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Improving the wear resistance of white cast iron using a new concept – High-entropy microstructure

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ABSTRACT

This study was conducted with attempt to break through the bottleneck using a new concept – high-entropy microstructure. It has been recently demonstrated that an alloy containing more than five elements with the concentration of each element in the range of 5–35% could have a so-called high-entropy microstructure, which is very fine without large-sized intermetallic phases that reduce the resistance to fracture during high-stress wear and impact wear. In this study, this new concept was applied to modify a white cast iron by adding a few carbide-forming elements to the material simultaneously. The carbide-forming elements mutually competed to form their own carbides and this competition also helped to suppress the growth of the carbides, so that carbide refinement could be achieved. Strong carbide-forming elements, Ti, V, Mo and W, were simultaneously added to Fe–20Cr–5C alloy. As the amount of added elements increased, primary M_7C_3 in the original white cast iron was eliminated with the formation of various finer carbides, including eutectic M_7C_3, MC and M_6C. Compared to unmodified white cast iron, the modified alloys have demonstrated promising improvement in the wear resistance.

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1. Introduction

White cast irons are ferrous based alloys with main alloying additions of chromium and carbon [1,2]. They are widely used as wear-resistant materials in various processes for mining, grinding, mineral handling, and oil sands slurry pumping. The wear resistance of the cast irons depends upon the type, morphology, amount and distribution of hard carbides and properties of the matrix. The hard carbides are crucial to the wear resistance, although the matrix makes a large contribution to the overall toughness [3].

Extensive industrial applications of high-chromium white cast irons have attracted researchers to try different carbide-forming elements such as Ti, V, Nb, Mo, and W to further improve this type of material through modification of carbides [4–9], e.g., introduction of harder carbides, though these elements may also improve the hardenability of the material.

Recently, a novel approach (so-called high-entropy microstructure) was proposed to design a new group of materials with very fine microstructures. A high-entropy alloy contains more than five elements and the concentration of each element is in the range of 5–35% [10–12]. Nanostructures or even amorphous phases could be obtained in a high-entropy alloy due to the high nucleation rate and low growth rates of formed second phases [10,11]. In this work, the high-entropy microstructure concept was applied to modify a white cast iron by alloying it with a few carbide-forming elements simultaneously. The fabricated new cast irons contained different types of hard carbides such as M_7C_3, MC and M_6C. Because of low atomic diffusivity or higher barriers to diffusion in a multi-component system, the growth rate of carbides was low, resulting in a microstructure with finer and harder carbides, which may further benefit the wear resistance of the material.

2. Materials and methods

Ti, V, Mo and W were added to a Fe–20Cr–5C white cast iron with equal mole percentage as shown in Table 1. These elements were selected based on their high carbide-forming abilities. The mole percentage of the elements was increased from alloy #2, through alloy #3, to alloy #4. Ingots of the alloys were prepared by melting mixed powders of Ti, V, Mo, W and Fe–20Cr–5C in an arc melting furnace with a high-purity argon atmosphere. The ingots were remelted five times in order to minimize the compositional inhomogeneity. The ingots were cut into pieces with required dimensions, and then ground using 240#, 400#, 600# and 800# silica paper and finally polished with a 1 μm-diamond suspension.

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Table 1
Chemical composition of the fabricated alloys.

Alloy no.	Wt%	At%
#1	Fe–20Cr–5C	62.64Fe–17.94Cr–19.42C
#2	Fe–20Cr–5C–1.99Ti2.12V4Mo7.64W	58.1Fe16.6Cr18C–1.8TiVMoW
#3	Fe–20Cr–5C–3.29Ti3.49V6.59Mo12.6W	55.5Fe15.9Cr17.2C–2.83TiVMoW
#4	Fe–20Cr–5C–3.57Ti3.8V7.15Mo13.7W	54Fe15.46Cr16.76C–3.45TiVMoW

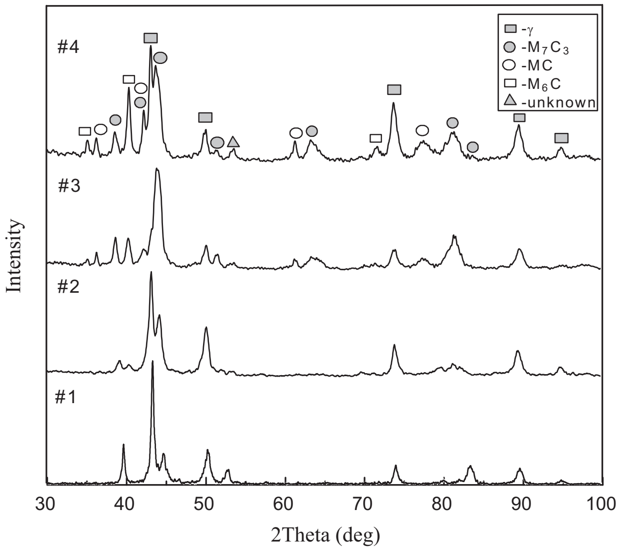

Fig. 1. XRD patterns of fabricated alloys.

