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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

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

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).

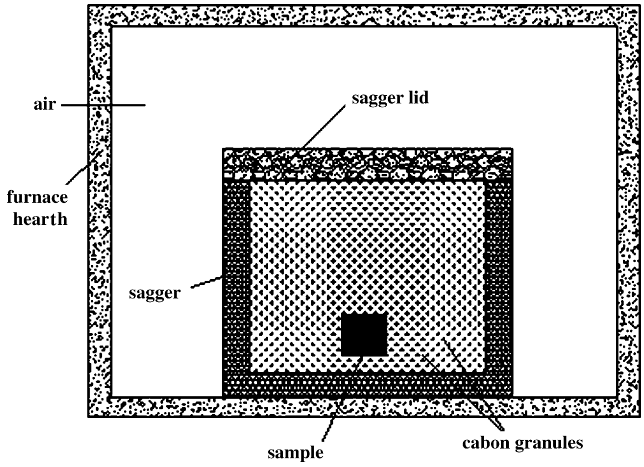

Fig. 1. Schematic diagram of preparation process.

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

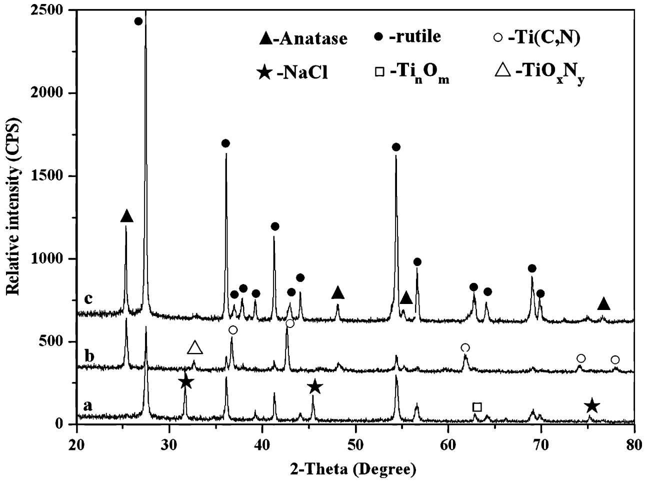

Fig. 2. XRD results of synthesized powder produced at 1100–1200 °C for 3 h: (a) 1100 °C + 10 wt.% NaCl; (b) 1200 °C + 10 wt.%; NaCl (c) 1200 °C without NaCl.

Fig. 3. The multi-hole structure of sample with NaCl after burning at or over than 1200 °C for 3 h.

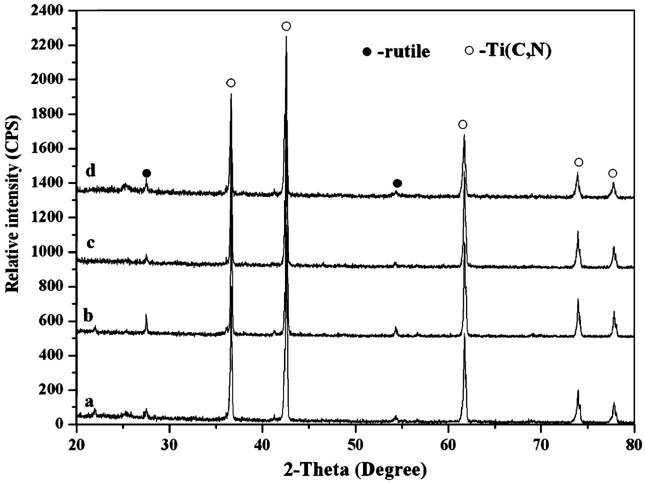

Fig. 5. XRD results of Ti(C, N) powder synthesized at 1400 °C for 3 h with different NaCl content (wt.%): (a) 5; (b) 10; (c) 15; (d) 20.

