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Mechanism and optimization of titanium carbide-reinforced iron composite formation through carbothermal reduction of hematite and anatase

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ABSTRACT

This study investigated an optimization of titanium carbide-reinforced iron composite fabricated using a combination of powder metallurgy and carbothermal reduction of hematite-anatase mixture using 2^k factorial design. The composite formation mechanism is described as well. Powders of hematite, anatase and graphite with mole ratio of 1:1:6 were mixed for 1 h together with 0 wt%, 1 wt% and 5 wt% $FeCl_3$. The mixture was pressed at 5 MPa, calcined for 1 h at 1000 °C, 1100 °C or 1200 °C and sintered at 1200 °C. X-ray diffraction of the calcined powder showed that with increasing temperature TiO_2 was reduced to TiC through formation of various suboxides (Ti_3O_5 and Ti_2O_3). Scanning electron microscope observation of the sintered composite indicated that addition of $FeCl_3$ enhanced the formation of TiC in iron matrix. Consequently, microhardness and density of the sintered composite improved noticeably. Based on microhardness, green density and sintered density measurements, design of experiment analysis suggested that an increase in both $FeCl_3$ content and calcination temperature increased the percentage of hematite and anatase reduction.

1. Introduction

Metal matrix composites (MMCs) have become the focus of intensive research and development due to their high specific modulus and strength, thermal stability, and excellent wear resistance, especially for light metals such as aluminum, magnesium and titanium [1]. Iron-based alloys are by far the most widely used metallic materials in MMCs because of their low cost and good mechanical properties. Similarly, TiC to be used as a reinforcing material in MMCs is attractive because of its low density, high melting point, extreme hardness and high resistance to oxidation and wear. Various routes of synthesis or fabrication of TiC-reinforced Fe-based (Fe–TiC) composites have evolved, including carbothermal reduction, combustion synthesis and thermic reduction, powder metallurgy and conventional melting and casting, respectively. Of these methods, carbothermal reduction is one of the more suitable routes to synthesize Fe–TiC composite powder due to the inexpensiveness of the raw materials and the simplicity of the process [2].

However, Suresh Gupta [3] have shown the difficulty of nucleating iron during reduction of synthetic ilmenite ($FeTiO_3$), but it can be overcome by the addition of a catalyst such as ferric chloride ($FeCl_3$). Moreover, the combination of addition of the catalyst and an increase in calcination temperature facilitated the reaction significantly. To the authors' knowledge, all published work on carbothermal reduction to synthesize Fe–TiC multi phase powder used ilmenite ($FeTiO_3$) [3–6]. On the other hand, carbothermal reduction synthesis of TiC single phase used anatase (TiO_2) has not done before [7–10]. In addition, all studies of Fe–TiC or TiC synthesis have focused on the characterization of the powder product without extending their investigation to bulk fabrication of the composite. The properties of composite produced in bulk fabrication must be characterized because the properties of the composite do not only depend on the formation of phases alone but also on densification of the powder during pressing and sintering.

We know of no previous study on the synthesis and fabrication of Fe/TiC using carbothermal reduction of a hematite (Fe_2O_3) and anatase (TiO_2) mixture. Unlike carbothermal reduction of ilmenite, carbothermal reduction of a Fe_2O_3 and TiO_2 mixture would give a significant advantage of relative ease of compositional control of the Fe matrix and TiC reinforcement in the composite product since the mole ratio of both oxides in the mixture can be tailored. In the case of ilmenite, in contrast, the Fe and TiO_2 ratio is constant, thus fabrication of a composite with various Fe and TiC compositions is impossible.

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This work, then, was conducted to investigate the mechanism for synthesis of a Fe–TiC composite powder through carbothermal reduction of Fe_2O_3 and (TiO_2), followed by densification of the composite powder via powder metallurgy. Optimization of composite fabrication was conducted in a 2^k factorial design to reduce time consumption and to account for the interaction between the investigated factors, i.e. the $FeCl_3$ catalyst and calcination temperature.

2. Materials and methodology

Of the raw materials, iron (III) oxide (Fe_2O_3, also known as hematite), carbon (C) and iron (III) chloride (or ferric chloride, $FeCl_3$) were supplied by Sigma–Aldrich Chemie Gmbh (Steinheim, Germany) while titanium dioxide (TiO_2, or anatase titania) was supplied by Merck KgaA (Darmstadt, Germany). Fe_2O_3, TiO_2 and C powders were mixed in a planetary mill for 1 h at a mole ratio of 1:1:6. $FeCl_3$ in the form of $FeCl_3 \cdot 6H_2O$ was added at 0, 1 or 5 wt%. The mixture was compacted in a steel die 13-mm in diameter at a pressure of 5 MPa. The pellets of the green body were heated slowly to a calcination temperature of either 1000 °C, 1100 °C or 1200 °C with 1 h soaking time in order to synthesize Fe–TiC composite powder. After calcination, the compacts were ground to powder in an agate mortar. Prior to sintering, the calcined powder was pressed in a 10-mm diameter die with a constant pressure of 15 MPa and sintered at 1200 °C with 1 h soaking time to yield a Fe–TiC bulk composite. The reduction paths of Fe_2O_3 and TiO_2 mixture are presented in percentage of weight loss. Phase evolution of the milled powder, calcined pellet and sintered pellet were investigated using X-ray diffraction (XRD). The morphology of reduced iron and titanium carbide in the composite was observed under scanning electron microscopy (SEM). Density and microhardness were measured to quantify the mechanical and physical properties of the sintered composite.

