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Microstructure Characteristics of Fe-Matrix Composites Reinforced by In-Situ Carbide Particulates

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Abstract. Carbide particulates reinforced iron-matrix composites were prepared by in-situ synthesis reaction between Ti, V and C on liquid alloys surface. The microstructure of the composite was characterized by SEM, TEM and OM. The results showed that the main phases were α-Fe, carbide particulate; besides, there were small amounts of γ-Fe and graphite (G) in the composite. The carbides were $TiVC_2$ and VC in the shape of short bar and graininess. The matrix consisted of martensite and small amounts of retained austenite.

1. Introduction

Particulates reinforced metal matrix composites (MMCs) have developed rapidly due to its promising advanced properties [1-2]. Mainly matrix materials in the composites were aluminum, magnesium and titanium; their applications were restricted due to high cost. Though Fe matrix composite developed latest, it has been attracted much attention owning to its excellent wear-resistance property. The most common reinforcement in Fe-matrix composites were VC, WC and NbC because of high hardness and thermal stability [3-5]. In the metal matrix composites, in-situ particulates reinforced composites had advantages over external additive ones [6]. Those particulates synthesized by in-situ reaction were fine in size, thermodynamically stable and evenly distributed [7]. In addition, in-situ techniques involved a chemical reaction on surface of the melt matrix alloy and formed clean and uncontaminated reinforcement interface with a stronger bonding interface [8].

As TiC and VC have the same lattice type and similar lattice constants (lattice constant of TiC is 4.329 Å, and that of VC is 4.16 Å) and also have proximate melting point, they can form a solid solution. Fe-matrix composites reinforced by TiC or VC particulates prepared by powder metallurgy and in-situ reaction casting method have been reported, but there were few special reports of hybrid-reinforced Fe-matrix composites synthesized by in-situ reaction casting method. In this paper, a hybrid iron matrix composite reinforced with $TiVC_2$ and VC particulates was prepared by in-situ reaction casting method, and then the microstructure of the composite was researched.

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2. Experiment Procedure

2.1. Preparation

The main raw materials used for the synthesis of the composite were Ti–Fe, V-Fe, C and low carbon steel (Steel 20). The composition of the low carbon steel, Ti–Fe and V-Fe were shown in Table 1. The mixed powders of Ti–Fe, V-Fe and C between 50 μm and 100 μm were taken which Ti, V and C was kept in an atomic ratio of 1:1:2. The investigated alloy was melt in a 50 kg medium-frequency induction furnace. When the melt temperature increased to 1650^{o} C, put 11.80 kg mixed powder on the surface of molten liquid-metal, the heat of liquid-metal impelled the reactions of Ti, V and C in the mixed powders. After all mixed powders' reaction completed, the melt should be degassed before it was poured in the casting ladle. Then the melt was poured into the moulds that were prepared with a mixture of sodium silicate and sand [9]. After cooled down to room temperature naturally, a standard Y-shape test block was obtained [10]. The specimens were heated at 950°C for 1 h and then oil quenching, subsequently tempered at 200°C for 3 h.

Table 1. The chemical composition of raw materials (wt. %)

Material	C	Si	Mn	S	P	Al	V	Ti	Fe
Ti-Fe	0.1	4.0	2.5	≤0.03	≤0.05	8	—	29.87	Balance
V-Fe	0.4	≤2	0.5	0.04	0.07	≤0.5	50	—	Balance
Steel 20	0.19	0.21	0.40	≤0.035	≤0.035	—	—	—	Balance

Table 2. The chemical composition of the composite (wt. %)

Elements	C	Si	Mn	S	P	V	Ti	Fe
Content (wt. %)	1.61	0..63	0.77	0.017	0.027	3.36	0.87	Balance

2.2. Characterization

The specimens were etched with a solution of 4% nitric acid and alcohol after polished by diamond paste, and they were examined by an optical microscope (OM) and a JSM-5800 scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS). Meanwhile the microstructure morphology and crystal structure of the composites were determined by a JEM-2100 transmission electron microscope (TEM). The chemical composition of the composite was tested by Optical Emission Spectrometry (showed in Table 2). The volume fraction of carbides in the composite was determined for 10 fields by line analysis method, in which the total lengths of carbides in specimen crossed by ruler (10 mm) were measured under 100 times microscope. Then calculate the ratio of total lengths of carbides to lengths of ruler. The formula is as follows:

$$vol.\% = \frac{\sum_{1}^{n} a_i}{\mathrm{L}} \times 100\% \quad (1)$$

Where: *vol.* % is the volume percentage, a_i is the length of carbide particle crossed by ruler, and L is the length of ruler.

