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Effects of vanadium addition on microstructure and tribological performance of bainite hardfacing coatings

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Abstract: New hardfacing coatings with different vanadium (V) additions were prepared by surfacing technology. The microstructures of the hardfacing coatings were analysed by field emission scanning electron microscope (FESEM) equipped with energy dispersive X-ray spectrometry (EDS) and examined by transmission electron microscope (TEM). The hardness and wear resistances of the hardfacing coatings were measured.Worn debris were collected at the end of wear test and analysed. The precipitation temperature of the phases in the hardfacing coatings and the mass fraction of MC carbide were calculated by Jmatpro software. The experimental results show that, the hardfacing coating mainly consists of granular bainite. No significant change in the size of linear martensite-austenite (M-A) islands is observed with increase of V addition,while the size of massive M-A islands is decreased. The wear resistance of the hardfacing coating reaches a maximum level with V content of 0.14wt.%. The calculated results show that, the mass fraction of MC carbide is increased with increase of V content. Based on calculation following two-dimensional mismatch theory, MC carbide is a heterogeneous nucleus of the ferrite resulting refined ferrite in the hardfacing coating.

Keywords: Hardfacing coating; Vanadium; Bainite; wear resistance; MC carbide.

1. Introduction

With the rapid development of the high speed railway, the requirement for the high quality material for rail manufacture and maintenance is in increasing demand [1,2]. At present, the high speed rail materials commonly used are pearlite steels such as steel U71Mn and U75V (GB 2581-81 material system). One main factor limiting wider applications of these materials is low toughness [3]. In addition, the wear resistance of the current material system used is not sufficient to achieve a longer service life, as, after being used for a period time, the high speed rail has to be replaced due to out of limit wear. In many case, remanufacture is required.

Hardfacing (harden-surface-welding) is an effective method to remanufacture failed rails. Hardfacing could be defined as "coating deposition process in which a wear resistant, usually harder, material is deposited on the surface of a component by welding techniques". In most cases, hardfacing is used for controlling abrasive and erosive wear, like in mining, crushing and grinding, and agriculture industries. It is considered as an economical way to improve the performance of components subjected to sever wear conditions, with a wide range of applicable filler materials [4]. By hardfacing, the shape and size of the worn rail could be restored, in the mean time , a better wear resistance can be achieved [5, 6]. Generally, the hardfacing consumables are divided into three main groups : pearlite consumable, austenite consumable and martensite consumable. When the pearlite hardfacing consumable is used to remanufacture failed rail, both the strength and toughness of the hardfacing coating couldn't fully meet the requirement on mechanical properties of high speed rail [7]. When the failed rail was remanufactured using the austenite hardfacing consumables, work hardening will occur on the surface of the hardfacing coating after being used for a period of time. During the work hardening process, the stress induces austenite to martensite transforms, which reduces the contact fatigue property of the hardfacing coating and shorten the service life.[8]. When the failed rail was remanufactured by the martensite hardfacing consumable, cracks usually initiate on the surface of the hardfacing coating [9]. In addition, the remanufactured rail needs to be preheated and heat-treated when using traditional welding consumables.

Due to itshigh strength and toughness, bainite steels have attracted the attention ofresearchers worldwide [10-13]. In order to meet the requirements of high speed rail, it is of significant potential and importance to develop novel bainite hardfacing consumable to remanufacture failed rails. As it is well-known that bainite steel can normally be obtained during isothermal process. However, hardfacing is a continuous cooling process, so it is a difficult and challenging task to obtain bainite structure during a hardfacing process with welding.

In recent years, alloy elements vanadium (V), niobium (Nb) and titanium (Ti) as micro-alloying elements are increasingly being used to improve the steel performances. [14, 15]. Alloy element V can not only control the transformation from γ-Fe to α-Fe, but also randomly precipitate in bainite steel as MC carbide, this strengthening mechanism is already successfully s used in developing high strength low alloy (HSLA) steels. However, there is very limited work on the design and development on bainite hardfacing coatings with V addition for rail remanufacturing. In this work, new bainite hardfacing consumables with V additions has been developed and analysed. The microstructure and the wear resistance of the hardfacing coatings with different V addition were tested , and the refinement mechanism of the hardfacing coating with V addition and the microstructure-wear resistance relationship was discussed.

