

Erosion-corrosion Assessment of Cr White Irons

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Abstract

Erosion-corrosion possesses a serious problem for the mining and mineral processing industries. Handling and processing of silica-based solids results in extremely severe wear conditions. Simultaneous action of erosion, corrosion and their synergistic interactions accelerates the material damage. Chrome white irons (CWI) are extensively used in the oilsands industry for slurry handling equipment. Erosion-corrosion resistance of CWI's depends on the chemical composition, matrix microstructure, types and volume fraction of carbides. In this study, high-Cr white irons were assessed using a slurry pot erosion-corrosion testing apparatus, where the total erosion-corrosion (E-C) rate as well as the separate components of synergy were determined. It was found that corrosion resistance of white irons largely depends on the amount of dissolved chromium in the matrix. On the other hand, erosion resistance is controlled by the type and volume fraction of carbides. During erosion-corrosion, corrosion enhanced erosion dominates the synergistic component. Material degradation rate depends on the involved wear mechanisms. SEM observation reveals that cutting of the metal matrix by erodent at low impingement angles, micro-fracture of the carbides and spallation are the dominant mechanisms.

Key words: Erosion-corrosion, synergistic effect, CWI, slurry pot testing

Introduction

Erosion-corrosion in the mineral and oil sands industries decreases the productivity and useful life of the slurry components. Material loss rate due to combined action of erosion and corrosion is significantly higher than the sum of material loss rates due to pure erosion and pure corrosion acting separately¹⁻⁷. Hence, materials employed in hydrotransport equipment must be able to resist the mechanical and electrochemical synergistic degradation by the sand/mineral containing corrosive media⁸⁻¹¹. Selection of appropriate material is crucial to reduce the overall maintenance cost and extend the service life of the equipment. High-Cr white irons are extensively used in mining and mineral processing industries to minimize the erosion-corrosion damage of critical areas in the slurry handling equipment (*i.e.* slurry pumps)^{4, 6, 12-21}.

Historically, high-Cr white irons were the first alloyed abrasion resistant (AR) irons in commercial production (since the early 1900s). With proper alloying, uniform hardness from surface to core could be achieved on a thick section. Wear and mechanical properties of high-Cr white irons are

derived from a well-controlled matrix microstructure and M_7C_3 carbides (M represents metallic species, most commonly Fe and Cr). During solidification, the first phase that solidifies in a hypo-eutectic white iron is austenite dendrites (γ). As the solidification progresses, primary austenite dendrites reject carbon and chromium to the liquid. This is mainly because of the complex interrelationship between the substitutional Cr atoms and the interstitial carbon atoms within the FCC crystalline structure of the austenite dendrite²². The remaining liquid is pushed towards higher C and Cr contents as it reaches to the eutectic valley (right and upward on the liquidus surface, indicated by an arrow in Figure 1). Once the eutectic solidification starts (liquid $\rightarrow \gamma + M_7C_3$), the carbide phase grows spontaneously, thus forming an interconnected eutectic structure in the bulk material²³. In the Fe–Cr–C system, the type and form of eutectic carbides changes with an increase in Cr content. In unalloyed white cast irons (<5% Cr and up to 2% C), continuous M_3C type carbides are formed during eutectic solidification. At 8–10% Cr, the eutectic carbides (M_3C) become less continuous and above 10% Cr, the eutectic carbides changes to the discontinuous M_7C_3 type^{14, 24–28}. A fully austenite matrix is retained at room temperature if the martensite start temperature (M_s) is below the room temperature and sufficient alloying elements are added to avoid pearlite formation during cooling, or the cooling is sufficiently fast that precipitation of secondary carbides in the matrix is avoided. This precipitation would decrease the alloy content of the matrix, and subsequently raise the M_s temperature. On the other hand, hyper-eutectic white irons solidify first in the primary M_7C_3 region. As Cr and C-rich carbides are formed, the remaining liquid is rapidly depleted of C and Cr (*i.e.* M_7C_3 requires approximately 8.9%C) as it reaches to the eutectic valley (left and downward on the liquidus surface, indicated by an arrow in Figure 1), followed by a eutectic of $\gamma + M_7C_3$.

