

The Effect of Mo on the Structure of High Cr-Mo Alloy Iron

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According to many former studies, the function of Mo in high Cr white iron is to increase its hardenability. In this paper, the results show that, as the precipitation of high Cr-Mo white iron takes place, the Mo precipitates in the form of χ phase from the austenitic matrix prior to other carbides, which results in a change of precipitate and precipitation.

Keywords microstructure, Mo, white iron

1. Introduction

High Cr white iron has been extensively used to resist various forms of abrasive wear. What role does Mo play in the white iron? There is not total agreement on views put forward by researchers.[1–4] Some think that Mo mainly lowers the solidus of Fe-Cr-C; others consider that Mo increases the hardenability of white iron. There is not a Fe-Cr-Mo-C phase diagram to use as a basis, except for Fe-Cr-C[5] or Fe-Cr-Mo.[6] The only way to recognize the role that Mo plays in white iron is through researching the effect of Mo on the Fe-Cr-C alloy iron.

2. Experiment

The compositions of samples can be seen in Table 1. The white iron is melted in a conduct furnace. The heat treatment process of as-cast iron and the structure of white iron are shown in Table 2. The microstructure of iron was surveyed by a transmission electron microscope (TEM) and a scanning electron microscope (SEM). The composition is analyzed in an energy-dispersive spectrometer. The thin foil specimens were made by melting the specimens, casting them into a bulk, heat treating them, using a spark machine to cut thin slices from the bulk, grinding them to a thickness of 0.1 mm using water-lubricated 500 grit abrasive paper, and finally thinning them at −15 °C, using 60 V and 80 mA in a solution of 10% $HClO_4$ + C_2H_5OH.

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3. Results

It was observed by SEM and TEM that the structure of the A sample of as-cast iron is eutectic austenite and eutectic carbide. The matrix appears as a bandlike structure parallel to eutectic M_7C_3 rod (Fig. 1). There are many stacking faults in the matrix of austenite. After heat treatment at 800 °C, there are some small square-block secondary phases precipitating along the boundary of austenite and M_7C_3 (Fig. 2). Progressively, the secondary phase changed from one phase to two phases (square blocklike phase and short rodlike phase) uniformly precipitated in matrix with an increase in temperature (Fig. 3). The small square blocklike phase is identified as χ phase and the short rodlike phase is identified as M_7C_{3II} by electron diffraction.

The microstructure and composition of the A sample is listed in Table 3. The matrix of as-cast iron contains about 19% Cr and 0.83% Mo; then, the alloy contents of elements Cr and Mo are reduced to 13.87% Cr and 0.02% Mo after being heat treated at 950 °C.

The microstructure of the B sample of as-cast iron is the same as that of the A sample as as-cast, but it precipitated granular secondary phase (Fig. 4) when it is heated at 950 °C. The granular secondary phase is identified by TEM to be $M_{23}C_{6II}$. This is completely different from the precipitate of the A sample. The matrix of the B sample contains about 19.86% Cr at as-cast, and then the Cr content is reduced to 11% Cr.

The structure of the C sample heat treated at 950 °C is M_7C_3, retained austenite, martensite, and granular secondary phase of M_7C_{3II} (Fig. 5). The matrix of martensite contains about 8% Cr and 2.58% Mo.

Table 1 Composition of high Cr and Cr-Mo white iron (wt.%)

Samples	C	Si	Mn	Cr	Mo	S	P	Cr/C
A	2.83	0.68	0.65	28.03	0.89	0.032	0.057	9.9
B	2.77	0.38	0.59	28.67	<0.06	0.029	0.059	10.4
C	3.01	0.62	0.74	16.04	2.84	0.037	0.046	5.3

