J Mater Sci (2010) 45:2538–2542
DOI 10.1007/s10853-010-4295-9

LETTER

Reaction synthesis of in situ vanadium carbide particulates-reinforced iron matrix composites by spark plasma sintering

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Received: 13 November 2009 / Accepted: 2 February 2010 / Published online: 25 February 2010

Introduction

In recent years, ceramic particulates have been widely used as reinforcements in metal matrix composites to improve the mechanical properties. Transition metal carbides have received much attention due to their various excellent properties, such as high melting points, high hardness, high-temperature strength, high thermal conductivity, and high chemical stability [1–4]. Among these carbides, vanadium carbide is important for industrial applications owing to its unique properties. Additionally, vanadium carbide is expected to be able to better incorporate into the iron matrix because of its better wettability by iron, as indicated by the smaller contact angle θ of 13° between vanadium carbide and iron [5]. Therefore, the vanadium carbide particulates-reinforced Fe matrix composites have received considerable attention owing to their potential use in cutting, machining, and wear resistance applications.

VC/Fe composites are commonly prepared by in situ synthesis of VC in the liquid iron by casting, which requires a high temperature and a long synthesis time, resulting in exaggerated growth of the VC grains. It also needs a bulky furnace to melt the iron alloy for an extended time period [6]. An alternative method which could decrease the reaction temperature and shorten the reaction time is needed. Therefore, spark plasma sintering (SPS) technique has received more and more attention. This technique has been developed as a novel in situ reactive synthesis technology to rapidly sinter a number of materials including metals, ceramics, and composites in a couple of minutes [7–10], which is potentially useful in producing VC/Fe composite. SPS utilizes pulsed high DC current along with uniaxial pressure to consolidate powders [11]. During the process, the sample is loaded in a graphite die, uniaxial pressure is applied during the sintering by the top and bottom punches, and a pulsed direct current is allowed to pass through the die and the sample. The pulses generate spark discharge and/or plasma in voids between the powders. Due to these discharges and/or plasma, the particle surface is activated and purified, and a self-heating phenomenon is generated between the powders, as a result of which heat transfer and mass transfer can be completed instantaneously [12, 13]. Therefore, SPS is capable of sintering ceramic particle-reinforced composites quickly to its full density at relatively low temperature within a very short time. SPS is an effective means of consolidating these carbides. Short-time consolidation is very useful in maintaining fine grain size and controlling the microstructure [14, 15]. However, little work has been done on the VC/Fe composite prepared by SPS technique.

In this investigation, an attempt has been made to fabricate vanadium carbide particulates-reinforced Fe matrix composites by SPS. VC particulates are synthesized by an in situ reaction of ferrovanadium and amorphous carbon powders during sintering. The phase evolution, microstructure, and mechanical properties of the composites have been studied. It is expected that the preliminary results can be significant in promoting the development of rapid reaction synthesis of vanadium carbide particulates-reinforced Fe matrix composites.

Experimental procedure

The commercial ferrovanadium (51.25 wt% V) and amorphous carbon powders with a mean particle size of

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100 nm are used as the starting materials in this study. Ferrovanadium powders were obtained by high energy planetary ball mill with stainless steel balls and vials in acetone for 2 h. Then the ferrovanadium and amorphous carbon powders were blended together in VC stoichiometric ratio (1:1). Powder mixtures were obtained by mechanical mixing in acetone for 1 h. The weight ratio of ball to powder is 3:1.

The mixed powders were dried and pre-compacted. Then, the mixed powders were put into a cylindrical graphite die with an inside diameter of 20 mm and sintered in vacuum using an SPS apparatus (model SPS1050, Sumitomo Coal Mining Co., Japan) at a sintering temperature range 650–1150 °C with 5 min holding time. In this process, the pressure was initially set at ~15 MPa at room temperature, and then 30 MPa pressure was applied when the maximum temperature was reached. The applied heating rate was about 80 °C/min. The temperature was monitored and regulated by a pyrometer which was focused on the die. In addition, with the aim of minimizing heat losses by thermal radiation, the die was covered with a layer of graphite felt.