It has been recognized that additional alloying elements (typically, a combination of Mo, Ni, Mn and Cu) are required in high-Cr white iron to achieve sufficient hardenability, particularly with larger sections^{22, 29–34}. Molybdenum (Mo) is added to suppress pearlite formation and to increase hardenability by effectively inhibiting secondary carbide precipitation during cooling^{1, 35–38}. It also has a synergistic effect on other alloying elements such as nickel and copper, which are more effective in delaying pearlite formation³⁹. Another advantage of Mo is that it has little effect on the M_s temperature, while most alloying elements tend to decrease the M_s temperature, which leads to overstabilisation of austenite⁴⁰. Nickel, copper, and manganese are commonly added to improve hardenability and inhibit pearlite formation. Nickel and copper are found exclusively in matrix regions, while manganese may partly segregate to the carbides⁴¹. Nickel when added in conjunction with molybdenum is the most effective combination to avoid pearlite formation⁴².

The primary role of the matrix is to provide mechanical support to the carbides. Previous research has suggested that during low stress abrasion, the effect of the matrix is related to the degree of protection offered by the carbides⁴³. If the carbides protect the matrix from the abrasive particles, the role of the matrix is primarily to provide mechanical support. However, if the matrix is preferentially removed by the abrasive, the carbides may become unsupported and susceptible to spalling and fracture. In this circumstance, the abrasion resistance of the matrix is critical, as this controls the rate at which the carbides become unsupported and fractured⁴⁴. However, the role of the matrix is more complex during erosion-corrosion. In order to provide mechanical support, matrix not only needs protection from the abrasive particle impact but also requires good corrosion resistance.

It's a long-held belief that the bulk hardness of a material determines its wear performance (harder material provides better wear resistance). However, it is now understood that numerous factors influence the wear performance of a material. For a given wear system (*i.e.* load, abrasive type, environment), the alloy microstructure plays an important role in influencing the wear resistance. In hypo-eutectic white irons, eutectic carbides (M_7C_3) constitutes between 20-35% of the microstructure, and are thought to be primarily responsible for the wear resistance of these alloys.

This is mainly because, M_7C_3 carbide is harder than most of the abrasives in service and is therefore shows excellent wear resistance ⁴⁵. For hyper-eutectic white irons, primary carbides determines the overall abrasion resistance. Many factors, such as carbide type, volume fraction, morphology, orientation, hardness and the mean free path between the carbides affect the wear resistance ^{29, 46–53, 20}. Among these factors, carbide volume fraction plays the most significant role in determining the wear performance of high-Cr white irons. Although intuitively, wear resistance is expected to increase with increase in volume fraction of the hard carbides, the actual behaviour is very much dependent on the wear system and involved wear mechanisms. Previous investigation shows that the wear resistance of hyper-eutectic white irons decreases with increase in carbide volume fraction, as the primary carbide often spalls and fractures ⁵⁴. This spalling is associated with the micro-fracture of primary carbide edges which become unsupported due to preferential matrix removal.

Erosion-corrosion is a complex phenomenon and suitable carbide-matrix combinations are required for better performance. The microstructure of high-Cr white iron affects its erosion, corrosion and erosion-corrosion resistance. Due to its broad compositional limit, as cast matrix can be ferrite, pearlite, bainite, austenite, martensite or a mixture with a varying amount of carbide volume fraction ^{55–58}. When changes in matrix microstructure and carbide volume fraction have contrary effects on erosion and corrosion, the optimization of the balance between erosion and corrosion resistance is required to achieve the least synergistic effect and total erosion-corrosion weight loss. In this study, erosion-corrosion resistance of white irons were assessed at 45 °C, in an aqueous slurry containing 35 wt% natural angular sand and 3.5 wt% NaCl. Surface examination was performed using a Hitachi S-3500N scanning electron microscope (SEM) to identify the possible wear mechanisms.

