Improving the Wear Resistance of High Chromium Cast Iron through High Entropy Alloys Concepts and Microstructure Refinement

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High Chromium Cast Iron (HCCI) has demonstrated its effectiveness as a potential material for applications in severe environments due to its remarkable wear resistance attributed to the volumetric fraction of carbides in the microstructure. This study investigates a novel high-alloyed composition of white cast iron named High Entropy White Cast Iron (HEWCI), which merges the concepts of HCCI and high entropy alloys. Specifically designed chemical compositions incorporating Vanadium (V), Molybdenum (Mo), and Nickel (Ni) were employed to enhance its wear resistance properties. The solidification path, microstructural characterization, and wear responses of HEWCI were evaluated. XRD and SEM techniques were carried out for characterization purposes. Linearly reciprocating ball-on-flat sliding wear tests were conducted using a high-frequency reciprocation rig (HFRR) tribometer, assessing wear volume, linear wear rate, specific wear rate (κ), and coefficient of friction (COF). The results revealed microstructural refinement and precipitation of new carbides through V, Ni, and Mo additions. This approach demonstrates that adding carbide-forming elements and refining the microstructure are promising strategies for enhancing wear performance in HEWCI alloys.

Keywords: high entropy alloys, high chromium cast irons, solidification, microstructures, wear resistance.

1. Introduction

White cast irons (WCIs) have been extensively utilized in many industries requiring wear resistance. WCIs for wear resistance proposes are typically classified into four groups: pearlitic, Ni-Hard (with $M_C$ eutectic carbides or $M_C$, eutectic carbides), High-Chromium Cast Iron (HCCI), and Multi-Component Cast Iron (MCCI).

Among these, Ni-Hard and HCCI are the most commonly utilized commercial alloys in industrial applications that require wear resistance. Ni-Hard refers to a group of white cast irons alloyed with Ni and Cr, with exceptional hardness and remarkable abrasion resistance. In scenarios where toughness, abrasion resistance, and, in some cases, corrosion resistance are considered, the HCCI stands unrivaled. Within the Ni-Hard family, Ni-Hard 4 exhibits the highest Ni, Cr, and Si levels. On the other hand, the HCCI family can have Cr content that is 2 to 3 times higher than that of Ni-Hard 4. Despite these differing chemical compositions, both alloys exhibit similar microstructures characterized by $M_C$, eutectic carbides.

MCCI contains Cr and other alloying elements that tend to form new carbides, such as Ti, V, Nb, Mo, and W. The carbon content of MCCI ranges between the carbon values of High-Speed Tool Steel, Ni-Hard, and HCCI. During solidification, carbides such as MC and $M_C$ precipitate in the microstructure of these alloys. MCCI demonstrates superior resistance to abrasive wear after heat treatment, compared to HCCI, even with a lower volume fraction of carbides.

The “base element approach” has been used in metallurgical history to develop metallic alloys. This method uses one primary element as the matrix and additional elements to improve properties. Recently, there has been a growing interest in developing a novel alloy design approach inspired by new systems that combine five or more elements. This approach created “High Entropy Alloys” (HEAs). This concept has greatly expanded alloy design and allowed the exploration of new alloy systems. HEAs were initially defined as alloys with at least five primary alloying elements in amounts ranging from 5 to 35 atomic percent, and these alloys have single-phase solid solution structures and configurational entropy ($\Delta S_{conf}$) greater than 12.5 kJ/mol (1.5R, where R is the gas constant).

However, as initially proposed, the strict definition of HEAs limited studies to alloys containing five or more principal elements and only single-phase solid-solutions microstructures.
Recognizing the complexities associated with attempting to fully define HEAs based on a single definition and microstructure new terminologies were introduced to overcome these limitations. These new terminologies include Complex Concentrated alloys (CCAs) and entropy-enhanced Conventional Alloys (EECAs) to encompass a broader range of alloy chemical compositions and microstructures.