same result was confirmed by chemical analysis. The melting point and boiling point of NaCl are known to be about 810 and 1413 °C, respectively. But in the Coke Powder Bed condition at 1200 °C, NaCl was driven out because of its good volatility and the release of the gaseous reaction product CO. Another difference between Fig. 2a and b was the formation of anatase, lower oxides Ti_nO_m and TiO_xN_y. The occurrence of lower oxides Ti_nO_m was the result of TiO_2 reduction by carbon black and CO. The possible reason for TiO_xN_y formation was the incorporation of nitrogen atoms into the lower oxides Ti_nO_m, leading to the formation of solid solutions, because Ti_nO_m such as Ti_3O_5 has a cubic crystal structure and nitrogen atoms has a strong tendency to be incorporated into the cubic crystal lattice [25]. As shown previously, complete transformation of anatase to rutile occurred before 1100 °C, but anatase was still found in the powders after reaction at 1200 °C, the reason for this is unclear at present and the further research is required to clarify this issue (Fig. 2). The important role of NaCl on formation of Ti(C, N) was also shown in Fig. 2. Comparing Fig. 2c with Fig. 2b suggests that the existence of NaCl significantly prompted the formation of Ti(C, N).

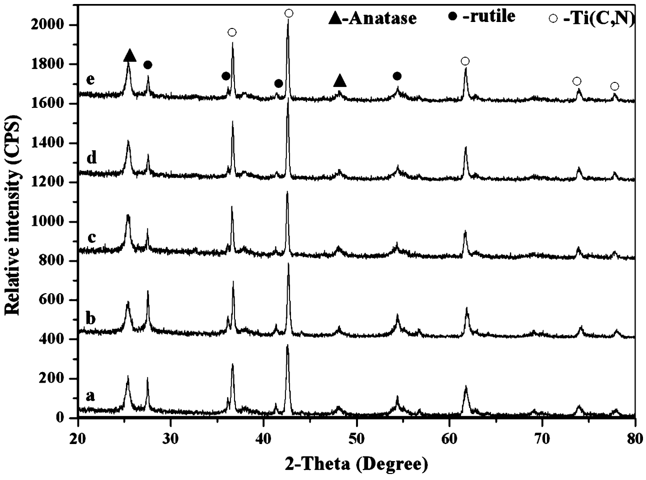

Fig. 4. XRD results of Ti(C, N) powder synthesized at 1300 °C for 3 h with different NaCl content (wt.%): (a) 5; (b) 10; (c) 15; (d) 20; (e) 30.

At 1300 °C or above the main phase found in XRD patterns, was Ti(C, N) (Fig. 4). Samples containing various amounts of NaCl were all brown in colour. Similar results were obtained at higher temperatures, i.e. 1400 °C. Comparing the XRD patterns at 1400 °C (Fig. 5) with those at 1300 °C (Fig. 4) showed that the intensity of Ti(C, N) peaks increased sharply with increasing temperature. Furthermore, the anatase and rutile peaks decreased greatly with increasing temperature. It became apparent from these results that higher temperatures were favorable for the synthesis reaction. When temperature was fixed, the XRD peak intensities of Ti(C, N) changed slightly with increasing NaCl content.

3.2. *Measurement of the residual carbon ratio*

Residual carbon content was measured and used to assess the purity of the powders. The dependence of NaCl content and the combustion temperature on the formation of Ti(C, N) was shown in Figs. 6 and 7, respectively. As can be seen in Fig. 6, the residual carbon ratio in the final product declined sharply with the addition of 5 wt.% NaCl and then changed very little with further addition of more NaCl up to 30 wt.%. Correspondingly, residual carbon ratio changed slightly from 5.6 to 3.1%, indicating that the addition of NaCl is beneficial to the reaction of TiO_2 with carbon as well as to a significant reduction of the residual carbon. Effects of temperature on the residual carbon ratio are shown in Fig. 7. It is apparent that at the temperature increasing from 1100 to 1300 °C the residual carbon ratio reduced significantly from 20.6 to 4.8%. With further temperature increase from 1300 to 1400 °C, the residual carbon ratio varied slightly from 4.8 to 2.1%. Thus, higher temperature is favorable for the formation reaction of Ti(C, N) and this reaction was close to completion at 1300 °C. It can be concluded from these results that the temperature of 1300 °C