Table 2 Structure and heat treatment process

Samples	As-cast	800 °C, air cooling	950 °C, air cooling	1050 °C, air cooling
A	M_7C_3 + A	M_7C_3 + A + χ	M_7C_3 + M + Ar + χ + M_7C_{3II}	M_7C_3 + M + Ar + χ + M_7C_{3II}
B	M_7C_3 + A	M_7C_3 + A	M_7C_3 + M + Ar + $M_{23}C_{6II}$	M_7C_3 + M + Ar + $M_{23}C_{6II}$
C	…	…	M_7C_3 + M + Ar + M_7C_{3II}	…

A = austenite; M = martensite; and the text provides descriptions of M_7C_{3II}, $M_{23}C_6$, and χ

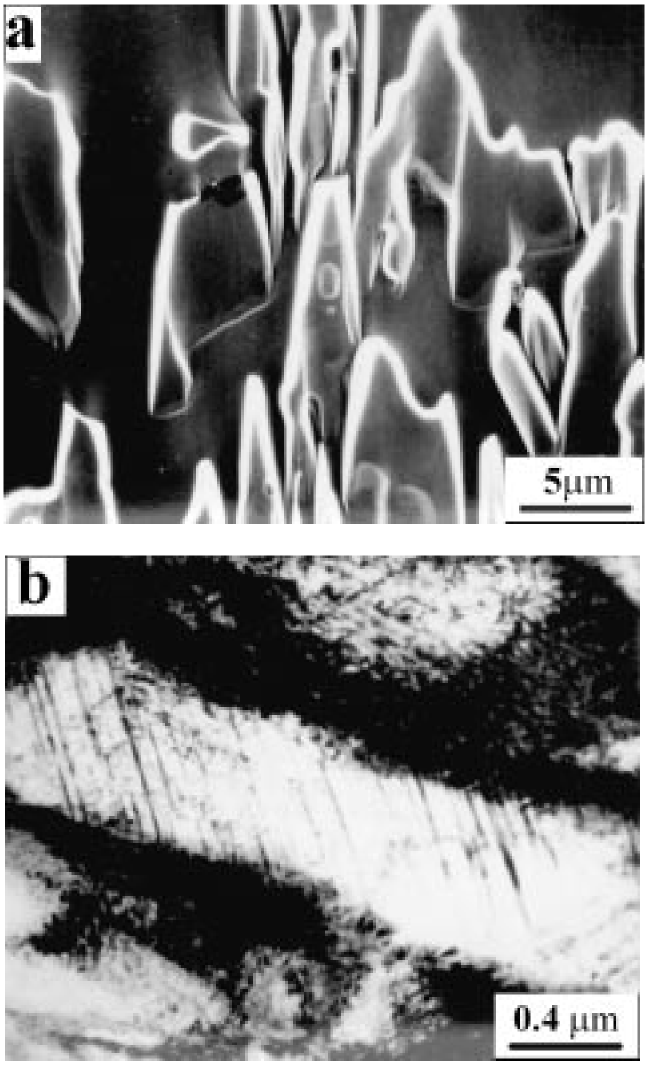

Fig. 1 The structure of as-cast iron: (a) SEM and (b) TEM

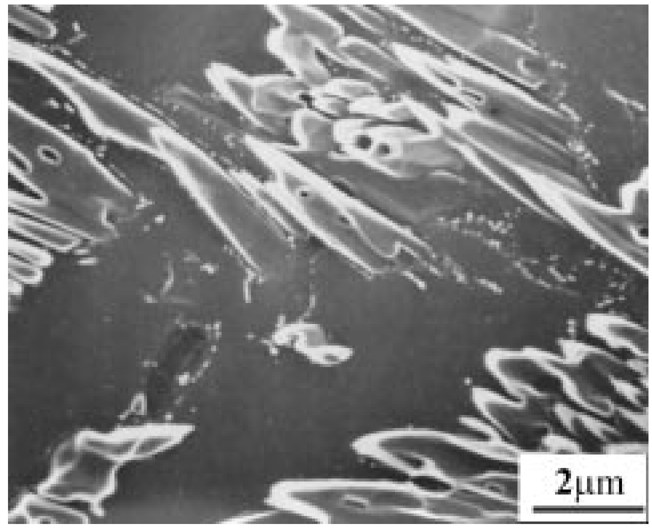

Fig. 2 The structure of white iron heated at 800 °C

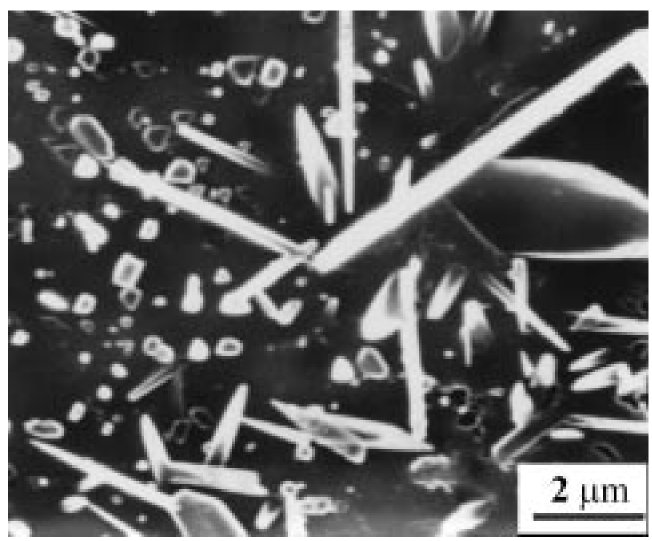

Fig. 3 The precipitation of secondary phases

4. Analysis and Discussion

The experimental results illustrate that there is a clear effect of the Mo element on the structure of high Cr white iron. The Mo can be dissolved in all the phases of iron, but the solubility in carbide is small. The Mo is dissolved mainly in austenite and ferrite. If the Mo is retained in matrix throughout, it plays a part in increasing hardenability and tempering stabilization and does not affect the regular pattern of precipitating a secondary phase; *i.e.*, with the increasing ratio of Cr/C, the order of precipitating secondary phase is M_3C_{II}-M_7C_{II}-$M_{23}C_{6II}$.[7] This can be demonstrated in the samples of B and C. Adding Mo to white iron, containing a relatively high Cr%, the above order will no longer survive. During the precipitating heat treatment of this high Cr-Mo iron, the Mo combines with Fe and Cr to form χ phase (a metallic compound) precipitating from the matrix of austenite, and this causes a change of the precipitating