Building upon the concepts of WCIs and HEAs, Wang et al.\textsuperscript{12,13} modified the chemical compositions of high-Cr cast irons by adding mixtures of various carbide-forming elements. They noticed that these tailored HCCIs showed high sliding wear resistance. The type, shape, phase fraction, and distribution of hard carbides in the microstructure, as well as the properties of the supporting matrix, significantly impact wear performance. It is well recognized that incorporating carbide-forming elements such as Mo, W, V, and Nb into the alloy can enhance wear resistance. Developing new abrasion-resistant cast iron based on a multi-component approach is a well-known research topic, with many studies supporting this hypothesis. Different high-alloyed cast iron compositions have been studied by diverse researchers such as Matsubara et al.\textsuperscript{14}, Kusumoto et al.\textsuperscript{6}, Purba et al.\textsuperscript{15}, Pasini et al.\textsuperscript{16} and Bedolla-Jacuinde et al.\textsuperscript{17}. The influence of Ni on the multi-component cast iron has also been studied by Kusumoto et al.\textsuperscript{7}.

This study explores High Entropy White Cast Iron (HEWCI), establishing a bridge between the metallurgy of white cast iron and high entropy alloy concepts. In this work, three different chemical compositions were proposed and selected to investigate solidification, mechanical properties, and sliding wear behavior.

2. Materials and Methods

2.1. Alloys Design

Modifications were made to a hypoeutectic High-Chromium Cast Iron (HCCI) alloy, considered the base alloy, to design the High Entropy White Cast Iron (HEWCI) alloys. The selected alloying elements for this purpose were V, Mo, and Ni, commonly employed in the metallurgy of steel and cast iron and have well-known effects on microstructures. Nickel was chosen because it aids in forming eutectic M\textsubscript{13}C\textsubscript{6} carbides with Cr and is required to produce a pearlite-free matrix structure. On the other hand, the V and Mo additions are due to a strong tendency to form hard carbides, elements widely used in the metallurgy of tool steels and high-speed steels. Adding high amounts of these elements to HEWCI alloys aims to improve the hardening ability.

During the design process, the following definitions of high entropy alloys were considered as design boundaries: (i) alloy containing at least five major elements; (ii) at least five percent concentration of each element; and (iii) having configurational entropy of mixing, $\Delta S_{\text{mix}} \geq 1.5$ R in the random-solution state. The chemical compositions of the HEWCI alloys were determined using optical emission spectrometry (MiniLab 300, GNR Analytical Instruments), and the obtained chemical compositions can be found in Table 1. As observed, the design criteria considered for high entropy alloys were achieved.

2.2. Alloys preparation and thermal analysis

To produce the HEWCI alloys, pure Ni and C, Fe-Si, Fe-Mn, Fe-V, and Fe-Mo master alloys were added to the hypoeutectic High Chromium Cast Iron (HCCI) base alloy. The HEWCI alloys were melted in a 4 kg coreless induction furnace. The metal was heated at 1400°C, and after removing any slag, the resulting molten alloys were poured into a cylindrical permanent copper mold to obtain samples for mechanical tests and a thermal-analysis samples cup. Approximately 700 g of each molten alloy was poured into two shell-molding sand cups instrumented with type-K thermocouples to analyze the solidification sequence of each new cast iron under near-equilibrium conditions. Computer-Aided Cooling Curve Analysis (CCA-CA) was performed during the solidification to reveal all the solid-liquid reactions and to determine the solidification path of the HEWCI alloys.

2.3. Microstructure characterization

For microstructure analysis, the HEWCIs were cut from the shell-molding sand thermal analysis cups near the type-K thermocouple and prepared by grinding with SiC papers ranging from 240 to 1200 grit, followed by fine polishing with alumina suspension. Scanning electron microscopy (SEM), utilizing backscattered electron (BSE) and secondary electron (SE) imaging modes associated with energy-dispersive X-ray spectroscopy (EDS), was used to characterize the matrix and carbides. X-ray diffraction (XRD, CuK\textalpha{}1 radiation, 40 kV, 30 mA, 20:20–100) analyses using powders obtained from each alloy were performed to identify the type and chemical composition of the phases.