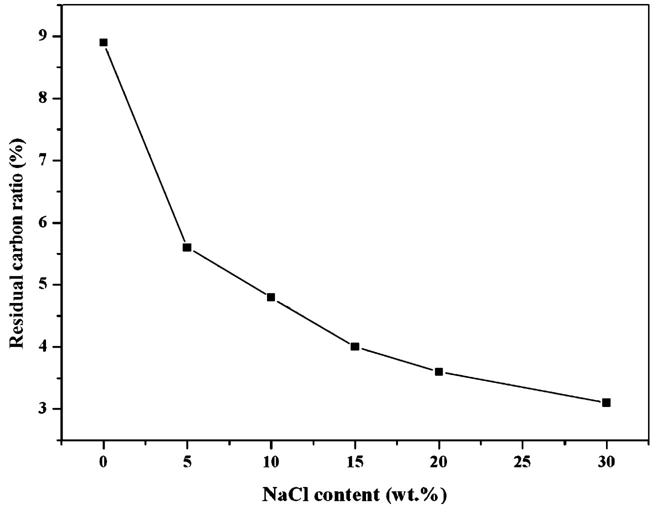

Fig. 6. The relationship between residual carbon ratio and NaCl content of specimen heated at 1300 °C for 3 h.

and 10 wt.% NaCl content are required for the carbothermic reduction and nitridation of TiO_2 to form Ti(C, N) in the presence of NaCl, requires a reaction temperature of 1300 °C and a NaCl content of 10 wt.%.

3.3. The microstructure analysis

SEM micrographs of powder products were taken form samples prepared under the conditions of different temperatures and different NaCl contents. The particle size and morphology of Ti(C, N) particles formed in the final product were affected apparently by temperature and by the amount of NaCl added. As can be seen in Fig. 8, after combusting at 1300 °C, the powders produced from the TiO_2 + C-black mixture consisted of oxides of titanium as the main crystalline phases with small amount of Ti(C, N). The very fine grains of Ti(C, N) make it very difficult to separate them in the SEM image. Fig. 9 shows SEM micrograph and EPMA analysis of the sample with 10 wt.% NaCl content after combusting at 1300 °C for 3 h. It illustrates the formation of Ti(C, N) particles with an uniform shape, a slide and tidy appearance, and a grain size in the range of 5–8 μm. Small degree of agglomeration was evident, but most particles were likely just overlapping each other. Increasing or decreasing NaCl content has little effect on

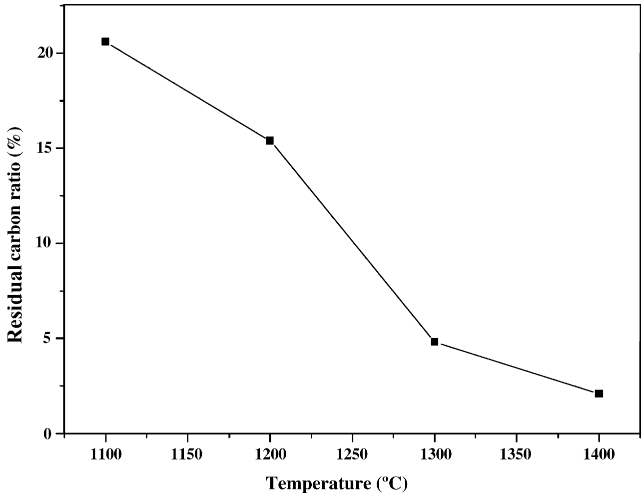

Fig. 7. The relationship between residual carbon ratio and heating temperature of sample with 10 wt.% NaCl.

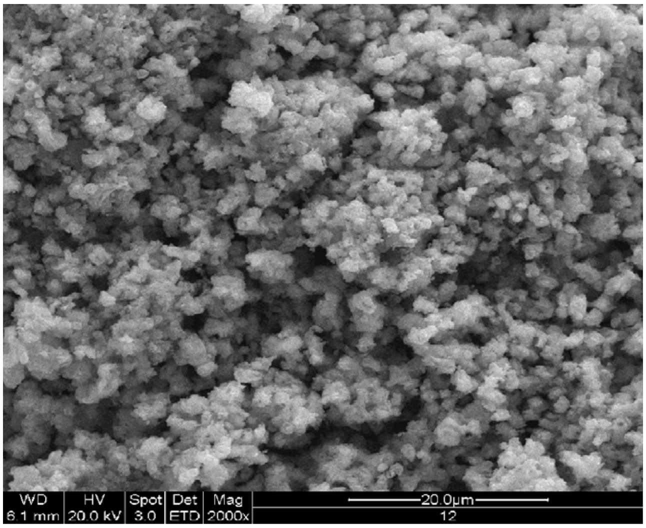

Fig. 8. SEM micrograph and element analysis of TiO_2/C-black specimen after firing at 1300 °C.

