

Microstructure and wear properties of TiC–VC reinforced iron based hardfacing layers

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TiC–VC reinforced Fe based hardfacing layers were obtained by shielded manual arc welding (SMAW) of which H08A rare electrodes were coated by different amounts of ferrotitanium (FeTi), ferrovanadium (FeV) and graphite. The microstructure of the hardfacing layers was investigated by means of scanning electron microscopy (SEM), transmission electron microscopy (TEM) and electron probe microanalysis (EPMA). The thermodynamics and effect of elements on the carbides were also discussed. It was shown that TiC–VC carbides could be formed during arc welding. The composition and amount of flux evidently affect the microstructure and properties of the coatings. Good crack resistance and higher hardness of the harfacing layer could be obtained, while the amounts of graphite, FeTi and FeV were controlled within a range of 8–10%, 15–18% and 8–12% respectively. TiC–VC reinforced Fe based hardfacing layers possess much greater wear resistance and a smaller friction coefficient than 1045 steel substrate.

Keywords: TiC–VC particles, Fe based hardfacing layer, Microstructure, Wear properties

Introduction

Wear related failure of machinery components is considered as one of the major reasons for the inefficiency of a variety of engineering applications. It is reported that surface modifying technology is one of the effective technologies that reduce the effects of wear.^{1–4} There are various surface methods for modifying the surface properties of substrates, such as plasma spraying, flame spraying, laser cladding, hardfacing, chemical and physical vapour deposition processes, etc. Among the proven techniques of surface modification, hardfacing has been especially effective in the cases that close dimensional tolerances are not required.⁵ Hardfacing coatings can be deposited as a thick alloy coating ranging from 750 μm to a few millimeters by welding deposition.

It is known that one of the most important parameters controlling the wear behaviour of the material is hardness.⁶ In general, the greater the hardness, the greater the abrasion resistance of the material. Therefore, a high content of carbon and carbides forming elements are added into the flux of the hardfacing electrode. For example, the composition of the deposited weld metal of coated electrode EDZ-B2-08 is 4.0–6.0Cr–8.5–14.0W–3.0C (wt-%), and its hardness is over 60 HRC. However, owing to the high solubility of Cr and W in steel, there are insufficient carbides in the hardfacing coating, and the matrix solid solution is

excessively strengthened. On the other hand, special carbides are produced in the matrix metal, such as the primary carbides and the secondary carbides either separately or in some combination, and some carbides form network carbides. Twinned martensite is also found in the matrix. This results in deterioration in toughness of the matrix metal, and consequently a fissured coating with a strong tendency to spalling.

In fact, wear resistance is a consequence of a specific favourable combination of hardness and toughness. It is reported that wear resistance can be improved when hard particles are embedded in a tough, metallic matrix where the particles act as bearings for the sliding surfaces, reducing friction coefficients or preventing adhesive metal transfer.^{7,8} In the recent developments, it has been shown that the toughness of the weld could be increased markedly when the carbides are granular in form and distributed evenly in the matrix metal.^{9–11} Some strong carbide forming elements, such as niobium (Nb), titanium (Ti), vanadium (V) and zirconium (Zr) could combine with carbon to form granular carbides and decrease the carbon content in the matrix, which is favourable for improving the toughness of the coating.

The aim of the present study is to achieve a harfacing layer containing a high volume fraction of carbide and a tough matrix. Ti and V are used as the main carbide forming elements together. The TiC–VC particles were formed from the reaction between Ti, V and C during welding.

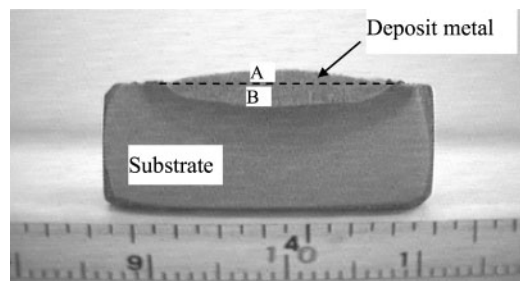
Experimental detail

An H08A bare electrode with 4 mm diameter was used as the core wire of the hardfacing electrode. It was coated with a marble–fluorspar–graphite systematic flux. The flux contains 15–18FeTi, 8–12FeV, 25–30TiO₂,

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1 Schematic illustration of dilution

6–10CaCO₃, 10–14CaF₂ and 8–10graphite (purity 99.5%) (wt-%).

