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Research on High Performance Fe_3Si-Si_3N_4-SiC Composite Used for Blast Furnace

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Abstract: Excellent Fe_3Si-Si_3N_4-SiC composites were successfully prepared with FeSi75 and SiC as main starting materials by nitridation reaction(at 1300°C for 8Hrs). The material properties were studied; the ferrosilicon nitridation mechanism was analyzed through chemical thermodynamics; phase composition, microstructure, corrosion resistance of products were also investigated. The results are shown that the comprehensive properties of Fe_3Si-Si_3N_4-SiC are outstanding. The nitridation products are fiber-like α-Si_3N_4 and rod-like β-Si_3N_4, which makes better mechanical behavior due to fiber reinforcement; a great deal of Fe_3Si intermetallic compounds uniformly distribute in matrix, which is one of the products of Fe-Si nitridation and as a plastic phase forming in grain boundary optimizes the performance of products. Chemical thermodynamic analysis is shown that the fiber-like α-Si_3N_4 is formed by SiO(g) and N_2(g) reaction which also increases the rate of nitridation. Fe_3Si-Si_3N_4-SiC material has high corrosion resistance. Now it has been successfully applied to one 2000M^3 domestic steel plant, the blast furnace operation goes well.

Keywords: Fe_3Si-Si_3N_4-SiC composite, nitridation mechanism, plastic phase Fe_3Si, corrosion resistance, blast furnace.

1. INTRODUCTION

Due to their excellent properties such as high temperature strength, low thermal expansion coefficient, high refractoriness under load and good chemical stability, silicon nitride bonded silicon carbide (Si_3N_4-SiC) materials have been used increasingly as a refractory in blast furnaces [1-10]. However, Si_3N_4-SiC possesses some weaknesses, such as great brittleness, poor thermal shock resistance and bad thermal conductivity, which restricts its further application. In order to farther improve properties of the material, a metallic plastic phase Fe_3Si was introduced into the grain boundary of Si_3N_4-SiC composite. For the sake of compounding metal with ceramic aggregates, preparation of Fe_3Si-Si_3N_4-SiC composites by nitriding ferrosilicon alloy based on Si_3N_4-SiC is proposed. Si_3N_4-SiC materials with uniformly dispersed metallic plastic phase is expected to have higher thermal conductivity and thermal shock resistance in favour of enhancing blast furnace cooling rate. At present, the research on Fe_3Si-Si_3N_4-SiC materials is rarely reported in domestic and oversea research [11-14], this research hopes to provide some useful reference.

2. EXPERIMENT

2.1. Raw Materials Preparation

The starting materials used in this study were SiC (5 ~ 3 mm, 3 ~ 1 mm, 1.5 ~ 0 mm, <0.088 mm.), ferrosilicon alloy powder (Namely FeSi75) (<0.088 mm,), Si_3N_4 (<0.088 mm, Si_3N_4 ≥ 97wt%), thermosetting resins and high purity nitrogen (φ (N_2) ≥ 99.99%). The chemical composition of FeSi75 and SiC was listed in Table **1**.

Table 1. Chemical Composition of Main Materials wt %

Material	SiC	Fe_2O_3	Al_2O_3	Si	Fe	Al	F.C
SiC	99.05	0.23	0.55	/	/	/	0.01
FeSi75	/	/	/	74.6	24.6	0.5	/

2.2. Experimental Formula

SiC and Si_3N_4 have different properties at high temperature. In order to maintain their virtues, some synthesized Si_3N_4 powder as starting materials was added to samples directly, which can not only increase the content of Si_3N_4 but also compare with Si_3N_4 generated through reaction, so 8wt% Si_3N_4 powder was added to samples uniformly.

The composition of samples was shown in Table **2**. Ferrosilicon powder content of samples was 12 wt%; the corresponding sample number was 1 #. 0 # was a blank sample without ferrosilicon. Thermosetting resin was binder.

2.3. Experimental Procedure

Specimen preparation can proceed as follows: after ball milling, mixing and 24 hours aging, the mixture of raw ingredients was pressed into green bodies by 1,000 tons of moulding press. The green bodies were fully dried, and then fired in flowing N_2 atmosphere (maintained at low positive pressure) in a furnace at 1300°C for 8 hours.

