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Reaction mechanism between porous ferrosilicon nitride ceramic and molten steel

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ABSTRACT

A novel porous ferrosilicon nitride ($Fe_3Si-Si_3N_4$) ceramic sliding gate was prepared and applied in a ladle in a steel mill; it was characterised by X-ray diffraction analysis, scanning electron microscopy, and energy-dispersive spectroscopy. The results showed that after use, the sliding gate consisted of a reaction layer (0–1.5 mm), a transition layer (1.5–2.2 mm), a gradient layer (2.2–20 mm), and an unaltered layer. In the reaction layer, Si_3N_4 is decomposed, and the structure is damaged; in the transition layer, Si_3N_4 is stable, and the structure shows no obvious change; in the gradient layer, Si_3N_4 is oxidised slightly. The reaction mechanism is as follows. The structure of the original porous ferrosilicon nitride resembles a sea urchin, and β-Si_3N_4 columns are bundled together by Fe_3Si. During operation, Fe_3Si reacts with molten steel to form an Fe/FeSi melt, which attacks the structure, whereas Si_3N_4 decomposes to the product N_2(g) [$Si_3N_4(s) + Fe(l) \rightarrow FeSi(l) + N_2(g)$]. N_2(g) forms a high-pressure gas cushion that blocks the molten steel, protecting the inner part of the sliding gate, so Si_3N_4 remains stable in the transition layer. Further inward, Si_3N_4 is oxidised slightly by trace [O] from the molten steel to generate silicon oxynitride. The reaction model was established.

1. Introduction

In recent decades, significant progress has been made in the development of ceramic materials [1]. Because of its good combination of mechanical, thermal, and thermomechanical properties, silicon nitride (Si_3N_4) is one of the most promising materials in this class. In particular, Si_3N_4 has high strength at high temperature, good fracture toughness, good thermal stress resistance resulting from the low coefficient of thermal expansion, a high decomposition temperature, relatively good resistance to oxidation, and excellent thermal shock resistance. Consequently, Si_3N_4 is widely used in structural applications at high temperatures, such as high-speed bearings, gas turbine blades, moulds, machinery parts, and other applications [2–7]. Silicon nitride ceramic products are produced by reaction-bonding or hot-pressing [8]. In the reaction-bonding method, a silicon powder compact is produced and then pre-nitrided at 1423–1473 K in a nitriding furnace. After reaching a certain strength, it can be machined to the required component shape and dimensions, and then further nitrided at 1623–1723 K until it turns entirely to silicon nitride. In the hot-pressing method, silicon nitride powders with a small amount of additives (such as MgO, Al_2O_3, MgF_2, AlF_3, or Fe_2O_3) are hot-pressed at a high pressure and temperature. Products obtained by hot-pressing generally have higher density and better performance than those obtained by reaction-bonding. However, both methods are costly owing to either the cost of the raw silicon powders or the high temperature and high pressure required for the process.

During recent years, a new generation of ceramics has been developed that are expected to provide an alternative to costly Si_3N_4 ceramics. Because they exhibit similar performance to Si_3N_4 and are inexpensive, novel porous ferrosilicon nitride ($Fe_3Si-Si_3N_4$) ceramics are among the most competitive materials in this class. They are prepared by flash combustion of economical FeSi75 powders. Technological expertise on this novel synthetic raw material has developed greatly since its introduction [9–14]. To date, $Fe_3Si-Si_3N_4$ has been used to replace Si_3N_4 in key applications such as large-scale blast furnace tapholes and blast furnace hot metal runners [10–13]. To broaden the range of applications, it is vital to explore the performance of $Fe_3Si-Si_3N_4$ in both the iron-making and steel-making industries.

The ladle sliding nozzle is a device for controlling the flow of

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molten steel and is a crucial component in the modern steel-making industry. The sliding gate is usually made of an alumina–carbon composite, which has good thermal conductivity, superior thermal shock resistance, and good wear resistance. However, the C in Al_2O_3–C materials is easily incorporated into molten steel, which is not ideal for clean and low-carbon steel production. Therefore, low-carbon and even carbon-free refractories are expected to be developed. The application of a porous ferrosilicon nitride ceramic sliding gate is a new attempt. This work focuses on the reaction mechanism between a porous ferrosilicon nitride ceramic and molten steel when the ceramic is used as a ladle sliding gate in a steel mill.

2. Experimental procedures

FeSi75 powders with a particle size of less than 0.074 mm were fed into a flash furnace continuously from the top, where they mixed with high-temperature N_2 flowing upward from the bottom; the FeSi75 powders combusted rapidly in the high-temperature nitrogen as they fell, generating a porous ferrosilicon nitride ceramic (Fe_3Si–Si_3N_4). The purity of N_2 is 99.999 vol.%, and the synthesis temperature is kept below 1823 K. The chemical composition of the FeSi75 powder is listed in Table 1. The physical properties, including the apparent porosity and bulk density, of the Fe_3Si–Si_3N_4 were measured according to ISO 5017-2013, the cold crushing strength was measured according to ISO 8895-2004, and the pore size distribution was determined according to ISO 15901-1-2016.

