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Processing of vacuum heat-treated MgO-densified silicon nitride crucible for molten cast iron handling

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Abstract

Silicon nitride with 3% MgO powder mix is uniaxially and cold isostatically pressed to form a green Si_3N_4 crucible. Liquid phase sintering was applied to the green Si_3N_4 crucible at 1600 °C for 30 min under the nitrogen atmosphere. Intergranular Mg–Si–O–N glass remained between the silicon nitride grains which reacted with the molten metal during melting. This grain boundary glass was removed by vacuum heat treatment at 1575 °C for 5 h. The vacuum heat treated crucible was used to melt cast iron to examine reactions between the molten metal and Si_3N_4 ceramic crucible. EDX spectra across the Si_3N_4–cast iron interface and XRD for silicon nitride sample after cast-iron melting side surface analysis were carried out. Optical microscopy and SEM image analysis were made to examine the interaction between Si_3N_4 crucible and cast iron melt. Surprisingly, no reaction was observed between the vacuum heat treated crucible and melted cast iron.

Keywords: Sintering; Grain boundaries; Corrosion; Si_3N_4; Vacuum heat-treatment; Crucible

1. Introduction

Ceramics have a high potential for their use in metallurgical processing because of the excellent refractoriness properties and wear resistance. They serve under many conditions, whereas metallic materials relatively fail to do so. So far, however, all applications of ceramic materials in contact with metals and metal melts have not been explored yet. This is mainly because of lack of information by the industrial users regarding the different types of ceramics, their characteristic properties and possible application.[1] Among the ceramics, 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.[2–4] It is essential to achieve high densification for obtaining these properties for Si_3N_4 ceramics, but it is impossible to sinter Si_3N_4 ceramics to full density without using sintering additives. Therefore, the liquid phase sintering mechanism which is provided by sintering additives is used for Si_3N_4.[3–5]

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, particularly under industrial conditions.[6–9] In previous researches, the environments were generally chosen to approach industrial conditions by avoiding an inert atmosphere commonly found in earlier scientific experiments.[10]

The researches carried out so far on nitrogen ceramics gave much emphasis to 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.[10–12] Thus, the reaction, which bonded silicon nitride with its 20% of porosity (but glass-free), is an excellent container material for the molten aluminium. One of the challenges of attempting 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.[12] In our previous study, the feasibility of melting cast-iron (melting point ≈ 1450 °C), copper (melting point 1089 °C) and aluminium (melting point 660 °C) in the vacuum heat treated silicon nitride crucible.[13] In this study,

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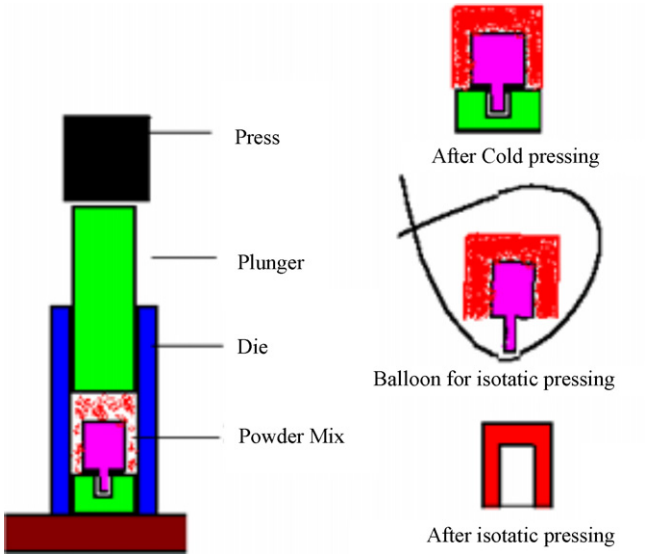

Fig. 1. Green crucible preparation by uniaxial and cold isostatic pressing.

however, the vacuum heat treatment has been applied for Si_3N_4 crucible to get rid of the glass phase and then used for the cast iron handling to examine the corrosion behaviour of materials.

