Study on VC formation mechanism and the microstructure of Fe-VC composite

Sijing Fu¹, Jing Wang²*

¹ College of Mechanical Engineering, Chengdu Technological University, No.1 Section 2, Zhongxin Avenue, Chengdu 611730, China;

² School of Materials Engineering, Chengdu Technological University, No.1 Section 2, Zhongxin Avenue, Chengdu 611730, China

Abstract

Iron matrix composite reinforced with VC reinforcement was produced through the synthesis reaction from FeV and C. VC formation mechanism was investigated using differential thermal analysis and X-ray diffraction analysis. The results show that FeV firstly decomposes into α-Fe and V, then V reacts with C to generate VC. The microstructure of Fe-VC composite was characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), the results indicate that the VC particles are distributed uniformly in the pearlite matrix, and the interface between VC reinforcement and pearlite matrix is clean. The abrasive wear test of Fe-VC composite was investigated with a MM-200 wear-test apparatus. The results show that as the load increases, the wear surface of Fe-VC composite is changed from the intermittent shallow grooves to long continuous deep grooves.

Keywords: iron matrix composite; VC particle; formation mechanism; microstructure; abrasive wear.

1. INTRODUCTION

Iron matrix composites reinforced with boride, nitride or carbide particulates have been the subject of significant investigation because they have superior mechanical properties in various conditions by combining all kinds of ceramic reinforcements with iron matrix (Cen et al., 2011; Srivastava et al., 2008; Akhtar, 2008; Das et al., 2004). Among these iron matrix composites, vanadium carbide (VC) particle reinforced iron matrix surface composites have recently received much attention due to VC particle high hardness and high melting point, good thermal and chemical stability, good wettability with iron matrix and low density (Euh et al., 2003; Wang et al., 2001; Thirumurugan et al., 2016; Dogan et al., 2001). However, the report on producing bulk Fe-VC composite is seldom. During the particulate reinforced iron matrix composite fabrication, there are main two processes: powder metallurgy technique and in situ synthesis technique. One of disadvantages for powder metallurgy technique is the interface between the iron matrix and particulate reinforcement is often a potential source of weakness because the surface of added particulates usually is polluted. However, the disadvantage can be overcome by in situ synthesis technique, in which the particulate reinforced phases can be formed directly by in situ reaction and have a clean interfacial structure with iron matrix (Yilmaz et al., 2009; Liu et al., 2009). In addition, in situ synthesis ceramic particles are fine and uniformly dispersed in iron matrix.
In this paper, bulk Fe-VC composite is prepared by in situ synthesis technique. The aim of this study is to investigate the microstructure of the Fe-VC composite and the VC formation mechanism.

2. MATERIALS AND METHODS

Iron powder, ferrovanadium powder (50wt%V), ferrochrome powder (70wt%Cr), ferromolybdenum powder (50wt%Mo) and carbon black powder as raw materials, were used to fabricate Fe-VC composite. The nominal chemical composition of Fe-VC composite was 40wt%V, 10wt%C, 2wt%Cr, 2wt%Mo and 46wt%Fe. The process conditions for preparing green compacts of Fe-VC composite were the same as that published in our team earlier work (Wang et al., 2008). The green compacts were 20mm in diameter and 35mm in height and the density of green compact was about 70% of the theoretical density. A vacuum furnace was used to sinter the green compacts at 800°C, 900°C, 1180°C for 60 minutes.

Fe-VC composites sintered at 1180°C were quenched and tempered. The holding temperature was 960°C, 200°C, respectively and the holding time was both 1 hour.

The specimens (10mm×10mm×10mm) were cut from Fe-VC composite (sintered at 1180°C, or quenched at 960°C and tempered at 200°C) for metallographic observation and polished on SiC emery papers up to 1200 mesh and finally etched with 4% nital (4ml HNO3+96 ml ethanol). The phase structure and microstructure of Fe-VC composite were examined by using X-ray diffraction (XRD), scanning electron microscopy (SEM) equipped with electron probe microanalyser (EPMA) and transmission electron microscopy (TEM).

