Carbide Characteristics of High Vanadium High-speed Steel Manufactured by Electroslag Remelting

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The carbide characteristics of high vanadium high-speed steel (W3Mo4Cr5V6) manufactured by electroslag remelting (ESR) are analyzed by field emission scanning electron microscopy (FESEM), electron probe microanalysis (EPMA) and micro-Vickers. The results illustrate that three types of carbides are mainly formed in W3Mo4Cr5V6 which includes the lumpy and strip-like MC in the intracrystalline, lamellar M2C at grain boundary with discontinuous network and globular secondary carbides dispersed in matrix, among these, the eutectic strip-like MC occupies the main part. The more uniform distribution and finer size for both MC and M2C are obtained with high solidification rate (SR). Both 2D and 3D morphologies of MC carbides show obvious symmetry with clustered distribution and various shapes. The MC and M2C are rich in V and Mo, W respectively, the compositional characteristics are not only related to the carbide type and morphology, but also the precipitation order and distribution density. The Vickers hardness of primary MC, eutectic MC and M2C are measured and the average values are 2205 HV, 850 HV and 896 HV respectively which includes the adverse effects of soft matrix on the test results of hard carbides. A new and exact test method for pure carbides should be developed in the future.

KEY WORDS: high vanadium high-speed steel; electroslag remelting; carbides; solidification.

1. Introduction

High-speed steel (HSS) is always considered as composite material of two phases: the carbides and matrix. Formation of carbides with high hardness is the main reason for high hardness and excellent wear resistance of HSS. Among the MC, M2C, M6C, M7C3, M23C6 and M3C carbides, MC formed mainly of V and C has the highest hardness value and HSS with massive MC carbides always has better wear resistance. The starting precipitation temperature and amount of MC increases with the increasing content of V in HSS and then the primary crystal reaction maybe change from L→γ to L→MC which can increase the amount of MC. As a tool for continuous plastic deformation of metal on rolling mill, high hardness and good wear resistance are very necessary for roller to improve the quality of rolled materials, increase rolling efficiency and reduce rolling cost. Therefore, composition of HSS with 1.9%–2.0% for carbon equivalent, 10%–11% for tungsten equivalent (W0=W+2Mo), and 5%–6% for vanadium has been recommended for the manufacture of roller. As the density difference between W2C(17 200), WC(15 800), Mo2C(9 100), VC(5 700), Fe3C(7 200) and residual molten steel (about 7 800) is huge, the vanadium carbides always located at the inner layer of a shell and the tungsten carbides at the outer layer of the shell under the action of centrifugal force during centrifugal casting process. In order to prevent segregation, decreasing W and Mo contents and adding a suitable amount of Nb to form (V, Nb)C composite carbide of a density near to that of molten steel can be used to decrease the gravity difference between VC and residual molten steel. But Nb increases the steel’s quenching temperature and decreases temperature at which the peak of secondary hardening is observed. In addition to composition adjustment, a suitable electromagnetic stirring can lessen the segregation of the alloyed elements and a larger solidification rate promotes the refinement and uniform distribution of eutectic carbides (MC + M2C) in centrifugal cast HSS roll. Therefore, electroslag remelting (ESR) with water-cooled mold has been used to manufacture HSS widely due to its advantages of increasing solidification rate, reducing elements segregation and refining grain. However, the previous reports mainly focus on the traditional high-speed tool steels, less of that is focused on the systematic microstructure analyses of HSS roll with high contents of C and V as used in the present study.
Here, the HSS with high C and V (W3Mo4Cr5V6) was manufactured by ESR and the carbide type, morphology, distribution and composition were analyzed in detail. The research results will provide references for preparing HSS composite roll with high C and V by the innovation method of electroslag remelting cladding (ESRC)\textsuperscript{15,16} developed by the authors.

2. Materials and Methods

The W3Mo4Cr5V6 used here was first prepared in 30 kg VIM furnace by using the industrial pure iron, high purity graphite and other ferroalloys. Then two as-cast ingots with the surface treatment were welded together as the consumable electrode. Finally, the as-cast ESR ingot with $\Phi$175/180 mm in diameter and 155 mm in length was obtained and its chemical composition was listed in Table 1.