2. Experimental methods

Essentially two methods can be used for this experiment. In the first case, the material is produced in the form of a crucible, into which is placed the powder (or some other commented form) of the metal, and this in then heated to the appropriate (high) temperature. Alternatively, a piece of the material is placed inside a refractory crucible, which again contains the metal powder. 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 the present work, both methods were used, and silicon nitride containing 3 w/o of MgO was used as the composition for making the refractory material. 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). It was desirable to achieve a good green density since it is well known that as Kingery[14] states, a high green density correlates with a high fired final density, and this is also important for the vacuum heat-treatment process. A pressure of 280 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 were pressureless sintered to high (>95%) densities as described in the previous work,[12] and then the vacuum heat treatment was carried out in the vacuum furnace to remove grain-boundary glass. When the crucible was placed inside the inner alumina tube of the vacuum furnace, care was taken to separate crucible and tube with a layer of boron nitride powder to prevent the chemical reactions from taking place as described in Demir.[12] A disadvantage of this route as discussed in previous works[12] is that it is essential to polish the sample after the initial pressureless sintering step to remove surface layers of oxide-rich material which might react with the carbon powder bed used during the vacuum heat treatment step to produce a silicon carbide coating. Whereas the samples used in the previous study by Demir[12] were in the form of rectangular blocks, polishing these samples is a simple process, and polishing inside surfaces of a cylindrical crucible is not easy as shown in Demir[12] unless all the surface layers are removed because it can reform during the vacuum heat treatment step. Due to this difficulty, the second procedure was developed as an alternative method of carrying out the molten metal compatibility test.

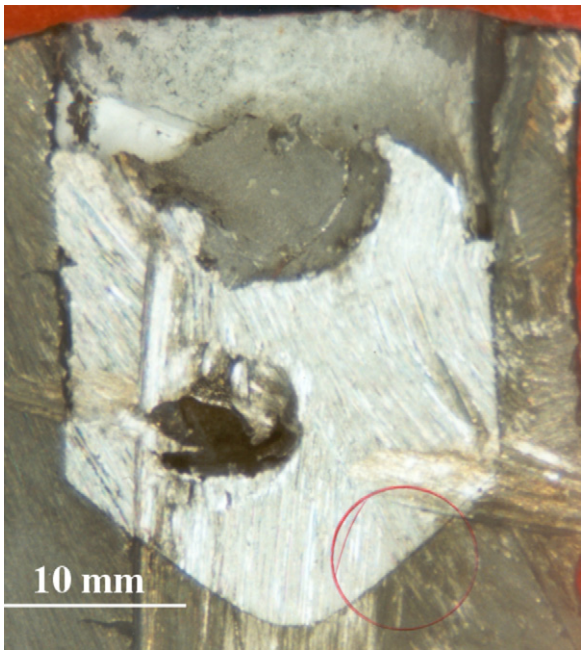

Fig. 2. Melting of cast iron in a silicon nitride crucible (without VHT) at 1450 °C in the air for ½ h.

For this purpose, blocks of pressureless sintered plus vacuum heat treated silicon nitride, initially densified with 3 w/o MgO, were prepared exactly as described in Demir[12] with any surface layers remaining after the pressureless sintering step removed by polishing. The iron metal block was put into the vacuum heat-treated crucible and heated to melt the cast iron block as shown in Figs. 2 and 3.

3. Results and discussion

Initial melting experiments on the cast iron were conducted in the air in silicon nitride crucibles which had been sintered and vacuum heat-treated, and the latter had a thin layer of silicon carbide on the surface due to the reaction with the carbon powder bed.

Fig. 2 (and the higher magnification photograph in Fig. 3) shows the appearance of the silicon nitride–cast iron interface after melting in the sintered crucible. Fig. 3 shows that some reaction does occur at the interface (the cast iron was firmly attached to the crucible after melting), and the thin black layer, corresponding to iron silicide ($FeSi_2$). Examination of the surface of the cast iron pellet after melting (Figs. 4 and 5) showed that a considerable amount of material had been trans-