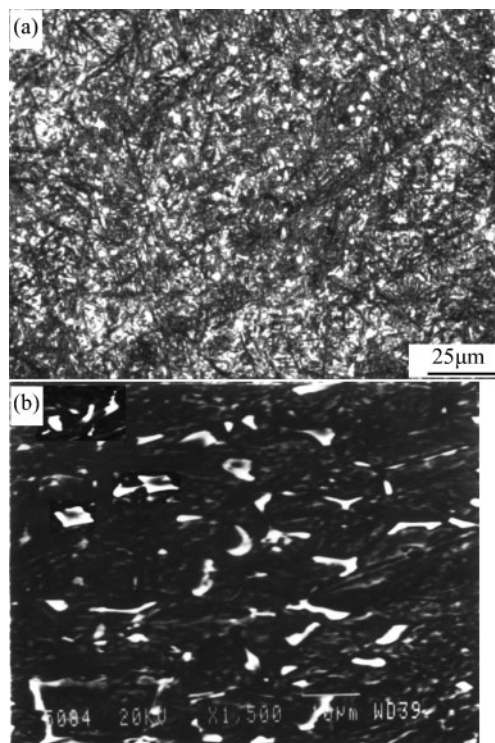
The hardfacing was done on a 1045 steel substrate using manual shielded metal arc welding (SMAW) under direct current with a reverse polarity. To assure the dryness of the electrode, it was baked in a furnace at 250°C for 1 h. The control of dilution is an important issue during welding. Dilution is the mixing of the base metal (substrate) and the applied metal, and is defined as the change in the chemical composition of a deposited metal caused by the admixture of the base metal or previous weld metal in the weld bead. It is measured by the percentage of the base metal or previous weld metal in the weld bead for bead-on-plate welds (Fig. 1). It can be calculated with the following equation

$$\text{Dilution} = \frac{S_B}{S_B + S_A} \times 100\% \quad (1)$$

where S_A and S_B are the area of the deposit metal and base metal, respectively. The more the base metal is melted, the greater the alloying of the deposit with the base metal. In general, the base metal has less carbon and alloy content than the deposit materials. Therefore, high admixture reduces the first layer alloy content and hardness. In most cases, the first layer of hardfacing has smaller wear resistance but greater impact resistance than that of the undiluted alloy. In order to avoid the effect of dilution, the hardfacing coating was deposited in a 2 mm thickness layer. Then hardfacing on the second and third layer was performed with the same electrode, which were about 3 mm in thickness, and with an interpass temperature below 40°C. The welding parameters were as follows: welding current 170–180 A, arc voltage 20–25 V.

Samples were cut from the hardfacing coating using an abrasive cutting machine under water cooling condition. The microstructure was observed with an optical microscopy (OM), a scanning electron microscopy (SEM) (JXA-840) and a transmission electron microscopy (TEM) (H-800). The phase distribution of elements was examined using electron probe microanalysis (EPMA) (JXA-8800R). The overall composition was determined by X-ray fluorescence analysis, and the micro-zone composition was investigated using energy dispersive spectrometer (EDS). The phase structure of the coatings was analysed using X-ray diffractometer (XRD) (D/Max-Rc). The hardness of the hardfacing coatings was measured by means of the average measurements taken from the surface of the coatings with an HR-150A hardness meter.

Tribological properties were performed on wear testing machine (model: MM-200, China) using block and ring specimens under dry sliding at room temperature. The test specimens were machined to



a OM; b SEM

2 Microstructure of third hardfacing layer

blocks with a size of 8 × 8 × 18 mm. The ring material of the wear couple was a hardmetal containing 92%WC and 8%Co. The wear conditions were 49 N normal load, 0.84 m s⁻¹ sliding speed with a sliding distance of 750 m. The coefficient of friction μ was calculated using the following equation

$$\mu = \frac{2M_f L}{D \sum Q_i L_i} \quad (2)$$

where M_f is the moment of torsion measured using a PY1 type moment speed gauge, L is the length of the pin arm, D is the diameter of the ring, and $\sum Q_i L_i$ is the sum of the parallel moments loaded on the lever.