A Rigaku X-ray diffractometer with Cu Kl radiation ($\lambda = 1.54056$ Å) was used to determine phases in the samples. The examinations using SEM and EDS were carried out with a Zeiss EVO MA 15. Sliding wear tests were performed on a pin-on-disc tribometer (CSEM Instruments, Neuchatel, Switzerland). The disc was the sample under study (15 mm × 8 mm × 5 mm) and the pin was a silicon nitride ball with its diameter equal to 6 mm. All tests were performed at a sliding speed of 0.5 cm/s along a circle path of 2.0 mm in diameter under a normal load of 10 N for 10,000 rotations. Each wear test was repeated at least 3 times. The calculation of volume loss was according to ASTM G99-05. Wear track width was determined by optical microscope and also examined using a profilometer. The hardness is measured by Mitutoyo hardness tester under a load of 5 N for 20 s. Each hardness value is an average of 10 measurements at randomly selected locations on each specimen.

3. Results and discussion

3.1. XRD

The XRD patterns of alloys #1, #2, #3 and #4 are presented in Fig. 1. Alloy #1, the base alloy, consisted by austenite γ and M_7C_3 carbide. Alloy #2 shows strong peaks of austenite γ and M_7C_3 and weak peaks of MC and M_6C. Alloys #3 and #4 also consist of γ, M_7C_3, MC and M_6C and intensities of the MC and M_6C peaks are higher, corresponding to increases in the volume fraction of the carbides. It needs to be noted that there are some unknown weak peaks present in the XRD patterns of all the three alloys. MC carbides have a simple crystal lattice and are usually crystallized with a significant carbon deficiency. M_7C_3 and M_6C carbides have complex crystal structures. The added carbide-forming elements introduced new carbides, MC and M_6C, in the material.

3.2. SEM

Microstructures of the four as-cast alloys are shown in Fig. 2. Large primary M_7C_3 can be seen in the Fe–20Cr–5C white cast iron. When Ti, V, Mo and W were added to Fe–20Cr–5C, the size of primary M_7C_3 decreased as shown in Fig. 2(c). No primary M_7C_3 were observed in alloys with a higher content of the added elements (see Fig. 2(e), (g)). This was attributed to the depletion of carbon in matrix when the strong carbide-forming elements were added, which reacted with carbon to form MC and M_6C. The amount of MC and M_6C increased with increasing the amount of added elements. In alloy #4, primary γ phase showed up and the microstructure appeared to be hypo-eutectic.

The high magnification images were taken to show the fine morphology of carbide. Alloys #3 and 4# contained higher-percentage finer eutectic carbides, in contrast with Fe–20Cr–5C and alloy #2. A duplex structure of carbide was observed as indicated by arrows in Fig. 2(f) and (h). The EDS results (Table 2) show that the core is rich in Ti and C, which should thus be MC carbide. The shell contained less Ti but more V, W and Mo, so it should be the carbide in the form of $(Ti, V, W, Mo)_xC_y$. Combined with the XRD results, the duplex zone might correspond to the unknown reflection peaks, which however cannot be indentified from the existing ICDD database. In summary, the MC carbide was enriched with Ti and V; M_7C_3 was enriched with Fe and Cr; and M_6C was enriched with W and Mo. Adding W and Mo to high-Cr cast irons lead to the formation of complex cubic M_6C carbide [13]. The M_7C_3 carbide in a hypereutectic high-chromium cast iron has a hexagonal lattice [3], which helps the primary M_7C_3 carbide grow into a long rod (as shown Fig. 2(a) and (b)). MC is a binary high-melting interstitial transition metal compound with a face-centered cubic (fcc) lattice like NaCl [14].

From the EDS results of alloy #4, one may see that each phase in the multi-element cast iron contained high quantities of multi-elements. For instance, MC phase can be denoted as (Ti,V)C, which may also contain other elements such as W, Cr, Mo and Fe. These affect the hardness of the MC carbide.

As expected, M (Ti, V, Mo, W, Cr and Fe) and C could dissolve into the molten iron and chemical reactions could take place at certain temperatures, as expressed as

$$x\,[\mathrm{M}] + y\,[\mathrm{C}] = \mathrm{M}_x\mathrm{C}_y\,(\mathrm{s}) \qquad (1)$$

In principle, the corresponding change in Gibbs free energy changes ΔG^* associated with the above reaction determines the order of carbide formation in the equilibrium state. However, it is difficult to calculate accurate ΔG^* for a specific carbide when it forms in multi-element iron melt. Lack of such information makes it difficult to use ΔG^* to predict the precipitation sequence for the present case. However, we may consider two other factors, the concentration of each carbide-forming element and its chemical affinity for carbon. The latter is determined by the mixing enthalpy as ΔH_{mix}. In this study, the mole concentration of each carbide-forming element is equal. Thus the carbide that has the largest negative ΔH_{mix} value would form preferentially. Table 3 lists the mixing enthalpies of the carbide-forming elements, Ti, V, Mo and W, with carbon in addition to that for chromium carbide. Due to the large negative ΔH_{mix} values of Ti and V, their carbides (MC) are expected to precipitate

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