Physical properties such as bulk density, apparent porosity, cold crushing strength and high temperature flexural strength of the nitridation products were measured by standard method(GB/T 2997-2000, GB/T 5072-2008, GB/T 3002-2004). The phase compositions of products were analyzed by X-ray diffraction (Rigaku D/MAX-RB), microstructures and micro-components of the products were examined by scanning electron microscope (PHILIPS XL30 type and Leica S440i) and

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Table 2. Composition of Samples wt %

Sample Number	SiC				Ferrosilicon	Si_3N_4	Additive
	5-3 mm	3-1 mm	1.5-0 mm	50μm	74μm	50μm	83μm
0	10	35	20	24	0	8	3
1	10	35	20	12	12	8	3

energy dispersive spectroscopy (EDS). The resistances of nitridation products to alkali corrosion, slag attack and hot metal penetration were tested by Research and Development Center of WuHan Iron and Steel Corp (abbreviation: WISGDRC).

3. RESULTS AND DISCUSSION

3.1. Performances of Fe_3Si-Si_3N_4-SiC Products

Physical properties of products are shown in Table **3**.

From the above results, the experimental prepared Fe_3Si-Si_3N_4-SiC products have excellent comprehensive performance. The composites contained metal plastic phase are better evidently than blank sample(0#). It means that metal plastic phase in Si_3N_4-SiC composite plays an important role for improving the performance of materials. Thus preparation of Fe_3Si-Si_3N_4-SiC composites by nitriding ferrosilicon is feasible. In order to give further explanation on the outstanding properties of Fe_3Si-Si_3N_4-SiC composites, their phase composition and microstructure need to be further analyzed.

3.2. Phase Composition of Fe_3Si-Si_3N_4-SiC Products

Phase composition of FeSi75 alloy powder and nitrided products were examined by XRD, the result is shown in Fig. (**1**). It shows that the main phases of FeSi75 are elemental Si and $FeSi_2$, which is consistent with Fe-Si binary system equilibrium phase diagram. SiC, α-Si_3N_4, β-Si_3N_4 and Fe_3Si are the main phases of Fe_3Si-Si_3N_4-SiC. α-Si_3N_4 is the primary nitridation reaction product, conversely β-Si_3N_4 is less, both of them are binder phases. Fe can not be nitridized [15] which finally exists as the form of Fe_3Si intermetallic compound.

3.3. Microstructure of Fe_3Si-Si_3N_4-SiC Products

Microstructure of Fe_3Si-Si_3N_4-SiC composites is shown in Fig. (**2**).

It reveals that the micro-morphologies of products are fiber-like and rod-like. Combined with the analysis of XRD, these substances are Si_3N_4 as binder phases. All the above microscopic appearances are the typical morphologies of Si_3N_4-SiC. So the ferrosilicon nitridation is similar to the Si nitridation. Generally, α-Si_3N_4 is fiber-like, while β-Si_3N_4 is rod-like [16]. Due to the existence of fiber-reinforced Si_3N_4 which makes crack deflection and healing, Fe_3Si-Si_3N_4-SiC composites have excellent mechanical behavior (shown in Table **3**). As binder phases, Si_3N_4 makes Fe_3Si-Si_3N_4-SiC composites dense.

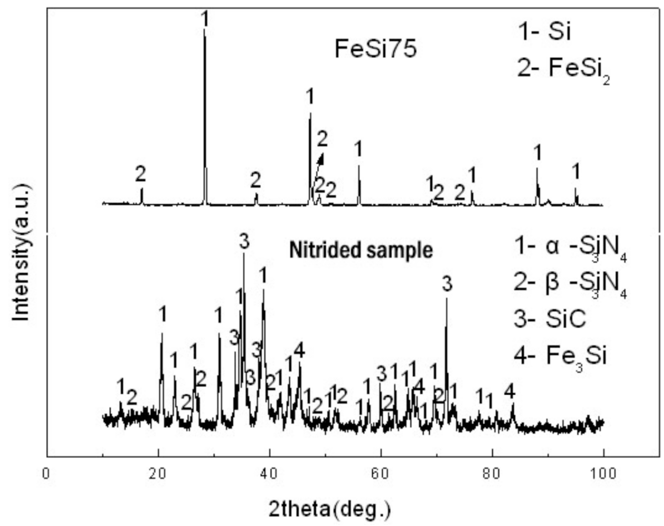

Fig. (1). XRD patterns of FeSi75 and specimen nitridized at 1 300 °C.

