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Stability of eutectic carbide in Fe-Cr-Mo-W-V-C alloy

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Abstract

The stability of the eutectic carbide in a self-designed Fe-Cr-Mo-W-V-C alloy during solidification was analyzed in this work. The carbide precipitation rule of the steel was calculated by Thermo-Calc.The typical microstructures at 1240 °C and 1200 °C were observed by optical microscope (OM),field emission scanning electron microscope (FESEM) and transmission electron microscope (TEM). The selected area diffraction patterns (SADPs) has been successfully used with TEM brightfields to identify the lattice structures of the carbides within a complex mixture of different types of carbides. The results show that the eutectic MC and M2C mix together along crystal grain boundary and exhibit the dendritic structure. The eutectic MC contains VC and WC, while the eutectic M2C contains V2C and Mo2C. The eutectic MC can exist stably and grows continuously, while the eutectic M2C disappears gradually.

1. Introduction

With excellent mechanical properties at different temperatures, Fe-Cr-Mo-W-V-C alloy is one of the important high alloying steel principally designed for cold work roll [1,2]. During solidification process, eutectic reaction occurs and eutectic carbide exists at room temperature [3,4], which make the cold work roll with higher hardness, better wear resistance and hardenability [5,6]. In recent years, the researches about eutectic carbides mainly focus on their morphology, distribution as well as the affecting factors [7–9]. Sun et al.[10]considered that the eutectic reaction of γ→MC occurs with varied solidification rate and the morphology of the eutectic MC differs from each other in a nickel-base superalloy. Buytoz [7] investigated the eutectic microstructure and properties of Fe-Cr-C coatings, and the morphology of the eutectic M7C3 was also observed. Luan et al.[11] indicated that with the increase of solidification rate, the eutectic carbides (MCþM2C) become finer and more uniformly dispersed in high speed steel roll. However, seldom reports about the stability of the eutectic carbide during cooling process can be found.

It is generally known that the as-cast microstructures of many alloys are obtained by non-equilibrium solidification, and the carbides at the room temperature are mainly the eutectic ones. Once the type, morphology and distribution of eutectic carbide get changed, the final microstructures and mechanical properties of the alloy after the subsequent heat treatment or hot working process will change as well. That is to say, the stability of eutectic carbide during the cooling process determines the as-cast micro- structures directly. Therefore, it is significant to study the stability of the eutectic carbide in the Fe-Cr-Mo-W-V-C alloy during cooling process.

In our previous work, a novel Fe-Cr-Mo-W-V-C alloy for cold work roll was designed and optimized by CALPHAD. The carbide precipitation rule of the novel alloy with different tungsten (W) content was calculated using Thermo-Calc [12]. The in- vestigation on the phase transformation and carbide precipitation in this alloy by our group showed that ternary eutectic reaction of

$$L\gamma \longrightarrow Fe + MC + M2C$$

occurs during solidification process and the microstructures consist of austenite, eutectic MC and eutectic M2C[13]. Meanwhile, the wear resistance was discussed [14]. In this work, in order to investigate the stability of the eutectic carbide during cooling process, the morphologies were firstly observed at characteristic temperatures. Lattice structures of the eutectic car- bides were determined by transmission electron microscopy (TEM) and the transformation of eutectic carbide was analyzed, which provide theoretical basis for their evolution during cooling process.

2. Experimental materials and methods

The specimen was taken from the self-designed Fe-Cr-Mo-W- V-C alloy for cold work roll. The chemical composition of the alloy 217is listed as follows: (wt%) C: 1.2, Cr: 11, Mo: 3, V: 3, W: 1.5, Mn: .5, Si: .5, Fe: Bal. Firstly, the non-equilibrium solidification curve and free energy curves of Fe-Cr-Mo-W-V-C alloy were forecasted by Scheil-Gulliver modeling via (Thermo-Calc) software (Version P, TCFE7 database). Secondly, according to the Fe–C isopleths and DSC results [13], 1240°C and 1200 °C are chosen as characteristic temperatures of the carbide precipitation. The specimens were firstly heated up to 1400 C and then cooled slowly to 1240 C and 1200 °C (the specimens quenching from 1200 C were held for 15 min and 30 min, respectively) in furnace, and quenched quickly into the water to fix the microstructures.

The specimens were polished and etched using Murakami etchant in which black M2C, brown M7C3, and gray MC were selectively etched, and then observed by Axiovert 200 MAT optical microscope (OM). Additionally, the matrix was deeply etched in an etchant of 5 g FeCl3+10 ml HNO3+3 ml HCl+

87 ml ethylalcohol to observe thethree-dimensional morphology of eutectic carbide by S4800-II field emission scanning electron microscope (FESEM). The com- positions of different carbides were analyzed quantitatively by energy dispersive spectroscopy (EDS).The foil specimens were prepared by cutting into sections about 3 mm in thickness and mechanically grinding to 30 mm. The observation holes were introduced by Model 691 precision ion polishing system (Model691 PIPS) and the samples were studied by aJEM-2010 transmission electron microscope (TEM). The microscopy was performed using bright field and selected area diffraction patterns (SADPs) to identify the lattice structures of carbides.

