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ORIGINAL RESEARCH

Novel approaches to produce Al_2O_3–TiC/TiCN–Fe composite powders directly from ilmenite

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Abstract Al_2O_3–TiC/TiCN–Fe composite powders were successfully prepared directly from ilmenite at 1300–1400 °C. The effects of Al/C ratio, sintering atmosphere, and reaction temperature and time on the reaction products were investigated. Results showed that the nitrogen atmosphere was beneficial to the reduction of ilmenite and the formation of Al_2O_3–TiC/TiCN–Fe composite powders. When the reaction temperature was between 600 and 1100 °C, the intermediate products, TiO_2, Ti_3O_5 and Ti_4O_7 were found, which changed to TiC or TiCN at higher temperature. Al/C ratio was found to affect the reaction process and synthesis products. When Al addition was 0.5 mol, the Al_2O_3 phase did not appear. The content of carbon in TiCN rose when the reaction temperature was increased.

1. Introduction

Alumina ceramics (Al_2O_3) have been used in the industry due to their low density, high hardness and good chemical inertness [1]. However, alumina ceramics have poor fracture toughness and thermal shock resistance, and wider application is limited. The incorporation of some second particulate phases into the ceramic matrix has been known to improve the mechanical properties of ceramics, such as the resistance to crack initiation and propagation. Among common reinforcing phases, TiC or TiCN with the same crystal structure as NaCl is preferred for its high hardness, low density, high melting point, high elastic modulus, excellent wear and corrosion resistance, appropriate electrical conductivity, high thermal shock resistance, and good wettability and stability in iron melt [2–6]. As a result, TiC or TiCN has been extensively utilized in Al_2O_3–TiC/TiCN composites and Fe-based compostes [7–9], and application of TiC or TiCN in surface coatings are also being investigated [10,11].

However, the TiC or TiCN powders prepared by traditional methods are very expensive, and many researchers tried to develop

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low cost preparing processes for TiC or TiCN powders. Ilmenite ($FeTiO_3$) is not only cheap but also very rich in China. The preparation of TiC or TiCN powders directly from ilmenite is very potential [12,13]. Besides, the surface contamination of the reinforcements is not avoidable when TiC or TiCN powders are added to Al_2O_3. The in-situ fabrication technique directly from ilmenite, aluminum and carbon not only overcomes the aforementioned disadvantages but also produces thermodynamically stable and impurity-free interfaces, similar to MC carbides in tool steels [14]. Therefore, the in-situ composites can result in better mechanical properties than traditionally processed composites [15].

Reaction synthesis of $FeTiO_3$–Al–C has attracted increasing interest. However, previous studies focused mainly on the formation of Fe–Al/Al–Ti intermetallic compounds using $FeTiO_3$–Al mixture [15–20], or TiO_2 was used to replace $FeTiO_3$, which is not cheap compared to $FeTiO_3$ [1,18,19,21–28]. Very few works on the direct synthesis of Al_2O_3–TiC/TiCN powders from ilmenite has been carried out.

In the present work, very cheap ilmenite ($FeTiO_3$) is used as one of starting materials. The reaction synthesis of Al_2O_3–TiC/TiCN–Fe composite powders from the mixture of ilmenite, Al and C was investigated, and the intermediate products during the reaction processes of the $FeTiO_3$–Al–C system at different reaction temperature were analyzed.

2. Experimental

Ilmenite ($FeTiO_3$, Panzhihua mineral from China), Al, and graphite powders were used as raw materials in the experiments. Al and graphite powders were used as reducing agents. Mixtures were prepared in accordance with Eq. (1), which is the thermodynamically predicted reaction:

$$FeTiO_3+x\mathrm{Al}+(4-3x/2)\mathrm{C}\rightarrow \mathrm{TiC}+(x/2)Al_2O_3+\mathrm{Fe}+(3-3x/2)\mathrm{CO} \quad (1)$$

x value changes from 0.5 to 1.5 mol for investigating the effects of Al addition on the reaction processes. The powder blend of ilmenite, Al, and graphite was ball milled for 4 h in a vertical planetary ball mill (QM-3SP4, China). The mill was operated at a speed of 300 rpm using different diameters of steel balls (6 and 10 mm). The mass ratio of ball-to-powder was maintained at 12:1. Ball milling was performed under an air atmosphere at room temperature.