According to SEM and EDS analysis (shown in Fig. **3**), the gray areas (represented by A) with well-preserved morphologies in Fig. (**3**) are SiC particles because of their low reactivity. While the gray areas (represented by B) with irregular morphologies are Si_3N_4 added as raw material and some produced by nitridation reaction. There are many white bright substances distributing in matrix (Fig. **3**), which is proved to be ferrosilicon intermetallic compounds Fe_3Si by EDS analysis (Fig. **3**). Those Fe_3Si substances are spherical and less than 10μm because of their bad wettability with Si_3N_4. There is no obvious residual Si in matrix. The one of nitridation products—ferrosilicon intermetallic compound Fe_3Si is as a plastic phase

Table 3. Properties of Fe_3Si-Si_3N_4-SiC Products

Sample Number / Test items	0#	1#
Apparent porosity (%)	12.3	9.7
Bulk density (g/cm^3)	2.75	2.87
Cold crushing strength (MPa)	114	181
High temperature flexural strength at 1400 °C (MPa)	16.79	27.43
High temperature flexural strength at 1200°C (MPa)	18.00	36.33
High temperature flexural strength at 1000°C (MPa)	23.44	39.76

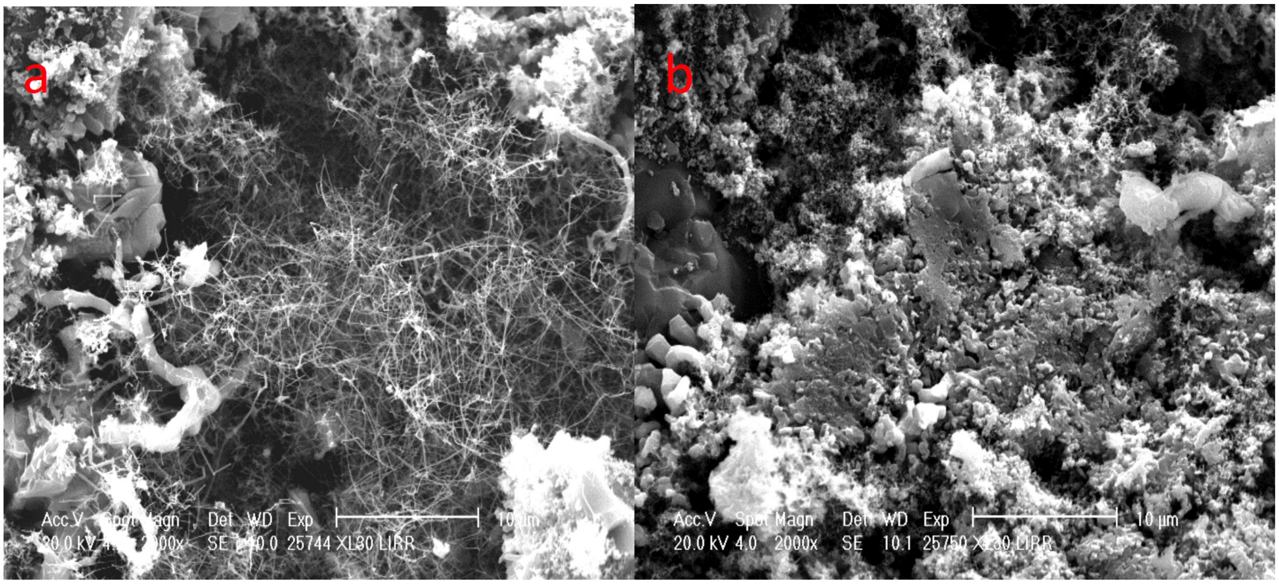

Fig. (2). SEM photographs of Fe_3Si-Si_3N_4-SiC composites.

to improve greatly the properties of products as shown in Table **3**. The existence of Fe_3Si can enhance the thermal conductivity of Fe_3Si-Si_3N_4-SiC composites and realize the fast cooling of blast furnace.