2. Experimental

2.1 Materials

A new hardfacing composition for remanufacturing the failed rail were designed to produce a bainite structure. The powders of the hardfacing coating consist of ferrosilicon, nickel, ferromolybdenum and so on. In order to analyze the effect of alloy element V on the microstructure and wear resistance of the hardfacing coating, the additions of ferrovanadium in the hardfacing coating were varied as 0wt.%, 1wt.%, 3wt.% and 5wt.% respectively. The steel core of the hardfacing consumable was made of low carbon steel H08A, with a composition of (%): C≤0.1, Mn=0.3-0.5, Si≤0.03, Cr≤0.2, Ni≤0.3, S≤0.03, P≤0.03.

2.2 Experimental Methods

The steel Q235 plates (Chinese standard GB T 708-1988)were used as the substrate. Multi-pass manual arc welding for three layers was deposited. The welding electric current is 140-150A, voltage is 24-26V and welding speed is 1.1-1.7mm/s. The chemical compositions of the hardfacing coatings were measured by ADVANT XP-381 X-ray fluorescence spectrophotometer, the result is listed in Table 1.

The hardfacing coatings were etched by 4% nitric acid alcohol after being polished metallographically. Subsequently, the microstructures were observed by field emission scanning electron microscope (FESEM) (Hitachi S3400), and examined by transmission electron microscope (TEM) type of Jem2010. The compositions of carbide were analyzed by energy dispersive X-ray spectrometry (EDS).

The macro hardnesses of the coatings were measured by a HR-105A Rockwell hardness tester. In the wear tests, a dry wear abrasion testing machine was specially designed, as shown in Fig. 1(a), in order to speed up the test. Fig. 1(b) shows the morphology of SiC abrasive particles on the abrasive belt. Fig. 1(c) is a cross-sectional drawing of the specimen holder. The size of abrasive particles is about 180 μm. The wear test velocity is 1.8×10^4 mm/min. The load is 100 g and the specimen size is 20 mm×10 mm×15 mm. In order to reduce experimental error, six specimens were tested from each composition. Electronic balance with accuracy of 0.1 mg was used to weigh the mass loss of the hardfacing coating every 60 minutes. After the wear tests, the worn debris were analysed by FESEM.

The Continuous-Cooling-Transformation (CCT) diagram and Time-Temperature-Transformation (TTT) diagram of the hardfacing alloys, and the precipitation temperature and mass fraction of MC carbide were calculated by Jmatpro software (Thermotech Ltd, UK). Refinement mechanism of MC carbide as the heterogeneous nuclei of ferrite was calculated according to the two-dimensional mismatch theory proposed by Bramfitt [17].

3. Experimental results

3.1 Microstructure

3.1.1 Metallographic microstructure

The microstructures of the hardfacing coatings with different V additions are shown in Fig.1. The structure mainly consist of granular bainite with martensite-austenite (M-A) islands dispersely distributed in the proeutectoid acicular ferrite. From **Fig. 2**, the microstructure of the hardfacing coating without V addition is relatively coarse. With increase of V addition, the structure becomes much finer. However, in the specimen with 0.27wt. %, carbon-poor (carbon depletion???) zone start to appear, which is damaging to the properties and performance of the hardfacing coating. This indicates that it is necessary to control the V addition in the hardfacing coating to achieve an optimum strengthening effects.

As shown in **Fig.2**, the M-A islands in the microstructure of the hardfacing coating can be divided into two types. One is massive island along the grain boundaries and another is linear island inside. With the increase of V addition, the microstructure of the hardfacing coating is refined slightly. There is limited change in the size of linear M-A island , while the size of the massive island is decreased with increasing V content. Because alloy element V is a strong carbide forming element, it is easier to capture carbon from grain boundaries than inside the grain. The existence of carbon-poor zone (*carbon-depleted zone???)* indicates that the excess V addition could have adverse influence on the property and performance of the the hardfacing coatings.

3.1.2 TEM analysis results

In order to further investigate the microstructures of the hardfacing coatings, TEM were used , typical result is shown in **Fig.3**. **Fig.3 (a)** shows the morphology of the typical triangular grain boundary in the equiaxed ferrite, and the high dislocation density exists around the ferrite grains. **Fig.3 (b)** shows the hybrid structure of the M-A islands and the lath ferrite. The dislocation cell structure can be formed by the entanglement of dislocation lines,the denser the dislocation cell structure is, the higher the intensity of dislocations.

The second-phase particles found in the ferrite is shown in **Fig.3 (c)**. It is clearly shown that , the second phase precipitates around the grain boundaries and the dislocation lines. Based on analysis of the diffraction spots, the second-phase particle is identified to be MC carbide, in which M is mainly the elements V and Mo. As shown in **Fig.3 (d)**, the grain boundaries turn to curl, this is probably due to the pinning effect of the second phase particle.

