Fabrication Approaches of Abrasion–Corrosion-Resistant High-Chromium White Cast Irons

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There is a huge demand for high-performance materials in extreme environments involving wear and corrosion. High chromium white cast irons (HCWCIs) display better performance than many materials since they are of sufficient hardness for wear protection and can be tailored in chemical compositions to improve corrosion resistance; however, their performance is often still inadequate.

Keywords: wear ; corrosion ; high chromium white cast irons (HCWCIs) ; casting ; heat treatment

1. Introduction

Material loss via wear is encountered in many processes, from earth movement, mining, mineral processing, slurry pumping, and machinery parts exposed to friction. Sometimes, the material under wear is also exposed to low pHs in an aqueous environment, for example, during wet grinding of sulfidic or phosphate ores and heavy pumping of acidic slurry containing hard particles [1][2][3]. It has been observed in studies by Jones [4] and Chelgani et al. [5] that combined wear–corrosion occurs even in neutral water during grinding in the presence of aeration. In such environments, the material media are exposed to harsh conditions because of the synergistic interactions between mechanical wear and corrosion, i.e., wear–corrosion [6][7][8]. Sometimes, abrasive particles accelerate wear–corrosion via repeated impact on the material, demanding materials with adequate impact toughness [9][10]. Thus, material design and selection become a difficult problem when wear and corrosion occur together. The best strategy in developing materials for such applications is to optimize mechanical strength and corrosion resistance [11][12]. Consequently, the material should be of sufficient hardness for wear protection and, at the same time, should contain enough elements like chromium (Cr), nickel (Ni), and molybdenum (Mo) in the matrix for corrosion resistance.

High chromium white cast irons (HCWCIs) display great potential in wear conditions, for example, in wet grinding of ores. HCWCIs are cast irons containing >1.8 wt% C and >11 wt% Cr and may contain other alloying elements, for example, Mo, manganese (Mn), copper (Cu), and Ni. Manganese (Hadfield) steels have a soft, ductile austenitic matrix and are applicable for rock mining because of their surface strain hardening on impact and high bulk impact toughness [13][14][15][16]. However, their drawbacks include low wear resistance compared to Ni-Hard/HCWCIs, low Cr contents to withstand corrosive environments, and they are relatively expensive to fabricate compared to HCWCIs [17]. Stainless steels are attractive because they have both good corrosion resistance and impact toughness; however, they are expensive and exhibit rapid wear in environments where wear dominates corrosion because of either the absence or low volume fraction of hard carbides in their microstructures [18][19]. Ni-hard alloys compete with HCWCIs in pure wear environments; however, they contain low Cr contents, making them inferior in environments where corrosion is aggressive [17][20]. Low alloy steels with pearlitic and martensitic microstructures contain low Cr contents to resist corrosive environments. They are mostly inferior to HCWCIs even in pure wear environments because of the low volume fraction of carbides [21]. Thus, steels and HCWCIs are potential materials for wear–corrosive environments, with steels being superior when corrosion dominates wear, while HCWCIs are superior when wear dominates corrosion [18]. Studies by Chenje et al. [21][22] show that HCWCIs perform better than steels and other materials like Ni hard alloys and forged and pearlitic steels in some environments such that they are replacing these materials.

HCWCIs are cheap, flexible to design due to wide chemical compositions and heat treatment options, and are easier to manufacture than steels, although their main drawback is low impact toughness [17][23]. Potential applications of HCWCIs include wet ore grinding mill liners or mill balls grinding media and slurry pump materials for mineral processing industries. HCWCIs with an optimum volume fraction of carbides for hardness and adequate elements like Cr and Mo in the matrix for corrosion resistance, together with acceptable impact toughness, are suitable for specific wear–corrosion environments. However, the main problem is that improvement in wear resistance in HCWCIs compromises corrosion resistance and vice versa.

The processing of HCWCIs should be controlled to ensure that the desired microstructure with appropriate chemical composition distributions within the phases is obtained. Solidification and heat treatment are mainly used to fabricate HCWCIs and will be considered as the main fabrication routes. The following section discusses the influence of casting and heat treatment variables on chemical composition and microstructure development.

2. Casting

The cooling rate during casting is mainly controlled by the type of mold used, i.e., sand, graphite, and metal. The microstructure, chemical compositions, and defects in HCWCIs are influenced by casting variables like superheat, inoculants additions, and solidification cooling rate [24]. Technologies like degassing and deoxidation are now widely employed to control defects. The effect of casting variables is discussed below to give some guidance on casting process design.