For the microstructure analysis, two specimens taken from the center and edge areas (3 mm from its surface) of the as-cast ESR ingot (marked as ESR-C and ESR-E respectively) were successively ground, mechanical or vibratory polished and etched by nital solution (4 ml HNO$_3$ + 96 ml C$_2$H$_5$OH). The two-dimensional (2D) and three-dimensional (3D) morphologies of carbides were carried out by using field emission scanning electron microscope (FESEM, Nova NanoSEM400, FEI, America) with energy dispersive spectrometer (EDS). In order to observe the 3D morphology of carbides, the specimens were firstly deeply etched with hydrochloric acid solution and then ultrasonically cleaned for several times. The carbide size was measured and analyzed by the image processing software of Image-Pro Plus 6.0. The carbide composition was analyzed by electron probe microanalyzer (EPMA, 8050G, Shimadzu, Japan). The Vickers hardness of carbides and matrix were measured by using HVS-2000PC micro-Vickers with the test load of 100 g (0.9807 N).

3. Carbide Morphology and Distribution

Figure 1 shows the microstructure of ESR-C and ESR-E specimens in backscatter mode of FESEM. The M$_2$C presents bright white and the MC presents dark grey or light grey in the SEM image due to their composition differences. On the whole, the lamellar M$_2$C are mainly distributed at grain boundaries with discontinuous network while the lumpy and strip-like MC are mainly inside the grains. The same characteristics are obtained in the study of HSS with Fe-1.9%C-4.8%Cr-4.5%Mo-7.4%V.\textsuperscript{17} Different from the obvious dendritic structure with coarse grains and poor distribution uniformity in ESR-C in Fig. 1(a), more uniform and finer grains are obtained in ESR-E which shows obvious equiaxed crystal morphology as shown in Fig. 1(c).

<table>
<thead>
<tr>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>V</th>
<th>Cr</th>
<th>Mo</th>
<th>W</th>
<th>Ni</th>
<th>N</th>
<th>Fe</th>
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<tr>
<td>1.92</td>
<td>0.87</td>
<td>0.93</td>
<td>0.018</td>
<td>0.006</td>
<td>5.77</td>
<td>5.29</td>
<td>4.08</td>
<td>2.76</td>
<td>1.10</td>
<td>0.0108</td>
<td>Bal.</td>
</tr>
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</table>

![Figure 1](https://example.com/fig1.png)

**Fig. 1.** Microstructure of the (a) ESR-C and (c) ESR-E specimens. (Online version in color.)
The average grain size (equivalent diameter) of ESR-C and ESR-E measured by the circular cutoff point method changes from 104 μm to 66 μm with the increasing solidification rate from center to edge areas of ESR ingot. In addition, huge differences between MC and M₂C in the two specimens are clear to us. For the lumpy MC, both its size and quantity decrease obviously from ESR-C to ESR-E. As the 2D morphology of lumpy MC is mostly quadrilateral in shape, its diagonal length is measured and used for the size comparison between ESR-C and ESR-E as shown in Fig. 2. It illustrates that the diagonal length of lumpy MC in ESR-C is mainly in the size range from 10 μm to 25 μm which occupies about 82.4%. Few lumpy MC with the diagonal length larger than 25 μm is found and the maximum value is 52.3 μm. However, that in ESR-E is mainly in the size range from 5 μm to 15 μm which occupies 96.7% and its quantity is much fewer than that in ESR-C. But for the strip-like MC, its quantity in ESR-E increases with a finer size and clustered shape as shown in Fig. 1(d). For the lamellar M₂C, its size and distribution in ESR-E (Fig. 1(c)) is much smaller and more uniform than that in ESR-C (Fig. 1(a)) which are beneficial to the transformation of M₂C + γ-Fe→M₆C + MC and refinement of carbides in the subsequent heat treatment and improvement of the finally mechanical properties of HSS. After a statistical analysis, the lamellar spacing of M₂C in ESR-C and ESR-E changes from 1.08–1.62 μm to 0.55–0.74 μm with the thinner slice in Figs. 1(b1) and 1(d1). In the former, the carbide branches are mainly straight, while in the latter, the bending deformation occurs for its branches with obviously finer size.