3. Results and Discussion

3.1. Thermodynamic Analysis

In this work, the feasibility of the reactions related to the synthesis carbide particulates in iron-based

composites was considered. The thermodynamic of in situ chemical reactions was researched [11-13]. The potential reactions' equations between the raw materials are as follows:

$$Ti + C = TiC \quad \Delta G_1 = -181.251 + 0.013T\ (kJ \cdot mol^{-1}) \quad (25\text{-}1670°C) \quad (2)$$

$$Fe + Ti = FeTi \quad \Delta G_2 = -41.261 + 0.012T\ (kJ \cdot mol^{-1}) \quad (727\text{-}1727°C) \quad (3)$$

$$2Fe + Ti = Fe_2Ti \quad \Delta G_3 = -90.885 + 0.027T\ (kJ \cdot mol^{-1}) \quad (727\text{-}1727°C) \quad (4)$$

$$2V + C = V_2C \quad \Delta G_4 = -146.4 - 0.00634T\ (kJ \cdot mol^{-1}) \quad (273\text{-}1727°C) \quad (5)$$

$$V + C = VC \quad \Delta G_5 = -117.04 + 0.0067T\ (kJ \cdot mol^{-1}) \quad (273\text{-}1727°C) \quad (6)$$

$$8V + 7C = V_8C_7 \quad \Delta G_6 = -98.7 + 1.26\times10^{-3}T\ln T + 0.835\times10^{-6}T^2 + 0.83\times10^{2}T^{-1} - 1.08T\times10^{-3}T\ (kJ \cdot mol^{-1}) \quad (273\text{-}1727°C) \quad (7)$$

The change of Gibbs free energies (ΔG) of TiC, FeTi, Fe_2Ti, V_2C, VC and V_8C_7 were calculated and plotted in Fig. 1 as a function of temperature. It was known that if the more negative of the ΔG in the interest temperature range, the higher tendency to form the substance. From Fig.1, it can be seen that TiC and V_2C had the most negative ΔG values, which indicated that TiC and V_2C phase were the most stable products under 1650°C. It was also found that the ΔG values were more and more negative from FeTi, Fe_2Ti, and V_8C_7 to VC.

3.2. Microstructure Analysis

Fig. 2 showed optical microscope images of the Fe-based composites reinforced by in-situ carbide particulates. It was evident from Fig.2 that there were three different forms of carbide in the composites, which included bar-shaped particles (marked as 1), square-shaped particles (marked as 2) and irregular-shaped particles (marked as 3). In addition, there was a small quantity of chrysanthemum graphite in the matrix microstructure (marked as 4). After etched by 4% Nital solution, the matrix microstructure was plate martensite (seen Fig. 2c, d). The hardness value of the composite achieved HRC54.3 and impact toughness reached to 9.0 $J \cdot cm^{-2}$. Through statistic analysis and calculations for 10 field, the volume fraction of carbide in the composite was about 15% .

In order to confirm the type of carbide particles, the line scanning analysis of the different type carbides was performed, and the analysis results were shown in Fig. 3. It was seen from Fig.3 that there were V and C elements in the bar-shaped carbides (see Fig. 3a), and V, Ti, and C element existed in the grainy carbide (see Fig. 3b). Therefore, it was inferred that the grainy carbides were multicarbide and the bar-shaped carbides were vanadium carbide. The reason for forming the different type of carbides was that the composition of the alloy melts surface area was hypereutectic after adding the mixed powders in liquid alloy, leading to multicarbide formation in the melts by in-situ reaction directly, and grown up to grainy carbides [14-15]. By electromagnetic stirring of the melts, the composition of the alloy melts transformed to uniform hypoeutectic state. Austenite precipitated from the liquid alloy and grown into dendrite during the freezing of cast, which led to melts achieved eutectic composition, and then the bar-shape carbide was formed during eutectic transformation.

