Wear 376-377 (2017) 587–594

Contents lists available at ScienceDirect

Wear

journal homepage: www.elsevier.com/locate/wear

Understanding effects of Cr content on the slurry erosion behavior of high-Cr cast irons through local property mapping and computational analysis

J. Cui, L. Guo, H. Lu, D.Y. Li [*]

Dept. of Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta, Canada T6G 1H9

ARTICLE INFO

Keywords:
High-Cr Cast Iron
slurry erosion
AFM
first-principles calculation

ABSTRACT

High-Cr cast irons (HCCIs) have demonstrated excellent performance during various industrial processes involving mining, oil sand slurry handling, and manufacturing. Attempts have been made to extend concentration ranges of carbon and chromium up to a higher level, e.g., 6%C and 35%Cr or higher. However, it is not clear how the Cr content influences properties of carbide, $(Fe, Cr)_7C_3$, and the ferrous matrix, and thus the performance of HCCIs during wear processes, e.g., slurry erosion for oil sand transport. In this study, we investigated how the chromium content, in the range of 5–35%Cr, affected the performance of HCCIs with 5%C during erosion tests in slurries at two pH levels and four velocities. In particular, local mechanical properties and electron work function which is a measure of electrochemical stability were analyzed for both carbides and the ferrous matrix in the HCCIs using a micro-indenter and a multi-mode atomic force microscope. First-principles calculation was conducted to understand mechanisms responsible for the observed phenomena.

1. Introduction

High Chromium Cast Irons (HCCIs) are widely used in mining, slurry pumping and manufacturing industries, where high resistance to wear, erosion and erosion-corrosion is required [1]. The excellent performance of HCCIs results from the combination of hard carbides, e.g., M_7C_3, and a ferrous matrix [2–4]. The matrix helps absorb impact energy and enhance toughness of the material, while the hard carbides play a crucial role in withstanding the wearing stress as the reinforcement [2]. Since Cr is a strong carbide-forming element, increasing Cr content helps form M_7C_3 carbides. Commercially used HCCIs have their chromium content in the range of 23–30 wt.% Cr, while in recent years efforts have been made to push both contents of carbon and chromium to higher levels in order to obtain higher strength and corrosion resistance for applications involving aggressive chemical conditions, such as dredging [4]. It appears that alloys with higher chromium concentrations exhibit higher resistance to erosion-corrosion. However, whether this trend is applicable to all HCCIs needs to be investigated, since the Cr content may affect compositions of carbides and matrix, leading to variations in their properties.

When concerning properties of M_7C_3 carbide, it is noticed that more Cr does not necessarily produce harder carbides. For example, the calculation by Zhang et al. shows that $Fe_4Cr_3C_3$ has the largest elastic modulus and hardness among all $(Fe, Cr)_7C_3$ carbides with different Cr/Fe ratios [5]. Xiao et al. [6] also computationally demonstrate that the elastic modulus of $Fe_{16}Cr_{12}C_6$ is larger than that of Cr_7C_3. Thus, it is worth investigating and determining the optimal Cr content for maximized benefits from the high-Cr cast irons.

Beside its influence on properties of carbide, alloyed chromium also affects the mechanical properties of the matrix through solid-solution strengthening mechanism. Furthermore, Cr renders the ferrous alloy resistant to corrosion, leading to elevated resistance to erosion-corrosion. Thus, it is also of importance to understand such effects in order to maximize the benefits from alloyed chromium.

In this study, we investigated effects of chromium content, in the range of 5–35%Cr, on the performance of HCCIs containing 5%C during erosion tests in slurries with two pH values and four velocities. In particular, local mechanical properties and electron work function which is a measure of electrochemical stability were analyzed for both the ferrous matrix and $(Fe, Cr)_7C_3$ carbides using a micro-indenter and a multi-mode atomic force microscope. First-principle calculation was conducted to analyze $(Fe, Cr)_7C_3$ carbides and the matrix to understand mechanisms responsible for observed phenomena.

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[*] Corresponding author.
E-mail address: dongyang.li@ualberta.ca (D.Y. Li).

http://dx.doi.org/10.1016/j.wear.2016.12.031
0043-1648/

2. Experiment details

2.1. Sample preparation

Materials under study are cast irons containing 5%C and Cr with its concentration from 5% to 35%, balanced by Fe and minor elements (Mn: 2.2–2.8 wt% and Si: 0.8–1.4 wt%). Ingots of the alloys were made using an induction furnace, from which specimens (10mm × 10mm × 1mm) were cut for microstructure characterization. The surface of specimen was wet ground with SiC papers (up to 2000 grit), and then polished using diamond paste (~0.5 μm). After the mechanical polishing, the specimens were etched using a solution of picral solution for 2 seconds in order to remove residual deformation or stress in the surface layer introduced by the mechanical polishing as well as for revealing microstructure features. The specimens were ultrasonically cleaned in ethanol and dried in a N_2 gas flow. In order to understand the role that Cr plays in affecting properties of the alloys, we selected samples containing 5%Cr, 10%Cr, 20%Cr and 35%Cr, respectively denoted as #5-5, #10-5, #20-5 and #35-5, for analyzing their local electron work function and Young's modulus. For slurry erosion tests, samples with dimensions of 9mm × 5mm × 50 mm were used.

