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Effects of high temperature and cryogenic treatment on the microstructure and abrasion resistance of a high chromium cast iron

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ABSTRACT

Effects of deep cryogenic treatment on the microstructure, hardening and abrasion resistance behaviors of 16Cr1Mo1Cu cast iron subjected to destabilization treatment were investigated. The results show that the cryogenic treatment can effectively reduce the retained austenite after destabilization heat treatment, but cannot make retained austenite transform completely. Cryogenic treatment can markedly improve bulk hardness and abrasion resistance of the high chromium cast iron. In the course of destabilization treatment and then cryogenic treatment, the amount of precipitated secondary carbide, $M_{23}C_6$, was more than that in air cooling. The additional fine secondary carbide precipitated during the cryogenics treat after destabilization heat treatment comparing with air cooling, is the main reason for the increase of the bulk hardness and wear resistance.

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1. Introduction

High chromium cast irons are commonly used for wearresistance applications in the mining and minerals industry due to their excellent abrasion resistance (Tabrett and Sare, 1998; Pearce, 2002). In the as-cast condition, the hard alloy eutectic carbides [(Fe,Cr)₇C₃] embedded in a predominant martensite matrix that always contains retained austenite resulting from heat treatment (Wang et al., 2005). For many applications, the castings are heat-treated prior to service. The destabilization heat treatment is the technique in common use (Tabrett et al., 1996; Wang et al., 2006) Nowadays, one of the most prevalent claims in low-temperature treatment is an increase in wear resistance of certain materials (Molinari et al.,

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2001; Yun et al., 1998; Huang et al., 2003; Liu et al., 2008) and cryogenic treatment is an inexpensive one time permanent treatment affecting the entire section of the component unlike coatings (Mohan Lal et al., 2001). Most researchers believed that the main reason for this was the almost complete transformation from austenite into martensite plus the formation of very small carbides dispersed in the tempered martensitic structure (Yun et al., 1998). But some researcher suggested that there was always the retained austenite after cryogenics treatment after destabilization treatment in high chromium cast iron (Tabrett and Sare, 1998; Hann and Gates, 1997). Hann called the retained austenite after cryogenics treated for "stable austenite" (Hann and Gates, 1997). So it would be in the interest to research the benefits of the cryogenics treatment and to know the conditions at which the treatment derives maximum benefits of the cryogenics treatment.

The present work is a systematic comparative study on the microstructure, hardening and abrasion resistance behaviors of cryogenic treated high chromium cast iron samples after subjected to destabilization heat treatment, want to give an insight of the effects of the cryogenics treatment on the cast iron and to understand the cryogenic mechanism.

2. Experimental procedure

The high chromium white iron was cast from 1773 K as 80 mm diameter balls into a chilled mould. The chemical composition is given in Table 1. The ball was cut into test samples by $10 \text{ mm} \times 10 \text{ mm} \times 10 \text{ mm}$ blocks. The test samples were subjected to destabilization treatment at serials of test temperatures. The holding time is 0.5 h for each temperature. After destabilization treatment, some of the samples were air cooled to room temperature and the others put into liquid nitrogen directly and held for 3 h.

The bulk hardness was measured using a Rockwell hardness tester with a load of 150 kg (HRC). Optical metallography and JSM-5900 LV scanning electron microscopy was performed after etching. The contents of the retained austenite and martensite were measured using XRD, with X'Pert Philip X-ray diffraction instrument that used a Cu K alpha X-ray source and a nickel filter. A continuously rotating/tilting sample holder was used to eliminate the effect of the texture. In the wear experiment using M-200 abrasion experimental tester with the 150-girt Al₂O₃, the load is 50 N and the rotational speed of the sample is 200 rpm.The losing weight of the sample was measured by TG328A photoelectric balance and the abrasive resistance was evaluated using the mean value of the tests.

3. Results and discussion

The microstructure and XRD profile of the cast iron in the ascast condition are illustrated in Figs. 1 and 2. Typically, the high chromium iron consists of hard eutectic carbides embedded in an austenitic matrix. Fig. 2 shows that the microstructural constituents of this cast iron are austenite, $(Fe,Cr)_7C_3$ [M₇C₃] and martensite. By calculation from the XRD results, the content of austenite, martensite is 77.0% and 7.2%, respectively. Using quantitative metallographic analysis, the eutectic carbide, M₇C₃ is 15.8%.