After sintering, the surfaces of samples with the dimension of 20-mm diameter and 4–10-mm height were ground for removing the graphite layer. The theoretical density of the samples is ~6.50 g/cm^3 and the volume fraction of the vanadium carbide particulates is ~64%. The phases of the fabricated composite specimens and the original powders were examined by a DX-2000 diffractometer with a graphite monochromator using Cu Kα radiation operated at 30 kV and 40 mA. The bulk densities of the sintered specimens were determined by Archimedes' method using water immersion. The hardness (HRA) was measured by a Rockwell sclerometer (HR-150A). The microstructure was characterized using JSM-6490LV scanning electron microscope (SEM). The micro-zone composition analysis was investigated using GENESIS 2000 XMS energy dispersive X-ray spectrometry (EDS) system which was attached to the SEM.

Results and discussion

Phase identification and evolution

The X-ray diffraction (XRD) patterns of the starting powders and the specimens sintered at various temperatures are shown in Fig. 1. As shown in Fig. 1, the phase detected in the starting materials is only FeV and no peaks of carbon can be found (Fig. 1a). The reason is that the carbon powders are amorphous. After sintering at 750 °C, the phases present in the specimen are α-Fe, V_8C_7, and $VC_{1\text{-}X}$ (1-X = 0.66–0.88) (Fig. 1d–f). It indicates that the FeV and C precursors have been reduced into vanadium carbide-reinforced iron matrix composites.

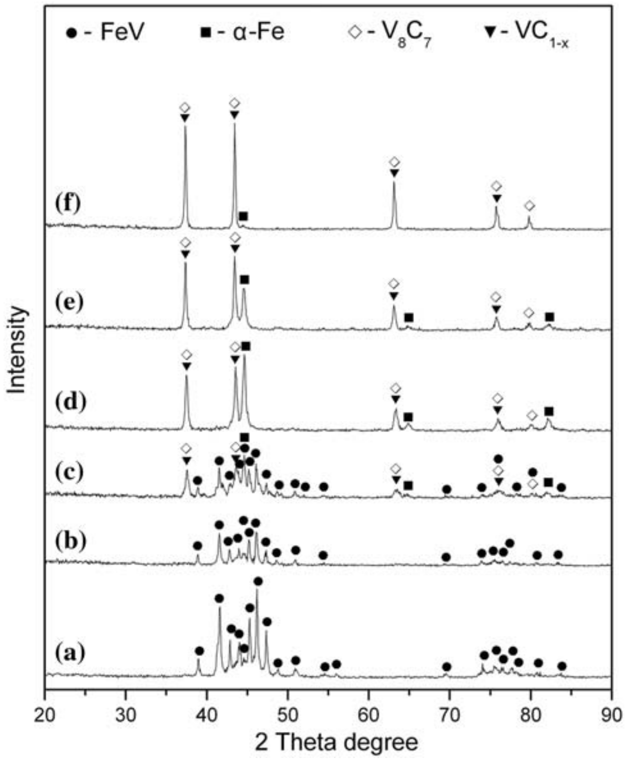

Fig. 1 XRD patterns of the specimens sintered at various temperatures: *a* starting materials, *b* 650 °C, *c* 700 °C, *d* 750 °C, *e* 950 °C, and *f* 1150 °C

Furthermore, as shown in Fig. 1, it indicates that the carbonification reaction between ferrovanadium and amorphous carbon hardly occurs below 650 °C and practically completed at 750 °C. The carbonification reactions of FeV maybe as follows

$$3\mathrm{FeV(s)} + 4\mathrm{C(s)} = 3\mathrm{VC(s)} + \mathrm{Fe_3C(s)}. \qquad (1)$$