2.1. Cooling Rate

Fast solidification cooling rate refines grains and reduces carbide sizes; the final locations of MC carbides in the matrix also depend on the interface velocity, which is influenced by the cooling rate. The cooling rate should be fast enough to avoid the formation of pearlite; additions of appropriate alloying elements like Mo, Ni, Mn, and Cu are sometimes used to stabilize the austenite phase in large castings [25][26]. In a study on the influence of cooling rate on wear resistance by Liu et al. [27], rapid cooling of 15 K/s refined the microstructure and increased hardness compared to a slow cooling rate of 1.5 K/s. However, the wear rate of as-cast samples with an austenite microstructure was almost similar independent of the hardness because the strengthening of all samples occurred via strain hardening and not grain refinement, although cracking of fine M_7C_3 carbides was experienced in a rapidly cooled alloy, showing that the slowly cooled alloy with coarse carbides was superior. In the heat treated martensitic matrix, the wear rate was less for the rapidly solidified sample, proving that the matrix could properly support small-sized carbides. It was shown in some studies that if carbide sizes are small, they can either break at high stresses or may be easily removed from the matrix [24][28]. The challenge with employing rapid cooling is that it cannot grain refine interiors of large components common in industry because of an inherent slow cooling rate at the center of the piece [24][29][30].

2.2. Superheat (Pouring Temperature)

Some researchers showed that large superheats resulted in coarse grains and carbides, thereby compromising toughness, corrosion, and wear resistance [24][30]. This is because of a large solidification range resulting in slow nucleation and cooling rates and elemental segregations. Thus, solidification will occur at higher temperatures, with slow nucleation accompanied by remelting and fast diffusion resulting in coarsening [31][32]. Therefore, nucleation should occur near the liquidus temperature for grain refinement to form an equiaxed morphology, but the main challenge is the increase in shrinkage porosity [33]. The appropriate superheat is selected based on the fluidity of the melt; thus, Si and manganese (Mn) are mostly added to enhance fluidity.

2.3. Inoculation

HCWCIs with high toughness and strength can be fabricated via a selection of appropriate inoculates with proper quantities. Grain refiners, for example, cerium (Ce) [34][35], strontium (Sr) [36], TiC [37], and ferrotitanium [38], are externally added to the melt as inoculations in HIWCIs and are effective in grain refinement via heterogeneous nucleation. Moreover, elements like B suppress C dissolution and enhance carbide precipitation from the melt to refine the melt. In this regard, they also act as inoculants [39]. Rare earths were also employed and proved to be effective modifiers [40][41].

2.4. External Forces

The application of external forces like mechanical, ultrasonic, electric pulse current, and electromagnetic vibrations in casting or mold during solidification causes a stirring of the melt, fragmentation, and nucleation [42][43], which control grain size and chemical segregation. In addition, external forces present in the selected casting method also affect grain refinement, e.g., centrifugal casting refines morphology better than sand casting. Grain refinement accompanied by mold vibration is attributed to either fragmentation of dendrite arms and high nucleation rate [44] or remelting [45][46] of dendrite necks due to stirring. An experiment on dynamic solidification [47] showed that sizes of the as-cast carbides were refined by solidification in the presence of mold vibration, enhancing the alloy hardness. An increase in vibration frequency enhanced microstructure refinement, alloy hardness, and impact toughness. In another study, the electric current pulse (ECP) method was employed and proved to be effective in breaking large clusters before solidification and dendrites during solidification to nucleate and refine the microstructure [48][49]. However, the challenge of the ECP method is the difficulty in applying it to large castings.

3. Heat Treatment

After the casting process, the HCWCIs can be used in the as-cast condition or are heat treated to modify the matrix microstructure depending on the intended application. Usually, the as-cast microstructure has a high content of Cr in the austenite matrix and is good for corrosion resistance but inferior in wear applications [50][51]. A destabilizing heat treatment is employed to destabilize the high alloy content austenite matrix at a temperature range of about 920–1060 °C for 1–6 h and transform it to martensite during cooling [31][51][52]. Transformation to martensite occurs because of secondary precipitation of carbides leaving an austenite matrix deficient in C and Cr, thereby increasing the martensite start (Ms) temperature; such that upon cooling, the matrix will transform to martensite with some retained austenite (about 35%). Soaking above 1100 °C mainly precipitates M_7C_3 carbides, while at below 1100 °C, a mixture of M_7C_3 and $M_{23}C_6$ is obtained [31][53][54]. Destabilization temperatures are mostly reached by first holding at intermediate temperatures to avoid cracking, especially when handling thick sections [31][53][54]. Pourasiabi and Gates [55] found that the presence of different sizes of carbides, i.e., primary and secondary, after heat treatment is beneficial in milling of different sizes of abrasives, i.e., coarse or fine ores. The martensite produced by destabilization is deficient in Cr and not suitable in wear–corrosion environments. The impact toughness of the quenched sample is finally improved by the tempering process; it is held at a low temperature, for example, at 200 °C for 2 h, to relieve stresses induced during transformation. Sometimes, the matrix with high martensite and low austenite content saturated with Cr can be developed for wear and corrosion applications.

