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Synthesis and characterization of TiB_2-reinforced iron-based composites

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Abstract

The TiB_2-reinforced iron matrix composite (Fe-TiB_2) was synthesized by a simple, cost-effective process involving aluminothermic reduction of blue dust (mainly Fe_2O_3), titanium dioxide (TiO_2) and boron trioxide (B_2O_3) powder. Aluminothermic reduction of these oxides, being highly exothermic in nature, essentially leads to a self-propagating high-temperature synthesis (SHS) of TiB_2-reinforced Fe-based composite. The composite has been subsequently characterized by scanning electron microscopy (SEM), image analysis, X-ray diffraction (XRD), and hardness measurement. It has been found that along with TiB_2, Fe_2B also forms during the synthesis of composite. Composite, synthesized by this process, possesses high hardness and high temperature stability. The abrasive wear resistance of the composite has been compared with that of a standard wear resistant material, i.e., high-chromium white cast iron, and found to be better than that of the standard material.

Keywords: Iron matrix composite; TiB_2; Aluminothermic reduction; Microstructure; Hardness; Wear resistance

1. Introduction

Search for superior wear resistant materials has been allotted a high priority in the field of materials research even these days. Although a vast reserve of wear resistant materials does exist in the present age, constant research activities are being carried out to produce some kind of new materials, which are better in terms of properties and less expensive compared to the existing ones. As for example, hot work tool steels are frequently used in die-castings, forging dies, punches and several other parts for hot working. These steels possess high machinability and toughness but suffer from inferior wear resistance. In order to increase their wear resistance, reinforcement with hard ceramic particles could be beneficial [1]. Apart from this specific case, composite materials with steel matrix and ceramic particle reinforcements provide a scope of producing relatively inexpensive wear resistant parts. Recently, however a limited numbers of iron and steel-based composites have emerged, which are inexpensive, versatile, and exhibit relatively good mechanical properties [2]. The most commonly used ceramic particles for reinforcement of various types of steel matrices include various oxides (e.g., Al_2O_3 and ZrO_2), nitrides (e.g., TiN and Si_3N_4), and carbides (e.g., TiC, Cr_3C_2, VC, and B_4C) [3]. A majority of these composite materials focuses on using TiC as the reinforcing particulate phase, primarily due to its capability of improving the wear resistance of the material [4–6]. Among the popular reinforcements, TiB_2 is considered as the best reinforcement for the following two reasons [2]. First, it exhibits an extremely high specific modulus of 120 GPa/Mg m^{-3} and hence would be desirable in applications where component weight as well as stiffness is important. Second, unlike most other ceramic reinforcements, which are reactive in molten iron, TiB_2 is stable in liquid Fe. Apart from these, TiB_2 is also well known for its high hardness and outstanding tribological properties. It's hardness (3400 HV) is greater than the more commonly used WC (2000 HV) and is almost as high as that of SiC (3500 HV) [7]. Furthermore, it has a high thermal conductivity ($\sim$110 Wm^{-1} K^{-1} at 25 °C) and a significantly lower coefficient of thermal expansion than steel ($\sim 13 \times 10^{-6}$ K^{-1} for steel and $\sim 7.2 \times 10^{-6}$ K^{-1} for TiB_2). Thus, steel-matrix composites with TiB_2 as the reinforcing phase have increased stiffness, hardness, and wear resistance, along with reduced coefficient of thermal expansion and only a moderate decrease in thermal conductivity properties [2].

Powder metallurgy is the most attractive processing route for these types of particulate-reinforced metal-matrix composites. But, there are several advantages in terms of production cost and efficiency, if such composites can be processed by liquid-based routes involving the in situ formation of the filler phase [8]. In the present study, the authors have made an attempt to synthesize TiB_2-reinforced Fe-based composites by aluminothermic

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reduction of Fe_2O_3, TiO_2 and B_2O_3. This type of reaction involves the reduction of a metallic or a non-metallic oxide with Al to form Al_2O_3 and the corresponding metal or non-metal. It is highly exothermic in nature and if it is initiated locally it can become self-sustaining. The study also includes the evaluation of the effect of heat treatment on the microstructure and abrasive wear resistance of the composite materials.

2. Experimental procedure

2.1. Materials

Blue dust, titanium dioxide, boron trioxide and aluminum powder are the main materials used for the synthesis of the composite. Blue dust is basically an oxide of iron of chemical formula Fe_2O_3 with 2.5 wt.% SiO_2. Laboratory grade TiO_2 (with 99% purity), B_2O_3 (99.5% purity) and Al powder (with 99% purity and ~50 μm size) were used in the present study. The as-received high-chromium iron contains 2.90% C, 1.00% Si, 1.00% Mn, 0.05% S, 0.032% P, 18.08% Cr, 0.80% Ni, 2.00% Mo, 0.30% Cu, and balance Fe (in wt.%) and has a hardness of R_c 60.