3. Results and analyses

3.1. Morphology of eutectic carbide

Fig. 1 is the non-equilibrium solidification curve of the steel and free energy curves of all phases versus carbon content at 1240 C, calculated by"Thermo-Calc"software. From Fig. 1(a), both MC and M2C precipitate from the liquid during solidification process. Combining with the analyses before, it is known that ternary eu- tectic reaction of

$L \rightarrow \gamma\text{-Fe} + MC + M_2C$

occurs, and the eutectic MC and M2C initiate simultaneously and almost instantaneously, which can't be clearly shown in Fig. 1(a). It is also can be seen from Fig. 1(a) that MC and M2C precipitate at 1200 C and 1150 C, which is in good accordance with the precipitation of secondary MC and M2C in this alloy [13]. From Fig. 1(b), it can be seen that, liquid, γ-Fe, eutectic MC and M2C exist in the alloy at 1240 C, and the free energy values of these phases are all less than zero. In the given carbon content range, the free energy of the eutectic MC is smaller than that of the eutectic M2C, which means that MC seems more stable than M2C. Fig. 2 shows the carbide morphology quenched at 1240 °C. From Fig. 2(a), the eutectic M2C is etched black by Murakami etchant and arranges tightly, while the eutectic MC is etched lighter and distributed sparsely. They mix together along crystal grain boundary. From three dimensional morphologies in Fig. 2(b), the eutectic M2C and MC are fibrous and leaf-like shape, respectively. They both exhibit the dendritical structure, which disperse a large number of branches with several to dozens of microns in length.

3.2. Attribution of eutectic carbide

In order to determine the element compositions and lattice structures of eutectic carbide, TEM experiment after quenching from 1240 °C was carried out, and the results are shown in Fig. 3. From Fig. 3(a), cubic VC in A region and orthorhombic V2C in B region are indexed. From Fig. 3(b), C, D regions stand for hexagonal WC and Mo2C. Accordingly, the eutectic carbide existing in the steel contains VC, WC, V2C and Mo2C. It also can be seen that eutectic carbide can't distinguished perfectly from each other ac- cording to TEM. The reason is that although the thickness of the eutectic MC and M2C are only 0.3-0.5 mm and 1–1.5 mm, their branch lengths reach tens even dozens of microns. Nevertheless, the connection phenomenon between the eutectic carbide is consistent with FESEM observation.

3.3. Stability of eutectic carbide

In our previous work [13], secondary MC with bulk-like shape was considered to appear at 1200 C. So, from 1240 C to 1200 C, how did eutectic MC and M2C evolve and what is the relationship between eutectic carbide and the growth of secondary MC need to be further analyzed and discussed. Therefore, in this work, 1200 C was also set as the characteristic temperature to observe the carbide variation from 1240 C. FESEM of carbide after holding15 min and 30 min at 1200 C are shown inFig. 4(a) and (b). From Fig. 4(a), at the early stage, the eutectic MC grows gradually, whose branches connect with each other, and exhibits in the form of blocky shape. The blocky MC swallows surrounding the eutectic MC and connects with adjacent eutectic M2C. Subsequently, the blocky MC swallows eutectic M2C accompanied by dissolving of M2C.Fig. 4(b) shows the growing traces of blocky MC “swallowing” eutectic M2C at the late stage. EDS analysis was performed to reveal element transfer in eu- tectic carbide and further verify microscopic observation.Fig. 4(c) is EDS line analysis of AB line in Fig. 4(a). From Fig. 4(c), the eutectic MC and connected blocky MC contain more V content, which is 10 wt% higher in blocky MC especially. V is the main element in MC and it can be seen that MC growing accompanies by V transfer in surrounding eutectic MC. Fig. 4(d) is EDS line analysis of CD line in Fig. 4(b). Compared with Fig. 4(c), V content in blocky MC continues to increase, while other elements change un-obviously. Eutectic M2C is a kind of Mo-rich carbide. From EDS analyses in Fig. 4(c) and (d), with the increase of holding time, Mo content in the eutectic M2C decreases, so does V content, which shows that the eutectic M2C dissolves gradually. Mo atoms enter in the matrix, while V atoms transfer to where blocky MC locates for its growth.

