Carbide Dispersion Carburizing (CDC) of Fe–Mo–V Based High-speed Steels

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The carbide dispersion carburizing process was applied to Fe-based high-speed steels, which contained multiple carbide-forming elements, Mo and V. Fine carbides precipitated during the carburization and the dispersed particles in the Fe–Mo–V–C alloys heat-treated at 1200°C were identified as VC, (Mo, V)₂C, and (Fe, Mo)₆C, which behave as effective inhibitors against the grain growth of austenite and as reinforcing results in increased hardness of the martensitic matrix. The maximum Vickers hardness of the Fe–10Mo–5V–2.05C alloy quenched from 1200°C and tempered at 600°C achieved values of 1100 and 1000, respectively. Thermodynamic calculation of the Fe–Mo–V–C quaternary system proved to be useful for optimizing the composition of carbide forming elements, the carburizing conditions, and the microstructure of carburized and solution-treated alloys.

KEY WORDS: high-speed steel; carburization; carbide; heat treatment; phase diagram; CALPHAD.

1. Introduction

Carburization is widely applied in various kinds of steel to improve the wear resistance of parts of industrial machines. In the conventional carburizing process to which low alloy steels are subjected, the composition of dissolved carbon at the surface of the austenite phase increases due to carburization, as shown in the case of ➀ of Fig. 1, and extensive hardness can be attained by quenching, which results in martensitic transformation of the austenite. The resulting gradient in carbon content below the surface of the carburized component causes a gradient in hardness, producing a strong, wear-resistant surface layer on a material. Most steels can be carburized by the carbon saturation–carbon diffusion type of cycle to obtain surface carbon content below 1.0 mass%. However, recent progress in carburizing technology, such as vacuum carburization, plasma carburization, etc., enables super-carburization, by which the carbon concentration at the surface of the specimen reaches 2–4 mass%. As a result, massive cementite particles precipitate in the austenite matrix, which results in an increase of hardness and wear resistance. Compared with cementite, as refractory carbides, MC, M₂C, M₆C, etc., have greater thermal stability and hardness as shown in Fig. 2. Further improvement of wear resistance and hardness of the surface layer can be expected by replacing cementite with other carbides. To this end, the carbide dispersion carburization (CDC) process has been developed, an outline of which is presented in Fig. 1. Figure 1(a) shows a schematic phase diagram of the Fe–M–C ternary system, where M represents a carbide-forming element (CFE) such as Ti, V, Cr, Nb, Mo, etc. In the case of a low-alloy steel, indicated by ➀, an austenite single phase with an inhomogeneous concentration profile of dissolved carbon can be obtained. When a certain amount of CFEs is added to the starting material, the carbon content at the surface exceeds the solubility limit of the MC carbide. Then, both an increase of dissolved carbon and precipitation of fine carbide particles in the austenite matrix can be attained simultaneously, which enhances the hardness and wear resistance of the surface layer of the specimen. Further addition of CFE extends options of the microstructure as shown in Fig. 1(b). For example, when steel containing higher alloying content is car-

Fig. 1. Outline of carbide dispersion carburizing (CDC) process.
burized, the microstructure is changed from $\alpha$ ($\alpha$ + MC) to $\gamma$ ($\gamma$ + MC) with increasing carbon content. An advanced alloy design is, therefore, required for multi-CFE systems.

Owing to recent progress of the CALPHAD (Calculation of Phase Diagrams) technique, calculation of the phase diagrams of multi-component systems can be performed with high reliability and can be utilized for the advanced alloy design of starting materials and optimization of the carburizing condition. In this paper, Fe–Mo–V multi-CFE alloys were subjected to carbide dispersion carburization, and the carburizing condition, microstructure and Vickers hardness were optimized on the basis of thermodynamic calculation.

### 2. Experimental Procedure

Samples of pre-carburized Fe–Mo–V alloys were prepared by induction melting under an argon atmosphere from electrolytic iron (99.99%), molybdenum scraps (99.7%), and vanadium bullion (99.7%). Nominal composition of prepared samples is listed in Table 1, which seems to be equivalent with actual composition because little loss of weight was recognized before and after the induction melting. Cylindrical ingots, 20 mm in diameter, were hot-rolled into 2-mm-thick plates at 1 000°C. After being cut into rectangular pieces, the samples were cold-rolled to arbitrary thickness, $d$, which determines the carbon content of each sample as explained in next section.