Approximately 20 g of the mixture was placed into a graphite crucible in a sintering furnace after milling. The furnace was evacuated to vacuum and then filled with flowing argon or nitrogen. Atmosphere flow rate was at 1 L/min. In order to understand the characteristics of the synthesis process, the samples were sintered for 30 min at different temperatures.

The starting materials, milled powders, and reaction products were characterized by XRD (D/MAX-1200, China) using Cu $K\alpha$ radiation within the range 10° to 90°. Peak positions were acquired from the International Center for Diffraction Data database. Raw XRD data were refined and analyzed through the MDI Jade 6.0 program (Materials Data Incorporated, Livermore, California, USA). NIST silicon powder (SRM640) was used as an external standard for correction because of instrumental broadening. Experimental errors were reduced as much as possible by fitting the curve. The microstructures of the sintered specimens were investigated using a scanning electron microscope (SEM) (TESCAN VEGAIILMU) equipped with an energy-dispersive X-ray spectroscopy system for elemental analysis (Oxford INCA).

3. Results

The XRD patterns of as-milled powders with different Al additions are shown in Fig. 1. The phases shown by the XRD patterns included the $FeTiO_3$, Al, and C phases, and no any new phases were found. This suggests that no significant reactions occur among the mixture of $FeTiO_3$, Al, and C during milling. The intensity of the Al peaks significantly increased with increasing Al content, whereas the intensity of the C peaks gradually decreased.

3.1. Reaction in argon atmosphere

To understand the reaction process of the $FeTiO_3$–xAl–$(4-3x/2)$C system in argon atmosphere, the $FeTiO_3$–1Al–2.5C system consisting of 1 mol $FeTiO_3$, 1 mol Al, and 2.5 mol C was investigated. Fig. 2 shows the XRD patterns of the $FeTiO_3$–1Al–2.5C mixture powders sintered at different temperatures for 0.5 h in argon atmosphere.

The results showed that no any new phases appeared as the sample heated at 600 °C, which suggests that no action occurred at 600 °C. When the sample was heated up to 700 °C, TiO_2, Ti_4O_7 and Ti_3O_5 were found, whereas ilmenite and Al disappeared, which indicated that ilmenite and Al reactions occurred during heating at 700 °C. In same cases, the compounds of iron and carbon, such as Fe_3C, was also found, and disappeared at higher temperature. TiO_2 is the initial reduction product from ilmenite. Fig. 2 shows that the intensity of TiO_2 phase decreased gradually as temperature increased, and TiO_2 disappeared at 900 °C, whereas the intensity of the Ti_3O_5 and Ti_4O_7 strengthened. The results in Fig. 2 suggest that the Ti_3O_5 and Ti_4O_7 phases form by the reaction of TiO_2 and Al. It was found that Al_2O_3 and Fe phase formed when oxides of titanium occurred. The results evidently showed that the following reactions occurred at 700 °C:

$$3FeTiO_3+2\mathrm{Al}\rightarrow 3TiO_2+Al_2O_3+3\mathrm{Fe} \quad (2)$$

$$9TiO_2+2\mathrm{Al}\rightarrow 3Ti_3O_5+Al_2O_3 \quad (3)$$

It was found that TiC peaks appeared at 1000 °C. When temperature increased from 1100 to 1300 °C, the intensity of Ti_3O_5 and carbon

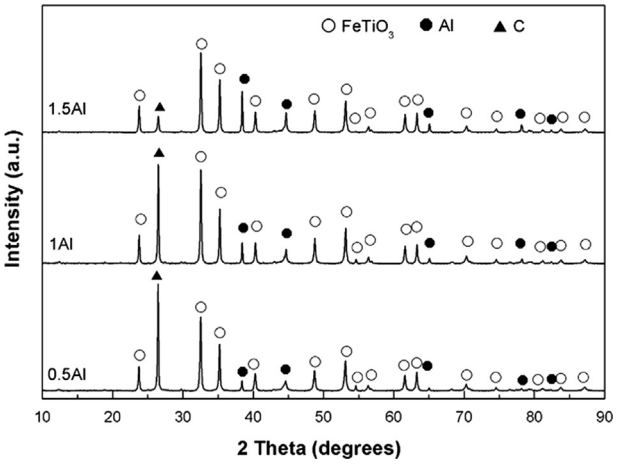

Fig. 1 XRD patterns of $FeTiO_3$–Al–C milled powders with the starting compositions given in Eq. (1) (x=0.5, 1, 1.5 mol).