The carbonification reactions of V and Fe are as follows [5, 16]

$$\begin{aligned} &\mathrm{V(s)} + \mathrm{C(s)} = \mathrm{VC(s)} \\ &\quad \Delta G_{\mathrm{VC}} = -102090 + 9.851T \text{ J/mol} \end{aligned} \qquad (2)$$

$$\begin{aligned} &3\mathrm{Fe(s)} + \mathrm{C(s)} = \mathrm{Fe_3C(s)} \\ &\quad \Delta G_{\mathrm{Fe_3C}} = 26668.4 - 24.7456T \text{ J/mol} \end{aligned} \qquad (3)$$

where ΔG_T is the reaction free energy, T is the temperature (K).

When the reaction temperature is in the range 650–750 °C, the carbonification reaction-free energy of V is below zero. Therefore, according to the thermodynamical theory, above the ignition temperature (650–700 °C), the carbonification reaction of V can be easily carried out. At this temperature range, $\Delta G_{\mathrm{Fe_3C}}$ is positive and Fe_3C cannot be formed. Even at the highest reaction temperature

1150 °C, ΔG_{Fe_3C} is only slightly negative (−8.5 kJ/mol). However, ΔG_{VC} is lower than −88 kJ/mol and much smaller than ΔG_{Fe_3C} in the entire experimental temperature range (0–1150 °C). So, the VC phase is by far the most thermodynamically favored product compared with Fe_3C. Moreover, the atomic ratio of V and C is 1:1, so the products are mainly containing V_8C_7 and VC_{1-X}.

To compare with VC, both V_8C_7 and VC_{1-X} may be regarded as substoichiometric vanadium carbides. VC_{1-X} belongs to space group *Fm*3*m* with a small amount of C vacancies. Its lattice parameter is $a = 0.4170$ nm, and the vacancies of C are randomly distributed in the VC_{1-X} lattice. V_8C_7 belongs to space group $P4_332$ with ordered C vacancies and its lattice parameter is $a = 0.8334$ nm. In spite of the difference in space group and lattice parameter, V_8C_7 and VC_{1-X} have the same atomic arrangement if the C vacancies are not taken into account. With the annealing temperature rising and not high enough, the positions of the C vacancies change from disorder to order, and the crystal structure changes from *Fm*3*m* (VC_{1-X}) to $P4_332$ (V_8C_7) [2, 3, 17].

Figure 1 also shows that the intensity of the V_8C_7 and VC_{1-X} peaks increases with the sintering temperature. However, the intensity of α-Fe decreases and it is almost disappeared at 1150 °C (Fig. 1d–f). The reason might be that the reaction between the vanadium and carbon solid solution in the matrix is more complete. Moreover, the iron matrix is volatilized, melted, and overflows from the bottom of the mold after 1050 °C, especially at 1150 °C.

Densification and hardness

The effects of sintering temperature on the density and hardness of VC/Fe composites are shown in Fig. 2. Figure 2 shows that densification increases as the sintering temperature increases, reaching a maximum for the specimen sintered at 1050 °C. A maximum density of 6.27 g/cm^3 (∼96.5% relative density) can be obtained due to the enhanced activation of the plasma. The reasons for the density increases might be that with the increase in sintering temperature, the wettability between liquid phase and vanadium carbide reinforcement is improved, which intensifies dissolution–precipitation of vanadium carbide particles and increases the amount of liquid phase. As a result, the densification increases. However, high sintering temperature needs a larger electric current, which results in the local temperature too high. And because of vacuum sintering, excess sintering temperature causes severe volatilization of metal, and the matrix is melted and overflows from the end of the mold after 1050 °C (especially at 1150 °C), which results in the formation of voids in the sintered specimen, thereby the density decreases.

