also show that Mg has diffused into the molten aluminium, with peaks in concentration at the surface of the silicon nitride.

Santos et al. [11] have also investigated molten metal handling properties of Si_3N_4 ceramic crucibles and revealed

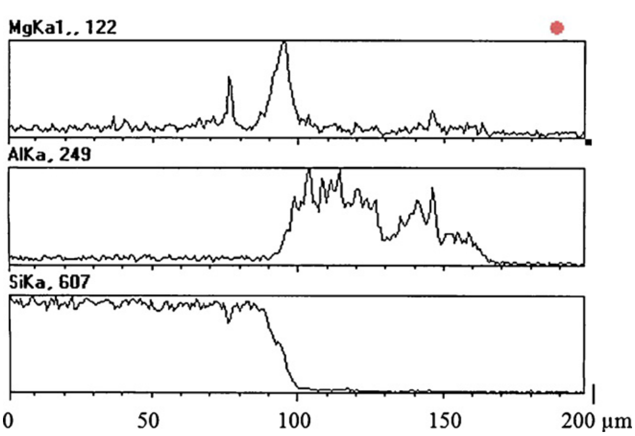

Fig. 4. Mg, Al and Si EDX traces across the white line shown in Fig. 3.

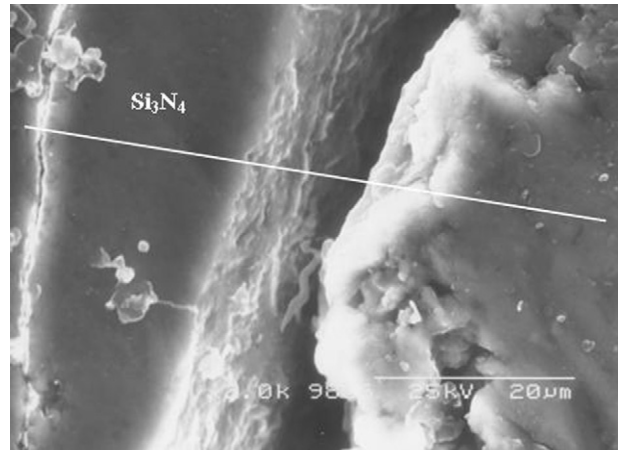

Fig. 5. Interface between the VHTed Si_3N_4 crucible in contact with Al melted at 700 °C in air.

that if the grain boundary glass of Si_3N_4 ceramic crucible is crystallized by post-sintering heat treatment, chemical bond can be prevented between molten aluminium and the crucible surface. The result obtained in that work is consistent with this study in terms of the grain boundary glass removal.

3.2. Melting copper at 1100 °C

Similar pressureless sintered and vacuum heat treated silicon nitride crucibles were prepared as described in the previous section, and used for the melting of copper by heating in air at 1100 °C. Both slugs of copper and copper came out of the crucibles cleanly, without sticking. Fig. 7 shows the appearance of the crucible (on the right) and the copper with slug (left). The silicon carbide layer which had formed during vacuum heat-treatment is still intact, and it was not surprising that this showed a clean break from the copper. The micrograph given in Fig. 8 shows the silicon nitride of the crucible (top part) with the bottom part of the picture (copper). The ragged interface shows some evidence for retaining part of the original silicon carbide layer.

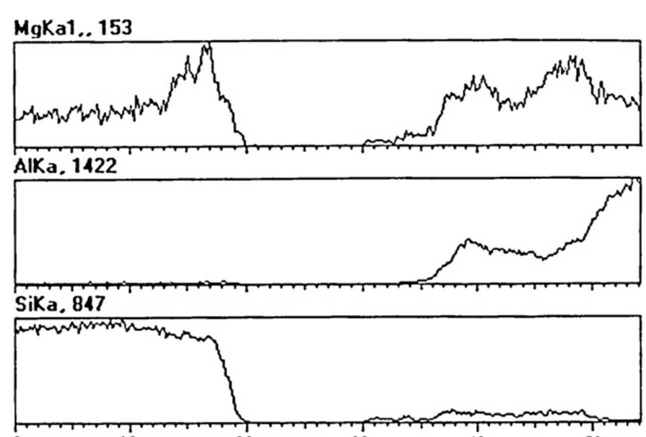

Fig. 6. Mg, Al and Si EDX traces taken across the yellow line shown in Fig. 5.

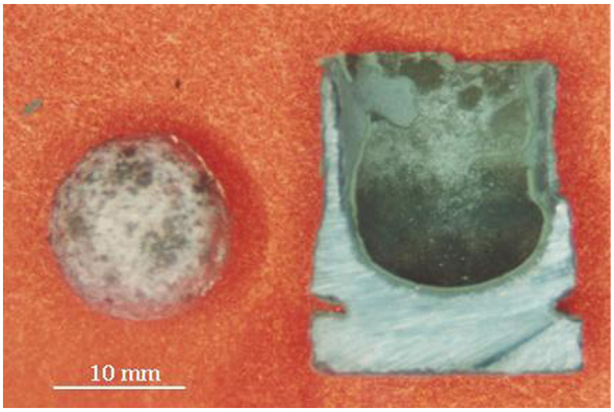

Fig. 7. VHT crucibles after Cu melting at 1100 °C for 1/2 h in air.

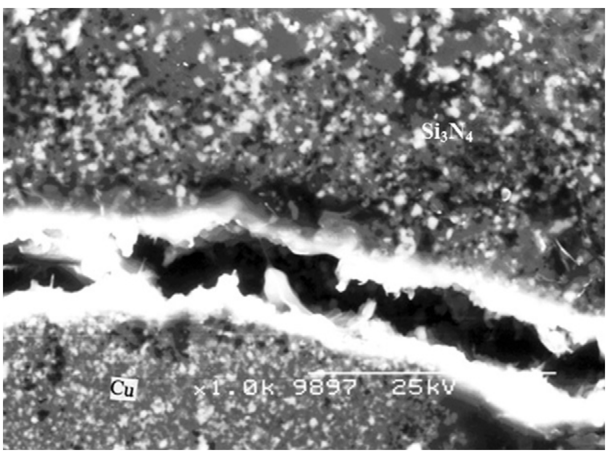

Fig. 8. SEM image of the Si_3N_4 (SiC)–Cu interface after melting copper at 1100 °C for 1/2 h in air in the VHT ed silicon nitride crucible.

4. Conclusion

High dense Si_3N_4 ceramic crucible was obtained by liquid phase sintering of the green crucibles. Grain boundary glass, resulting from liquid phase sintering, was successfully removed by the vacuum heat treatment. Molten aluminium was stuck and reacted with as sintered Si_3N_4 crucible surface, but it was not chemically reacted with the vacuum heat-treated crucible during melting or handling. SiC layer occurred at the Si_3N_4 crucible surfaces during sintering was also behaved as non-stick surface. The Si_3N_4 crucible produced in this study is harder, tougher and more stable than other non-oxide ceramic crucible which can be used for molten aluminium and cooper handling.

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