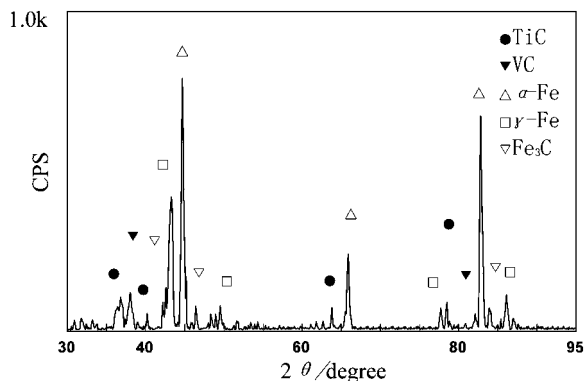
Results and discussion

The overall composition of the hardfacing layer is 1.1C–0.08Si–0.34Mn–3.96V–1.44Ti–0.01S–0.014P (wt-%). The average hardness of the coating is 58–62 HRC.

Microstructural characteristics

The microstructural features of the top surface of the hardfacing coating is shown in Fig. 2. The structure reveals dark areas of martensite in the matrix and a number of small white carbide particles embedded in it. The carbides are in irregularly cuboidal form with a dispersed distribution in the matrix. Their sizes vary from 2 to 4 μm. Although some areas show more carbides than others, the distribution of carbides is, in general, uniform in the matrix.

Figure 3 shows the X-ray diffraction spectrum of the hardfacing coating. It can be found that the coating is composed of TiC, VC, Fe₃C, α -Fe and γ -Fe, which means that the TiC and VC carbides can be formed during the welding procedure. In addition, no remaining graphite, ferrotitanium or ferrovanadium identified in



3 X-ray diffraction spectrum of hardfacing coating

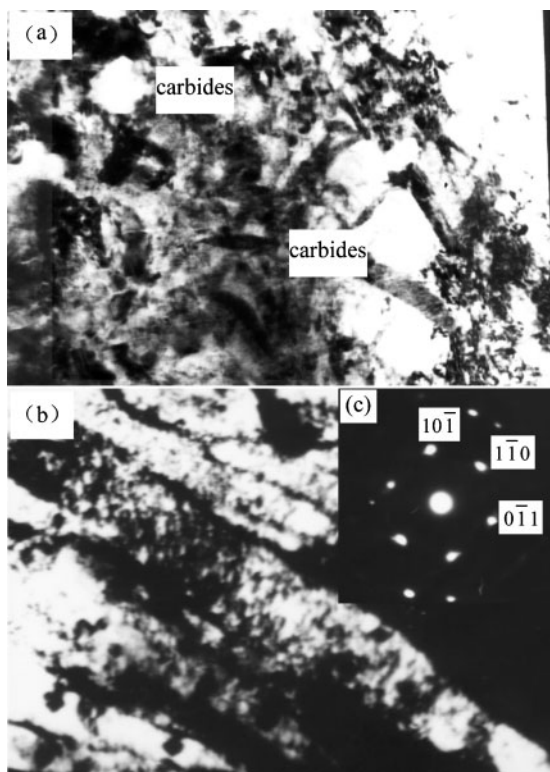
the X-ray diffraction pattern shows that the reaction synthesising TiC and VC is almost complete.

A TEM image of the hardfacing layer is shown in Fig. 4. It indicates that bulk carbide was embedded in the lath martensite and retained austenite matrix. Lath martensite contains low carbon and possesses good strength and toughness. The thin austenite film is favourable to the prevention of the propagation of cracks. The formation of low carbon martensite mainly resulted in carbide precipitation, which consumed the carbon in the matrix.

Figure 5 shows the phase distribution based on the results of EPMA analysis for elements [Ti] and [V] in the coating. The carbides of titanium and vanadium were detected in the cubic or granular particles.