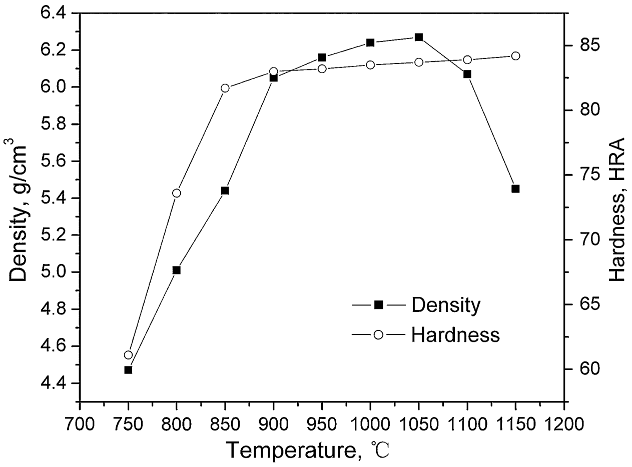

Fig. 2 Effects of sintering temperature on the density and hardness of VC/Fe composites

The relation between sintering temperature and hardness is also shown in Fig. 2. Figure 2 shows that the hardness continuously increases with temperature. However, the increase in hardness becomes slow above 900 °C. A maximum of 84.2 HRA can be obtained when the specimen was sintered at 1150 °C. The hardness could be affected by porosity, reinforcement content, and grain size [18]. Pores in materials have no resistance to applied stress, so dense materials with less porosity own higher hardness. Part of the increase below 1050 °C in hardness could be explained by the density's influence. Moreover, the content of vanadium carbide reinforcements increases with the temperature. The formation of vanadium carbide, which exhibits high hardness (2400 VHN for V_8C_7) [19], is beneficial to improve the hardness of the composites. However, the size of grains is increased significantly with sintering temperature, which will decrease the hardness. Therefore, the increase in hardness is slow between 900 and 1050 °C. The reason for the hardness increase at 1050 °C might be as follows: when the temperature is higher than 1050 °C, a part of iron matrixes, which exhibits low hardness, overflows from the specimens. Therefore, the ratio of reinforcements to iron matrix is larger, which causes the hardness increases while the relative density decreasing. However, with the increase in the sintering temperature between 1050 and 1150 °C, the porosity also increases, which can be confirmed from the SEM pictures. Thereby, the increase in the hardness is not significant.

Microstructure of the composite

The SEM micrographs and EDS analysis of VC/Fe composite are shown in Fig. 3. Figure 3a shows the SEM image of the specimen sintered at 1050 °C. The dark particles are vanadium carbide, and the white matrix is Fe. Figure 3a shows that the vanadium carbide particulates are near spherical and their sizes are about 1–3 μm. The reinforcements and the iron ones are homogenously