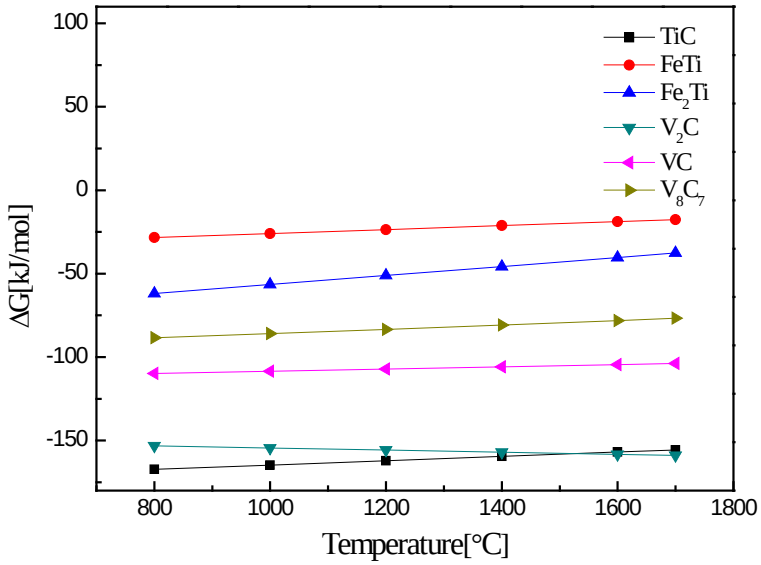


Figure 1. Change of Gibbs free energies (ΔG) as a function of temperature for TiC, FeTi, Fe_2Ti, V_2C, VC and V_8C_7.