3.4. Chemical Thermodynamic Analysis of FeSi75 Nitridation

The flowing N_2 (φ (N_2) $\geq$ 99.99%) has trace O_2 and green bodies are put in saggers without vacuum-pumping, so there is still a small amount of O_2 in the furnace. When green bodies fired in flowing N_2 atmosphere (maintained at low positive pressure) in the furnace at 1300°C for 8 hours, some reactions which may occur in this condition have been plotted as $\Delta G_T^{\ominus}$.~T relationship in Fig. (**4**) to show their reation order [17, 18]. Because the FeSi75 contains two phases : Si and $FeSi_2$, FeSi75 nitridation can be divided into two parts: Si nitridation and $FeSi_2$ nitridation.

It can be seen from Fig. (**4**) that the reaction order is SiO_2 forming firstly, then to form SiO(g)→(Si_3N_4+Fe_3Si)→Si_3N_4 as the oxygen partial pressure decreases gradually. Two points must be paid attention: (a) When oxygen partial presure P_{O_2} in the system is reduced by forming SiO_2 to a low value, SiO(g) can be formed through follows reaction:

$$3Si(s) + 1.5O_2(g) = 3SiO(g) \quad (1)$$

This reaction will create a condition (P_{O_2} reducing farther) for realization of Si direct nitriding and prepares the raw material for nitridation farther as Reaction (2) and (3).

$$3Si(s) + 2N_2(g) = Si_3N_4(s) \quad (2)$$

$$3SiO(g) + 2N_2(g) = Si_3N_4(s) + 1.5O_2(g) \quad (3)$$

Actually, Reaction (2) can be got from Reaction (1) plus (3). It means Si_3N_4 can be formed by two formats: direct nitridation of Si through Reaction (2) and indirect nitridation through Reaction (1) and (3). Moreover the rate of the latter reaction will be higher than former, because the indirect nitridation contains a gas-gas reaction which increases the reaction rate, so the trace O_2 is catalyst. Also the product α-Si_3N_4 of the latter reaction becomes fiber-like [19-21], because it is separate out from gaseous.

(b) Si_3N_4 and Fe_3Si can be generated by nitriding $FeSi_2$ at very low P_{O_2} through the reaction as follows:

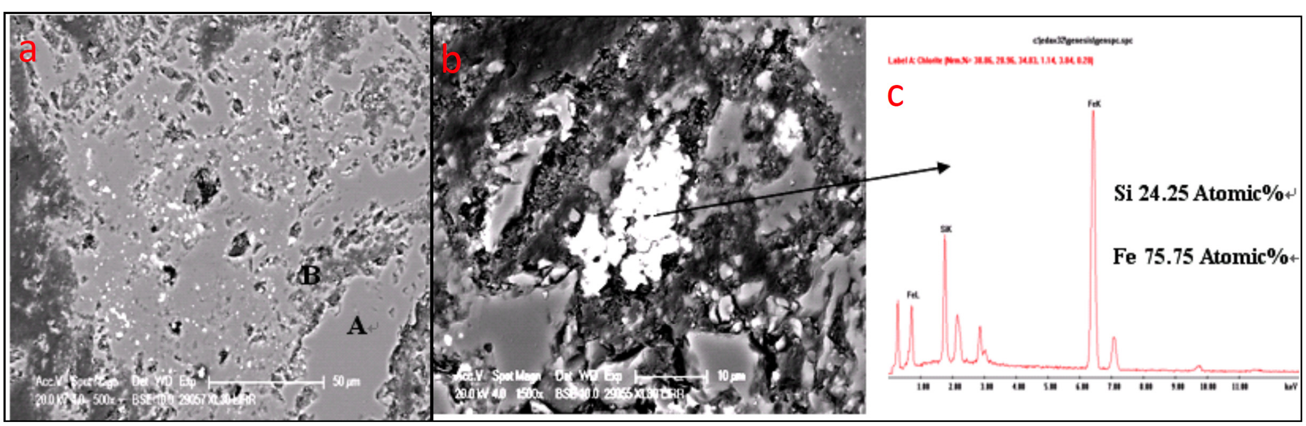

Fig. (3). SEM photographs and EDS analysis of Fe_3Si-Si_3N_4-SiC composites.