According to the classical nucleation theory, higher solidification rate leads to higher supercooling which results in a smaller critical nucleation radius and then much more carbide nucleation occurs per unit area in the microstructure. It is the main reason for the size refinement of grain and carbide from ESR-C to ESR-E. The above phenomenon has good consistency with the influence results of solidification rate on the carbide characteristics. Once the type, morphology and distribution of carbides get changed, the final microstructures and mechanical properties of W3Mo4Cr5V6 after the subsequent heat treatment or hot working process will change as well. For the W3Mo4Cr5V6, the eutectic MC precipitated after the primary crystal reaction of L→MC mainly grows into clustered shape with many small branches in ESR-E as shown in Fig. 1(d). At large magnification in Fig. 3, the partial morphology of eutectic MC shows a distinct symmetry as a wind turbine with three blades (Fig. 3(a)), four leaf clover (Fig. 3(b)) or hollow square (Fig. 3(c)) to some extent. Maybe this morphology characteristic is closely related to the formation and growth mechanism of eutectic MC which needs further study.

Figure 4 shows the carbides morphology with vibration polishing of ESR-E specimen and it has more clear display of carbides morphology when compared with that observed with mechanical polishing in Fig. 1. Through Fig. 4(a), it
clearly illustrates that the eutectic strip-like MC occupies the main part of all the carbides and the phenomenon of MC being symbiotic with M₂C can be found as they are connected with each other in some regions in Figs. 4(b) and 4(d). The globular secondary carbides in Fig. 4(b) and the matrix of plate martensite in Fig. 4(c) are also clearly observed. In order to give the more clear display, the 3D morphology of carbides in ESR-E after a deep etching is given as shown in Fig. 5.

Through Fig. 5(a), it also clearly illustrates that the MC is the main precipitated phase due to its massive existence where few M₂C is found. In addition, different from the 2D strip-like or rod-like eutectic MC, it shows coral-shaped, skull-shape, fan-shaped or leaf-shaped flakes eutectic MC with clustered distribution in the 3D view and it also shows a certain symmetry. For the primary lumpy MC, the quad-

Fig. 4. Morphology of carbides with vibration polishing of ESR-E specimen. (Online version in color.)

Fig. 5. Three-dimensional morphology analyses of carbides in ESR-E. (Online version in color.)
rilateral morphology in 2D view changes to hexahedral magic-square shaped in Fig. 5(d), complex polyhedral shaped in Fig. 5(e) or petals-shaped in Fig. 5(f). In fact, different hexahedral MC or polyhedral MC have different orientations, an equivalent cutting of that is carried in the 2D observation of the grinding and polishing specimen. With different cutting angles, the rhombic quadrilateral shapes obtained in the 2D view are also different, or it shows a non-quadrilateral morphology.

4. Carbide Composition

Figure 6 shows the compositional analysis of lumpy and strip-like MC by EPMA. As high V content promotes the formation of primary V-enrich MC instead of primary \( \gamma \)\(^3\),\(^1\),\(^7\),\(^17\),\(^23\) it clearly indicates that the MC is rich in V, C, N and certain contents of Mo, W, oppositely, the contents of Cr and Fe in MC is very low. It is also found that N is mainly presented in the interior of lumpy MC in Fig. 6(b) which is starting from a N-enrich core and then the successive shells are rich in C as shown in Fig. 6(c). As the solubility product of VN is much more thermodynamically stable than vanadium carbide in austenite\(^24\),\(^25\) and then the former is preferentially precipitated. Through the thermodynamic calculation and experimental measurement, a certain amount of N in HSS promotes the formation of primary \( M(C,N) \) which includes higher content of N than that of C, while in the eutectic MC, the content of N is much fewer than that of C\(^26\)—\(^28\).

The maximum contents of V, C and N in MC are 77.89%, 9.20% and 4.05% respectively and the average contents of Cr, Mo and W in MC are about 5.60%, 7.19% and 9.57% respectively. In fact, a certain difference of the contents of alloy elements in primary lumpy MC and eutectic strip-like MC occurs and a new scale bar of V content is used to clearly display the difference as shown in Fig. 7. On the whole, the content of V in lumpy MC is higher than that in strip-like MC and the opposite trend is obtained for Mo, but for both V and Mo, its uniformity in lumpy MC is better. In other words, a fluctuation of V content in strip-like MC occurs, specifically, the V in strip-like MC between the outer circle and inner circle is higher than that in strip-like MC inside the inner circle, for the strip-like MC outside the outer circle, the content of V shows a gradual decrease trend along the direction to the grain boundary due to the gradual increase of other elements (such as Mo in Fig. 7(b)) under the micro-segregation effect. Figure 8 shows the elements distribution mainly for the eutectic MC in ESR-E. In the main skeleton, the contents of V and Mo is less, and that of Fe increases outside the main skeleton. A point-scan analysis for the elements of MC in ESR-C by SEM-EDS is carried out and the result is shown in Fig. 9. On the whole, from point A to point J, that is, from the inside of the grain to the grain boundary, the content of V in MC decreases obviously and that of W, Mo and Cr increases to different degrees. It shows that the MC formed first has higher V than that of the MC formed later, while the contents of W, Mo and Cr have a certain increase, the variation trend of MC composition is in good agreement.