Fig. 3 shows the micrographs of cryogenically treated and non-treated sample after destabilization treatment at 1000 °C for 0.5 h. As shown in them, there precipitates some secondary carbides during heat treatment, the etched secondary carbides appear dark in microstructure. The secondary carbides are distributed more homogeneously in the cryogenic treated sample than in the non-cryogenically treated one. And after the cryogenics treated, the proportion of martensite in the matrix appears to increase. By calculated from XRD results, the amounts of retained austenite in cryogenically treated and

Table 1 – Chemical composition of the high chromium cast iron (mass%)								
Element	С	Si	Mn	S	Р	Cr	Cu	Мо
Mass%	2.77	0.7	1.90	0.063	0.05	16.38	0.9	1.08



Fig. 1 – The microstructure of the as-cast high chromium cast irons.



Fig. 2 – The XRD pattern of the as-cast high chromium cast iron.

non-treated are change into 18.99% and 9.93%, respectively. The netted eutectic carbide is unchanged after heat treatment.

The XRD profiles of two different states are shown in Fig. 4. Comparing with the XRD in as-cast condition (Fig. 2), it illustrates that the content of martensite increase markedly while that of retained austenite lessened greatly. Under the as-cast state, there is so little secondary carbide, M₂₃C₆, in microstructure that cannot be clear shown. Both of cryogenic treatment and air cooling after destabilization treatment, the secondary carbides, M₂₃C₆, are increasing. Additionally, as shown in Fig. 4, the content of $M_{23}C_6$ in cryogenic treatment is greatly more than that of in air cooling. This is because the martensite becomes more supersaturated under cryo-temperature due to the solid solubility of alloy elements and carbon in martensite lessened after destabilization treatment. This increases the lattice distortion and thermodynamic instability of the martensite, both of which drive carbon and alloying atoms to segregate. Because of this, the secondary carbide precipitation occurs with higher activation energy, thus leading to a higher nucleation rate and, in turn, to finer dimensions and a more homogenous distribution (Molinari et al., 2001; Yun et al., 1998). Therefore, the amount of precipitated fine



Fig. 3 – The microstructure of the high chromium cast irons in different heat-treated states (a) air cooling (b) cryogenic treatment after destabilization treatment at 1000 °C.



Fig. 4 – The XRD profile of high chromium cast iron in two kinds of heat-treated states.

secondary carbides of cryogenic treated sample after destabilization treatment is more than that non-cryogenically treated sample after destabilization treatment.

The contents of retained austenite of alloy subjected to air cooling and cryogenic after destabilization treatment are shown in Fig. 5. As mentioned above, the as-cast matrix of the alloy is thermodynamically unstable because it is



Fig. 5 – The content of retained austenite at different heat-treated states (heated for 0.5 h).



Fig. 6 – The hardening curves of high chromium cast irons after air cool and cryogenic.

super-saturated with alloying elements. These elements will precipitate from the matrix in the form of secondary carbides during destabilization heat-treating, the depletion of carbon and chromium content of matrix increases the Ms temperature. This causes abundant austenite transform to martensite during cooling. So retained austenite lessens markedly. Furthermore, after cryogenic treatment, retained austenite reduced more remarkably than that after air cooling. This is because retained austenite is soft and unstable at lower temperatures, and it is likely to transform into fresh martensite (Mohan Lal et al., 2001), however, the cryogenic treatment cannot make retained austenite transform into martensite completely, which highlights the difficulty in reducing the austenite content to very low levels.

The hardening behavior of the alloy subjected to destabilization with air cooling and cryogenic are illustrate in Fig. 6. In destabilization treatment with air cooling, the hardness of the alloy increases until the temperature reaches $1000 \,^{\circ}$ C, and then the hardness falls. For the deep cryogenic treated samples, there is similar rule in hardening behavior. But its hardness is higher than that of air cooling and more stable against the change with the treated temperature.



