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Carbothermic reduction synthesis of Ti(C, N) powder in the presence of molten salt

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Abstract

In the presence of sodium chloride (NaCl), Ti(C, N) powder was successfully obtained by the carbothermal reduction of TiO_2 in lab-scale experiments. The effects of NaCl addition and reaction temperature on the formation of the powder were studied in the temperature range of 1100–1600 °C, the reaction time used in all cases was 3 h. The final powder was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and electron probe microanalysis (EPMA). The results indicated that addition of NaCl played a facilitating role in the formation process of Ti(C, N). Ti(C, N) was detected at 1100–1200 °C, and the yield of powder was purer at about 1300 °C when 10 wt.% NaCl was added. The as-prepared Ti(C, N) was uniform in shape and the particle size was about 5–8 μm. With increasing temperature, the residual carbon content in the products decreased but the degree of oxidation increased at temperatures above 1300 °C. The possible mechanism involved in the reactions was discussed.

Keywords: Ti(C, N); Molten salt; Carbothermic reduction

1. Introduction

Titanium carbonitride, Ti(C, N), has been of practical interest because of its unique and outstanding combination of physical properties such as high melting point, high hardness, good thermal and chemical stability, excellent electrical and thermal conductivity and metallic luster appearance [1]. It is more stable against molten steel than TiC at high temperatures [2], which make it has wide applications such as coatings [3–5], cutting tools [6,7], cermets [8,9].

Various methods of synthesizing Ti(C, N) exist. Ti(C, N) is conventionally prepared from TiN–TiC powder blends through high-temperature solid-state diffusion in a temperature range between 1700 °C and 1800 °C [10], or by self-propagating high-temperature synthesis (SHS) method by igniting a using titanium and carbon mixture in gaseous nitrogen [11,12]. Slifirski and Teyssandier [13] obtained titanium carbonitride by chemical vapor deposition from organometallic precursor in the temperature range of 450–800 °C. Aleksandrovskii et al. [14] synthesized Ti(C, N) by reduction of CCl_4–$TiCl_4$ mixtures in argon or nitrogen atmosphere using magnesium. Angerera et al. [15] prepared nanostructured titanium carbonitride powders using spark-plasma-sintering (SPS) method at 1600 and 1800 °C (sintering time = 1 min). Alekseev et al. [16] synthesized titanium carbonitride ultra-fine powders from titanium hydride in arc discharge plasma jet of nitrogen at high temperatures. Pierson [17] reported the synthesis of Ti(C, N) using amines as a source of carbon and nitrogen at temperatures of 550–650 °C. Other methods were also adopted such as pyrolysis of poly(titanylcarbodiimide) [18], hot metal [19] and ion implantation [20]. However, most of the methods available for the synthesis of Ti(C, N) require complex manipulation procedures, complicated synthetic steps, expensive equipments, high temperatures and long holding times. Therefore, a convenient and economical route for producing Ti(C, N) is desirable.

Carbothermic reduction is an economical method for synthesizing carbides, nitrides and carbonitrides [21]. This method relies on the supply of inexpensive raw materials and is capable of producing Ti(C, N) with a range of N and C content. This technique, therefore, can be adopted in processing a

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functionally gradient ceramic material, with properties controlled in a range those of between TiC and TiN by adjusting C and N potentials to achieve the required concentration gradient of C and N [22]. But the limitations of this technique include the presence of residual oxides and the use of excess carbon, high combustion temperature, which make it unattractive. Molten salt method is a new material synthesis method [23] that offers the possibility of overcoming these limitations, it can increase the diffusing rates of the reaction ions and thus greatly reduce the synthetic temperature, which make it easier to control the morphology of the particles produced.

Nersisyan et al. synthesized WC powder using WO_3, Mg, C and sodium salts (NaCl, Na_2CO_3) as raw materials and found that the activation energy for the formation of WC in the molten salts was at a comparative low value of 35 kJ/mol [24]. In this paper, the combination of carbothermic reduction technique and molten salt method is applied to synthesize Ti(C, N) powder using TiO_2, carbon black and molten salt (NaCl) as raw materials, which are readily attainable.

2. Experimental procedure

TiO_2 (>98.5% purity, anatase type, $D_{v50} = 1.18\ \mu m$), Carbon black (>98% purity, 40 nm) and NaCl (>99.8% purity) were used as the starting materials.

The molar ratio of [carbon]/[TiO_2] used was 2 in line with the stoichiometry of the following reaction

$$TiO_2(s) + (3-x)C(s) + \tfrac{x}{2}N_2(g) \rightarrow 2CO(g) + Ti(C_{1-x}N_x)(s) \quad (1)$$

The weight ratios of TiO_2 to carbon black to NaCl were 79.87:24.02:y, where $y = 0$, 5.195, 10.389, 15.584, 20.778 and 31.167. Six types of powder mixtures were prepared by dry ball milling (using alumina balls) in a ball mill for 40 min. The mixtures were then die-pressed into cylindrical specimens with diameter and height dimensions of about 20 mm under a pressure of 100 MPa. The green cylinders were buried in carbon granules (0.5–2 mm) in a sagger and heated in a furnace to temperatures of 1100–1600 °C and then soaked for 3 h (shown in Fig. 1).