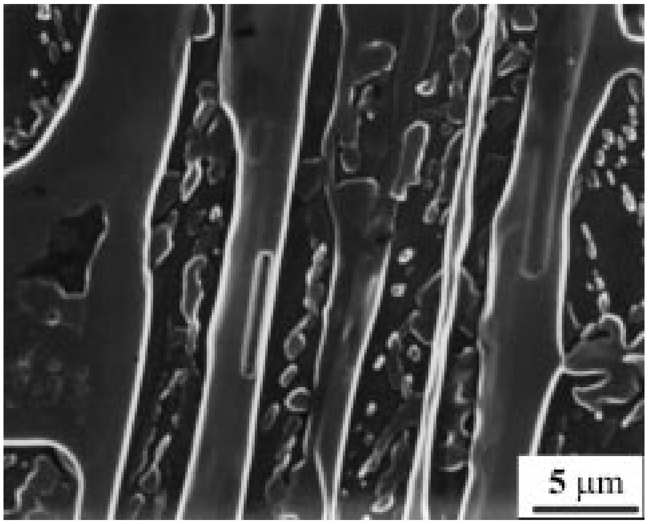

Fig. 4 The precipitated phase of B sample heated at 950 °C

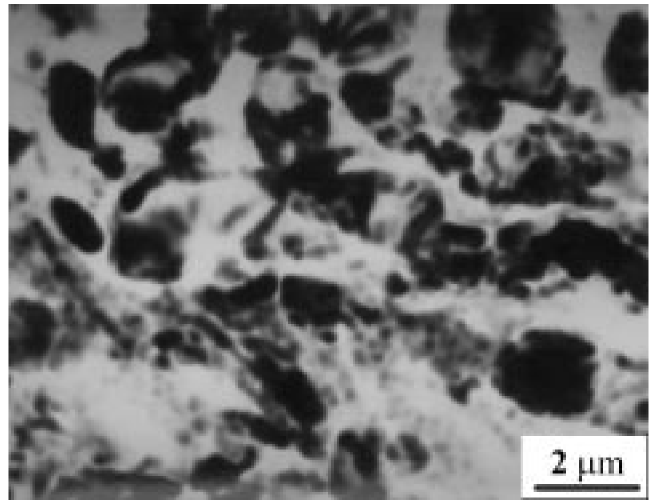

Fig. 5 The precipitated phase of C sample heated at 950 °C

Table 3 The Cr and Mo content of the matrix

Element	A as-cast	A 950 °C, air cooling	B as-cast	B 950 °C, air cooling	C 950 °C, air cooling
Cr	19.11	13.87	19.86	11.35	8.06
Mo	0.83	0.02	…	…	2.58

phase from $M_{23}C_{6II}$ to M_7C_{3II}. Now, the Mo does not play a part in increasing hardenability but alters the rule of precipitation. The properties of white iron have been changed.

The χ phase appearing in high Cr-Mo white iron depends not only on having the Mo element but also on the amount of Cr in the matrix austenite. Comparing the A sample with the C sample, both contain Mo, with even more Mo in the C sample, but the C sample does not precipitate χ phase at all. Mo is retained in the matrix. This is because the C sample contains relatively low Cr%. According to Maratray,[8] the $Cr_m\% = 1.95 \times Cr/C - 2.47$, C sample contains about 8% Cr, which is very low compared to the A sample containing 19% Cr. How much Cr% is required to form the χ phase in white iron? No certain answer has been found. This problem will be researched further.

The χ phase is a metallic compound with a body-centered cubic crystal lattice containing the three elements of Cr, Mo, and Fe. The standard molecular formula is $Fe_{18}Cr_6Mo_5$. Actually, the constituent of the χ phase may be altered to even contain some carbon atoms. The χ phase widely exists in high Cr-Mo alloy iron and precipitating hardening stainless steel. It is part of the strengthening phase and is useful for high Cr-Mo iron.

The χ phase is close to the σ phase in the chemical constituent and crystal structure. Sometimes the χ phase, as a transitional phase, gradually changes into σ phase and lowers the properties of iron.[9] In high Cr-Mo alloy iron, the χ phase is very stable. No σ phase has been found in my experiment.

The temperature of the precipitating χ phase is lower than that of M_7C_{3II} in high Cr-Mo alloy iron. At a low temperature, the χ phase nucleates heterogeneously at the phase boundary and precipitates along the M_7C_3 boundary. Upon raising the heating temperature, the χ phase homogeneously nucleates inside of the grain, so the χ phase particles disperse at the matrix. The growth rate of the χ phase is low. Even when the iron is held at high temperature long enough, the χ phase is not more than 1 μm. Therefore, the precipitating hardening should be performed at high temperature so the iron can be strengthened effectively by a small dispersed χ phase.

It is χ phase prior precipitation that alters the rule of secondary precipitation. A precipitated χ phase takes much of the Cr of the matrix; this causes the Cr/C to be reduced and the secondary carbide modified from $M_{23}C_{6II}$, into M_3C_{3II}. The morphology of M_7C_{3II} also has changed from short rodlike into granular.

5. Conclusions

The Mo is a useful alloy element for high Cr white iron. What role it plays depends on the alloy constituent. When the Cr content of iron is low, such as about 15% Cr, the Mo dissolved in the matrix plays a part in increasing hardenability, but when the Cr content is up to about 28% Cr, the Mo forms the χ phase prior to precipitating from the matrix, which leads to the precipitation rule of the secondary phase being changed.

The secondary phase of high Cr-Mo white iron is of a small square blocklike χ phase and a short, rodlike M_7C_{3II} carbide. The white iron can be strengthened effectively by dispersed phases.

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