Rectangular plates (20 $\times$ 10 $\times$ $d$ mm) were put into a stainless steel container with a mixture of activated charcoal and sodium carbonate. The pot was covered with a stainless steel lid and carburization was carried out in an electrical furnace at 900°C for three hours. After the carburization treatment, the container was quenched into an oil bath. Each sample was cut into pieces. Some of them were heat-treated at 1 200°C for 20 min for solution and homogenization with respect to carbon concentration. After being quenched in an oil bath, one of them was used for chemical analysis of carbon content and another was tempered at temperatures between 500°C and 650°C for 1 h and quenched in iced water. Microstructures of as-carburized, as-quenched and tempered samples were examined using an optical microscope (OM) and a scanning electron microscope (SEM). The composition of precipitated carbides in the as-quenched samples was determined by an electron probe micro-analyzer (JEOL JXA-8100). Micro-vickers hardness was measured from the surface to the center of all the specimens with a load of 0.5 kg.

Thermodynamic calculations were performed by Thermo-Calc using thermodynamic database, SSOL2 (SGTE Solution database v.2). Stability of the $M_2C$ carbide was corrected so as to reproduce phase equilibria in the Fe–10Mo–5V–C (mass%) alloys by introducing a negative interaction between molybdenum and vanadium as following equation.

$$G_{\text{HCP-A3, MO, V : C; 0}} = -16000$$ (1)

In the above equation, HCP_A3 represents not only a hexagonal-closed-pack solid solution but also $M_2C$-type carbide.

### 3. Experimental Results

In the present carburizing process, the total amount of carbon which permeates from the surface area of rectangular plates ($= 4 \text{ cm}^2$) during the carburization process (3 h) is assumed to be constant, $m_c$ (g). Then, the carbon content of each sample, $w_c$ (mass%), can be approximated by

$$w_c = \frac{100 \times m_c / (m + m_c) = 100 \times m_c / m}$$ (2)

where $m$ represents the weight of each sample, which is directly proportional to its thickness, $d$. Figure 3 shows the relationship between the carbon content, $w_c$, and the thickness of samples, $d$. The carbon content of each sample was controlled by its thickness on the basis of the obtained equation shown in Fig. 3.

Figures 4(a), 4(b) and 4(c) show backscattered electron (BSE) images of the microstructure of as-carburized Fe–10Mo–5V alloy ($d=0.72$ mm). In the magnified images, (b)
and (c), three kinds of carbides; namely, (1) black, (2) globular white and (3) acicular white, can be observed. These carbides were identified as VC, (Mo, V)$_2$C, and (Fe, Mo)$_6$C, respectively, these results being compared with the calculated phase diagram shown in Fig. 4(d). It is supposed that (Fe, Mo)$_6$C precipitates during cooling after carburization. The carbon content of the sample was measured by EPMA and the result is shown in Fig. 4(d) by an open circle and a solid circle for the center and surface, respectively, which indicates that the carbon content in the as-carburized sample is inhomogeneous.

In order to relieve the inhomogeneity of carbon concentration and to dissolve a certain amount of alloying elements, the as-carburized samples were subjected to a heat treatment at 1200°C for 20 min. This temperature was chosen on the basis of calculated phase diagrams, an example of the Fe–10Mo–5V alloy being shown in Fig. 5(c), so as not to form the liquid phase. Figures 5(a) and 5(b) show a comparison between as-quenched samples prepared by (a) the casting process and (b) the CDC process. It is apparent that the microstructure of the CDC-processed sample is much finer than that of the cast sample. Not only the grain size of austenite matrix but also the size of carbides is very fine for the CDC sample, where the average diameters of matrix grains and carbide particles are 2.1 μm and 0.4 μm, respectively. Figure 5(c) clearly explains the difference of the both process. In the casting process, 2 mass% carbon was added to the Fe–10Mo–5V alloy beforehand and melted up to the homogeneous liquid phase. The melt was then cast into a mold. During solidification, some kinds of carbide formed from the melt, which resulted in coarsening of the obtained carbide particles as shown in Fig. 5(a). On the other hand in the CDC process, pre-carburized alloys were prepared without carbon, which enables deformation of ingots into near net shape of products. The samples were then carburized, solution treated, and quenched. Finely and ho-

Fig. 4. Backscattered electron images of the as-carburized Fe–10Mo–5V (mass%) alloy and corresponding isothermal section phase diagram calculated at 900°C. M$_2$C and M$_6$C represent (Mo, V)$_2$C and (Fe, Mo)$_6$C, respectively.