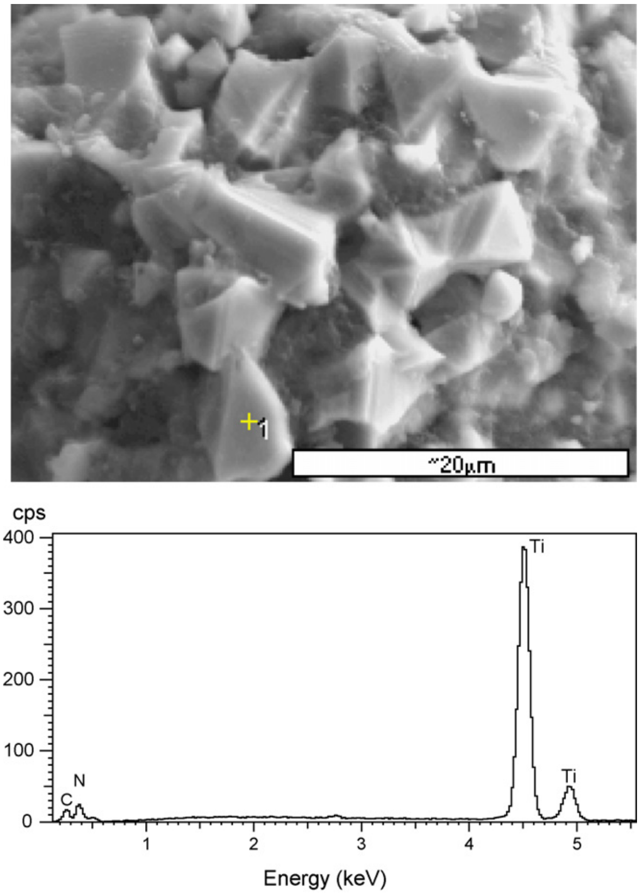

Fig. 9. EPMA analysis of specimen with 10 wt.% NaCl after burning at 1300 °C for 3 h.

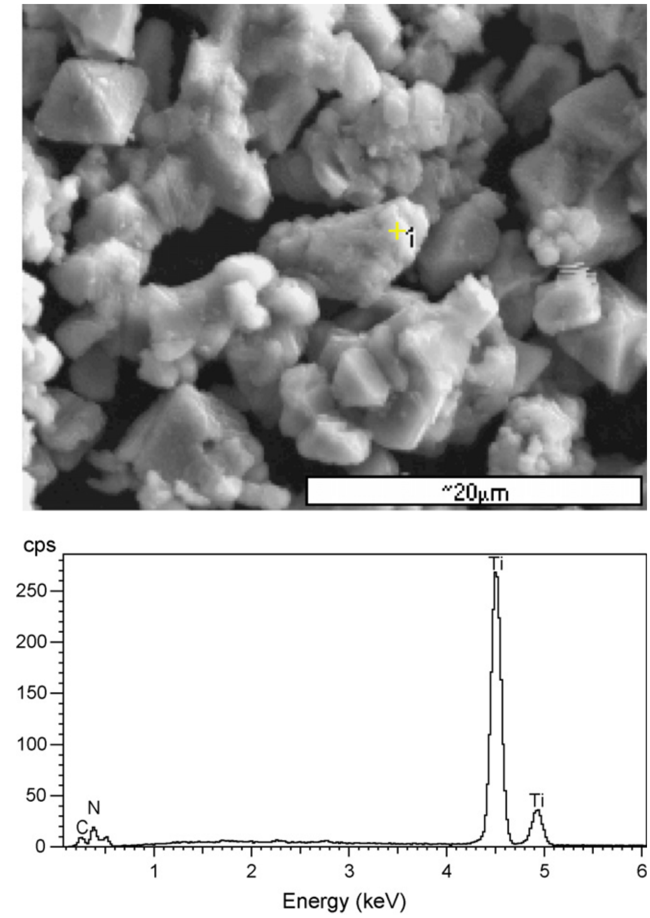

Fig. 10. EPMA analysis of specimen with 10 wt.% NaCl after burning at 1400 °C for 3 h.

