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Effect of dilution and additive on direct nitridation of ferrosilicon

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Abstract

Ferrosilicon nitrides were fabricated by direct nitridation of ferrosilicon, and the effects of ferrosilicon nitride and α-Si_3N_4 dilution and ammonium chloride (NH_4Cl) additive on characteristics of the nitride products were investigated. The phases of final nitride products consist of α-Si_3N_4, β-Si_3N_4 and iron silicides with various compositions. Long columnar crystals, equiaxed crystals and flower-like crystals were observed in the final products, and fiber or whisker-like crystals with a low degree of crystallization were also found in the nitrides. Both the diluents and additive can improve the nitridation degree, but only the additive can increase the content of α-Si_3N_4 in the nitride products. As a diluent, ferrosilicon nitride can decrease the cost of nitride products, and increase their nitridation degree more than α-Si_3N_4. NH_4Cl made the products fluffy and expansive, while the dimensions of the compact without addition of NH_4Cl remain unchanged during nitridation.

Keywords: Direct nitridation; Ferrosilicon nitrides; Dilution; Additive

1. Introduction

Silicon nitride (Si_3N_4) based ceramics are used in a variety of structural applications such as engine and turbine component, heat exchanger, pump seal materials, ball bearings, cutting tools, corrosion-resistant protective jackets for thermocouples, high-temperature filters for corrosive liquids and so on, owing to their excellent mechanical properties at both room and elevated temperatures, high resistance to thermal shock and chemical attack, high erosion and corrosion resistance, high crack resistance, high strength retention at elevated temperatures, outstanding creep resistance and very good tribological properties.[1–4] Silicon nitride powders can be prepared by various processes, which determine their engineering performance and, eventually, application area.[5] Among the known methods for producing silicon nitride, the direct nitridation of silicon has been recognized as one of the commercial methods for mass production of silicon nitride containing predominantly the α-form. This process is an inexpensive option for applications in which metal impurities, originating from silicon, contained in the product silicon nitride can be tolerated.[3]

The demands for Si_3N_4 powders as a raw material are constantly growing, therefore simpler and cheaper methods for its production are required.[6] Using cheaper raw materials instead of expensive pure silicon is considered to be a feasible way, since the use of a cheaper substitute allows one to significantly decrease the prime cost of the produced silicon nitride powders. Numerous researches and tests[4,7–11] have shown that silicon nitride can be obtained from commercial ferrosilicon powders as well as from a dust fraction which arises when ferrosilicon is milled (RF Patent No. 2257338). Removal of iron and accompanying impurities from a raw material can be achieved by acid enrichment technique.[10,11] On the other hand, ferrosilicon nitrides themselves are widely used in tap-hole and gutter materials for the blast furnace as a refractory as well as used in smelting corrosion-resistant steel as alloying material.[2,12]

Current reports about synthesis of silicon nitride and ferrosilicon nitride from ferrosilicon are mainly focused on SHS (Self-propagating High-temperature Synthesis).[4,5,7–12] However, the process of SHS is hard to control. On the other hand, direct nitridation of ferrosilicon can be a simple, common and commercialized method to synthesize silicon nitride and related materials. But, study of this method was rarely reported.

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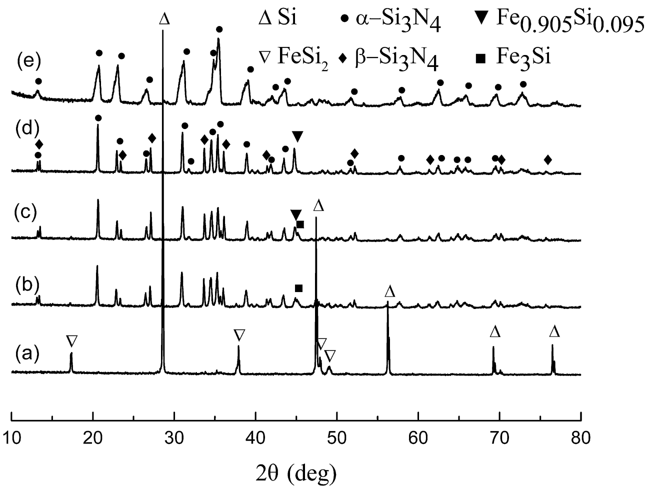

Fig. 1. X-ray diffraction patterns of (a) ferrosilicon and the nitride products formed by direct nitridation of (b) ferrosilicon, (c) ferrosilicon with 20 wt% ferrosilicon nitride, (d) ferrosilicon with 20 wt% ferrosilicon nitride and 2 wt% NH_4Cl and (e) the fiber-like nitride products.

