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Effects of Secondary Carbide Precipitation and Transformation on Abrasion Resistance of the 16Cr-1Mo-1Cu White Iron

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The relationship between secondary carbide precipitation and transformation of the 16Cr-1Mo-1Cu white iron and abrasion resistance were investigated. The results show that secondary carbide precipitation and transformation at holding stage play an important role in the hardness and abrasion resistance. After being held for a certain time at 853 K for subcritical treatment, the grainy secondary carbide, $(Fe,Cr)_{23}C_6$, precipitated first and then Fe_2MoC or MoC carbides precipitated in the alloy, both of which improve the bulk hardness and abrasion resistance of the alloy. The reasons for these improvements are the secondary carbide precipitates from the austenite and the retained austenite transforms into the martensite, both make the matrix strengthen. So the matrix has more effective support to the harder eutectic carbide against exterior abrasion. With expanding the holding time, the in situ transformation from the granular $(Fe,Cr)_{23}C_6$ carbide into laminar M_3C carbide causes the formation of the pearlitic matrix and an associated decrease of the alloy abrasion resistance.

Keywords abrasion resistance, high-chromium white iron, precipitation, secondary carbide

1. Introduction

High-chromium white irons are commonly used in wear-resistant applications in the mining and minerals industry because of their excellent abrasion resistance, which is imparted by the hard alloy eutectic carbides presenting in the microstructure (Ref 1, 2). The influence of the microstructure for the high-chromium white irons after certain heat treatments on the abrasion resistance has been studied extensively. Previous research has revealed that the abrasion resistance of these alloys is primarily determined by the features of the hard alloy carbides that form, such as the carbide volume fraction, primary carbide structure, and the eutectic carbide orientation (Ref 3-5). The structure of the matrix that supported the carbides may be varied extensively by alloy selection, processing route, and thermal treatment; it has also been shown to influence the wear behavior (Ref 5, 6). A number of studies have considered the effect of the retained austenite content on the abrasion resistance of alloy white irons (Ref 5-7).

Furthermore, the characteristics of the secondary carbides that precipitate in the matrix during heat treatments also play important roles in influencing the wear resistance (Ref 8-12). Radulovic found that high-chromium cast irons alloyed with vanadium would produce more secondary carbides and improve the abrasion resistance (Ref 8). Minoru found that the addition of molybdenum into high-chromium cast irons could form the more finely dispersed carbide, which was harder than Cr_7C_3 and was expected to impart good wear resistance to the alloy (Ref 9). He also found that the micropitting wear resistance of martensite steel could be improved by the separated secondary carbide transformation during three-body abrasion wear (Ref 10). However, it is not clear how secondary carbide precipitation from the matrix and transformation influence the abrasion resistance of the high-chromium white iron.

This study describes further research into the effect of the secondary carbide precipitation and transformation on the abrasion resistance of a high-chromium white iron subjected to subcritical heat treatment.

2. Experimental Procedures

The high-chromium white iron was a 16Cr-1Mo-1Cu alloy (actual composition: 16.38% Cr-1.08% Mo-0.9%Cu-2.77% C, all in mass %). The casting and manufacture process have been described previously (Ref 11). The test specimens were soaked at 833 K for various times and were then air-cooled to room temperature.

The carbides and matrix structure were investigated by using an optical microscope and analytical electron microscopy (AEM). Philips Tecnai 20 HR-TEM (high-resolution transmission electron microscopy, Phillips Electronic Instruments Corp., Mahwah, NJ) equipped with EDX (energy-dispersive x-ray analyzer). The contents of the retained austenite and martensite were measured by x-ray diffraction (XRD), with a Philips X'Pert XRD instrument. A continuously rotating/tilting sample holder was used to eliminate the effect of the preferred orientation of columnar structure.