A Shimadzu DT-2A differential thermal analyzer was used to conduct the differential thermal analysis (DSC) for Fe-V-C system. The heating rate and cooling rate were both 10°C min⁻¹, and the heating maximum temperature was up to 1000°C. High purity argon was inflated to protect Fe-V-C system in the whole test process and the flow rate of argon gas was 150 mL min⁻¹.

A MM-200 wear-test apparatus was used to perform the abrasive wear test of Fe-VC composite (sintered at 1180°C, quenched at 960°C and tempered at 200°C). The counterpart was hardened GCr15 steel ring with a hardness of 60 HRC. Before the abrasive wear test, a 200 mesh SiC abrasive paper was attached to the GCr15 steel ring which rotated at 400 rev min⁻¹. Each wear test was carried out on a fresh SiC abrasive paper. The loads were 29.4N, 50N and 100N, and the wear distance was 600m.

3. RESULTS AND DISCUSSION

3.1 VC formation mechanism

3.1.1 The DSC analysis of Fe-V-C system

Fig.1 shows the result of differential thermal analysis thermogram for Fe-V-C system. It can be observed that there are one endothermic peak and one exothermic peak. The endothermic peak with a maximum at 752.3°C may arise from allotropic change and carbon diffusion in the iron caused the decrease from 912°C (value for pure iron) according to our team previous work (Wang et al., 2008). The exothermic peak with a maximum at 814.5°C is attributed to exothermic reaction between FeV and C.

3.1.2 XRD analysis

XRD results of Fe-VC composites sintered at 25°C, 800°C and 900°C are shown in Fig.2(a)~(c), respectively. Fig.2(a) reveals that Fe-VC composite sintered at 25°C consists
of α-Fe, σ(FeV) and C(graphite). Fig. 2(b) reveals that Fe-VC composite sintered at 800°C is composed of α-Fe, σ(FeV), C(graphite) and V. Compared Fig. 2(b) with Fig. 2(a), it can be seen that a few of V has separated from σ(FeV). According to Fe-V binary alloy phase diagram (Nagasaki et al., 2002) shown in Fig. 3, it can be found that FeV(50wt%V) can decompose into α-Fe and V only the temperature being beyond 1227°C. Therefore, it can be rationally deduced that σ(FeV) stability decreases due to the addition of C(graphite). Fig. 2(c) reveals that Fe-VC composite sintered at 900°C is composed of α-Fe, σ(FeV), C(graphite) and VC. Compared Fig. 2(c) with Fig. 2(b), it can be found that a few of V has separated from σ(FeV). According to Fe-V binary alloy phase diagram (Nagasaki et al., 2002) shown in Fig. 3, it can be found that FeV(50wt%V) can decompose into α-Fe and V only the temperature being beyond 1227°C. Therefore, it can be rationally deduced that σ(FeV) stability decreases due to the addition of C(graphite).

3.1.3 The kinetic investigation of formation VC particles

The relationship between the rate of chemical reaction $K$ and the temperature of chemical reaction $T$ is defined by the equation (1) (McCartney D.G., 1989).

$$d\ln K/dT = E/RT^2 (1)$$

Where $T$ is thermodynamic temperature, $R$ is gas constant, $E$ is activation energy of chemical reaction.

Because $E$, $R$ and $T$ are greater than zero, $d\ln K/dT$ is greater than zero ($d\ln K/dT > 0$), indicating that the rate of chemical reaction $K$ increases as the temperature of chemical reaction increases.
reaction increasing. Thus, the rate of forming VC can be improved by appropriately raising the temperature of chemical reaction, and more and more fine VC particles can be formed in Fe-VC composite, which is beneficial to the microstructure and mechanical properties of Fe-VC composite.

![Figure 2. X-ray diffraction patterns of Fe-VC composites at different sintering temperatures (a) 25°C; (b) 800°C; (c) 900°C.](image)

![Figure 3. Fe-V binary alloy phase diagram.](image)

Nucleation rate of VC precipitated from liquid phase can be expressed by the following equation (2) (Yao et al., 2005).
\[ I = C N_0^p \exp \left( -16\pi \sigma \alpha a_{\alpha,L-S} f(\theta) / (3 K_B \Delta S \Delta T^2) \right) \] (2)

Where \( C \) is a coefficient associated with atomic diffusion, \( N_0^p \) is the embryos number per unit volume of melt, \( \Delta S \) is nucleation entropy, \( \Delta T \) is the degree of supercooling, \( \sigma_{\alpha,L-S} \) is the solid-liquid interfacial tension, \( K_B \) is the Boltzmann constant.