A ladle sliding gate was fabricated from the prepared porous ferrosilicon nitride ceramic, as shown in Fig. 1, and was used in a steel mill. The steel grades are Q235, Q345, SWRH77B, etc., the capacity of the ladle is 100 tons, and the average casting time is 40 min. The sliding gate was used for two cycles and then cut into block samples for characterisation.

The X-ray diffraction (XRD) pattern was measured on a Rigaku instrument using Cu Kα radiation (wavelength: 1.5415 nm). A scan speed of 5°/min in continuous mode was applied, and the data were collected in a 2θ range of 10–90°. The microstructure was investigated by an environmental scanning electron microscope (SEM) (Quanta FEG450, FEI, America) equipped with an energy-dispersive spectroscope (EDS). A gold coating was used to make the sample electrically conductive enough for SEM investigation after being polished.

3. Results

3.1. Phase and microstructure of porous ferrosilicon nitride ceramic

The XRD pattern of the porous ferrosilicon nitride ceramic prepared by flash combustion is shown in Fig. 2. The ceramic is composed of β-Si_3N_4, α-Si_3N_4, and Fe_3Si, where β-Si_3N_4 is the major phase, and α-Si_3N_4 and Fe_3Si are minor phases. FeSi75 is nitrided into β-Si_3N_4 and α-Si_3N_4, whereas Fe is present in the form of Fe_3Si.

The microstructure of the porous ferrosilicon nitride ceramic prepared by flash combustion is shown in Fig. 3. As shown in Fig. 3(a), the ceramic is composed of sea-urchin-like units that include two typical morphologies, which appear as grey hexagonal prisms and bright white spheres. According to the XRD results, the grey hexagonal prism-like crystals are β-Si_3N_4, which has sharp edges and clean surfaces; the bright white spheres are mainly Fe_3Si. Fe_3Si acts as a core to fix and bind β-Si_3N_4 columns together into structures resembling sea urchins, and the β-Si_3N_4 columns overlap each other so that each sea urchin structure overlaps to form a porous block.

Table 1
Chemical composition of FeSi75 powder (mass fraction, wt.%).

Item	Si	Fe	Al	Cr	C	S	P
Result	75.80	22.03	1.66	0.35	0.12	0.01	0.03

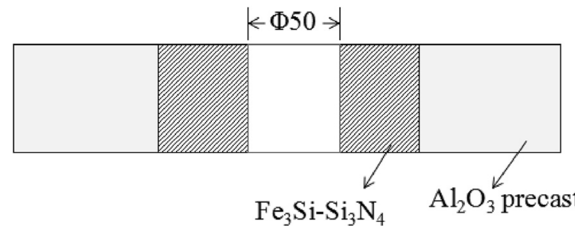

Fig. 1. Schematic diagram of the porous ferrosilicon nitride ceramic sliding gate.

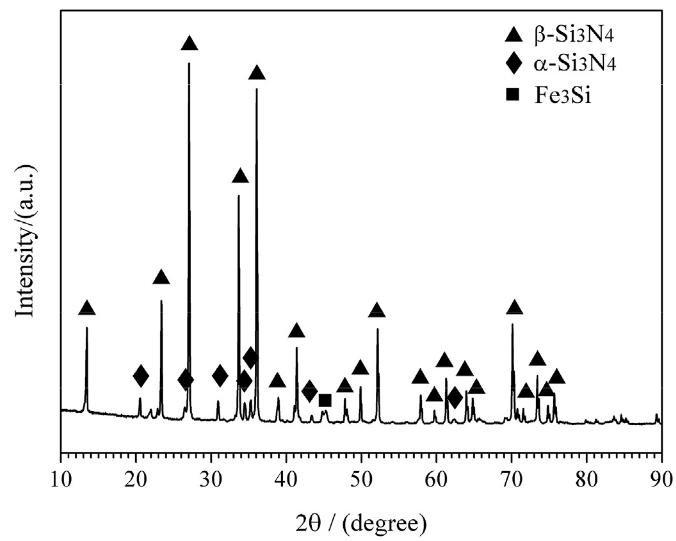

Fig. 2. XRD pattern of porous ferrosilicon nitride ceramic prepared by flash combustion.

3.2. Physical properties of porous ferrosilicon nitride ceramic

The physical properties of the porous ferrosilicon nitride ceramic produced by nitridation of FeSi75 powders are as flows. The apparent porosity is 54.4%, and the bulk density is 1.56 g/cm^3, indicating that the product is a porous material. Further, the average pore size is 10.4 μm, and the <1 μm pore volume ratio is 3.18%. The cold crushing strength is 90 MPa, which is promising for industrial steel-making applications.

3.3. Microstructure of the porous ferrosilicon nitride ceramic sliding gate after use

Fig. 4 shows the morphology of the porous ferrosilicon nitride ceramic sliding gate after use (from the hot face). The morphology changes with the distance from the hot face, and its structure consists of a reaction layer (I: 0–1.5 mm), a transition layer (II: 1.5–2.2 mm), a gradient layer (III: 2.2–20 mm), and an unaltered layer. To exploration the morphology in more detail, the microstructures of each layer were observed further.

Fig. 5 shows the microstructures of various layers of the porous ferrosilicon nitride ceramic sliding gate after use. As shown in