The bulk hardness was measured by the Rockwell hardness meter with a load of 150 kg. In the wear experiment, the M-200

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abrasion experimental instrument was used, coupled with the 150 grit Al_2O_3 sandpaper. The load is 50 N, and the rotational speed of the lower sample is 200 rpm. The mass loss of the sample was measured by TG328A photoelectric balance.

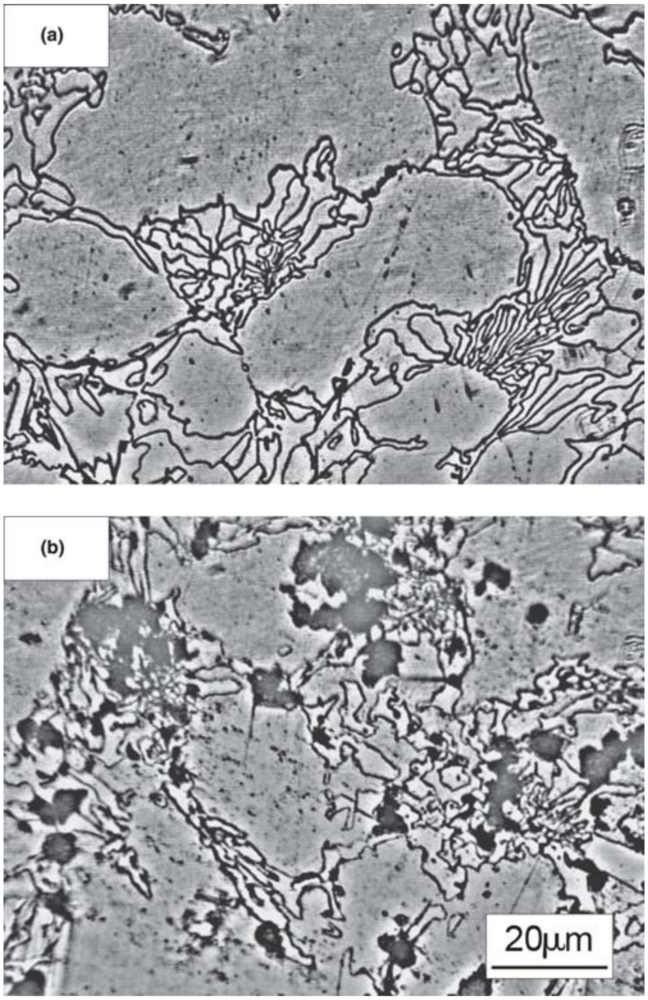

Fig. 1 Microstructures of the alloy (a) in as-cast condition and (b) at 853 K for 10 h

3. Results

3.1 Microstructure

The microstructures of the high-chromium white iron by the way of as-cast and the subcritical treatment at 853 K for 10 h are shown in Fig. 1. In the as-cast state, the alloy's microstructure consists of predominantly austenite dendrites with a eutectic of austenite and carbides. For the subcritically treated alloy, the eutectic carbide is unchanged, while most retained austenite has transformed into martensite after the subcritical treatment. Holding at 853 K for 10 h, the copious secondary carbide precipitated from bulks of the austenite dendrite (Fig. 1b). The etched secondary carbide in the microstructure is dark in the optical morphology observation. The secondary carbides precipitated from the random austenite that grains and did not nucleate and grow on the eutectic carbide.

The XRD profiles of the two different states are shown in Fig. 2. After subcritical treatment, the microstructure changed significantly. A mass of secondary carbides precipitated; the substantive fresh martensite transformed, and retained austenite lessened greatly. Analysis of XRD indicated that, under the as-cast state, the microstructure mainly consists of the retained austenite, martensite, and eutectic carbides, $(Fe,Cr)_7C_3$. The content of the retained austenite of the high-chromium white iron is 77%. By quantitative metallography analysis, the content of eutectic carbides is 15.8%. After holding at 853 K for 10 h, the amount of austenite decreases sharply to about 10%.