2.2. Slurry erosion testing

For applications of HCCIs in slurry transport for the oil sand operation, slurry erosion tests were carried out using a home-made slurry-pot tester. The tester had a cylindrical tank of 29 cm in diameter and 22 cm in height. In the tank, four baffles were mounted on the internal wall to block the slurry flow so that the samples would travel in the slurry at a velocity that was equal or close to the nominal velocity. A slurry solution consisting of 20 Vol.% silica sand (sand particle size: 500 um in diameter) and 80 Vol.% water was placed in the slurry container. pH value of the solution was adjusted by adding HCl. Samples (9mm × 5mm × 50 mm) were held by a holder, which was connected to a motor that rotated during erosion test and thus drove the samples to move in the slurry. The sand impingement angle was set to be 45 °and the moving velocity was 2.5, 5.0, 6.5 and 8.0 m/s respectively. For each slurry-erosion test, the total distance that samples travelled in the slurry was 15 km. With initial deviation assessment, it was turned out that the distance of 15km was sufficient for obtained repeatable results. Standard deviations were generally in the range of ± 10% for our slurry-pot erosion testing arrangement for HCCIs. After the test, the samples were rinsed and lightly brushed to remove corrosion products and then further cleaned by rinsing with distilled water. The weight loss of each sample was measured using a balance with a precision of 0.1 mg. More details about the home-made slurry pot erosion tester and the experimental set-up can be found in our previous publication [7].

Electron work function and reduced Young's moduli of carbide and matrix were mapped using a Bruker MultiMode atomic force microscope (AFM)8 with PeakForce KPFM capability. The modulus given by AFM is a reduced Young's Modulus by fitting the retract curve using the Derjaguin, Muller, Toropov (DMT) model [8]. Bruker magnetic probes (MESP) with its force constant of 2.8 N/m were used for measuring the modulus and work function. The purpose of *in situ* mapping both work function and the reduced modulus is to view the relation between the modulus and work function.

For more precise information, a micro-indenter (Fischer Technology, Inc., Windsor, CT, USA) was employed to measure micro-hardness and Young's modulus for carbides and matrix in the HCCIs under a load of 1N. The overall hardness or macro-hardness of the samples was determined using Rockwell Hardness testing machine (Zwick Roell Group, UK). Each measurement was repeated 4–5 times.

Microstructures of the alloys were characterized using a scanning electron microscope and corresponding compositions were analyzed with Energy-dispersive X-ray spectroscopy (EDX).

3. Computation details

Calculations were conducted with the first-principles density functional theory (DFT) as implemented in the Vienna ab-initio simulation package (VASP) [9,10]. DFT is a computational quantum mechanical modelling method used to investigate the electronic structure of many-body systems [11]. This method can describe structural and electronic properties of various systems, ranging from atoms, molecules, simple crystals and complex material systems. Electron interactions were treated with the projector-augmented wave method. The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) was used for the exchange and correlation effects [12]. The cut-off energy for plane wave basis was set to 400 eV. M7C3 is determined by Herbstein and Snyman to be isostructural to Ru_7B_3 with space group P63mc (nr. 186) [13]. A Monkhorst-pack [14] sampling of 7 × 7 × 9 k-point mesh was adopted to achieve self-consist field convergence, and 11 × 11 × 13 k-point mesh was adopted to compute total energy, charge density and electronic structure. In all calculations, self-consistency was achieved when the total energy difference between cycles was smaller than 0.1 meV. The geometry relaxation tolerance in all forces was below 0.01 eV/Å. The moduli were calculated with Yu's method [15] as well as Voigt–Reuss–Hill approximation. The alloy matrix was determined to be a bcc structure with 15 Fe atoms and 1 Cr atom according to real Cr concentration in matrix.

4. Results and discussion

4.1. Microstructure

Fig. 1 illustrates typical SEM microstructure images of fabricated alloys with 5%C and different Cr concentrations, 5%, 10%, 20%, 30% and 35%. The alloys show hypereutectic microstructures. The volume fractions of 5%C alloys with different Cr contents were determined by image analysis based on obtained SEM figures. The Cr content did not show a significant influence on the volume fractions of carbides, which were 61%, 65.7%, 56.2%, 57.5%,and 59.6% for samples of 5-5 (Fe-5%Cr-5%C) to 35-5 (Fe-35%Cr-5%C), respectively. Since all these alloys were in the hypereutectic state with their carbide fraction around 60%, difference in their performance during erosion tests as shown later is likely more attributed to variations in compositions of carbides and the matrix in the alloys.

As for why %Cr had no significant influence on the volume fraction of carbides, Table 1 may provide a hint, which presents concentrations of Cr and Fe in both carbide and ferrous matrix of the HCCIs measured using EDX. As shown, with increasing Cr concentration, the Cr/Fe ratio varies in both carbide and the matrix. However, the overall contents of Cr and Fe in the carbide and matrix (in form of ferrite) keep approximately unchanged. Or in other words, adding Cr changes the Cr/Fe ratio but the total amount of metallic elements (Cr and Fe) for forming M7C3 carbides and the matrix are approximately constant, bear in mind that the carbon content is the same for all these HCCIs. This could be the reason why the carbide volume fraction did not show significant changes when %Cr was varied. However, for full understanding, one may need to look into how Cr influences the Fe-C