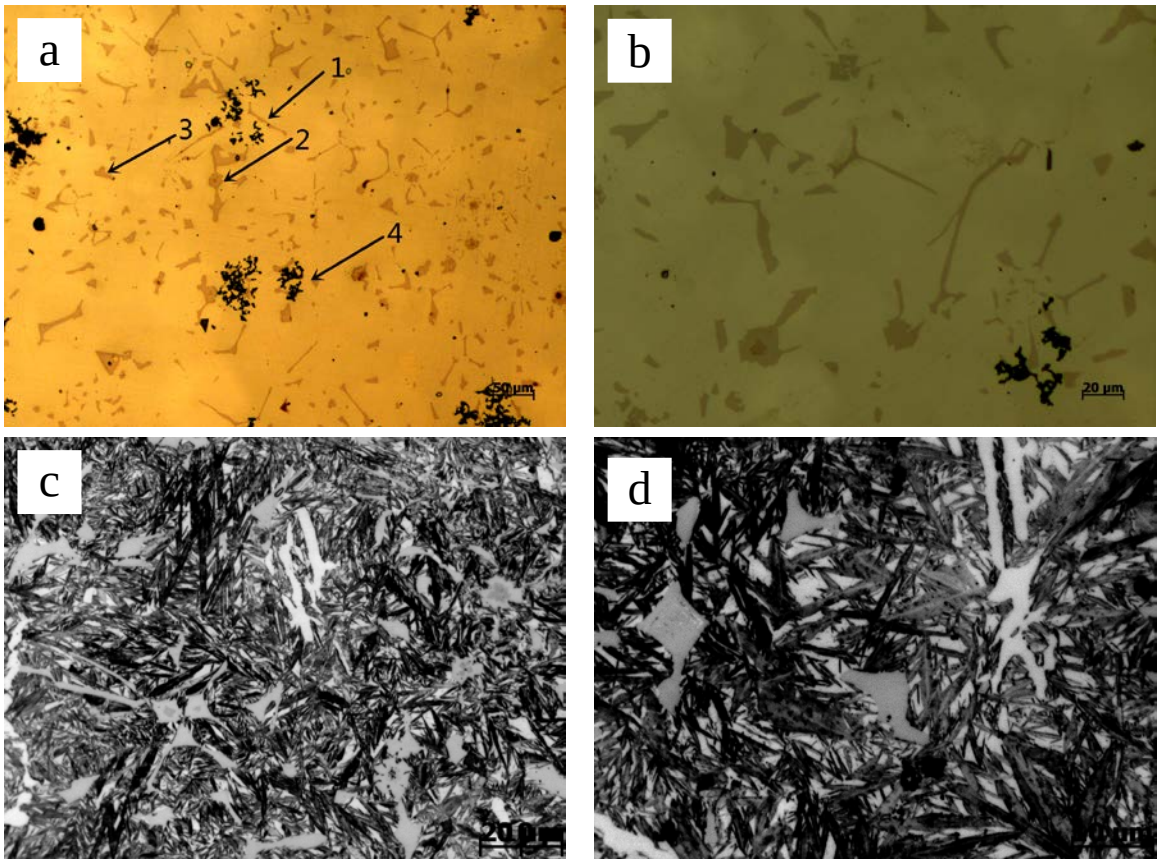


Figure 2. Optical microscope images: (a) without etched under 200 times; (b) without etched under 500 times; (c) etched by 4% Nital solution under 500 times; (d) etched by 4% Nital solution under 1000 times.

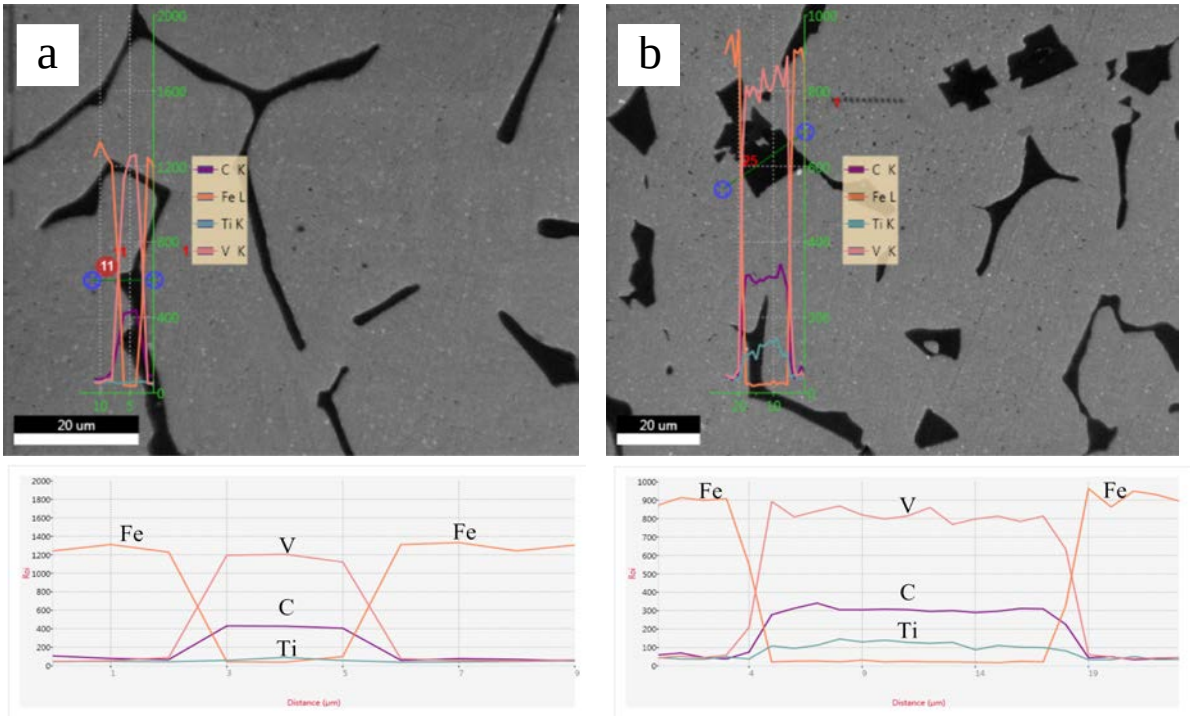
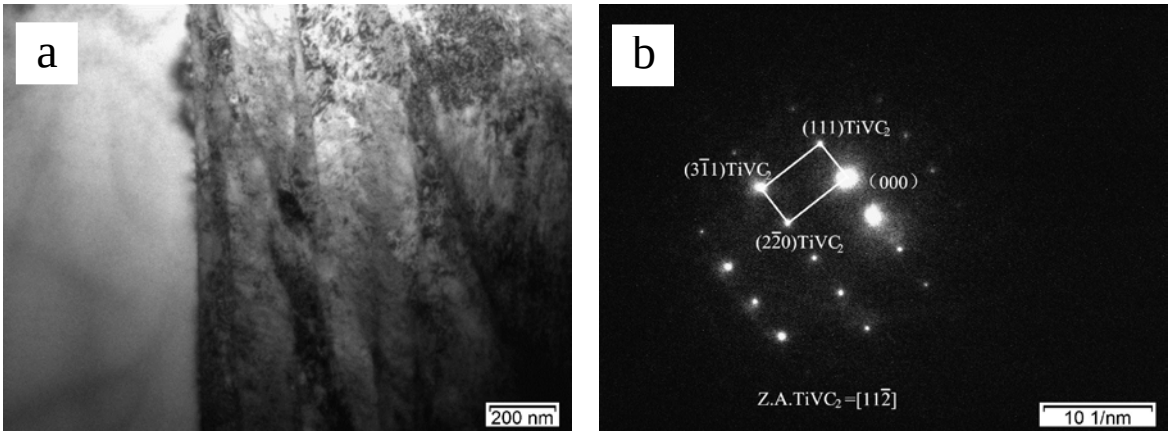