2.4. Mechanical properties

The ultimate tensile strength (UTS) responses of the HCCI, HEWCI-A, HEWCI-B, and HEWCI-C alloys were investigated through room-temperature monotonic tensile testing.

<table>
<thead>
<tr>
<th>Table 1. Chemical compositions of the hypoeutectic cast irons (at. %).</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Cr</th>
<th>Mo</th>
<th>V</th>
<th>Ni</th>
<th>$\Delta S_{\text{mix}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCCI</td>
<td>2.47</td>
<td>1.67</td>
<td>1.37</td>
<td>18.90</td>
<td>0.02</td>
<td>0.11</td>
<td>0.12</td>
<td>0.96 R</td>
</tr>
<tr>
<td>HEWCI-A</td>
<td>2.31</td>
<td>1.51</td>
<td>1.27</td>
<td>18.49</td>
<td>6.32</td>
<td>4.05</td>
<td>10.38</td>
<td>1.50 R</td>
</tr>
<tr>
<td>HEWCI-B</td>
<td>2.33</td>
<td>1.71</td>
<td>1.41</td>
<td>18.62</td>
<td>12.78</td>
<td>3.56</td>
<td>4.76</td>
<td>1.50 R</td>
</tr>
<tr>
<td>HEWCI-C</td>
<td>2.39</td>
<td>2.67</td>
<td>1.41</td>
<td>18.47</td>
<td>11.60</td>
<td>5.96</td>
<td>9.62</td>
<td>1.65 R</td>
</tr>
</tbody>
</table>
3. Results and Discussion

3.1. Solidification and thermal analysis

Considering that the HEWCI alloys consist of multiple components with significant carbide-forming abilities and the need for well-established phase diagrams for such multi-component systems in the literature, accurately estimating all stages of solidification solely based on the as-cast structure is challenging. In order to gain further insights into the solidification path of the HCCI, HEWCI-A, HEWCI-B, and HEWCI-C alloys, X-ray diffraction (XRD), backscattered electron (BSE) images and Newtonian thermal analyses were conducted. Figure 2 illustrates the results of phase identification for the as-cast alloys obtained from XRD spectra (Figure 2a) and BSE images (Figure 2b). The XRD analyses revealed the presence of austenite (γ), M\(_2\)C carbides (Mo\(_2\)C and V\(_2\)C), M\(_7\)C\(_3\) carbide, and M\(_6\)C carbide in the alloys.

The Newtonian analysis method, utilizing the first derivative of the cooling curve, was employed to determine the temperatures at which phase transitions occurred during the cooling of the alloys. Additionally, the first derivative of the cooling curve was compared to the Zero Curve, which represents the cooling rate of the alloy without any phase transformations, to gain further insights. This methodology allows the identification of peaks and inflections in the cooling rate curves corresponding to phase transformations, which are influenced by the heat transfer between the latent heat released during solidification and the heat dissipated to the environment.\(^{20}\)

The cooling curve of the HCCI alloy, as shown in Figure 3a, exhibits three distinct reaction or arrest points labeled as R1, R3, and T\(_\text{sol}\) occurring at temperatures of \(1324°C\), \(1247°C\), and \(1233°C\), respectively. The identification of the solidification reactions at each arrest point was conducted by examining the final microstructure of the alloy and comparing it to the findings of previous studies on the Fe-Cr-C system carried out by Thorpe and Chicco.\(^{21}\) The first arrest point (R1) on the
Figure 2. (a) Identification of austenite, $\text{M}_2\text{C}$, $\text{M}_7\text{C}_3$, and $\text{M}_6\text{C}$ phases by XRD diffraction analyses, and (b) BSE images of the as-cast microstructures of HEWCI-B and HCCI alloys.