Experimental Procedure

Materials characterization

Four high-Cr white irons were used for this study. Nominal chemical compositions, Cr/C ratio and bulk hardness of these chrome white irons (CWIs) are listed in Table 1. Based on chromium and carbon content, relative positions of these white irons are shown in the iron-rich corner of the Fe-Cr-C phase diagram (Figure 1) ^{59–61}.

Table 1
Nominal chemical composition and bulk hardness of high-Cr white irons (CWIs).

Material	Nominal chemical composition*							Cr/C ratio	Hardness (HRC)
	C	Cr	Ni	Mn	Si	Mo	Fe		
Low C-high Cr	2.1	27.1	-	-	-	-	Bal	12.9	57.4 ± 1.7
Low Cr WI	2.75	19.2	0.66	0.86	0.45	1.85	Bal	7.0	54.9 ± 1.2
Near eutectic-Cr25Mo	2.9	26.1	0.35	0.80	0.50	1.90	Bal	9.0	63.6 ± 0.8
Hyper-eutectic	5.0	35.0	-	-	-	-	Bal	7.0	63.5 ± 1.0

* Chemical compositions from manufactures data sheet

Figure 2 shows the SEM micrograph of hypo-eutectic low C-high Cr white iron. The microstructure consists of primary austenite dendrite and inter-dendrite eutectic colonies. Based on bulk carbon and chromium concentration, Maratray has suggested an empirical formula for determining the eutectic carbide volume fraction ($12.33\%C + 0.55\%Cr - 15.2$)³⁷. Carbon is the main alloying element that determines the total carbide volume fraction. Low C-high Cr white iron has the lowest carbon content among the evaluated irons, which results in lower carbide volume fraction and improved toughness. It also has the highest Cr/C ratio, which results in higher Cr content in the matrix and better corrosion resistance. The microstructure of hypo-eutectic low Cr white iron consists of primary austenite dendrites in eutectic colonies of M_7C_3 carbides and austenite (Figure 3). Low Cr WI contains slightly higher carbon and significantly lower Cr than low C-high Cr white iron, which results in comparatively higher carbide volume fraction and lower corrosion resistance. Figure 4 shows the micrograph of near eutectic white iron. The microstructure contains mostly eutectic structure with uniformly distributed fine carbides and a small amount of primary austenitic dendrites. As evident in Figure 4 (b), carbides are uniformly distributed throughout the structure providing smaller mean free path. There is also some evidence of secondary carbide precipitation inside the austenite dendrites (Figure 4 (d)). The microstructure of hyper-eutectic white iron consists of primary carbides in eutectic matrix (Figure 5). Some martensite is also present in the eutectic structure, predominantly in localized regions adjacent to the eutectic/primary carbides where the depletion of chromium and carbon from austenite has raised the M_s temperature sufficiently to permit the transformation of austenite to martensite.