3.2 Hardness and wear resistance of the new hardfacings

3.2.1 Hardness

The hardness of the hardfacing coatings with different V addition are listed in Table 1 together with the compositions. the hardness of the hardfacing coating Without V is HRC 25. With 0.05wt.%, Vthe hardness is much higher at HRC 32. Further increasing V addition to 0.14wt.%, the hardness of the hardfacing coating reaches a maximum at HRC 33. The hardness then starts to drop with V content. When V content is 0.27wt.%, the hardness value is HRC 30.

3.2.2 Wear resistance

The wear resistance can be expressed as follows:

$$\varepsilon = 1/\omega \tag{1}$$

$$\omega = \left(m_0 - m_1\right)/t \tag{2}$$

where ε is the wear resistance; ω is the wear rate; m_0 is the initial weight; m_1 is the final weight; t is the time.

Calculated based on formula (1) and test data of the weights before and after each test, the wear resistances of the hardfacing coatings are shown in **Fig.4**. The data show that, with increase of V addition, the wear resistances of the hardfacing coatings increase. The highest value is 4320 (g/ min)$^{-1}$ with the sample of 0.14wt.% V. .

The morphologies of worn debris from the wear tests of the hardfacing coatings are shown in **Fig.5**. As shown in **Fig.5 (a)**, the debris from the hardfacing without V addition, are uneven, and the particle are much larger (about 100 μm in length). With the hardfacing containing0.14wt.%, V, the debris are much smaller **(Fig.5 (b))**. The debris are machining chip shapedwitha larger aspect ratio about 0.2-0.4, as shown at higher magnification in **Fig.5 (c)**. **Fig.5 (d) is a close-up view of one of the debris**, the regular longitudinal grooves and horizontal creases with straight edge can be clearly seen. Because of the uneven deformation in the shear zone, the debris is curled.

In addition, it is clear that some smaller chips has also been generated during wear process.

The experimental result shows that both hardness and wear resistance of the coating with 0.14wt.% V is higher than those with 0.27wt.% V.The reason may be that, with a higher V content, more MC carbides can be formed in the coating with 0.27wt.% V , this cause a decrease of C contents in the M-A islands around MC carbides resulting in a a lower macro-hardness of the coating and wear resistance.

4. Discussion

4.1 MC precipitation regularity

It is known, alloy element V can refine the austenite grain, and improve the performance of the low alloy steel significantly [16]. As a strong carbide forming element, V can increase the transition temperature of γ-Fe→α-Fe, so the free energy between austenite and ferrite and the transition driving force increases, which is a beneficial favctor for forming bainite during the hardfacing process.

Fig.6 is the CCT and TTT diagrams showing the effects of V content calculated by Jmatpro software. **It is clearly shown that** V can delay the pearlite transformation and decrease the Ms point. The incubation period of bainite transformation gets shorter by adding V in the hardfacing.. Therefore, the bainite can be obtained relatively easily during the hardfacing process.

The precipitation temperatures of the hardfacing coatings with a V content of 0.05wt.%, 0.14wt.% and 0.27wt.% were calculated, the result is shown in **Fig.7 (a)**. As shown in the figure, with increasing amount of V addition, the precipitation temperatures of the austenite in the hardfacing coatings decreased, 1468℃, 1467℃ and 1465℃ respectively for the three hardfacing sample of different V content. While the precipitation temperatures of MC carbide in the hardfacing coatings are increased, which are 816℃, 890℃ and 930℃ respectively for the three V contents. The precipitation temperature of the ferrite in the hardfacing coatings also increased, which are 791℃, 797℃ and 803℃ respectively. Because precipitation temperature of MC carbides is lower than that of the austenite, MC carbides can play the role of pinning the grain boundaries during the cooling process. Moreover, as the precipitation temperature of the MC carbide is higher than that of the ferrite, MC carbide can play the role of heterogeneous nucleation, which could refine the ferrite and improve the wear resistance of the hardfacing coating.