Figure 3. The cooling curves, zero curve, 1st and 2nd derivative: a) HCCI, b) HEWCI-A, c) HEWCI-B, d) HEWCI-C.
cooling curve (Figure 3a) corresponds to the formation of primary γ-austenite. The second arrest point (R3) represents the transformation of liquid to the eutectic mixture of γ and M₇C₃ carbides. The Tsol point indicates the minimum value of the second derivative of the cooling curve, corresponding to the end of solidification or the cross-point between the first derivative and the Zero Curve.

The XRD diffractograms of the HEWCI-A, HEWCI-B, and HEWCI-C alloys exhibited similar patterns, indicating the presence of almost identical indexed carbide phases. The solidification sequence of these alloys involved the formation of primary γ-austenite (R1), M₇C₃ (Cr-rich) carbide (R2), M₇C₃ (Cr-rich) carbide (R3), and M₇C₃ (Mo-rich) carbide (R4). The cooling curves for HEWCI alloys are presented in Figures 3b-d. In the case of HEWCI-B and HEWCI-C, the curves showed an additional peak on the first derivative curve, labeled as R5 in Figure 3c and Figure 3d. Based on this observation and the identification of M₆C carbide through XRD analyses in the HEWCI-B and HEWCI-C alloys, it can be inferred that M₆C is formed as the final phase transformation during solidification. The temperatures of the arrest reactions are summarized in Table 2.

3.2. Microstructure characterization

Microstructure observations obtained by SEM in BSE mode indicate the presence of five constituent phases, which have been indexed by XRD and are shown in Figure 4. These phases include (a) M₇C₃ carbides (light gray), (b) M₇C₃ carbides (dark gray), (c) M₇C₃ carbides (white), and (d) M₇C₃ carbides (fuzzy gray). The M₇C₃ (V-rich) carbides are primarily within the Solidification Cell (SC). In contrast, the M₇C₃ (Cr-rich), M₇C₃ (Mo-rich), and M₇C₃ (Mo, Fe-rich) carbides are distributed along the Cell Boundaries (CB) following the solidification direction.

In Figure 5, a micrograph of HEWCI reveals the presence of different carbides, indicated by the letters “a” through “d”, where EDS analyses were conducted. The areas marked by the letter (a) exhibits the highest concentration of V, indicating the presence of an M₇C₃ (high-V) carbide. The dark-gray region marked by the letter (b) corresponds to an M₇C₃ carbide, primarily composed of Cr. The white-colored region marked by the letter (c) shows a higher Mo content compared to other carbide-forming elements, identifying it as an M₆C carbide with a lamellar morphology. The areas marked by the letter (d) are identified as an M₆C carbide, consisting predominantly of Fe and Mo elements.

The HEWCI alloy has multiple elements that exhibit a pronounced tendency to form carbides. Figure 6 illustrates the distribution of chemical elements, revealing the partial solubility of carbide-forming elements within one or more carbides across different alloy regions. Mo demonstrates partial solubility in V-rich carbides, forming M₇C (Mo-rich) carbides at the boundaries of the M₇C (V-rich) phase. The remaining liquid phase precipitates as M₇C carbides with relatively lower V content. As mentioned, the carbides observed in the HEWCI alloys are multi-component and enriched with V, Cr, and Mo, as these elements exhibit a stronger affinity for carbon than iron.

Table 2. Estimated solidification sequence for the HCCI and HEWCI alloys.