Fig. 7 – Relationship between abrasive wear loss and holding temperature of destabilization heat treatment.

The change of the hardness after different destabilization temperature can be ascribed in: (a) the amount of retained austenite changed with treated temperature (Fig. 4) and (b) the secondary carbide precipitated during the heat treat and coarsened at high treated temperature.

After cryogenic treatment, the hardness of the alloy is higher than that of air cooling was associated that cryogenic treatment can effectively reducing the amount of austenite and increasing the fresh martensite content after the destabilization treatment, comparing with the air cooling conditions, and that cryogenic treatment can make more fine secondary carbides precipitates, which can cause the dispersing strengthening effect, so the hardness are higher than that of air cooling.

The correlation between abrasive resistance of the cast iron and treating temperatures are shown in Fig. 7. As shown in it, the abrasive wear loss of cryogenic treated sample represents a similar change with that of non-cryogenic treated sample. At first, the wear resistance changed better with the treated temperature ascending from 900 to 1050 °C, attained the optimal wear resistance. And then, with the treated temperature ascending, the wear resistance worsened. The reason for the wear resistance change may be ascribed the hardness change of alloy, mainly in change of contents of retained austenite and volume of secondary carbide precipitates. The content of carbon and alloys in the matrix is also the important factor for considered.

The abrasion resistance of cryogenic treated sample is always better than that of non-cryogenic treated in the whole of treated temperature domain. There are two important factors to be considered to account for the observed improvement of cryogenic treatment on wear resistance. One is the transformation of abundant retained austenite into martensite during the cryogenic treatment, which can offer stronger support for carbides to inhibit its spalling and prevent large grooves forming during abrasion course (Wang et al., 2006). Another is that the precipitation of fine carbides and the more homogeneous carbide distribution as a result of cryogenic treatment is responsible for the improved wear resistance (Yun et al., 1998; Huang et al., 2003). As mentioned above, the distribution of the carbides in the cryogenic treated samples are more homogeneous than that in the non-cryogenic treated samples, and the carbide volume fraction in the cryogenically treated samples is more than that in the non-cryogenically treated. The precipitation of more hard carbides in the cryogenically treated samples can reduce the carbon and alloy contents in the matrix, which improves the toughness of the matrix. So, in cryogenic treatment, the combination of higher carbide content and tougher matrix enhanced the wear resistance.

Additionally, the more fine carbide precipitated in the process of cryogenics treatment, truly, in the course of restore to ambient temperature from -196 °C (liquid nitrogen), may have lowered the stability of the austenite in the heat-treated structure. Lower austenite stability could increase the degree of work-hardening during abrasion and improve the wear resistance (Tabrett and Sare, 1998; Sinatora et al., 1995).

A comparison of the wear surfaces of cryogenic treated and the non-cryogenic treated sample following abrasion 150-girt Al_2O_3 are provided in Fig. 8. The cryogenic treated sample developed ground surfaces (Fig. 8b) similar to that of the non-cryogenic treated (Fig. 8a) at 1000 °C for 0.5 h. Both ploughing marks (long ribbon) and delaminated fragments could be observed. But a distinct effect of cryogenic treated sample is that the width and the depth of the long ribbon type chips decreased and the proportion of flaky chips produced by delamination decreased after cryogenic treatment. This differ-



Fig. 8 – Scanning electron micrographs of abrasion surface of different treated sample (a) air cooling and (b) cryogenics treatment after 1000 °C, 0.5 h.

ence can be resulted from the microstructure change during the cryogenics treatment as discussed above.

4. Conclusion

Cryogenic treatment can effectively reduce the retained austenite content after the destabilization heat treatment, but cryogenic treatment cannot make retained austenite transform to martensite completely. Cryogenic treatment can markedly improve hardness and abrasion resistance of high chromium white cast irons. In the course of destabilization treatment and then cryogenic treatment, the amount of precipitated secondary carbide, $M_{23}C_6$, was more than that in air cooling. The additional fine secondary carbide precipitated during the cryogenics treat after destabilization comparing with air cooling, is the main reason for the improve of the hardness and wear resistance.

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