Fig. 5. Comparison of microstructures of as-quenched Fe–10Mo–5V–2C (mass%) alloy prepared by (a) casting and (b) CDC process. M$_2$C and M$_6$C represent (Mo, V)$_2$C and (Fe, Mo)$_6$C, respectively. Differences between two processes are explained in the isoplethal phase diagram.
mogeneously dispersed particles prevented the grain growth of the matrix by Zener drag during solution treatment and resulted in a fine polycrystalline microstructure as shown in Fig. 5(b).

Figure 6 shows BSE images of the as-quenched microstructure of the Fe–Mo–V–C alloys. The morphology of carbides changes depending upon the composition of Mo, V and C. With the increase of Mo, the volume fraction of white carbides increases. EPMA measurement was carried out on relatively large carbides, resulting in identification of three kinds of carbide, i.e., VC (black), (Mo, V)\(_2\)C (globular white), and (Fe, Mo)\(_6\)C (acicular white), which is consistent with the as-carburized alloy in Fig. 4. The (Mo, V)\(_2\)C carbide is dominant when the Mo/V ratio is large as shown in Fig. 6(c). The (Fe, Mo)\(_6\)C carbide was observed only in the Fe–12Mo–3V–C alloy, while only black precipitate, VC, was identified in the Fe–8Mo–5V–C alloy, whose Mo/V ratio is smallest in the five samples. Coarsening of carbides is remarkable in two such extremes. A fine carbide microstructure can be realized in the moderate condition of the Mo/V ratio (Mo/V = 2–3) as shown in Figs. 6(a), 6(b) and 6(e).

Tempering treatment at temperatures between 500°C and 650°C on some solution-treated alloys was performed to attain secondary hardening due to decomposition of the quenched martensite. Vickers hardness at the center of as-tempered samples was measured. The result is shown in Fig. 7. The tempering temperature was optimized to be 600°C at which the maximum hardness was obtained. The tempering treatment at 600°C was then applied to all the alloys and Vickers hardness was examined from the surface to the center of the sample plates. Figure 8 shows selected results of the Vickers hardness for the as-quenched and as-tempered samples. The maximum hardness was obtained in the Fe–10Mo–5V–2.05C alloy. The as-quenched and as-tempered samples achieved a hardness of 1 100 and 1 000, respectively, values at least 100 higher than those in super-

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**Fig. 6.** Backscattered electron images of as quenched microstructure of Fe–Mo–V–C alloys. White particles represent either (Mo, V)\(_2\)C or (Fe, Mo)\(_6\)C and the black ones represent VC.

**Fig. 7.** Optimization of the heat treatment for tempering of Fe–10Mo–3V–1.39C and Fe–12Mo–3V–1.15C (mass%) alloys. The maximum hardness was obtained by tempering at 600°C.

**Fig. 8.** Comparison of micro-Vickers hardness of quenched and tempered Fe–Mo–V–C alloys.
carburized steels with massive cementite dispersions.5)

4. Discussion

In this study, the adequate carbon content and the temperature of heat treatment for a solution were determined on the basis of thermodynamic calculation. Furthermore, it was found the microstructure and hardness could be optimized in accordance with the obtained result. A suitable microstructure was obtained in the moderate condition of the Mo/V ratio as shown in Fig. 6. Improvement of toughness is expected with the fine microstructure with respect to the matrix grains and dispersion carbides. In addition, hardness of samples depends on the volume fraction of hard carbides and on the carbon content of austenite matrix phase, which transforms into the martensite by quenching from 1200°C and results in secondary hardening by tempering at 600°C.