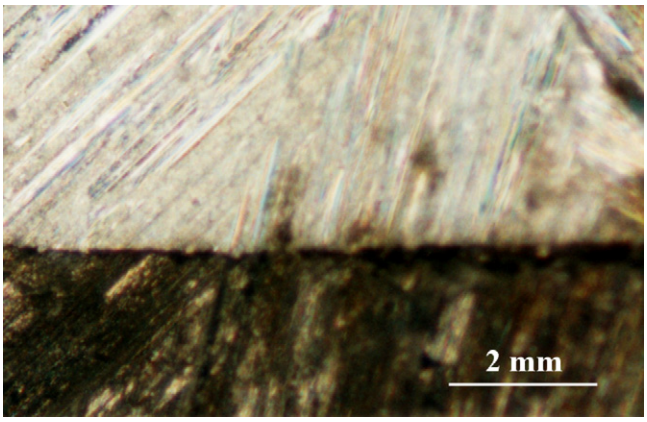

Fig. 3. Higher magnification photograph of the area circled in red in Fig. 2. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

ferred from the crucible to the metal by chemical reaction. The bubbled appearance of the debris combined with EDX evidence suggested that this was mainly Mg–Al–Si–O glass which had come out of the silicon nitride, oxidising at the same time.

Melting experiments carried out in the silicon nitride crucible resulted in the cast iron, sticking to the side of the crucible after melting. Fig. 6 shows the SEM image of the interface (Si_3N_4 on the left of the picture) where clearly some reactions have taken place. The micrograph shown in Fig. 6 is from an edge region of the area of contact, and shows that some contamination has occurred. The EDX spectra (Fig. 7) indicate a rather ragged elemental distribution in agreement with the ragged nature of the interface shown in Fig. 6. The reason for this may be ingress of oxygen from the air which at the edges of the sample resulted in

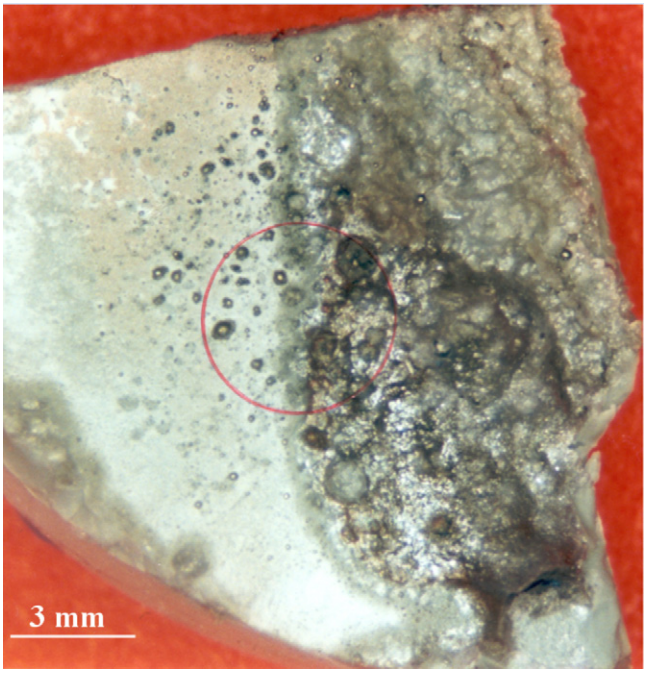

Fig. 4. Cast iron pellet after melting in a silicon nitride crucible (without vacuum heat treatment) at 1450 °C for ½ h.

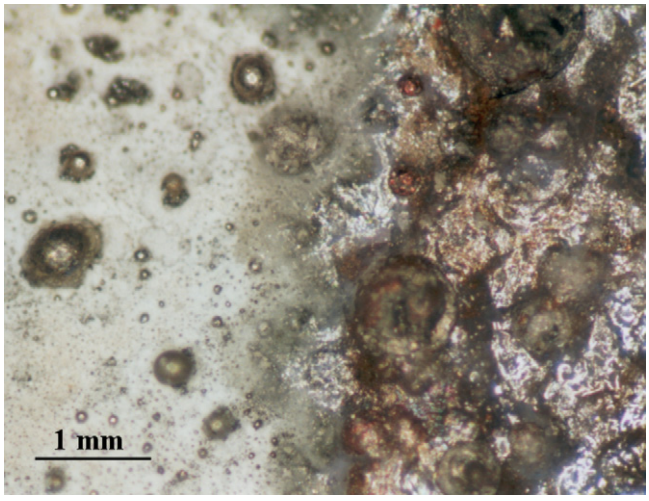

Fig. 5. Higher magnification photograph of the region circled in red in Fig. 4. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