Ti(C, N) formation and growth. The small and black non-crystalline particles in Fig. 9 were unreacted carbon due to incomplete mixing between carbon and titanium oxide. Fig. 10 shows SEM images and EPMA analysis micrographs of the sample with 10 wt.% NaCl after firing at 1400 °C for 3 h. Up to the temperature of 1400 °C, Ti(C, N) was oxided slightly and at a higher temperature of 1600 °C, the surface of Ti(C, N) was covered completely by a layer of oxidation film, with a popcorn-like shape (Fig. 11). It implies that temperatures higher than 1300 °C caused the oxidation of Ti(C, N) and was unfavorable for the formation of Ti(C, N). The oxidation behavior of Ti(C, N) should be investigated in the future work.

3.4. Description of the reaction mechanism

The overall reaction of carbothermal reduction and nitridation of titanium oxide by heating with carbon black in a carbonaceous atmosphere to produce carbonitrides was shown previously in Eq. (1), which was actually the sum of a more complex set of reactions. The initial stage of the reaction was the reduction of TiO_2 to its lower oxides Ti_nO_m as well as simultaneous nitridation, shown in Eqs. (2)–(4)

$$a\mathrm{TiO_2(s)} + b\mathrm{C(s)} \rightarrow c\mathrm{Ti}_n\mathrm{O}_m\mathrm{(s)} + d\mathrm{CO(g)} \tag{2}$$

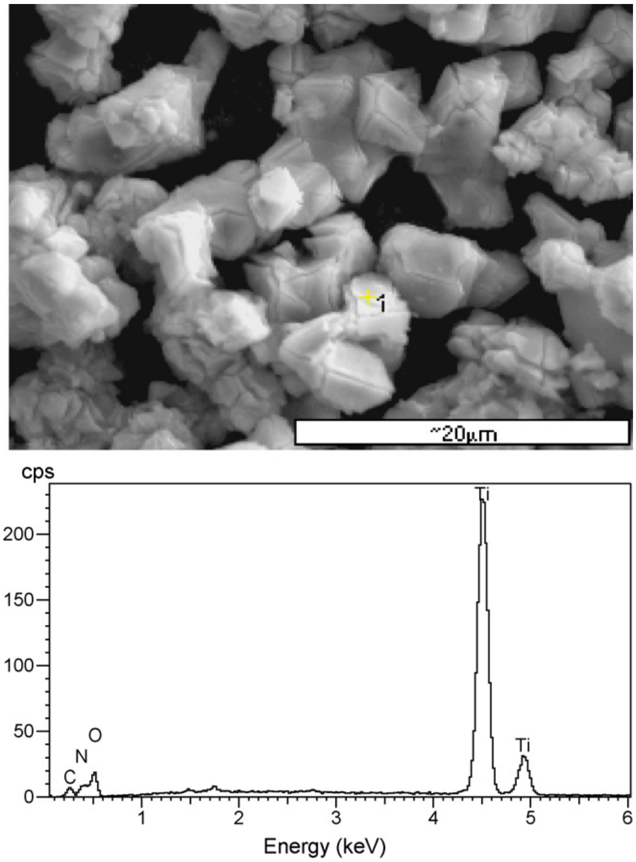

Fig. 11. EPMA analysis of specimen with 10 wt.% NaCl after firing at 1600 °C for 3 h.

$$a\mathrm{TiO_2(s)} + b\mathrm{CO(g)} \rightarrow c\mathrm{Ti}_n\mathrm{O}_m\mathrm{(s)} + d\mathrm{CO_2(g)} \tag{3}$$

$$a\mathrm{Ti}_n\mathrm{O}_m\mathrm{(s)} + b\mathrm{N_2(g)} \rightarrow c\mathrm{TiO}_x\mathrm{N}_y\mathrm{(s)} \tag{4}$$

In addition, as the reaction temperature increases, TiO_xN_y reacting with C or CO leads to the formation of Ti(C, N), as shown in Eqs. (5) and (6):

$$a\mathrm{TiO}_x\mathrm{N}_y\mathrm{(s)} + b\mathrm{C} + c\mathrm{N_2} \rightarrow d\mathrm{Ti(C,N)} + e\mathrm{CO} \tag{5}$$

$$a\mathrm{TiO}_x\mathrm{N}_y\mathrm{(s)} + b\mathrm{CO} + c\mathrm{N_2} \rightarrow d\mathrm{Ti(C,N)} + e\mathrm{CO_2} \tag{6}$$

The CO_2 formed in reactions (3) and (6) further reacts with C to form CO.