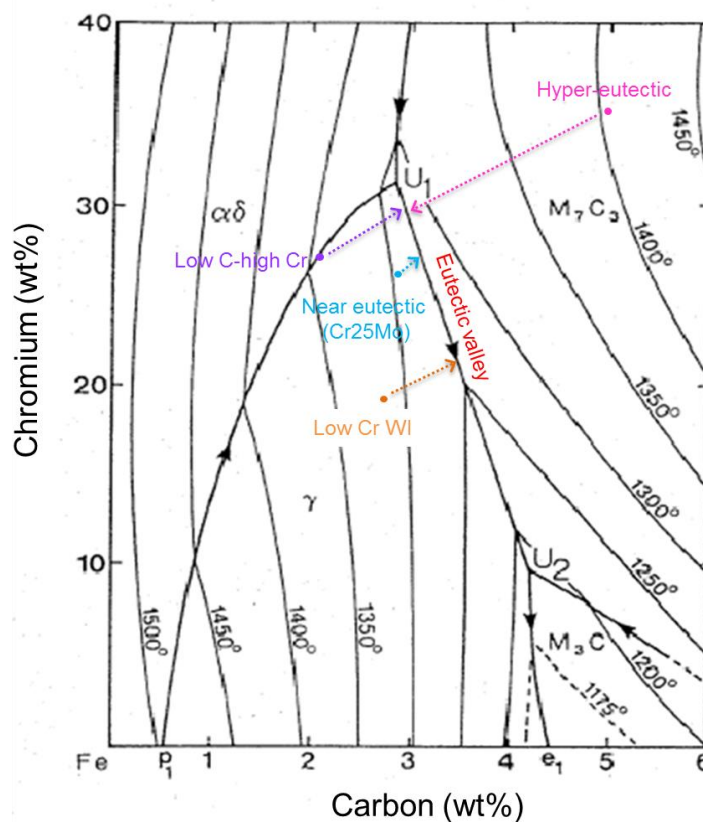


Figure 1 : Fe-Cr-C metastable liquidus surface (contour lines represent constant liquidus temperature).

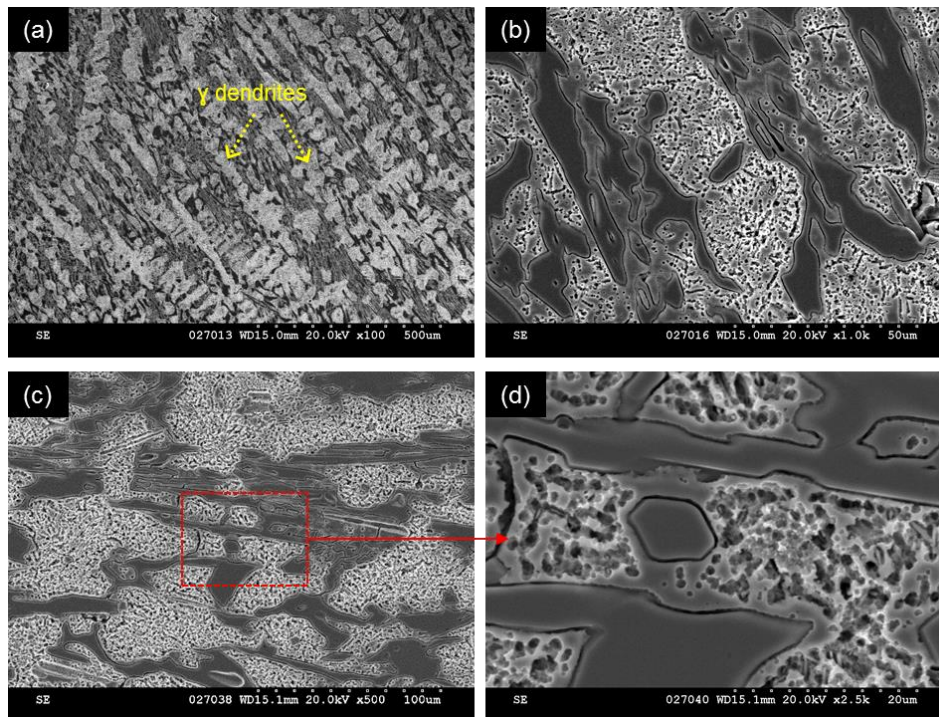


Figure 2: Low C-high Cr white iron microstructure consists of primary austenite dendrite and inter-dendrite eutectic colonies.