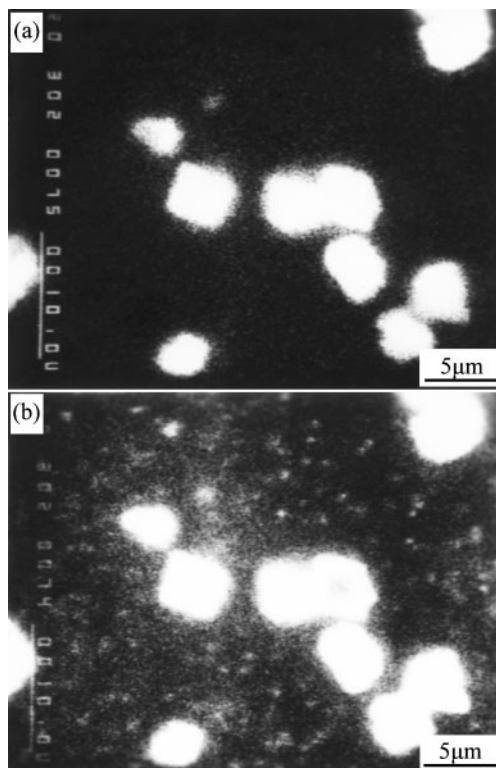
Thermodynamic analysis and predictions

For thermodynamic predictions, it is essential to consider all possible reactions for the Fe-Ti-V-C



a carbides in hardfacing layer; b matrix; c electron diffraction pattern of martensite

4 TEM image of hardfacing coating



a Ti; b V

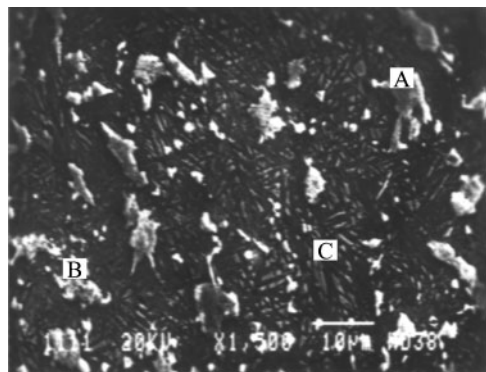
5 EPMA analysis of TiC and VC particles

system. Several researchers¹²⁻¹⁶ have studied thermodynamics of Fe-Ti-C system. It has been concluded that the system is very active and complex owing to the temperature and activities of the elements. For the Fe-Ti-V-C system, possible reactions between Ti-C, V-C, Fe-Ti and Fe-C are being considered. Various reaction equations accompanied by their respective free energy changes for the formation of carbides from respective elemental state are extracted from various sources, which are listed in Table 1. The free energy values help with predicting the formation of carbides relative to each other.

From the Gibbs free energy, it is evident that TiC and VC are the stable carbides, and the free energy of formation does not change significantly with temperature. This implies that the entropy of the formation of the carbides is almost negligible. Therefore, it is reasonable to assume that free energy of the carbides varies in a similar manner even at the temperature attained during the arc welding process. Moreover, it can be seen that

Table 1 Free energy of reaction as function of temperature¹²⁻¹⁶

Reaction	Free energy, J mole ⁻¹	Temperature range, K
Ti+C=TiC	-183172+10.09T -186731+13.20T	298-1155 1155-2000
3Fe+C=Fe ₃ C	25958-23.27T 26711-24.78T	298-463 463-1115
2Fe+C=Fe ₂ C	10360-10.17T 19860-10T 18420-10T	1155-1808 298-1155 1155-1808
Ti+2Fe=Fe ₂ Ti	-53300+53.7T	298-2000
Ti+Fe=FeTi	-39822+14.9T	298-2000
V+C=VC	-102090+9.581T	298-2000