From above observations and EDS results, the element transfer in eutectic MC, M2C and secondary MC fully supports our speculation about the evolution of eutectic carbide and precipitation of secondary MC during the cooling process. During the slow cooling from 1240°C to 1200 C, the branches of eutectic MC grow up and connect each other to form secondary MC. As the holding time prolongs at 1200°C, the secondary MC continues to grow until reach the edge of eutectic M2C area. Then, the eutectic M2C gradually dissolves and provides alloy elements for the growth of secondary MC. Therefore, it can be seen that the eutectic MC exists stably all the time and goes on growing to form secondary MC, while the eutectic M2C dissolves gradually during the cooling process and thus can be considered as a kind of meta-stable phase. That is to say eutectic MC is more stable than eutectic M2C.

4. Conclusion

Ternary eutectic reaction occurs when the specimen is cooled slowly to 1240 C. The eutectic MC distributes sparsely, while the eutectic M2C arranges tightly. They mix together along crystal grain boundary. The eutectic MC contains VC and WC, while the eutectic M2C contains V2C and Mo2C.

At the early stage of cooling process, the eutectic MC grows with branches connecting with each other, and exhibits in the form of blocky shape; then the eutectic M2C is swallowed by MC and disappears gradually, which shows that the eutectic MC can exist stably, instead of M2C.

Acknowledgments

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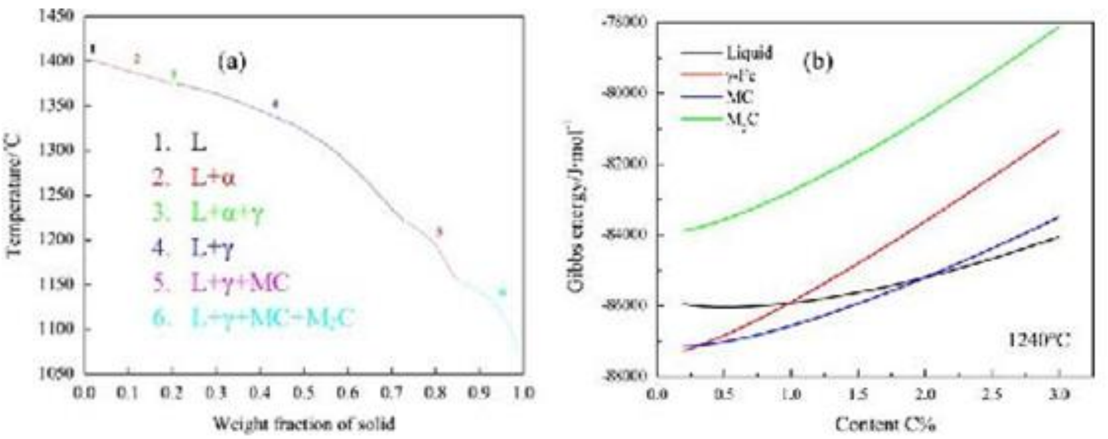

Fig. 1. Non-equilibrium solidification curve of the steel and free energy curves of all phases at 1240 °C: (a) solidification curve, (b) free energy curves.

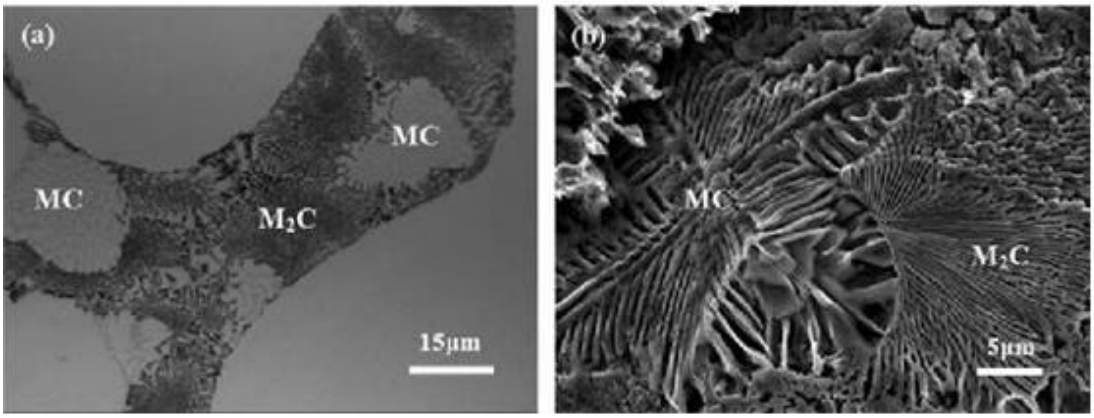

Fig. 2. Morphologies of eutectic carbides: (a) Microstructure, (b) three dimensional morphology.