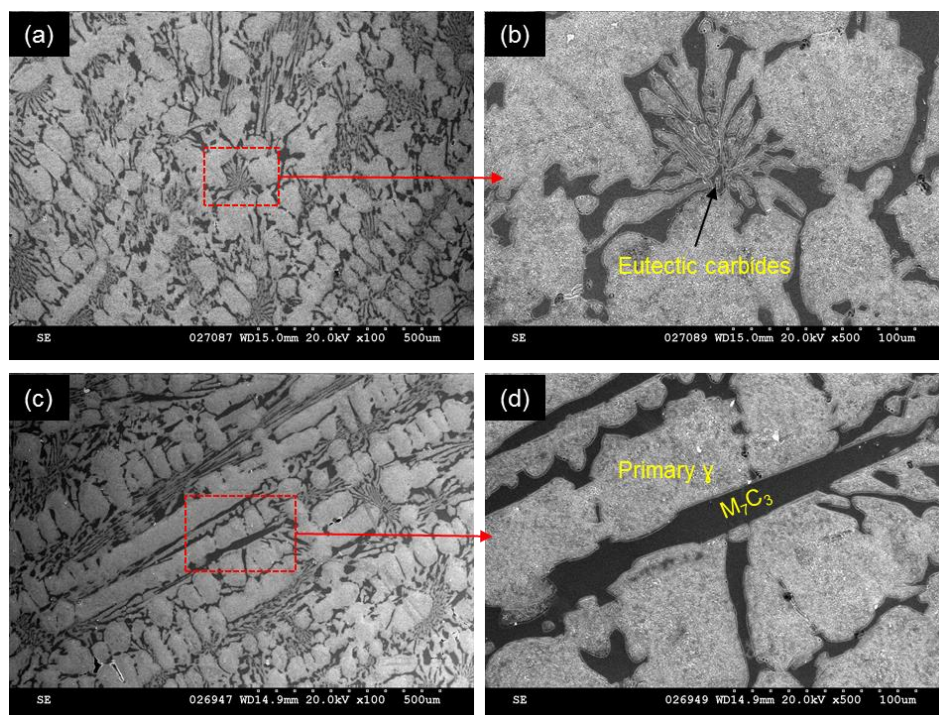


Figure 3: The microstructure of low Cr white iron contains primary austenite dendrites in eutectic colonies of M_7C_3 carbides and austenite.

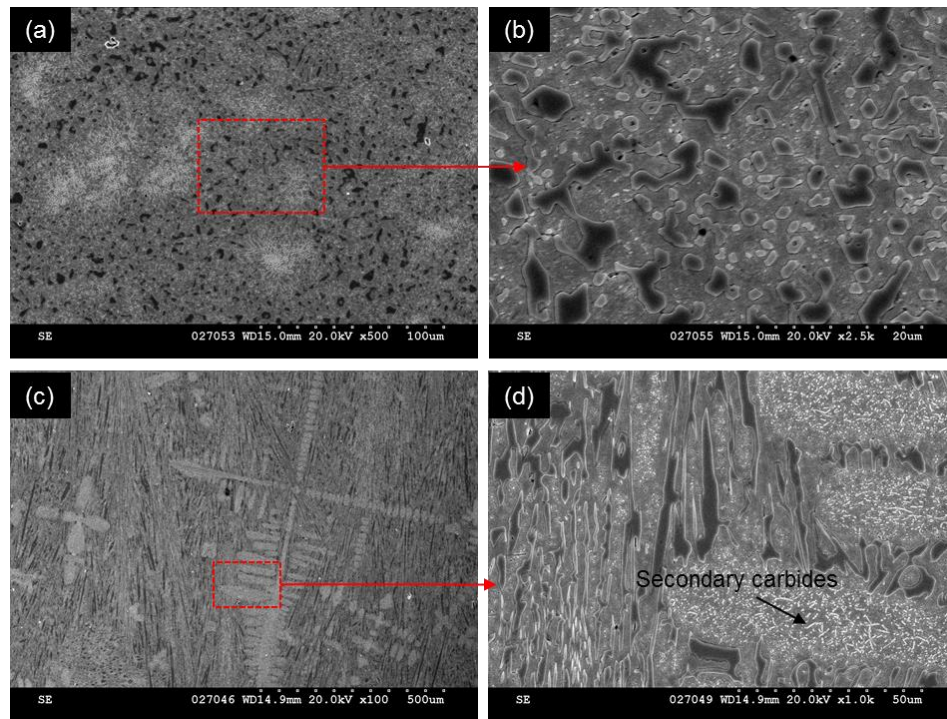


Figure 4: Near eutectic Cr white iron contains mostly eutectic structure with uniformly distributed fine carbides and a small amount of primary austenitic dendrites.