$9/5FeSi_2+2N_2(g)=3/5Fe_3Si+Si_3N_4(s)$ (4)

It is clearly from Fig. (**4**) that this reaction is easier to occur than Reaction (2).

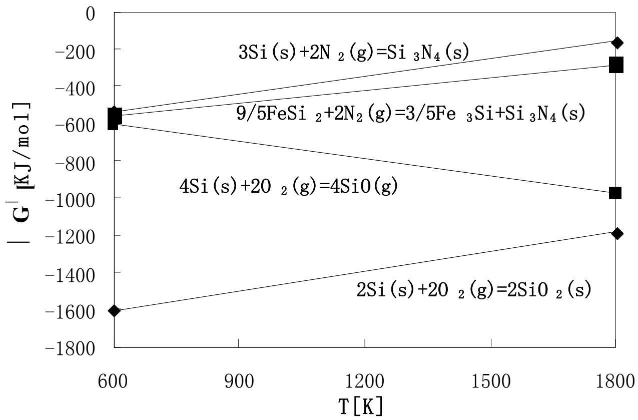

Fig. (4). Relationship between free energy ΔG_T^{Θ} and temperature of the reactions.

3.5. Existent Form of Fe

There are various Fe-Si intermetallic compounds. The following reaction may take place in nitridation process(listed in Table **4**).

We can see from Table 4. that only Reaction (8)(9)(10) can occur at 1573 K. It means the products of nitriding ferrosilicon are Fe_3Si and $Si_3N_4(s)$. Fe_3Si plays a role of plastic phase in the composite, which highly improves the performance of Fe_3Si-Si_3N_4-SiC composites.

3.6. Corrosion Resistance Tests

Blast furnace lining brick plays an important role for the blast furnace to obtain a long lining life. In the ironmaking process, the refractory lining is not only exposed to high temperature corrosion, more importantly, it will suffer from chemical corrosion of molten slag, molten iron and alkali metal oxides. Obviously only testing conventional properties of refractories cannot meet the performance requirements of blast furnace under working conditions, so operational performance of the refractory materials used for blast furnace needs to be detected. In this experiment, the resistances of Fe_3Si-Si_3N_4-SiC materials to alkali corrosion, slag attack and hot metal penetration were commissioned to test by Research and Development Center of WuHan Iron and Steel Corp (abbreviation: WISGDRC) which is a professional testing center of refractory material in China.

According to the national standard test method(GB/T 14983—2008, GB/T 8931—2007, GB/T 24201—2009)[23], the corrosion resistance of Fe_3Si-Si_3N_4-SiC materials is measured, the results are listed in Table 5. It indicates that the corrosion resistance of Fe_3Si-Si_3N_4-SiC materials is excellent.

During ironmaking process, the surface of Si_3N_4 and SiC particles is likely to form SiO_2 oxidation film when Si_3N_4-SiC materials are applied to blast furnace. These SiO_2 will react with alkali metal oxides (K_2O, Na_2O) and molten slag (i.e. CaO, MgO) in blast furnace at high temperature and form low-melting-point eutectics, which would reduce materials high-temperature strength, cause materials volume expansion or spalling and finally result in lining materials failure [24]. Hot metal drops along the furnace wall and make the refractory erosion and wear.