Figures 9(a)–9(c) show as-quenched microstructures of Fe–10Mo–5V–xC alloys. Figure 9(d) and 9(e) shows the relationship between carbon content, phase fraction, and hardness of the Fe–10Mo–5V alloy at 1200°C which suggests the maximum hardness is obtained in the austenite+VC+(Mo,V)2C region.

The obtained phase constitutions shown in Figs. 9(a)–9(c) are consistent with the calculated result shown in Fig. 9(d) where the suitable microstructure is the constitution of the γ+VC+(Mo,V)2C three-phase region. The maximum hardness can be realized on the verge of the high carbon limit where the carbon content in the austenite matrix phase is approximately 0.8 mass% in accordance with the calculated composition. In Fe–8Mo–5V and Fe–10Mo–3V alloys, the maximum hardness can be attained at 1.9 mass% C and 1.5 mass% C, respectively, just below the upper limit of the suitable phase constitution. The carbon content in the austenite matrix of the two hardest alloys was calculated to be 0.76 mass% C and 0.79 mass% C, respectively.

Figure 10 shows the relationship between the maximum hardness attained in the Fe–Mo–V–C alloys fabricated by the CDC process and the volume fraction of carbides in the as-quenched samples. In both as-quenched and as-tempered samples, the following linear relationships were observed:

\[ H_v = 941 + 1.443 \times f_C \quad \text{(as-quenched from 1200°C)} \]  
\[ H_v = 827 + 1.405 \times f_C \quad \text{(as-tempered at 600°C)} \]

where \( f_C \) represents the total volume fraction of existing carbides measured on samples quenched from 1200°C. Even though ultra-fine carbides were precipitated extensively during tempering treatment at 600°C, the above equations were derived in accordance with the measurable \( f_C \) at 1200°C. In this diagram, the offset of the fitted lines represents the hardness of the matrix itself and the extra hardness increases linearly with the increasing volume fraction of carbides. Therefore, the role of carbide can be summarized as (1) inhibitor of the matrix grain growth, which improves toughness, and (2) reinforcer of hardness, which results in desirable wear resistance. Comparison between measured and calculated volume fractions of total carbides showed good agreement as shown in Fig. 9(d). Hence, the maximum hardness of the CD carburized alloys can be estimated using the above equations and calculated volume fractions above which the liquid phase appears, hardness drops abruptly and remarkable coarsening of both the austenite matrix and carbides takes place as shown in Fig. 9(c).
fraction of the carbide phases. Finally, Fig. 11 shows calculated phase diagrams at 1200°C under fixed carbon content, (a) 2.0 mass% C and (b) 1.2 mass% C. Iso-carbon content curves in the austenite matrix phase are superimposed by dashed lines on the phase diagrams. An experimentally optimized sample is marked by a solid diamond in Fig. 11(a). On the basis of such diagram, the microstructure, compositions of alloying element, the temperature of heat-treatment, etc., can be optimized as shown by an open diamond in Fig. 11(b), which indicates the availability of thermodynamic calculation for alloy design of practical materials.

5. Conclusions

A carbide dispersion carburization (CDC) process was devised and the method was applied to develop high-speed steels. This carburization process was applied to Fe–Mo–V alloys at 900°C and formation of finely and homogeneously dispersed carbides was attained. The temperature of heat-treatment for solution and homogenization was determined on the basis of thermodynamic calculation. The growth of the austenite matrix grains during the solution treatment at 1200°C was effectively retarded by Zener drag induced by carbide particles. Secondary hardening was achieved by tempering heat-treatment at 600°C. The maximum Vickers hardness reached 1100 and 1000 in the as-quenched and as-tempered Fe–10Mo–5V–2.05C alloy, respectively, values 150 higher than the conventional high-speed steel, SKH9 (AISI M2) tempered at 550°C. The thermodynamic calculations have proved to be useful for alloy design with respect to the microstructure, the composition of the alloying elements, the temperature of heat-treatment, the volume fraction of carbides, etc. It is important to make multiple kinds of carbides precipitate to maintain fine polycrystalline microstructures during solution treatment. In addition, carbon content in the austenite matrix phase during the solution treatment should be optimized to attain the desirable secondary hardening during the tempering process.

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