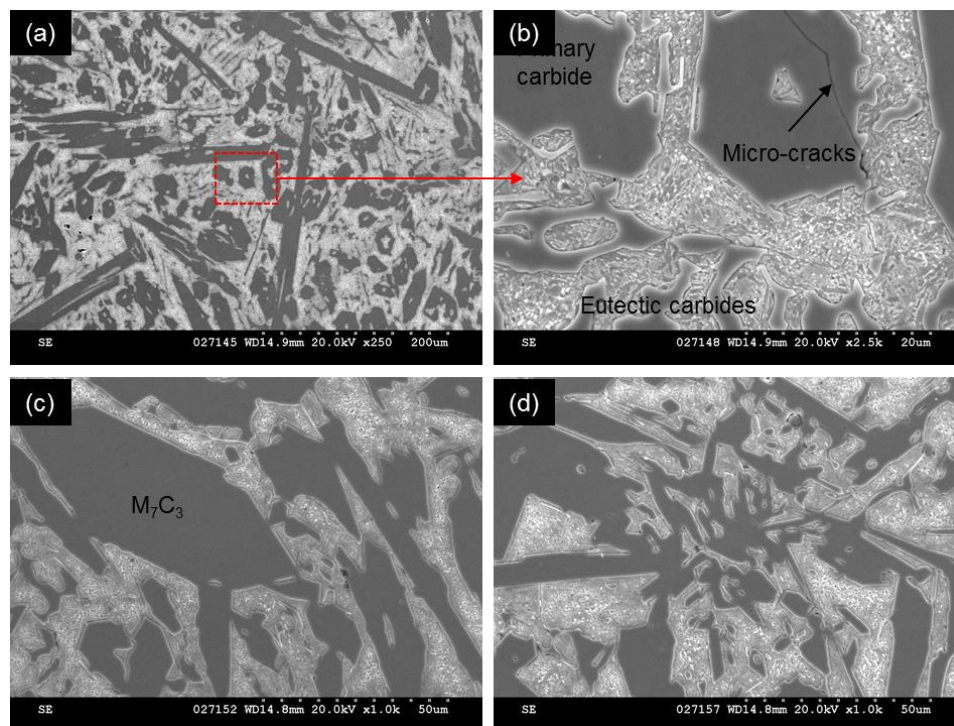


Figure 5: The microstructure of hyper-eutectic Cr white iron consists of primary carbides in eutectic matrix.