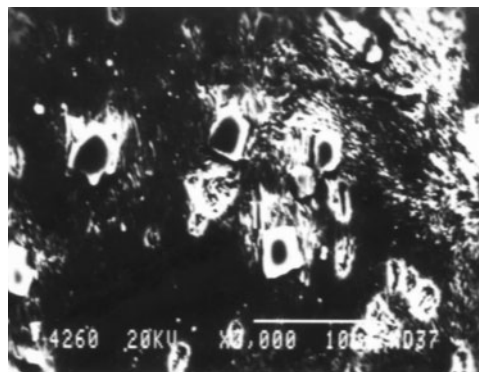
6 Microstructure of droplet

the Gibbs free energy for the formation of both TiC and VC is always negative at the arc welding temperature, indicating the possibility of the formation of TiC and VC. In addition, it implies that the formation of TiC and VC occurs at the stage of droplet reaction during welding. This result can be conformed by the chill droplet test. Figure 6 shows the microstructure of the chill droplet. EDS analysis of phases A, B and C shown in Fig. 5 reveals that the composition of phase A is 44.11Ti-50.97V-4.92Fe, of phase B 34.61Ti-61.76V-3.60Fe, and of phase C 0.09Ti-1.34V-1.08Mn-97.49Fe (wt-%), it indicates that phases A and B are TiC-VC carbides, and phase C is the Fe based matrix.

Owing to the sublimation and exothermicity of graphite and the decomposition of CaCO_3 at high temperature, CO and CO_2 gases were produced during welding. Moreover, slag forming constituents of the flux, such as CaCO_3 , TiO_2 and CaF_2 , etc. formed the slag, which covered the surface of the molten metal. Both CO or CO_2 and slag can prevent N_2 from air entering into the arc and protect the molten metal during welding. Therefore, the reaction between Ti/V and N can be avoided effectively. Oxygen, however, cannot be avoided from entering into the arc atmosphere, so that the arc atmosphere and slag have strong oxidation. Therefore, FeTi acts as carbide forming element and deoxidiser, and depletes at the stage of droplet reaction. Consequently, there are few active Ti atoms in the subsequent reaction stage in the molten pool, and the quantity of Fe_2Ti in the microstructure will be very small even if it can be formed during arc welding, resulting in no Fe_2Ti peaks (Fig. 3). It is noteworthy that apart from the temperature, the activity of carbon also plays an important role in the formation of various reaction products. Some carbon diffuses into the melted Fe to form Fe_3C during the solidification, therefore, a Fe_3C peak was observed, as shown in Fig. 3.

Effect of elements on microstructure and properties

The present study shows that the key factor affecting the microstructure and properties is the amount of FeTi, FeV and graphite. The hardness increases rapidly with increasing content of graphite when the amount of graphite is less than 12%. A large quantity of cementite or ledeburite can be observed around the TiC-VC carbides or in the matrix when the amount of graphite is over 12% (Fig. 7), which leads to poor crack resistance. However, while the amount of graphite is less than 5%, there are fewer alloy carbides, which decreases wear



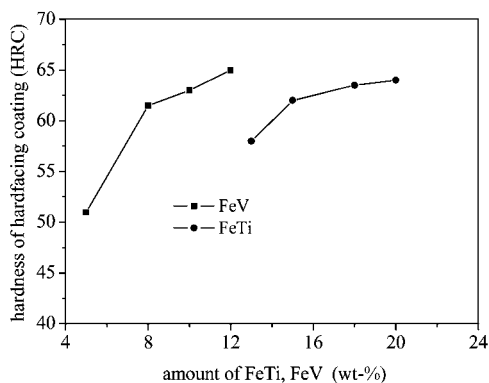
7 Microstructure of cementite around TiC-VC carbides

resistance. Therefore, it is useful to control the amount of graphite within a range of 8–10%.

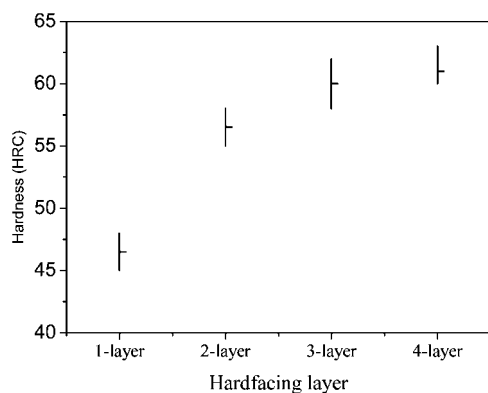
Both of titanium and vanadium are strong carbide forming elements. Figure 8 shows the relationship between the hardness and amount of FeTi and FeV. It indicates that with an increase in the amount of FeTi and FeV, the hardness of the coating increases. This may be attributed to the increase in the quantity of TiC (3200 HV) and VC (2800 HV) in the hardfacing coatings. TiC and VC also have a good thermal stability, which can restrain boundary movement and prevent grains from coarsening. However, because of the diffusion at the stage of solidification, some TiC and VC diffuses into the slag, resulting in an increase of the melting point and the viscosity of the slag. Slag detachability and fluidity become bad, when the amounts of FeTi and FeV in the flux are over 20% and 12%, respectively.