oxidation of the silicon nitride, with Mg from the grain boundaries in the sample diffusing to the surface and forming an Mg–Si–O glass which then allowed further diffusion of Mg to pass across into the cast iron. The EDX spectra of the interface (Fig. 7) showed a fairly sharp demarcation between Si-rich and Mg-rich regions; the peaks in the Mg spectrum are due to localised regions of Mg-rich glass trapped in the interface. The apparent evenness of the magnesium concentrations on either side of the interface shows that Mg has diffused out of the glass and into the metal, and the chemistry associated with this

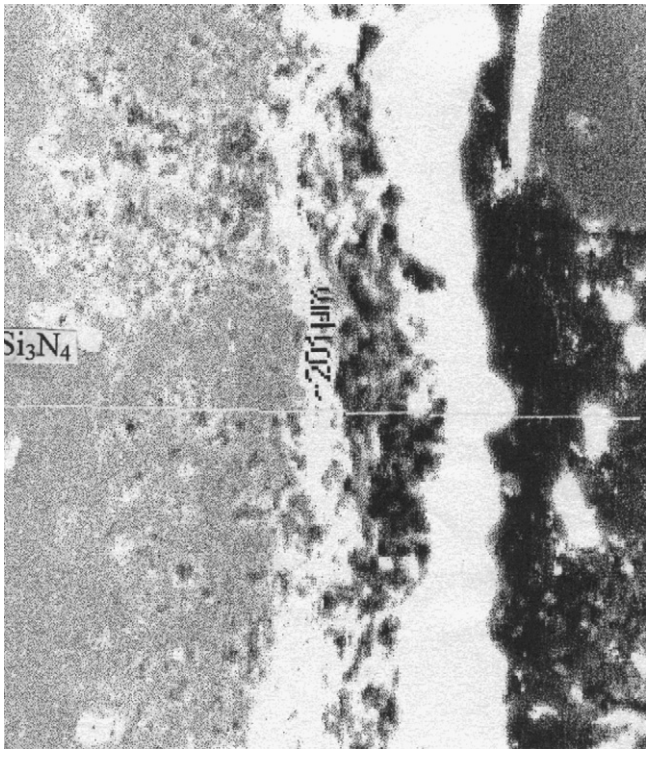

Fig. 6. Cast-iron–silicon nitride interface for cast iron melted in a silicon nitride crucible (without vacuum heat treatment) at 1450 °C for ½ h.

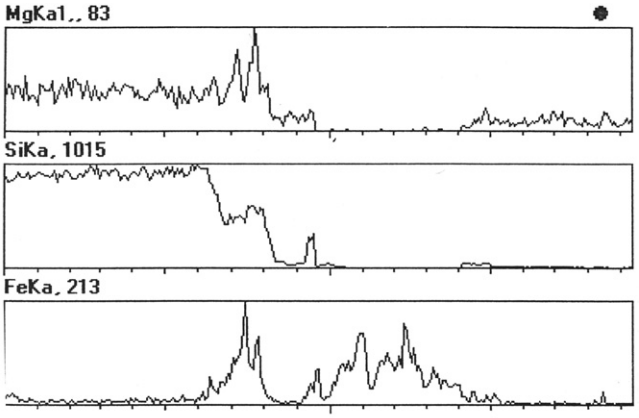

Fig. 7. EDX spectra across the Si_3N_4–cast iron interface show as the yellow line in Fig. 6. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

diffusion evenness activity may be responsible for the sticking observed at the interface.