Table 1
Compositions of the starting powder mixtures.

Sample	FS75 (wt%)	Dilution (wt%)*	NH_4Cl (wt%)
0	100	0	0
1	90	10	0
2	80	20	0
3	70	30	0
4	60	40	0
5	50	50	0
6	40	60	0
7	98	0	2
8	96	0	4
9	94	0	6
10	92	0	8
11	90	0	10
12	88	0	12
13	86	0	14
14	84	0	16
15	82	0	18
16	80	0	20

* The content of two kinds of diluents was same in two different diluting process.

In this work, feasibility of fabricating Si_3N_4-related materials by direct nitridation of ferrosilicon was preliminarily confirmed, and the phase composition and morphology of nitride products as well as the effects of dilution and additive were investigated.

2. Experimental procedure

2.1. Raw materials

The FS 75 ferrosilicon with a particle size less than 75 μm and a silicon content of 75% (Ningxia Puhua Metallurgical Products Co., Ltd., Ningxia, China) was used as the main raw material while the self-made ferrosilicon nitride (Nitrogen content ≈30%) and Si_3N_4 powders (α-Si_3N_4 > 93%, D_{50} < 0.5 μm, F_{Si} < 0.8%, Beijing Tsinghua Unisplendor Founder High-Tech Ceramics Co., Ltd., Beijing, China) served as diluents. X-ray phase analysis showed that the ferrosilicon alloy was a two-phase material consisting of silicon and high-temperature lebeauite $FeSi_2$ (Fig. 1 (a)). NH_4Cl (99.5 wt% purity, Hubei ShuangHuan Science and Technology Co., Ltd., Yingcheng, China) was used as additive.

2.2. Preparation process

Starting powder mixtures were mixed using FS 75, self-made ferrosilicon nitride, silicon nitride and NH_4Cl additive according to the proportions listed in Table 1. The homogeneously blended mixtures of ferrosilicon and two kinds of diluents were prepared as bar-like samples by mold pressing, the same as mixtures of ferrosilicon and additive. Before nitridation, the samples were dried at a temperature of 150–200 °C to remove moisture and volatile impurities. The as-prepared green samples were laid separately in a graphite crucible which is 350 mm high and 180 mm in diameter, then placed into the sintering furnace (ECM Industrial Furnaces, 46, rue Jean Vaujany-TECHNISUD-38029 GRENOBLE CEDEX 2-FRANCE) for subsequent nitriding. For security considerations, the nitriding process was performed in a pressure range from 0.03 MPa to 0.05 MPa with nitrogen gas (99.999% purity, Xi'an Weiguang Gas Co., Ltd., Xi'an, China) as the atmosphere. Before filled with high-purity nitrogen, the furnace was hermetically vacuumized. The temperature was measured by a thermocouple inserted in the furnace. After nitridation, the samples were cooled down in nitrogen and then extracted from the furnace for further investigations.

2.3. Characterization

Morphology and EDS analysis of the nitride products was investigated by scanning electron microscope (SEM, S-4700, Hitachi, Japan). The phase compositions of reaction products were determined by an X-ray diffractometer (Cu Kα, D8 ADVANCE, Bruker, Germany). The phase content of α- and β-Si_3N_4 in the products was calculated according to the method proposed by Zhou.[13] The nitridation degree was defined as the ratio of the nitrided silicon amount to the silicon amount in raw ferrosilicon. Thermo gravimetry and differential scanning calorimetry (TG–DSC) were performed in N_2 at a heating rate of 10 °C/min using a high-temperature synchronous thermal analyzer (STA429CD/3/7, Netzsch Co., Germany).

3. Results and discussion

3.1. Effect of dilution

According to the results of X-ray phase analysis, the product by direct nitridation of ferrosilicon is a composite of silicon nitride and iron silicide when nitridation is relatively complete, while free silicon is present when nitridation is incomplete (Figs. 1 and 2). The SEM micrographs of products by direct nitridation of pure ferrosilicon show that a variety of morphologies are present which include acicular, prismy and flower-like lamellar crystals (Fig. 3). Diversity of the morphology reveals