3.2 Hardening and Abrasion-Resistance Behaviors

The effects of subcritical heat treatment time on hardness and abrasive mass loss of the 16Cr-1Mo-1Cu alloy at 853 K is shown in Fig. 3. There is a dramatic increase in the bulk hardness of the alloy from 2 to 10 h of treatment. The bulk hardness then decreases smoothly. But at about 16 to 20 h, more or less, the bulk hardness has little increase. The change of abrasive resistance with heat-treatment time has some similarity in some sense. When the alloy is hardening at the first holding stage, the abrasive mass loss decreases observably. Along with the prolonged holding time, abrasion resistance has weakened on the whole.

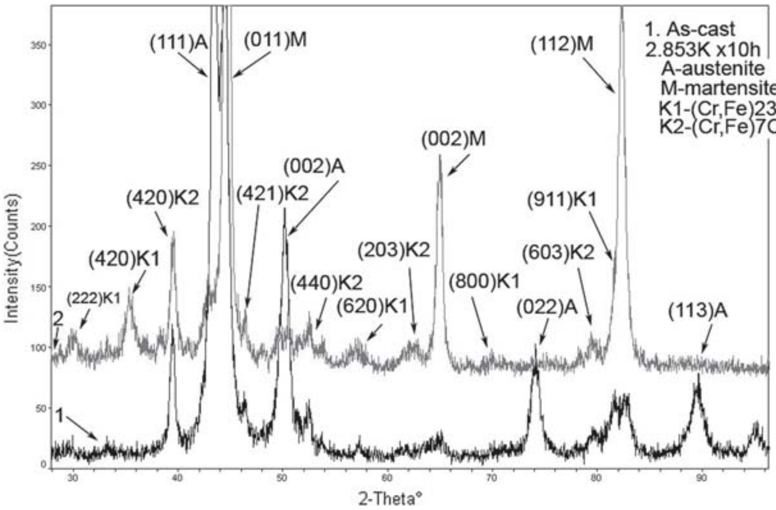

Fig. 2 XRD profiles of alloy in as-cast and subcritical heat treatment at 853 K for 10 h

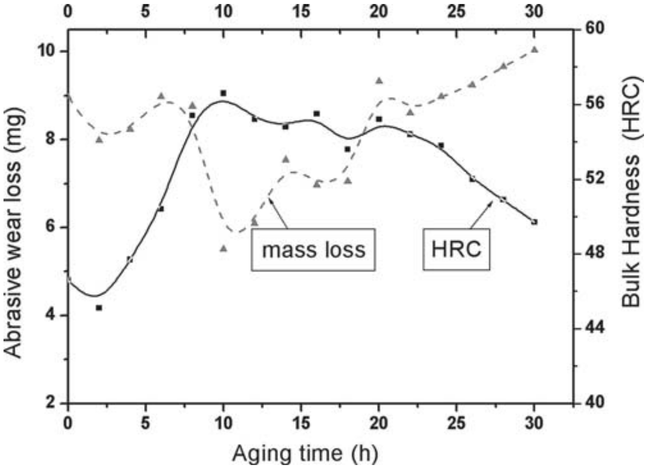

Fig. 3 Hardening and wear behaviors of the alloy subjected to subcritical heat treatment at 853 K

4. Discussion

The as-cast matrix of the alloy has more supersaturated alloy elements. So, it is thermodynamically unstable. After subcritical treatment, the alloy elements will precipitate from the matrix as a form of secondary carbide. A detailed discussion of secondary carbide precipitation during subcritical treatment at 853 K has been given previously (Ref 11). The main precipitation process is as described below.

First, after the temperature was held for 10 h, there was copious precipitate of grainy $(Fe,Cr)_{23}C_6$ carbide (Fig. 4a). Second, after soaking at this temperature for 16 h, the especially smaller sized carbide, Fe_2MoC or MoC, precipitated from the matrix (Fig. 4b) and rod-shaped ε-carbide precipitated from martensite. Then, along with increasing the holding time, an in situ transformation from $(Fe,Cr)_{23}C_6$ into M_3C carbide was observed (Fig. 4c) after soaking 22 h at 853 K, synchronously the matrix begins to transform into pearlite.