$$\mathrm{CO_2} + \mathrm{C} \rightarrow 2\mathrm{CO} \tag{7}$$

Because the reactants are in the form of separate particles, the extent of the reactions was limited by the contact area between the reactants and by the degree of mixing the carbon and TiO_2, resulting in a product that contains unacceptable quantities of unreacted carbon and oxides of titanium [26]. In these reactions, carbon monoxide is produced by reactions between atmospheric oxygen and carbon granules in the sagger, shown in Eqs. (2), (5) and (7). The nitrogen source is in air. In the reactions where no volatile titanium oxide intermediates existed, the mass transfer was realized solely by the CO/CO_2 mass transport mechanism. Carbon was either a CO_2

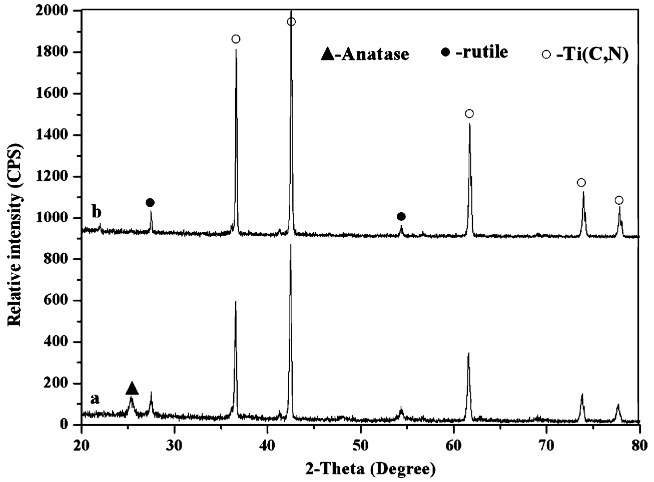

Fig. 12. XRD results of Ti(C, N) powder synthesized under different conditions: (a) 1600 °C without NaCl; (b)1400 °C + 10 wt.% NaCl.

reducer or a CO generator which kept the CO/CO_2 ratio high enough to make the reduction of TiO_2 possible by gas phase reduction. So the intimate contact of carbon with TiO_2 and continuous supply of CO was essential during reduction in order for well conversion of TiO_2 into Ti(C, N).

Molten salt method is a simple and cost-effective technique for preparing single crystalline particles in a low-melting point flux. In this experiment, NaCl was used as a reaction aid or medium, which supplied a liquid-phase at lower temperatures (about 810 °C). It aided transportation of the reactant species reduced combustion temperature and thus leads the production of uniform powders. The mutual diffusion of various atoms is much more rapid in the molten salt than in the solid state. Meanwhile, pure Ti(C, N) powder can be obtained because of the good volatility for NaCl. As clearly seen in Fig. 3, the sample with 10 wt.% molten salt of a cellular-like structure and the similar appearance was observed at higher temperatures, revealing that the multi-holes were made by the volatility of molten salt, which supplied channels for nitrogen and CO flowing into the sample to take part in the reaction. NaCl decreased the reaction temperature significantly as also seen in Fig. 12. It is obvious that the formation of Ti(C, N) was drastically enhanced and the synthetic temperature was greatly decreased by adding 10 wt.% NaCl. It was rational to expect that the packed agglomeration of the Ti(C, N) powder was avoided, the reaction temperature in the presence of NaCl decreased about 200 °C compared to that without NaCl.

4. Conclusions

Molten salt-assisted carbothermal reduction synthesis of Ti(C, N) powder was investigated experimentally. Ideal yield of Ti(C, N) powder was successfully obtained by the carbothermal reduction reaction of TiO_2 and C in the presence of 10 wt.% NaCl at 1300 °C for 3 h. The presence of NaCl had a strong positive effect on the formation of Ti(C, N) during the reaction process, which decreased the residual carbon content contained in the final powders and initial reaction temperature and prompted significantly the formation of Ti(C, N). At 1300 °C, the shape of Ti(C, N) prepared was uniform and the particle size was about 5–8 μm. But at temperatures higher than 1300 °C Ti(C, N) was oxided and turned to a popcorn-like shape as temperature further increased. The advantages of this process were that it requires a relatively low reaction temperature and were easy to control. So this method may be extended to prepare other carbonitrides, which is underway.

Acknowledgements

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