2.2. Composite synthesis

The charge calculation was done by simple stoichiometric method considering 20 vol.% TiB_2 in Fe matrix. Anticipating the loss of B_2O_3 and TiO_2 into the slag phase, 20 and 40% excess amounts of B_2O_3 and TiO_2, respectively were added to the charge composition. Stoichiometric amount of aluminum, needed to reduce all the oxides, was added to the charge. Blue dust (375 g) was mixed with predetermined amount of TiO_2 (62 g), B_2O_3 (82 g) and Al powder (190 g). The charge was preheated in a pit furnace at a temperature of about 750 °C for about half an hour in a zircon coated clay–graphite crucible. After preheating, the crucible was removed from the furnace and magnesium turnings were then added to trigger the self-propagating high-temperature synthesis (SHS) reaction. The heat generated due to aluminothermic reduction was high enough to melt the charge completely and uniformly. The heavier metallic phase and the lighter slag phase was well separated by gravity. A bottom pouring arrangement was made so that the liquid metal could be poured directly into a metal mould by opening the plug at the bottom of the crucible.

2.3. Microscopy, image analysis, and X-ray diffraction (XRD) study

Metallographic samples of dimension 12 mm × 12 mm × 10 mm were cut from the middle portion of castings of original size. The specimens were etched with 2% nital (2 ml HNO_3 + 98 ml ethanol) and were examined using an optical microscope as well as a scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectrometer (EDS). Leica QWIN image analysis software was used to find out the volume fraction of different phases. X-ray diffraction (XRD) was used to analyze the presence of the phases in the composites using Co Kα radiation.

2.4. Hardness test

Hardness values of the composites in as-cast as well as annealed condition were measured in R_c scale using diamond indentor and 150-kg load. The micro-hardness values of the individual phases, present in the composites, were determined using Vicker's indentor. The average of 10 measurements has been taken as the hardness of the material/individual phase.

2.5. Abrasive wear test

Abrasive wear tests were carried out on 12 mm × 12 mm × 10 mm samples of composite and high-Cr iron, against 220 grit SiC paper affixed to a rotating flat disc of 250 mm diameter [9]. The rotating speed was 500 r.p.m. and the duration of the test was 12 min. The sliding velocity was fixed at 2.61 ms^{-1} and track diameter was 100 mm. The experiments were carried out at different loads, e.g., 9.8, 14.7 and 19.6 N. Each test was repeated thrice. Wear rate of the specimens was computed by the weight loss technique. Prior to weighing, the specimens were cleaned with ethanol. The cumulative weight loss was converted to cumulative volume loss by dividing the weight loss by experimentally determined density. Wear rate has been calculated by using the following formula:

$$\text{Wear rate}(\text{mm}^3\,\text{m}^{-1}) = \frac{\text{cumulative weight loss(gm)}/\text{density(gm/mm}^3)}{\text{sliding distance}\,(m)}$$

Wear data have been plotted as either cumulative volume loss or wear rate as a function of sliding distance.

3. Results and discussion

3.1. Thermodynamic analysis

The feasibility of the reactions involved in synthesizing TiB_2-reinforced Fe-based composite has been considered. The important reactions leading to the formation of Fe-TiB_2 composite can be written as:

$$3TiO_2(s) + 3B_2O_3(l) + 10Al(l) = 3TiB_2(s) + 5Al_2O_3(s) \quad (1)$$

$$Fe_2O_3(s) + 2Al(l) = 2Fe(l) + Al_2O_3(s) \quad (2)$$

where (s) and (1) denote solid and liquid states, respectively.

It is quite likely that liquid B_2O_3 reacts with liquid Al during the initial stage of SHS due to its low melting point and raises the temperature, which triggers the reduction reaction of solid TiO_2 and Fe_2O_3 by liquid Al and releases huge amount of heat. Iron oxide is reduced into Fe and thus forms the matrix. On the other hand reduced Ti reacts with B and forms TiB_2 reinforcement. The standard free energy change, ΔG_T° and the standard enthalpy change, ΔH_T° for reactions (1) and (2) have been calculated using data from Kubaschewski et al. [10] and Gaskell [11]. The thermodynamic calculation indicates that ΔG_T° and ΔH_T° values are:

For reaction (1)

$$\Delta G_T^\circ = -2\,761\,726 - 833\,T + 160\,T\,\ln T - 87\,T^2 + 27 \times 10^5/T\ \text{J/mol}$$

$$\Delta H_T^\circ = -2\,762\,027 - 160\,T + 36 \times 10^{-3}\,T^2 + 56 \times 10^5/T\ \text{J/mol}$$

For reaction (2)

$$\Delta G_T^\circ = -834\,399 + 223\,T - 31\,T\,\ln T + 35 \times 10^{-3}\,T^2 - 5 \times 10^5/T\ \text{J/mol}$$

$$\Delta H_T^\circ = -854\,398 + 30\,T - 35 \times 10^{-3}T^2 - 12 \times 10^5/T\ \text{J/mol}$$

The ΔG_T° and ΔH_T° for both reactions (1) and (2) are plotted in Fig. 1 as a function of temperature. For both reactions they are negative and hence, these reactions can occur with evolution of heat. The first and foremost requirement for a reaction