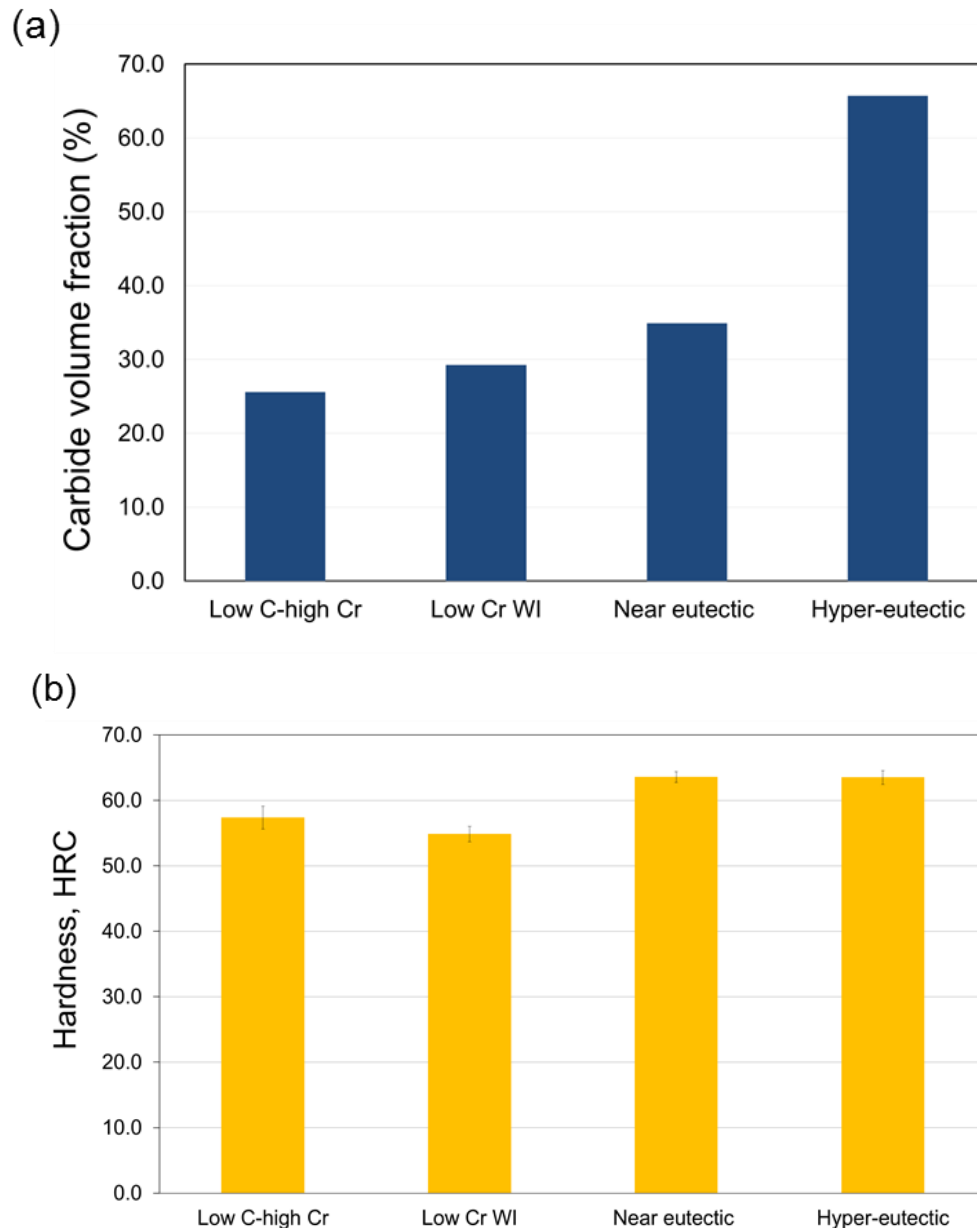


Figure 6: (a) Carbide volume fraction and (b) hardness of chrome white irons.

Figure 6 shows the measured carbide volume fraction and hardness of the evaluated white irons. As expected, the carbide volume fraction increases with increase in carbon concentration. Hyper-eutectic white iron contains the maximum amount of carbon and chromium which results in the maximum carbide volume fraction (66%). Near eutectic white irons contain around 35 vol% of eutectic carbides. Carbide volume fraction of low C-high Cr and low Cr white irons are 26% and 29%, respectively. It is interesting to note that, despite of slightly lower carbide volume fraction, low C-high Cr white iron exhibits higher bulk hardness than low Cr white iron due to its finer microstructure (Figure 2). Both near eutectic and hyper-eutectic white irons exhibit similar bulk hardness.

Alloy content affects the wear performance of high-Cr white iron by influencing not only the overall physical property but also the local mechanical behaviour of the matrix and carbides. Figure 7 shows the micro-hardness measurement performed on the matrix, primary and eutectic carbides. Low C-high Cr and hyper-eutectic white irons has similar matrix hardness. This might be due to similar liquid composition of these white irons before eutectic solidification (as evident from Figure 1). Low Cr white irons has the lowest matrix hardness. Primary carbides has comparatively higher hardness than eutectic carbides. However, these primary carbides are more brittle in nature and susceptible to micro-fracture which is apparent from the crack formation near the indentation (Figure 7 (d)).