3.1. Effect of Destabilization Temperature, Time, and Quenching Rate

Low destabilization temperatures cause extensive precipitation of secondary carbides consuming C and Cr from the austenite matrix, forming soft martensite, while very high temperatures will retain high C and Cr contents in the matrix to form hard martensite saturated in Cr with a high volume of retained austenite impairing hardness. In their work, Girelli et al. [56] investigated the influence of heat treatment on the corrosion performance of a 27%wt Cr HCWCI. It was shown that heat treating at a temperature of 1160 °C for 1 h significantly improved corrosion resistance by retaining high Cr content in the matrix because of high dissolution rates of carbides. Moreover, some investigators [54][57] reported that increasing austenitizing temperature decreased the hardness and wear resistance of HCWCIs. An optimum destabilization temperature for required hardness (martensite content) and Cr content should be a temperature that is not too high to avoid much C and Cr dissolution in the matrix and not too low to avoid depleting all C and Cr from the matrix. Cryogenic treatment can be used after destabilization by cooling below the Ms temperature to reduce retained austenite levels to <5 wt%. Cryogenic treatments may also be used in as-cast austenitic structures by cooling them below Ms to eliminate destabilization, thereby avoiding stresses to enhance toughness [31][53]. In this way, high saturated C and Cr content can be maintained in the martensite for enhanced wear and corrosion resistance. Such innovative heat treatments show potential in the development of HCWCIs for wear–corrosion environments.

The effect of holding time on the hardness of HCWCIs shows that with an increase in holding time, the hardness increases up to an optimum before decreasing due to precipitation and coarsening of secondary carbides [31][32]. Prolonged holding times coarsen carbides via Ostwald ripening and reduce wear resistance [31][58]. Moderate cooling during quenching of destabilized austenite causes additional precipitation of secondary carbides, which is advantageous, while very slow cooling rates result in the formation of pearlite matrix with low hardness and corrosion resistance [59]. Very fast cooling is desirable but may cause cracking and residual stresses. The De-MQ-Sct process was proposed by Jia et al. [59] as an innovative destabilizing fast-cooling heat treatment that uses multi-cycle alternate water quenching and air cooling to reduce pearlite formation and enhance martensite content to obtain alloys with high hardness and toughness.

3.2. Effect of Alloying Elements

The influence of alloying elements on the heat treatment of HCWCIs was studied [60][61][62] using a hypoeutectic HCWCI, and the relationship between the number of alloying elements (Ni, V, Mo Cu) and hardness of retained austenite was established. Alloying elements, for example, Si, promote the decomposition of austenite by reducing C solubility in the austenite matrix, thereby raising the Ms temperature [31]. Elements that enhance C solubility retain more Cr in the matrix for corrosion protection, while those reducing C precipitation eliminate Cr from the matrix. Thus, alloying elements should be optimized to develop wear–corrosion-resistant HCWCIs. For example, at high C content, Cr in the matrix will be deficient, so alloying elements like Mo, Ni, and Cu should be added to prevent pearlite formation in favor of the austenite matrix [31].

3.3. Heat Treatment Design

The heat treatment of HCWCIs is difficult to optimize using trial and error approaches because of the multiple variables involved, including temperature, time, and cooling rates. Optimum values of parameters like destabilization temperature and holding times should depend upon the selected composition and must be properly determined. Many researchers used the same destabilization temperatures and holding times for alloys with different compositions, and such an approach does not lead to the fast development of HCWCI alloys. A few studies used computational modeling to optimize heat treatment parameters. Albertin et al. [11] used computational thermodynamics calculations to design the heat treatment parameters of wear-resistant HCWCI rings for the blast furnace feeding system. Other computational modeling approaches, including machine learning, demonstrate potential in designing HCWCIs since they can handle large volumes of data from composition selection, casting variables, and heat treatment to predict appropriate compositions, microstructures, and fabrication conditions [63][64].

Regarding computational thermodynamics, it has been proven to be a reliable tool for predicting the microstructure of HCWCIs [65][66]. It allows, for example, to evaluate the effect of the solutes on the formation of primary carbides during solidification [67]. Wang et al. [68] used computational thermodynamics to understand the mechanism for the formation of core–shell carbides in HCWCIs, while Pranav Nayak et al. [69] were able to successfully predict the eutectic carbide phase fraction in two HCWCIs.

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