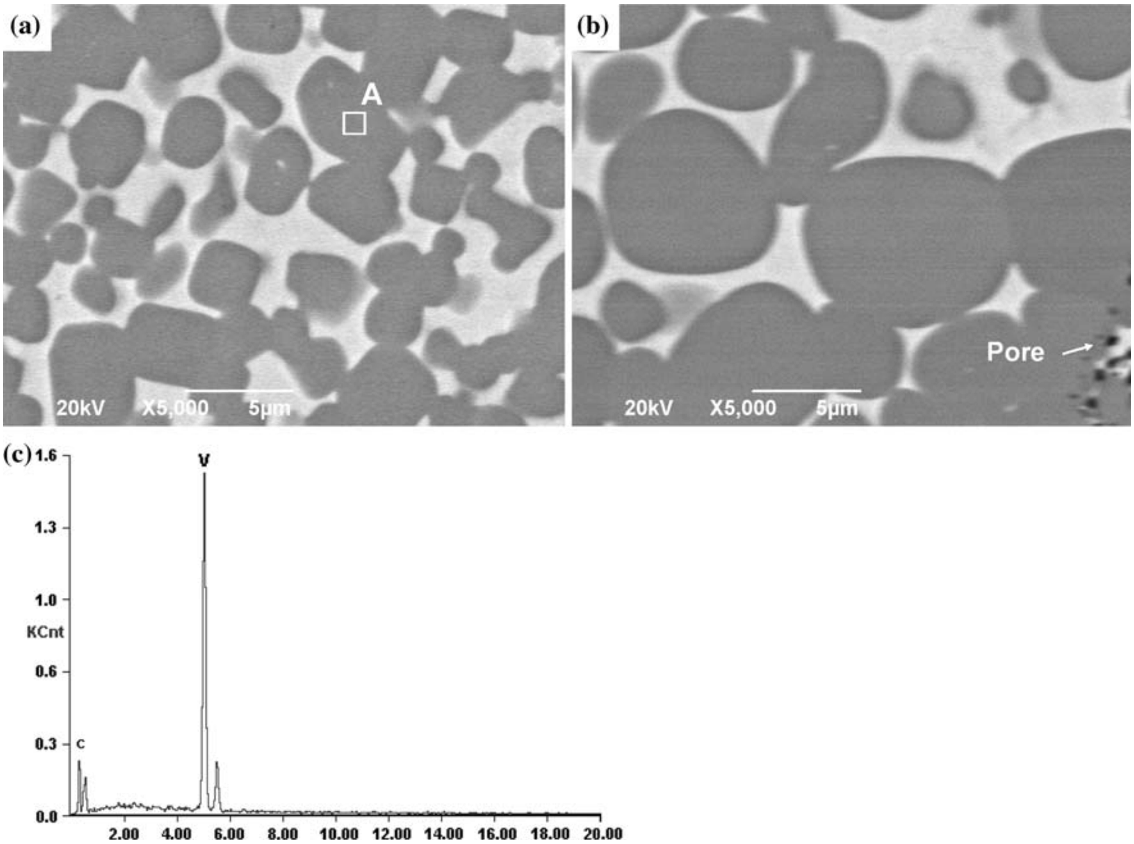

Fig. 3 SEM micrographs and EDS analysis of VC/Fe composite: **a** micrograph of the composite sintered at 1050 °C, **b** micrograph of the composite sintered at 1150 °C, and **c** EDS of point A

distributed. It is very important to obtain homogeneous and fine reinforcements in the matrix phase in order to enhance mechanical properties. The SEM image of the specimen sintered at 1150 °C is shown in Fig. 3b. It can be seen that the size of reinforcements is increased markedly. Obviously, the amount of matrix is also decreased, which results in the ratio of reinforcements to iron matrix becoming larger. In addition, some micropores can also be seen in the composites. It could explain the reason for the densities decreasing but the hardness having a slight increase after 1050 °C. In order to confirm the dark particulates are vanadium carbide, EDS analysis is carried out. Figure 3c shows the EDS spectra of the dark particulates (marked by point A in Fig. 3a). Obviously, this region is rich in vanadium and carbon. With the combination of the XRD results, it is evident that the dark particulates can be identified as V_8C_7 and VC_{1-X}.

Conclusion

SPS technique has been successfully applied to the reaction synthesis of vanadium carbide-reinforced iron matrix composite in situ using commercial ferrovanadium and amorphous carbon powders. After a relatively low onset temperature (650–700 °C), it can realize solid-phase diffusion between reactant V and C and the carbonification reactions of V easily. The densities increase at first and then decrease with the temperature. A maximum density of 6.27 g/cm^3 ($\sim$96.5% relative density) is obtained at 1050 °C for 5 min by the method. The hardness continuously increases with temperature, but grows slowly after 900 °C. A maximum of 84.2 HRA can be obtained at 1150 °C. The vanadium carbide particulates contain V_8C_7 and VC_{1-X} ($1-X = 0.66$–0.88). Moreover, the vanadium carbide particulates, that are in a size of 1–3 μm, and the iron ones are homogenously distributed when the composite is sintered at 1050 °C.

Acknowledgement This study was supported by a grant from the National High Technology Research and Development Program of China (863 Program) (No. 2008AA031105).

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