Because of the obvious limitations of carrying out these experiments in crucibles which were coated with a thin layer of silicon carbide after the vacuum heat-treatment step, further experiments were carried out using dense vacuum heat treated pieces of silicon nitride as described in the second method given in Section 2. These pieces were included with a small block of cast iron in an alumina crucible and melted in the air at 1450 °C for 30 min. The main difference observed in these experiments was that the cast iron pellet separated easily from the silicon nitride piece after melting. Fig. 8 shows the appearance of the silicon nitride piece and the cast iron pellet after melting and both surfaces are relatively unmarked. XRD spectra are shown in Fig. 9 for cast-iron and Fig. 10 for the silicon nitride surfaces which were in contact after melting; the former shows strong peaks of iron plus additional peaks for trace impurities in the cast iron, and the latter shows mainly peaks of α- and β-silicon nitride as expected. The outline of the silicon nitride sample is still clearly visible on the surface of the cast iron, emphasising the cleanness of the break. This shows that significant reaction occurred between the vacuum heat treated Si_3N_4 sample and cast iron melt. After the liquid phase sintering of Si_3N_4 with MgO sintering additive, Mg–Si–O–N glass remains within the grain

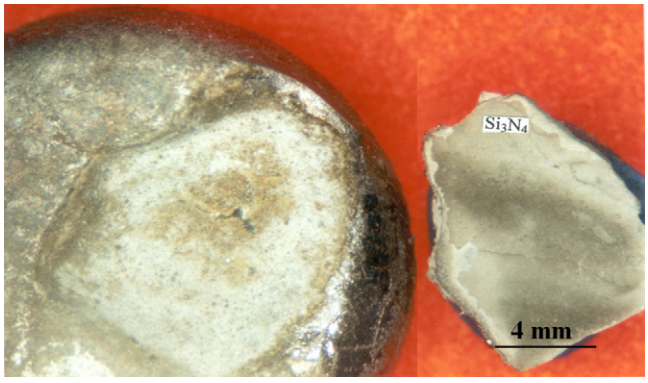

Fig. 8. Vacuum heat treated sample after melting cast-iron.

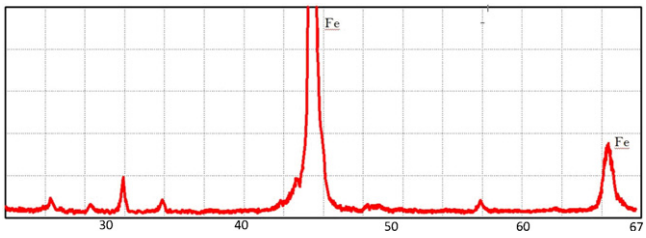

Fig. 9. XRD for cast-iron melting after silicon nitride sample side surface analysis in Fig. 8 left side.

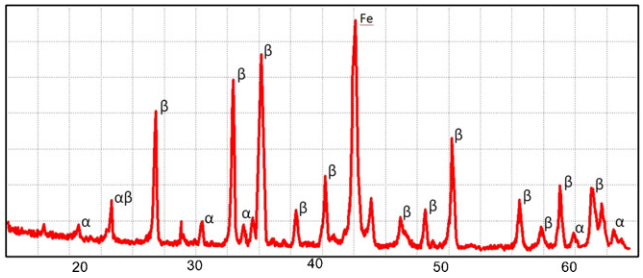

Fig. 10. XRD for silicon nitride sample after cast-iron melting side surface analysis in Fig. 8 right side.

boundaries. Unless these grain boundary glasses are removed, chemical reaction takes place, and Si_3N_4 crucible and cast iron melt stick together as illustrated in Figs. 3 and 4. Hence, it is essential to remove the grain boundary glass by using vacuum heat treatment method, so that MgO densified Si_3N_4 ceramic crucible can be used for the cast iron melting and handling.

4. Conclusions

Results obtained from the melting of cast iron in contact with vacuum heat-treated samples of silicon nitride showed negligible signs of attack, even when the melting was carried out in air. These results are very exciting and suggest that the total removal of glass from the silicon nitride removes the main driving force for the reaction between silicon nitride and cast iron, which is between grain boundary glass in the silicon nitride and slag on the surface of the molten cast iron.

Unfortunately, the technology of producing good quality VHTed materials only came out at the end of the research programme, and there was no time to carry out a detailed study on either the molten cast iron/silicon nitride materials, or the similar samples prepared by melting aluminium and copper in vacuum heat treated crucibles. In the latter cases, silicon nitride crucible was coated with a thin layer of silicon carbide after the VHT process, and therefore also contained residual grain boundary glass within the ceramic. These always showed some signs of attack with interfacial layers developing, even though the SiC layer was quite protective especially at lower temperatures.

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