It can be known by the equation (2) that the nucleation \( I \) has an exponential-law dependence on the nucleation entropy \( \Delta S \) and a small change of \( \Delta S \) can result in apparent change of \( I \). In addition, \( \Delta S \) increases with the increase of \( V \) content, and the VC crystal nucleuses formed have high interfacial energy, as a result, the nucleation rate of VC is very high in the interface of C and V particles, and a lot of VC crystal nucleuses are formed in the driving force of nucleation.

In order to build the kinetics model of VC, three hypotheses are made in reaction process: (1) VC particles are spherical and the radius of the sphere is \( r \); (2) the whole reaction film is formed; (3) the double diffusion of reaction atoms V and C occurs in the interface of VC particles and the melt.

Reacting unit whose the cross-sectional area is \( A \) is selected in the radial direction. If the mole concentration gradient \( (dN_i) \) of reaction atom \( i \) in this reacting unit is \( dC_i / dr \), and there are \( dN_i (mol) \) reactants passing the cross-sectional area \( A \) in \( dt \) time, and the diffusion rate of the reactant is defined by the equation (3).

\[ -dN_i / dt = D_i A dC_i / dr \] (3)

If supposed \( N \) in the equation (3) is the volume of diffusion system, \( N_i / V = C_i \),

\[ dC_i / dr = A C_i / (V \delta) \], the equation (3) is changed to the equation (4).

\[ -dC_i / dt = D_i A dC_i / (V \delta) \] (4)

Where \( D_i \) is the diffusion rate of the reactant \( i \) in the reaction film, \( \delta \) is the thickness of the reaction film, \( A/V \) is the dispersion of the reaction system, \( C_i \) is the concentration difference of the reactant \( i \) in the interface of reaction film.

It is not difficult from the equation (4) that the factors influencing \( D_i \), \( \delta \), \( A/V \) and \( dC_i \), will effect the reaction rate, that is to say, the rate of generating VC is inversely proportional to the thickness of the reaction film, and is proportional to the concentration difference of V and C in reaction film and the dispersion of V and C in the Fe-V-C system.

The Gibbs Thomson-Law equation (5) defines the relationship between the VC particle radius and the interfacial tension.

\[ C_r = C_0 - [2M \delta_{PL} / (RT \rho_r)]C_0 \] (5)

Where \( C_r, C_0 \) is the solute concentration when the VC particle radius is \( r, r_0 \), \( M \) is the molar quantity of VC particle, \( \delta_{PL} \) is the interfacial tension between the VC particle and the melt, \( R \) is the gas constant, \( T \) is the thermodynamic temperature and \( \rho_r \) is the VC particle density.

According to the diffusion first law, the diffusive flux of the solute in the spherical area (\( R_C \) radius) is defined by the equation (6).

\[ J = (-4\pi R_C^2 D) dC_r / dR_C \] (6)

Where \( J \) is the diffusive flux of the solute, \( D \) is the diffusive coefficient of the solute, \( R_C \) is the radius of VC particle.
If supposed that the growing velocity of VC particle is \( \frac{dr}{dt} \), the moles of solute needed in unit time when VC particle grows is \( \frac{dn}{dt} = \frac{\rho 4\pi r^2}{M} \frac{dr}{dt} \).

The needed concentration of VC particle growth is provided by the diffusive flux of solute, and the relationship between the concentration and the diffusive flux of solute can be defined by the equation (7).

\[
\frac{(-4\pi R_c^2) dC_r}{dR_c} = (\rho 4\pi r^2 / M) dr/dt \quad (7)
\]

When VC particle grows from \( R_c = r \) to \( R_c = \infty \), the solute concentration in the melt is changed from \( C_0 \) to \( C_r \), the equation (7) is changed to the following formula (8).

\[
-1/r = \frac{DM}{[\rho r^2 (dr/dt)]} (C_r - C_0) \quad (8)
\]

According to the equation (5),(6),(7) and (8), the equation (9) can be obtained.

\[
dr/dt = 2DM_2 \delta l C_0 (RT^2 r^2) \quad (9)
\]

The growing velocity of VC particle is proportion to the melt concentration and inversely proportion to squared radius of VC particle.