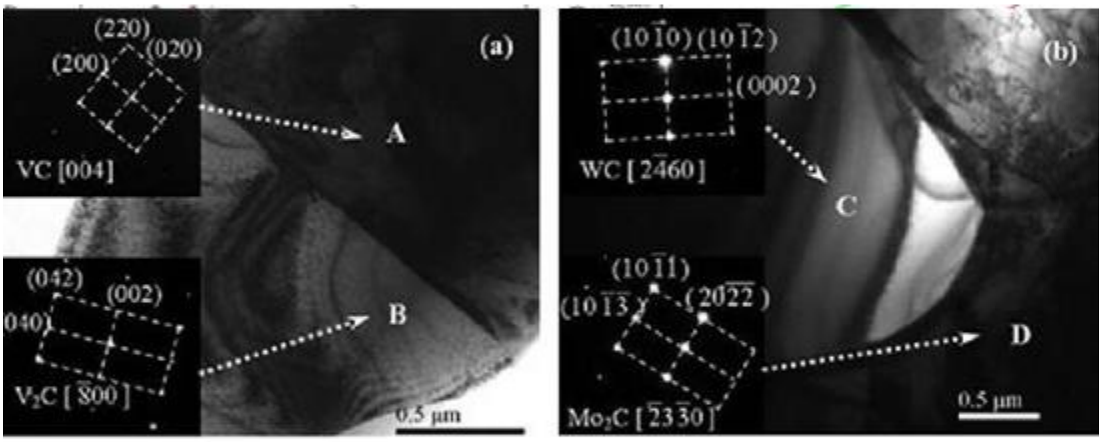

Fig. 3.High-resolution TEM images and SADPs of eutectic carbides: (a) VC in A region, V2C in B region and (b) WC in C region, Mo2C in D region.

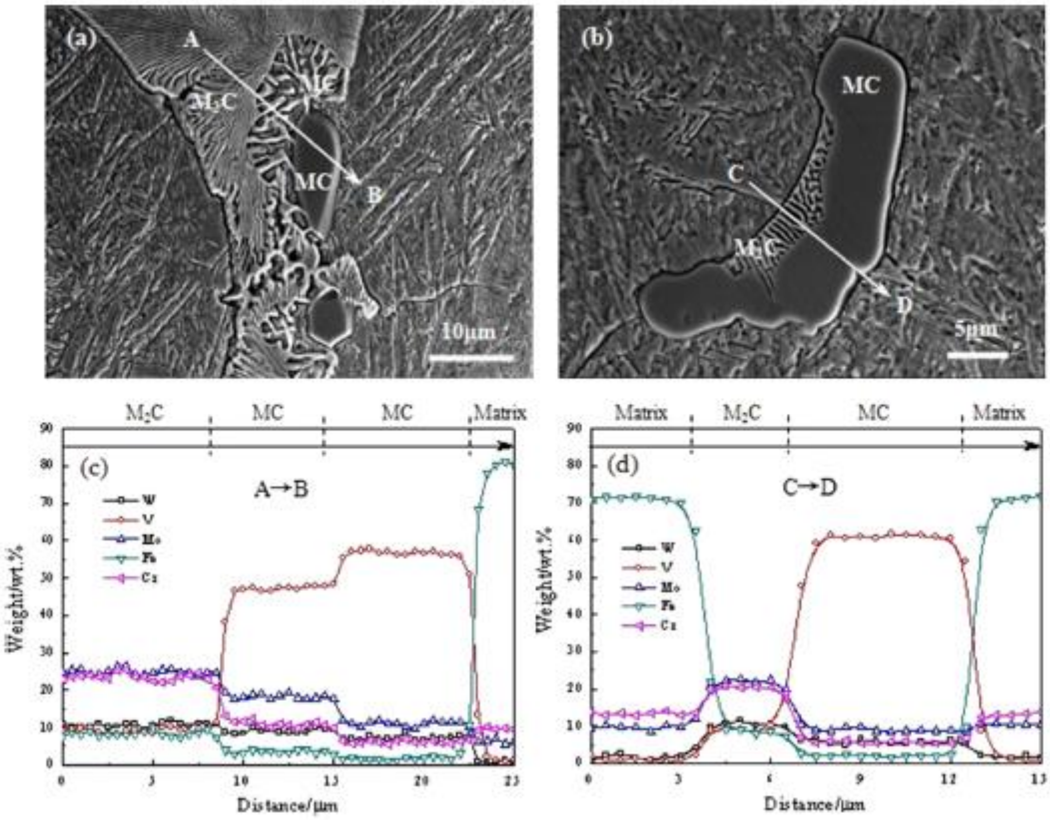

Fig. 4. Growing traces of eutectic carbides: (a) eutectic MC grows, connects with each other and becomes block-shape, (b) the block MC"swallows" adjacent eutectic M2C and eutectic M2C dissolves gradually, (c) EDS line analysis of AB line in (a), (d) EDS line analysis of CD line in (b).