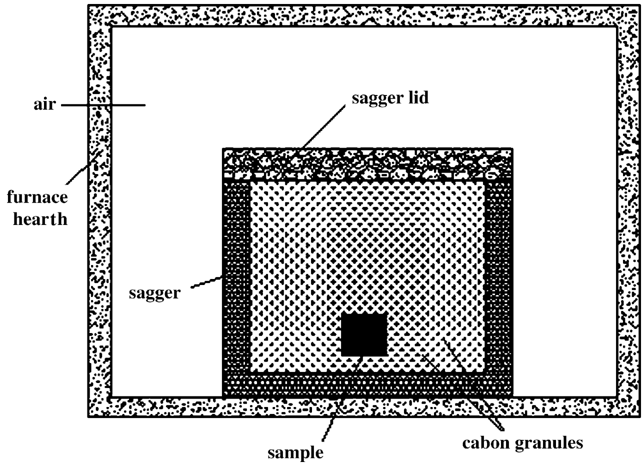

Fig. 1. Schematic diagram of preparation process.

The weight percentage of residual free carbon content in the final powders was determined by burn off experiment, which was conducted in air at 650 °C for 2 h. It was calculated according to $(W_1 - W_2)/W_1$, where W_1 and W_2 are the powder weight before and after burn off, respectively.

In order to identify the exact amount of NaCl in the final powders a chemical analysis was required. XRD patterns (XPERT PRO) were obtained by using Ni-filtered, Cu Kα radiation at a scanning speed of $2^\circ\ min^{-1}$ of 16 °C. The microstructure and microprobe analysis were carried out by using scanning electron microscopy (SEM) (JXA-880) and electron probe microanalysis (EPMA) (ISIS).

3. Results and discussion

3.1. Phase evolution (characterization)

The air contains approximately 21 vol% oxygen and 79 vol% nitrogen. Under Coke Powder Bed condition, it was presumed that the oxygen reacted with carbon granules completely and produced carbon monoxide. According to the reaction $2C(s) + N_2(g) + O_2(g) = 2CO(g) + N_2(g)$, the partial pressure of CO and N_2 produced would be about 3.5×10^4 and 6.5×10^4 Pa, respectively.

Fig. 2 is the XRD results of TiO_2/C-black mixtures with or without NaCl after reaction between 1100 and 1200 °C. Up to a reaction temperature of 1100 °C, the sample with 10 wt.% NaCl appeared unreacted, no Ti(C, N) peak was observed in Fig. 2a, indicating that the synthesis reaction to form Ti(C, N) unoccurred. Meanwhile, anatase was converted to rutile completely but there was plenty of NaCl (about 9.28 wt.%) in the final product. At 1200 °C, the sample with 10 wt.% NaCl was of a dim-brown colour and had a multi-hole structure (Fig. 3). XRD pattern revealed that Ti(C, N) was formed in the sample (shown in Fig. 2b). At the same time, no NaCl peaks were identified and other compounds containing the elements Na or Cl were not detected in the XRD pattern (Fig. 2). The

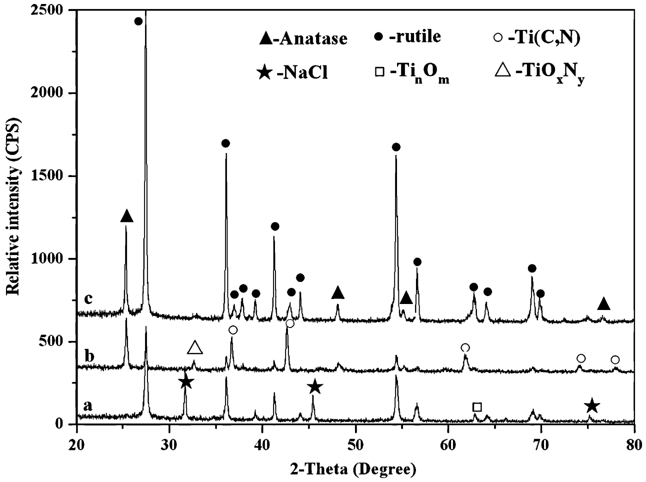

Fig. 2. XRD results of synthesized powder produced at 1100–1200 °C for 3 h: (a) 1100 °C + 10 wt.% NaCl; (b) 1200 °C + 10 wt.%; NaCl (c) 1200 °C without NaCl.