The retained austenite is destabilized by precipitation of secondary carbide, and the martensite transformation start (Ms) temperature is increased. So during subsequent cooling to ambient temperature, the destabilized austenite more likely transforms into the fresh martensite. The retained austenite content in the matrix decreases greatly along with the prolonging holding time, from 77.0% in the as-cast state to 10.0% in subcritical treatment for 10 h at 853 K.

With the secondary carbide precipitating from the austenite during the holding stage, more and more fresh martensite is formed during the subsequent cooling stage. So the bulk hardness of the alloy increases. The secondary carbide precipitate strengthens the alloy by a precipitation hardening mechanism, which also increases the bulk hardness. But the ε-carbide precipitating from the martensite during the holding stage at elevated temperature (Ref 11) decreased the carbon content in martensite and decreased the microhardness of martensite. When the hardness increased with precipitation of $(Fe,Cr)_{23}C_6$ but could not make up for the decreased martensite microhardness caused by the matrix carbon content lessening, the bulk hardness drops. After being held at 853 K for 16 h, the special secondary carbide, Fe_2MoC or MoC, precipitates from the matrix and increases the bulk hardness slightly. With the prolonged holding time, the $(Fe,Cr)_{23}C_6$ transforms in situ into the cementite (M_3C), correspondingly, the matrix changes into pearlitic from the martensite matrix, as shown in Fig. 3, so the bulk hardness deteriorates ultimately.