Due to the uniformly dispersed metallic plastic phase Fe_3Si, Fe_3Si-Si_3N_4-SiC composites have high thermal conductivity, which will benefit blast furnace cooling. When brick linings temperature is lowered, the molten slag attack, alkali corrosion, hot metal penetration will be slowed down and even all the erosive substance becomes solidified, so reactions between erosive substance and refractories are stopped. Moreover the intermetallic compound Fe_3Si is preferentially oxidized in comparison with Si_3N_4 and SiC, so Si_3N_4 and SiC can be better reserved to resist corrosion [25, 26]. Besides, Fe_3Si-Si_3N_4-SiC composites are dense so the erosive substance is difficult to penetrate into refractory. Therefore, the corrosion resistance of Fe_3Si-Si_3N_4-SiC materials is excellent.

3.7. Industrial Trial

Based on the excellent properties of Fe_3Si-Si_3N_4-SiC materials, they have been successfully applied to one $2000M^3$ blast furnace installed in Sep.2009 in a domestic steel plant. So far, the blast furnace operates well. It shows that Fe-Si_3N_4-SiC materials are outstanding refractory materials for blast furnace.

CONCLUSIONS

(1) Excellent Fe_3Si-Si_3N_4-SiC composites are successfully prepared with FeSi75, Si_3N_4 and SiC as main starting materials by nitridation reaction (at 1300°C for 8Hrs).

Table 4. Changes of Gibbs Free Energy in Nitridation of Ferrosilicon Intermetallic Compounds [22]

Reaction	ΔG_T^{Θ} (J • mol^{-1})	$T_{conversion}$(K)	No.
$3Fe_3Si+2N_2(g)\rightarrow Si_3N_4(s)+9Fe$	$\Delta G_T^{\Theta}=-204\ 208+657.396T$	310.6	(5)
$Fe_5Si_3+2N_2(g)\rightarrow Si_3N_4(s)+5Fe$	$\Delta G_T^{\Theta}=-496\ 704+340.961T$	1456.8	(6)
$3FeSi+2N_2(g)\rightarrow Si_3N_4(s)+3Fe$	$\Delta G_T^{\Theta}=-507\ 628+377.967T$	1343.0	(7)
$9Fe_5Si_3+8N_2(g)\rightarrow 4Si_3N_4(s)+15Fe_3Si$	$\Delta G_T^{\Theta}=-3\ 449\ 298-218.333T$	15798.0	(8)
$9FeSi+4N_2(g)\rightarrow 2Si_3N_4(s)+3Fe_3Si$	$\Delta G_T^{\Theta}=-1\ 318\ 676+476.507T$	2767.4	(9)
$9FeSi_2+10N_2(g)\rightarrow 5Si_3N_4(s)+3Fe_3Si$	$\Delta G_T^{\Theta}=-3\ 467\ 760+1131.8T$	3063.9	(10)

Table 5. Test Results of Corrosion Resistance from WISGDRC

Alkali resistance of Fe_3Si-Si_3N_4-SiC	Original cold crushing strength	MPa	120.59
	Post cold crushing strength	MPa	132.37
	Change rate of strength	%	+9.77
	Change rate of volume	%	0.52
	Sample appearance		No crack
	Evaluation		Excellent
Slag corrosion rate of test sample	weight change	%	5.98
Hot metal corrosion rate of test sample	weight change	%	0.53

(2) The main phases of Fe_3Si-Si_3N_4-SiC composite are SiC、α-Si_3N_4、β-Si_3N_4 and Fe_3Si. The morphologies of α-Si_3N_4、β-Si_3N_4 are fiber-like and rod-like and the intermetallic compund Fe_3Si distributes uniformly in grain boundary.

(3) Chemical thermodynamic anlysis is shown that Si and FeSi75 can be nitridized to form Si_3N_4 and Fe_3Si. The processing of nitridation incluing two ways, direct nitriding and indirect nitriding. In the latter format SiO(g) is a middle product, which increases the rate of reaction and makes the product α-Si_3N_4 becomes fiber-like to improve greatly the performance of composite.

(4) Ferrosilicon alloy nitridation is easier than Si and the product Fe_3Si plays a role of plastic phase which also improves the mechanical properties of composite.

(5) Fe_3Si-Si_3N_4-SiC material has high corrosion resistance. Now the Fe_3Si-Si_3N_4-SiC composites have been successfully applied to one $2000M^3$ domestic steel plant, the blast furnace operation goes well.

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