Statistical design of experiment typically involves planning the experiment to collect and analyze appropriate data by statistical method. In the present work, 2^k factorial design was implemented to estimate the effect of each factor (calcination temperature and weight percentage of the added catalyst $FeCl_3$) on the formation of Fe–TiC composite through carbothermal reduction of hematite and anatase mixture powder during mechanical milling and consolidated through sintering. This experimental design involved a series of experiments with k factors where in each factor had two levels ('low' – and 'high' +). In a design in the 2^k series, only two factors (A and B) run at two levels. The design used in this work was a 2^2 factorial design. The term A refers to the effect of calcination temperature and B refers to the effect of weight percentage of the added catalyst $FeCl_3$, while the term AB refers to the interaction between the two factors. The lower level for A was 1000 °C and the higher level was 1200 °C while for B, the lower level was 0 wt% and its higher level was 5 wt%.

3. Results and discussion

3.1. Weight loss reduction

The weight loss was defined as a fraction of oxygen in titanium dioxide removed in the course of reduction. The reduction efficiency of Fe_2O_3–TiO_2–C mixture during calcination in terms of weight percentage of $FeCl_3$ catalyst were determined as indicated in Fig. 1. Apparently the addition of $FeCl_3$ increased the reaction rate significantly as the initial and overall rates of weight loss reduction increased significantly with calcination temperature. At 1200 °C, the effect of the temperature was much more pronounced than at lower temperatures. This is because the heat produced during milling was insufficient to removed oxygen in titanium dioxide therefore higher temperature is needed to reduce the oxygen. Moreover, the addition of $FeCl_3$ catalyst at 5 wt% was found to be more effective than at 0 wt% or at 1 wt%. The addition of $FeCl_3$ catalyst indeed accelerated the weight loss during reduction of hematite and titania.

3.2. Effects of calcination temperature and added $FeCl_3$ catalyst

The formation of phases after carbothermal reduction was investigated for different weight percentages of $FeCl_3$ catalyst and calcination temperatures. Figs. 2–4 show XRD patterns of composite powder synthesized with addition of 0 wt%, 1 wt% or 5 wt% $FeCl_3$ catalyst for calcination temperatures of 1000 °C, 1100 °C and

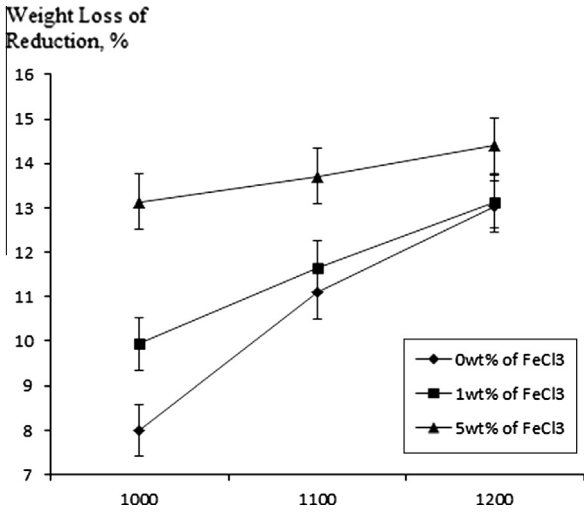

Fig. 1. Weight loss of reduction with different calcination temperatures and content of added catalyst.

1200 °C. Apparently without $FeCl_3$, TiO_2 was reduced to Ti_3O_5 phase with some residual graphite. Furthermore, peaks of Fe were also detected at 44.5° and 65°. With addition of 1 wt% $FeCl_3$, Ti_2O_3 phases formed while Ti_3O_5 peak intensity disappeared. Simultaneously, the peak intensity of C decreased, indicating a decrease in residual C content. With addition of 5 wt% $FeCl_3$, TiC phase appeared while the peak intensity of Ti_2O_3 decreased. These findings are consistent with those of Sen [2] who synthesized TiC powders through carbothermal reduction of TiO_2. In the present work, carbothermal reduction of TiO_2 to TiC started at 1000 °C, which is considerably lower than temperatures (1700 °C–2100 °C) used in conventional melting and casting [11]. Thus, based on XRD results in Figs. 2–4 the reactions phases between Fe_2O_3, TiO_2 and TiC and their Gibbs energy were proposed according to the following equations:

$$Fe_2O_3 + 3TiO_2 + 4C = 2Fe + Ti_3O_5 + 4CO \quad (1)$$

$$\Delta G^\circ = 711339.8 - 695.786T \text{ (J)}$$

$$Fe_2O_3 + 2Ti_3O_5 + 3C = 2Fe + 3Ti_2O_3 + 3CO \quad (2)$$

$$\Delta G^\circ = 826986 - 569.79T \text{ (J)}$$

$$Fe_2O_3 + Ti_2O_3 + 4C = 2Fe + 2TiO + 4CO \quad (3)$$

$$\Delta G^\circ = 766738.4 - 660.384T \text{ (J)}$$

$$Fe_2O_3 + TiO + 5C = 2Fe + TiC + 4CO \quad (4)$$

$$\Delta G^\circ = 690583.4 - 661.018T \text{ (J)}$$

These equations describe the steps, one after the other, of the reduction process. The standard Gibbs free energy changes of the reactions were calculated in the range of 1027 °C–1527 °C. According to Mohammad Dewan [7], in solid-state carbothermal reduction, the reaction is executed by the transfer of carbon from the graphite phase to the oxide phase and of oxygen from the oxide phase to graphite. This suggestion is consistent with the experimental results in the present work as TiO_2 was reduced first to Ti_3O_5, then Ti_2O_3 and finally to solid TiC phase.