![Fig. 6. Surface scanning analysis of the (a) MC and (b) M_2C carbides. (Online version in color.)](image-url)
with the calculated and measured results. Based on the analysis results from Figs. 6 to 9, it can be summarized in two points. Firstly, the content of V in primary lumpy MC is higher than that in eutectic strip-like MC and an opposite trend is obtained for that of Mo, W and Cr. Among these carbide formers, the affinity of V and C is greater and the V-enriched MC is preferentially formed. Secondly, for the eutectic MC, its composition is also closely related to the distribution of carbides, that is, the denser the eutectic MC is distributed, the lower the content of V inside it. With the dense distribution, the finite concentration of V at solidification front (low partition coefficient leads to segregation and enrichment) is allocated to the multitude branches, therefore, the average content of V in each branch decreases. In the areas with fewer MC branches (outside the circle in Figs. 7 and 8), the V in each branch allocated from the solidification front is much more and then its final content is higher. In addition, the phenomenon of MC symbiotic M2C can be found near point J (around the grain boundary) in Fig. 9(a) and now the MC is light gray or greyish-white which is brighter than that of the primary MC and eutectic MC located inside the grains. Through Fig. 9(b), it also can be seen that the V of point J is low and the W, Mo, Cr of point J is high, which is consistent with the brightness change of carbides.

Figure 10 shows the compositional analysis of eutectic M2C by EPMA. W and Mo in HSS are always excreted into the retained liquid phase during solidification and accelerate the eutectic reaction which results in the increase of M2C at grain boundaries. The M2C has obvious lamellar structure and it contains lots of Mo and a certain content of W, Cr and V. Both MC and M2C are all poor in Fe as it is the weakest carbide former when compared with V, Mo, W and Cr.

![Fig. 7. Distribution of (a) V and (b) Mo in eutectic MC of ESR-E specimen. (Online version in color.)](image)

![Fig. 8. Distribution of (b) V, (c) Mo and (d) Fe in eutectic MC of ESR-E specimen. (Online version in color.)](image)

![Fig. 9. Composition of MC in ESR-C specimen (a) measured points, (b) measured result. (Online version in color.)](image)
order to clearly describe the elements distribution characteristics in lamellar M₂C, two lines scanning analyses marked as L1 and L2 by EPMA are carried out in Figs. 10(a) and 10(e) and the results are shown in Fig. 11.

For the L1, the measurement starts from the matrix and ends at the matrix, it goes through the matrix, MC, M₂C and matrix successively. From the corresponding result in Fig. 11(a), an obvious phenomenon is that the content of Fe in both MC and M₂C is always complementary to the contents of other carbide forming elements, that is, the variation trend between Fe and V, Mo, W, Cr is opposite. Consistent with the report, the major forming elements in MC and M₂C are V and Mo respectively. For the L2, the distribution of alloy elements presents an obvious sinusoidal waveform shape in Fig. 11(b) and its minimum period length depends on the lamellar spacing of M₂C. Here, the average lamellar spacing of M₂C is about 1.04 μm.

Figure 12 shows the morphology and composition of globular secondary carbides in ESR-C and ESR-E. Obviously, most of those are less than 500 nm in size with the dispersed distribution and few of those are in chain distribution. Based on the composition analysis, the contents of C, W, Mo, Cr and V in secondary carbides are all higher than that in matrix and that of Fe is opposite which is con-
sistent with the analysis results in Fig. 6. Among the above alloy elements, Fe and V is the major forming elements. Based on the equilibrium phase diagram calculation of W3Mo4Cr5V6$^{(10)}$ and the previous report,$^{31)}$ the secondary carbides are considered as $M_23C_6$ which mainly contains Fe, V, C and few Cr, Mo and W. Meanwhile, the contents of alloy elements in matrix are lower than the initial composition of W3Mo4Cr5V6 in Table 1.