Figure 3. Line scanning of Fe, C, Ti and V in carbide particles.

The in-situ carbide morphology and micro-crystal structure of the composites were determined by transmission electron microscopy. The results were shown in Fig. 4. Plate martensites and carbide can be seen in Fig. 4a. Through selected area electron diffraction (SAED) of the carbide (see Fig. 4b), the type of the carbide was determined as $TiVC_2$ crystal with a face-centered cubic (fcc) structure and a lattice parameter of a=4.255Å. There was twin structure in area A (see Fig. 4c). Fig. 4(d) was the SAED pattern of reinforced particulates and matrix microstructure in Fig. 4(c). It can also be found that there were α-Fe, γ-Fe and VC in the composites. Therefore, the composite was consisted of martensite, small amounts of retained austenite, $TiVC_2$ and VC.



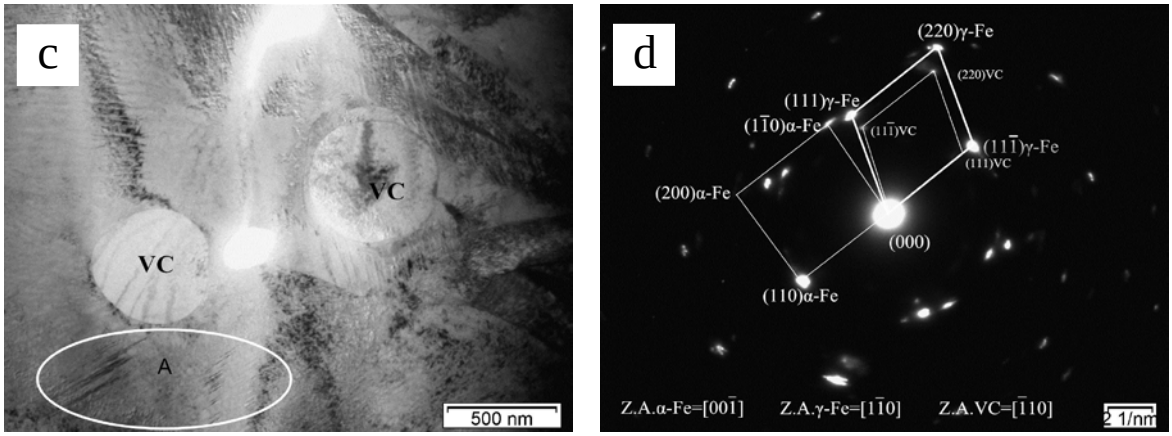


Figure 4. TEM characterization of (Ti,V)C/Fe composites: (a) TEM image of selected area; (b) selected area electron diffraction of reinforcing particulate in (a); (c) TEM image of selected area; (d) selected area electron diffraction of reinforcing particulates and matrix in (c).

4. Conclusions

An iron-based hybrid composite reinforced by carbide particles was prepared through in-situ reactions between Ti, V and C. There were grainy shape and bar shape carbides in the composite. Grainy carbides were $TiVC_2$ multicarbide formed from liquid alloy by in-situ reaction directly. Bar-shaped carbides were VC formed during eutectic solidification.

The matrix of the composite was consisted of plate martensite, small amounts of retained austenite and graphite.

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