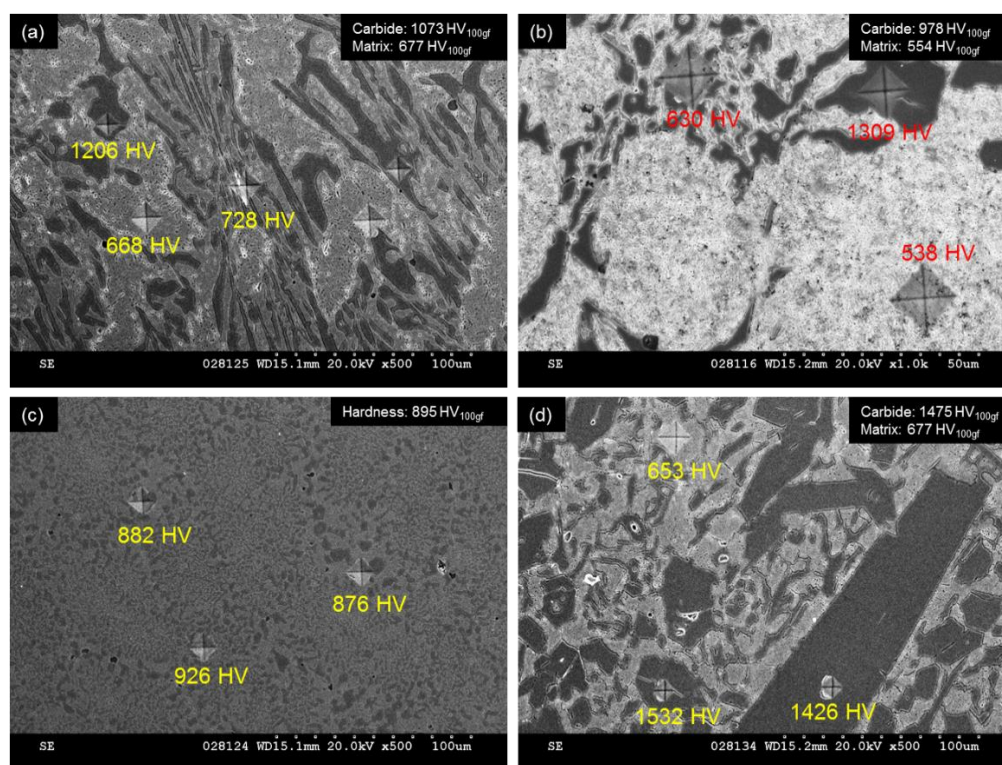


Figure 7: Micro-hardness measurement (using 100 gf load) on (a) low C-high Cr, (b) low Cr, (c) near eutectic and (d) hyper-eutectic white irons.

Slurry pot erosion-corrosion (SPEC) test

Erosion-corrosion test was conducted on a slurry pot erosion-corrosion tester (Figure 8). The unit consists of a 4-litre glass vessel to hold the slurry, a neoprene-lined impeller that is rotated to impel the slurry against the test surfaces, a heating/cooling system (chiller) and a three-electrode cell with a Gamry PC4/750 potentiostat to allow for electrochemical assessment and cathodic protection control⁶². Electrochemical tests were conducted in-situ vs. saturated calomel electrode (SCE) and Pt counter electrode. The specimen dimensions are 18 ± 0.5 mm x 10 ± 0.5 mm x 5 ± 0.5 mm, where 18 mm x 10 mm is the test surface which constitutes a test area of 1.80 cm^2 . All surfaces adjacent to the test surface are ground perpendicular to each other. The testing surface is polished to 1 μm diamond suspension prior to the experiments. All specimens are mounted in epoxy, leaving only the test surface exposed to the testing environment. An electrical contact is attached to the specimen requiring electrochemical assessment/control before embedding in epoxy.