### 3.3 Microstructure of Fe-VC composite

Fig.4 shows the result of X-ray diffraction pattern about the Fe-VC composite sintered at 1180°C. It can be seen that the Fe-VC composite consists of \( \alpha \)-Fe, VC and \( Fe_3C \), which confirms that VC reinforcements generate in Fe-VC composite. In light of VC formation mechanism, it can be known that the reaction (\( FeV+C=Fe+VC \)) happens. The equation (10) about the Gibbs free energy of the reaction is as follow.

\[
\Delta G^0 (J/m^3) = -102100 + 9.58T(298K < T < 2000K) \quad (10)
\]

In the range of sintering temperature investigated in this paper, it can be calculated that the Gibbs free energy of the reaction (\( FeV+C=Fe+VC \)) is negative, indicating the reaction can occur spontaneously in thermodynamics.

![Figure 4. X-ray diffraction patterns of Fe-VC composite sintered at 1180°C](image)

The micrographs of Fe-VC composites sintered at 800°C, 900°C and 1180°C are shown in Fig.5(a)~(c), respectively. In Fig.5(a), it can be found that there are many interconnected voids in composite, and the various kinds of particles are discrete, therefore the densification of the composite is very low. The compositions of point 1 and
point 2 in Fig.5(a) are analyzed by using electron probe microanalyser. The result shows that the composition of point 1 is 50.1wt%Fe and 49.9wt%V and the composition of point 2 is 100wt%C, indicating the particle in point 2 is graphite. Based on the composition of point 1 and the result of Fig.2(b), it can be concluded that the particle in point 1 is FeV, and the reaction (FeV+C=Fe+VC) does not happen in 800°C. In Fig.5(b), it can be observed that there are many small white particles as indicated by arrows. The content of V and C in the small white particle is 60.2wt% and 12.5wt% by using electron probe microanalysis, which confirms the small white particles are VC. This result is consistent with that of Fig.2(c). In Fig.5(c), it can be seen that the composite mainly consists of the spherical gray particles and the light areas, and the gray particles are uniform distribution relatively in the light areas. The electron probe microanalysis indicates that the content of V, C and Fe in gray particle is 70.7wt%, 15.4% and 2.5wt%, whereas the content of Fe, C and V in light areas is 90.3%, 0.9% and 3.5%, which indicates that the gray particles are VC and the light areas are Fe matrix. It can be also seen that the size of VC is 1-3μm and the interface between VC particles and Fe matrix is clean.

In addition, a few of voids in Fe-VC composite sintered at 1180°C can be found in Fig.5(c) (indicated by arrows). In order to obtain a complete dense Fe-VC composite, Patril et al. (2002) reported that the relationship between the minimum liquid content, the green density and the solubility of VC in the liquid.

\[
f_{l}^{\min} = \varepsilon_0 \frac{1 - X_i^L}{X_i^L + \varepsilon_0(1 - X_i^L)} (11)
\]

Where \( \varepsilon_0 \) is the initial porosity, and \( X_i^L \) is the solubility of element \( i \) in the liquid.

In light of the the formula (11), when the initial porosity (\( \varepsilon_0 \)) in Fe-VC green compact is 0.3, the VC solubility in liquid must reach 0.23~0.41 for purpose of preparing a fully dense composite. However, the VC solubility in liquid is only 0.013 when the sintering
temperature is $1180^\circ C$. If the VC solubility in liquid is only 0.013, the initial porosity ($\varepsilon_0$) in Fe-VC green compact has to be below 0.015, which is impossible for Fe-VC green compact pressed by traditional powder metallurgy technique.