5. Carbide Hardness

Figure 13 shows the measured results of Vickers microhardness of MC, $M_2C$ and matrix. On the whole, the microhardness values of MC are highest and most unstable among the tests. Obviously, the indentation size in Fig. 13(a) is smaller than that in Fig. 13(b) with the same test load which is inversely proportional to the hardness value. Here, the Vickers hardness values of lumpy MC in Figs. 13(a) and 13(b) are 2 494 HV and 1 916 HV respectively. Two aspects will lead to the instability and inaccuracy of the measured results, on one side, it is hard to exactly measure the diagonal length of the indentation which has a direct influence on the calculation of Vickers microhardness through the equation of $V(HV) = \frac{0.1891 \times F}{d^2}$, where $F$ is the test load (N) and $d$ is the arithmetic mean value of the two diagonal lengths of the indentation (mm). On the other hand, few cracks on the surface of lumpy MC are found around the indentations in Figs. 13(a), 13(b) which fully illustrates that the lumpy MC is hard and brittle, and the relatively soft matrix may affect the accuracy of the measured results. Through Figs. 13(c) and 13(d), the Vickers hardness values of eutectic MC are 865 HV and 835 HV respectively which is the double action of strip-like MC and the matrix between the MC branches. Similar to the eutectic MC, the Vickers hardness values of eutectic $M_2C$ are 895 HV and 896 HV in Figs. 13(e) and 13(f) respectively. As it is difficult to separate the carbides and matrix effectively for separate measurement, the accurate hardness values of pure primary MC, eutectic MC and eutectic $M_2C$ are also difficult to obtain through the conventional hardness test methods which should be given further research in the future.

As mentioned above, there are many secondary carbides distributed on the martensite matrix, in addition, a certain content of residual austenite in matrix is obtained through the X-ray diffraction (XRD) analysis. Based on the combined action of the above three parts, the Vickers hardness values of matrix in Figs. 13(g) and 13(h) are 658 HV and 609 HV respectively. Through Figs. 4(b) and 4(c), it can be seen that the content and distribution of secondary carbides and martensite in matrix may be very different which is closely related to the grain size and the type or distribution of surrounding carbides. Then it results in the inhomogeneity of matrix hardness as shown in Figs. 13(g) and 13(h).

6. Conclusions

(1) The carbides in high carbon W3Mo4Cr5V6 manufactured by ESR mainly contain primary MC and eutectic MC in the intracrystalline, eutectic $M_2C$ in the grain boundary and globular secondary carbide in matrix. Among these carbides, eutectic MC occupies the main part. The 2D morphology of primary lumpy MC is mainly quadrilateral with different diagonal lengths and its 3D morphology is hexahedral magic square or complex polyhedral shape with few branches. The eutectic MC is mostly in strip-like shape and has a certain symmetry, its 3D morphology is fan-shaped or leaf-shaped flakes with clustered distribution.
The lamellar and fibrous $\text{M}_2\text{C}$ with discontinuous network are formed at grain boundary. The more uniform distribution and finer size for both $\text{MC}$ and $\text{M}_2\text{C}$ were obtained with high solidification rate.

(2) Both primary $\text{MC}$ and eutectic $\text{MC}$ are mainly rich in $\text{V}$ and the former has a higher content, while the eutectic $\text{M}_2\text{C}$ is mainly rich in $\text{Mo}$. As a result, the above three types of carbides always present dark grey, light grey and bright white in the SEM image with backscattering mode. During the transition from the inside part of grain to the grain boundary, the content of $\text{V}$ in eutectic $\text{MC}$ decreases slightly and then forms the eutectic $\text{M}_2\text{C}$ in the grain boundary. Also, the contents of alloy elements in $\text{MC}$ are closely related to its distribution characteristic, that is, the denser the eutectic $\text{MC}$ is distributed, the lower the content of the major forming element of $\text{V}$ inside it. For the lamellar $\text{M}_2\text{C}$, the distribution of alloy elements presents an obvious sinusoidal waveform shape and its minimum period length depends on the lamellar spacing of $\text{M}_2\text{C}$.

(3) As it is difficult to separate the carbides and matrix effectively for separate measurement, the accurate hardness values of pure primary $\text{MC}$, eutectic $\text{MC}$ and eutectic $\text{M}_2\text{C}$ are also difficult to obtain. Influenced by the soft matrix, the average Vickers hardness of primary $\text{MC}$, eutectic $\text{MC}$ and eutectic $\text{M}_2\text{C}$ are about 205 HV, 850 HV and 896 HV respectively which can be used as a reference. The convenient and accurate test methods of hardness for the pure carbides should be developed in the future.

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