Effect of dilution on hardness and microstructure

In order to analyse the effect of layers on hardness, some samples were deposited in four layers. Figure 9 shows the variation of hardness with hardfacing layers under investigation. The average hardness of the first layer is 46.5 HRC, the second layer 56 HRC and the third layer 60.5 HRC. However, the average hardness of the fourth layer is only 61 HRC. It suggests that the hardness of the hardfacing layer increases as the number of the deposited layers increases, but the hardness increases slowly when there are more than three hardfacing layers. The variations in chemical composition of hardfacing layers are listed in Table 2. As shown in Fig. 9 and



8 Effect of amount of FeTi and FeV on hardness of coatings



9 Relationship between number of layers and hardness

Table 2, it indicates that the dilution of the substrate becomes less while there are more than three hardfacing layers.

Figure 10 shows the SEM morphology of the first hardfacing layer. Compared with the third layer (Fig. 2b), there is less carbide particles in the first layer. It also indicates that the dilution of the substrate obviously influences on the microstructure of the first layer.

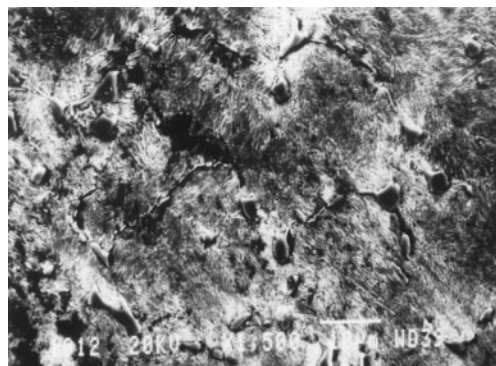
Wear properties

Figure 11 shows the wear volume of the TiC-VC particle reinforced Fe based hardfacing layer as a function of sliding distance with an applied load of 49 N, compared with the hardfacing layer of EDZ-B2-08 and 1045 steel substrate. From Fig. 8, it can be seen that the hardfacing layer causes significantly enhanced wear resistance. The hardfacing layer reinforced by TiC-VC particles has the smallest wear volume and wear rate.

In general, the wear resistance of the material increases with increasing hardness. Compared with 1045 steel, hardfacing layers have greater hardness, therefore greater wear resistance. However, wear resistance is a consequence of a specific favourable combination of hardness and toughness. The hardfacing layer reinforced by TiC-VC particles has almost the same hardness as the hardfacing layer deposited by EDZ-B2-08, but it has much greater wear resistance than that of the hardfacing layer deposited by EDZ-B2-08. For the hardfacing layer of EDZ-B2-08, there are insufficient carbides in the hardfacing coating owing to the high solubility of Cr and W in steel, the carbon cannot diffuse out of the carbide and react with the matrix metal. Therefore, special carbides in the matrix are produced, which cause undesirable embrittlement.⁷ In the case of carbide, the carbides of Cr and W tend to precipitate along grain boundaries, which results in deterioration in toughness of the matrix metal. The consequence is a fissured coating with a strong tendency to spalling. For TiC-VC particle reinforced hardfacing layer, Ti and V