A larger amount of MC carbide is beneficial to refine the ferrite and pin the austenite grain boundaries. So the mass fractions of MC carbide in the hardfacing coating with different V addition has been studied and the result is shown in **Fig.7 (b)**. With the increase of V addition, the mass fraction of MC carbide in the hardfacing coating increase accordingly. For a given V content, with decreasingtemperature, the mass fraction of MC carbides is increased first and then decreased. When the temperature reaches 700℃, the mass faction of MC is at its peak value. The reason for this is that when $M_{23}C_6$ carbide begins to precipitate at 700℃, it will capture the C, so the mass fraction of MC carbide is decreased. At room temperature, the mass fractions of MC carbide in the hardfacing coatings with V contents of 0.05wt.%, 0.14wt.% and 0.27wt.% is found to be 0.12%, 0.27% and 0.45%, respectively, demonstrating that, mass fraction of MC carbide increases with V addition.

4.2 Refinement mechanism

Among the material compositions studied, the wear resistance of the hardfacing coating with 0.14wt.%, V is the best one. Therefore, the optimized content of alloy element V is 0.14wt.% for this application. The carbide morphology and its EDS were further analyzed, as shown in the

Fig.8. The Auger peaks of alloy element Mo, V and C can be found in the carbide, indicating that the carbide type is the MC carbide.

According to the two-dimensional mismatch theory proposed by Bramfitt [17], the criterion can be used to estimate whether the carbide can act as a heterogeneous nuclei during the hardfacing process. The equation is as follows:

$$\delta_{(hkl)_n}^{(hkl)_s} = \sum_{i=1}^{3} [(\left| d_{[uvw]_s}^{\ i} \cos\theta - d_{[uvw]_n}^{\ i} \right| / d_{[uvw]_s}^{\ i}) / 3] \times 100\% \tag{3}$$

where $(hkl)_s$ is a low-index plane of the substrate; $[uvw]_s$ is a low-index direction in $(hkl)_s$; $(hkl)_n$ is a low-index plane in the nucleated solid; $[uvw]_n$ is a low-index direction in $(hkl)_n$; $d_{[uvw]n}$ is the interatomic spacing along $[uvw]_n$; $d_{[uvw]s}$ is the interatomic spacing along $[uvw]_s$; θ is the angle between the $[uvw]_s$ and $[uvw]_n$.

Bramfitt proposed the theory that the inoculating agents are most effective if the mismatch is less than 6%. It will be moderately effective if the mismatch is between 6 - 12%, and it is almost not effective if the mismatch is more than 12% in heterogeneous nucleation. The calculated result for MC carbide acting as the heterogeneous nuclei of ferrite is listed in Table 2 and the mismatch of MC carbide with ferrite is 2.92%. The data clearly indicates that MC carbide can act as the most effective heterogeneous nuclei of ferrite and promote the refinement of microstructure.

4.3Relationship between wear resistance and microstructure

Fig.4 shows that, with the increase of the V addition, the wear resistance of the hardfacing coating is firstly increased reaching the highest value in the sample with 0.14wt.%, V. This indicates that the wear resistance of the hardfacing coating is related with the microstructure in terms of the reinforcing particle and the matrix. Firstly, with increase of V addition, VC is precipitated from austenite and as wear resistant phase, VC particles improve the wear resistance of the hardfacing coating. However, with excessive V addition, the formation of carbon-poor zone causing a decrease in the hardness of the hardfacing coatings. So the wear resistance of the hardfacing coating is decreased again and the optimized V content is 0.14wt. %. Secondly, with the increase of V addition, more VC is formed. Based on the result detailed in 4,2, VC is an effective heterogeneous nuclei of ferrite promoting the refinement of microstructure. It is known that the refinement of microstructure can improve the strength and hardness of the materials, thus directly influencing the wear resistance of the hardfacing coating.. Therefore, it is reasonable to conclude that the wear resistance of the hardfacing coating is decided by the precipitation of VC carbide and refinement of microstructure.

5. Conclusion

1. The microstructures of the hardfacing coatings designed with different V addition, are granular bainite with dispersely distributed M-A islands. The wear resistance of the hardfacing coating with 0.14wt.% V reaches the highest value at 4320 (g/ min)$^{-1}$.

2. For hardfacing with 0.05wt.%, 0.14wt.% and 0.27wt.% V,the precipitation temperatures of austenite in the hardfacing coating are 1468℃, 1467℃ and 1465℃, respectively, precipitation temperature of ferrite are 791℃, 797℃ and 803℃, respectively and the precipitation temperature of the MC carbide are 816℃, 890℃ and 930℃, respectively. The corresponding mass fractions of MC carbide are 0.12%, 0.27% and 0.45%, respectively.

3. The mismatch of MC carbide with ferrite is 2.92%. Following the Bramfitt theory, the MC carbide could be the heterogeneous nucleus of the ferrite and refine the ferrite in the hardfacing.

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