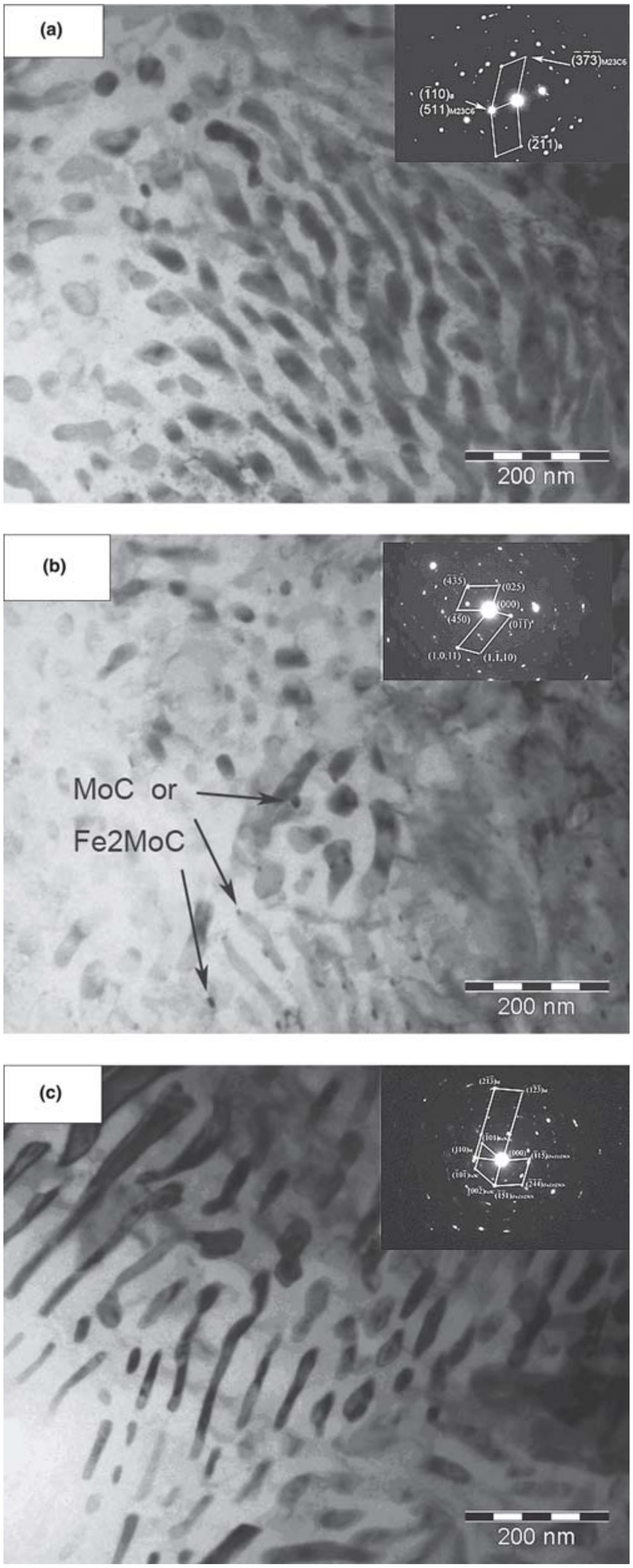

Fig. 4 TEM showing (a) $(Fe,Cr)_{23}C_6$, (b) Fe2MoC or MoC carbides, and (c) in-situ transformation of $(Fe,Cr)_{23}C_6 \rightarrow M_3C$; a, b, and c were heat treated at 853 K and held for 10, 16, and 22 h, respectively (Ref 11)

As shown in Fig. 3, when secondary carbides $(Fe,Cr)_{23}C_6$ precipitate from the austenite dendrites (and cause fresh martensite to form at the cooling stage), the bulk hardness decreases and the alloy's abrasive resistance is improved. The reason for the former is the microhardness of martensite lessening due to the ε-carbide precipitating from the martensite and the carbon content in the pro-transformation-destabilized austenite reduction. The reason for the latter is the secondary carbide precipitating from the matrix during the subcritical heat treatment, which strengthens the matrix through the dispersion hardening effect and alters the mean free path of matrix between the carbides (Ref 12). The strengthened matrix gives a better mechanical support to the harder eutectic carbide for resistance the external abrasion to inhibit its spalling and fracturing and prevents large grooves forming during the abrasion wear (Ref 1, 13, 14). Eckhard suggested that the primary carbides together with the secondary carbide and the harder matrix are responsible for the high wear resistance (Ref 15).

Interestingly, when the special carbide precipitates from the matrix, the matrix strengthens again, and the abrasive resistance becomes better correspondingly. The reason for this phenomenon is that the newly special carbides, Fe_2MoC or MoC, precipitate and strengthen the matrix mainly by causing the crystal lattice deformation.

With expansion of the holding time, the $(Fe,Cr)_{23}C_6$ carbide transforms in situ into long, plate-shaped M_3C carbide, and the matrix transforms into pearlitic structure, which not only causes the carbide amount to decrease, but also makes the morphology of carbides change from a granular shape into lamina, which has a larger impairment effect on the matrix. The pearlitic structure decreases the support of the matrix to carbides, which causes carbides to more easily spall and fracture during abrasion wear. All of these changes severely reduce abrasion resistance. Several researchers have shown that a pearlitic matrix reduced the abrasion resistance, and this matrix structure is generally avoided if good abrasion resistance is required (Ref 12, 14, 15).

5. Conclusions

After subcritical treatment at 853 K, copious secondary carbide precipitated from the austenite in the 16Cr-1Mo-1Cu white iron, which caused the more martensite formation.

$(Fe,Cr)_{23}C_6$ carbide and Fe_2MoC or MoC carbides precipitated at the holding stage in subcritical heat treatment for 16Cr-1Mo-1Cu white iron and improved the bulk hardness and abrasion resistance of the alloy by strengthening the matrix, which more effectively supported the harder eutectic carbide against exterior wear.

With expanded holding times, $(Fe,Cr)_{23}C_6$ carbide transformed in situ into M_3C carbide and the pearlititic matrix structure formed, which sharply weakened the hardness and abrasion resistance of the alloy.

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