Table 2 Variation of chemical composition with hardfacing layers, wt-%

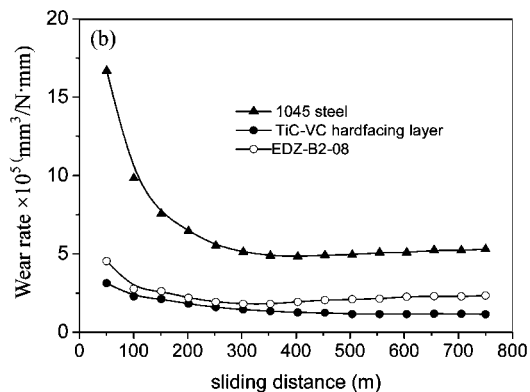
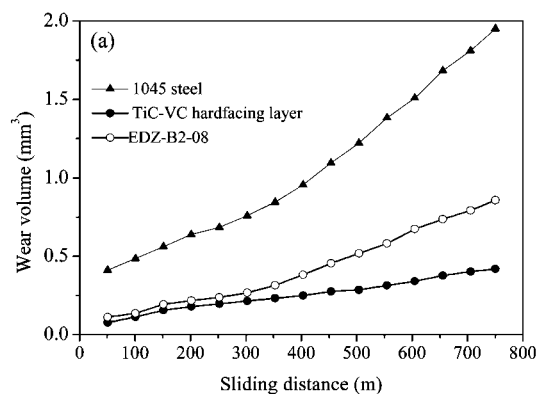
Layer no.	C	Si	Mn	V	Ti	S	P	Fe
1	0.7	0.32	0.48	0.73	0.36	0.012	0.002	Bal.
2	0.9	0.15	0.42	1.05	0.64	0.01	0.018	Bal.
3	1.2	0.08	0.34	1.66	1.44	0.01	0.014	Bal.
4	1.31	0.06	0.21	1.81	1.42	0.01	0.008	Bal.



10 SEM morphology of first layer

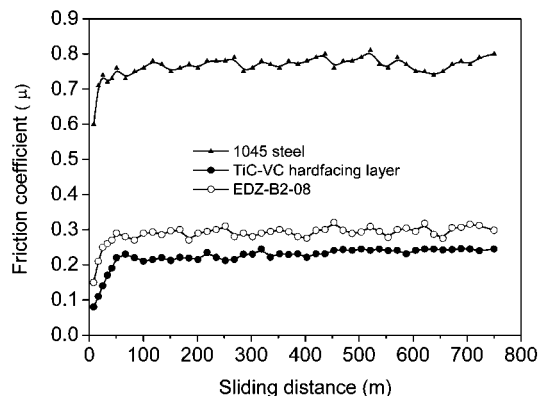
are strong carbide forming elements. This combines with carbon to form TiC or VC carbides, which have a high melting point and high hardness. Meanwhile, the structure of the matrix is lath martensite, which contains a low content of carbides and shows a good combination of strength and toughness. This kind of structure provides the weld metal with both high hardness and crack resistance. The hard TiC-VC particles do not easily come out in the matrix during dry sliding. Therefore, the hardfacing layer reinforced by TiC-VC shows higher wear resistance than that of hardfacing layer deposited by EDZ-B2-08.

The friction coefficient of the TiC-VC particles reinforced Fe based hardfacing layer is smaller than that of the steel substrate and EDZ-B2-08 hardfacing layer (Fig. 12). With increasing sliding distance the friction coefficient of the substrate undergoes a slight increase while that of the hardfacing layers decreases slightly. In addition, a lot of fluctuation in the values of the friction coefficient is seen. A possible explanation for



a wear volume; b wear rate

11 Wear volume and wear rate v. sliding distance



12 Friction coefficients v. sliding distance

such fluctuation in the friction coefficient values has been suggested on the basis of a 'stick and slip' mechanism.¹⁷ As the asperities adhere during the wear, the moving parts stick, leading to high friction values. As the junction ruptures under the applied load the friction tends to zero.

Conclusions

1. Fe based hardfacing layers reinforced by TiC-VC particles were produced by arc welding. TiC-VC particles are formed by metallurgical reaction during arc welding. TiC-VC particles with size ranging from 2 to 4 μm are found to be uniformly dispersed in the matrix.

2. The amount of FeTi, FeV and graphite affects the microstructure and hardness of the hardfacing coating. Excellent microstructure and hardness of hardfacing coating can be obtained, while the amounts of graphite, FeTi and FeV are controlled within a range of 8–10%, 15–18% and 8–12%, respectively.

3. The TiC-VC reinforced Fe based hardfacing layer possesses much higher wear resistance and a lower

friction coefficient than 1045 steel and the hardfacing layer deposited by EDZ-B2-08.

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