Fig.6 shows the TEM micrographs of the Fe-VC composite sintered at $1180^\circ C$. It can be seen that the interface between the matrix and VC reinforcement is clean. The micrograph of the Fe-VC composite etched is shown in Fig.7. It can be found that the microstructure of matrix is pearlite, which is line with the TEM micrograph(Shown in Fig.6(c)).

When Fe-VC composite is sintered at $1180^\circ C$, liquid phase appears, indicating liquid sintering process occurs in fabricating Fe-VC composite. With the decreasing of system temperature and the temperature dropping below the liquidus temperature, it becomes solidified and the solidification process can be discussed by the Fe-V-C ternary phase diagram (shown in Fig.8)(Euh et al., 2003). Firstly, primary ferrites nucleate and grow from the liquid phase, and C and V elements become progressively poor in the liquid phase. The composition of liquid phase changes to ‘L’ along the dotted line. Eutectic reaction occurs at ‘L’. Secondly, when the temperature decreases to ‘U1’-1370°C (ternary quasi-peritectic temperature), some liquid phases are transformed to VC and austenite($\gamma$). As the temperature continues to drop until reaching ‘E2’-1120°C (ternary eutectic temperature), eutectic reaction ($L=\gamma+VC+Fe_3C$) takes place, and the residual liquid phase is transformed to VC, Fe$_3$C and austenite. Thirdly, further lowering the temperature, reaching 1000K, eutectoid reaction ($\gamma$=Pearlite) takes place, and the austenite is transformed to pearlite and the reaction is terminated.

As shown in Fig.9, a number of fine VC particles are precipitated in the tempered martensitic matrix, which leads to the hardness increase of Fe-VC composite. Fig.10 shows the XRD result of Fe-VC composite quenched and tempered, and the result is line with that of Fig.9.

**Figure 6.** TEM micrograph of Fe-VC composite sintered at $1180^\circ C$ (a)morphology of VC; (b)selected area electron diffraction of VC; (c)morphology of Fe matrix
Figure 7. SEM micrograph of Fe-VC composite (sintered at 1180°C) etched by 4wt% nital.

Figure 8. Liquidus projection of the iron-rich region of the ternary Fe-V-C phase diagram.

Figure 9. SEM micrograph of Fe-VC composite (sintered at 1180°C, quenched at 960°C and tempered at 200°C).
Figure 10. X-ray diffraction patterns of Fe-VC composite (sintered at 1180°C, quenched at 960°C and tempered at 200°C).

Figure 11. SEM micrographs of wear surface of Fe-VC composite at different loads. (a) 29.4N; (b) 50N; (c) 100N

3.4 Wear behavior of Fe-VC composite

Fig.11(a)~(c) shows the wear surface morphologies of Fe-VC composite at different load. In all micrographs, the wear surfaces of Fe-VC composite are characterized by grooves, which form as the SiC abrasive particles plough across the surface of Fe-VC composite and eventually remove material along sides. It can be seen that as the load increases, the abrasive wear becomes severe and the wear surface morphologies gradually changes from intermittent shallow grooves to long continuous deep grooves which are parallel to the sliding direction. During the wear process, the SiC abrasive particles deform the matrix of Fe-VC composite and cause microploughing and grooving in the surface of iron matrix. When the load is small, the depth of SiC abrasive particles penetrating the matrix of Fe-VC composite is shallow and the distance of SiC abrasive particles ploughing the matrix is short, resulting in the intermittent shallow grooves shown in Fig.11(a). As the load increases, the penetrating depth and the ploughing distance increase, as a result, long continuous deep grooves form, as shown in Fig.11(c).
4. CONCLUSION

Using Fe powders, Fe-50wt%V powders, Fe-70wt%Cr powders, Fe-50wt%Mo powders and carbon black powders, bulk Fe-VC composite is prepared by using in situ synthesis technique. Fine VC particles distribute evenly in pearlite matrix and the the interface between VC particles and pearlite matrix is clean. The VC formation mechanism may be as follows. First, FeV decomposes into α-Fe and V. Second, V reacts with C to generate VC. As the load increases, the wear surface of Fe-VC composite is from the intermittent shallow grooves to long continuous deep grooves.

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6. REFERENCES