<table>
<thead>
<tr>
<th>Solidification sequence</th>
<th>Alloy</th>
<th>R1</th>
<th>R2</th>
<th>R3</th>
<th>R4</th>
<th>R5</th>
<th>Tsol</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1: Lₐ→γ+Lₜ</td>
<td>HCCI</td>
<td>1324</td>
<td>-</td>
<td>1246</td>
<td>-</td>
<td>-</td>
<td>1231</td>
</tr>
<tr>
<td>R2: γ+ M₇C₃(V-rich)+Lₜ</td>
<td>HEWCI-A</td>
<td>1319</td>
<td>1259</td>
<td>1246</td>
<td>1202</td>
<td>-</td>
<td>1195</td>
</tr>
<tr>
<td>R3: γ+ M₇C₃+Lₜ</td>
<td>HEWCI-B</td>
<td>1305</td>
<td>1225</td>
<td>1210</td>
<td>1198</td>
<td>1182</td>
<td>1164</td>
</tr>
<tr>
<td>R4: γ+ M₇C₃(Mo-rich)+Lₜ</td>
<td>HEWCI-C</td>
<td>1303</td>
<td>1234</td>
<td>1229</td>
<td>1223</td>
<td>1161</td>
<td>1140</td>
</tr>
</tbody>
</table>

Lₐ, Lₜ are solute-rich liquid phases.
3.3. Mechanical properties and sliding wear behavior

The ultimate tensile strength and strain-to-fracture results of the HEWCI alloys are presented in Table 3. The alloying element additions resulted in an improvement in both tensile strength and strain values. This can be attributed to the microstructural refinement achieved in the HEWCI alloys, the formation of new second-phase precipitates, and the solid solution strengthening. The microstructural refinement can be observed in Figure 7, where a comparison is made between HCCI and HEWCI alloys. These findings agree with previous studies by Hashimoto et al.,22-25 supporting the notion that the influences of elements V, Mo, and Ni significantly enhance the mechanical properties of HEWCI alloys.

The ASTM G133 standard describes a method for evaluating material wear through a linearly reciprocating ball-on-flat sliding wear test. The results are summarized in Table 3. The wear tracks were characterized using three-dimensional optical profilometry (Bruker 3D Optical Profilometer - GTK M, CONTOUR GTK). A three-dimensional surface profile was generated for each track, allowing for the measurement of the wear volume and the acquisition of the central profile, track depth, and width, as illustrated in Figure 8.

Figure 8a presents the wear volume (V) and specific wear rate (κ) of the alloys, while Figure 8b compares the cross-section profiles of the wear tracks between the HEWCI and HCCI alloys after the tests. It is observed in Table 3 and Figure 8 that the high-entropy alloys with added V, Mo, and Ni exhibited improved wear resistance. The specific wear rate decreases for all HEWCI alloys as the content of alloying elements increases. The HEWCI-A alloy has a specific wear rate that is 48% lower than that of the base HCCI alloy, while the HEWCI-B alloy has a wear rate that is 37% lower than HCCI. In terms of wear resistance, the HEWCI-C alloy exhibits similar behavior to the HEWCI-A alloy. The coefficients of friction were measured during the sliding wear tests. Initially, the coefficient of friction increased rapidly, and after a 10m sliding distance, it reached a steady-state regime. According to Table 3, the COFs of the HEWCI alloys in the investigated conditions ranged from 0.27 to 0.33. No evident differences in the COFs among the alloys were observed.
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Table 3. Tensile strength (σ_{UTS}), strain-to-fracture, coefficient of friction (COF), wear volume (V), and specific wear rate (κ) of HCCI and HEWCI alloys.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>σ_{UTS} (MPa)</th>
<th>Strain-to-Fracture (%)</th>
<th>COF</th>
<th>V (mm³)</th>
<th>κ (mm³/Nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCCI</td>
<td>571</td>
<td>0.21</td>
<td>0.302</td>
<td>0.0026</td>
<td>1.87 E-8</td>
</tr>
<tr>
<td>HEWCI A</td>
<td>657</td>
<td>0.62</td>
<td>0.276</td>
<td>0.0013</td>
<td>0.98 E-8</td>
</tr>
<tr>
<td>HEWCI B</td>
<td>854</td>
<td>0.88</td>
<td>0.324</td>
<td>0.0015</td>
<td>1.16 E-8</td>
</tr>
<tr>
<td>HEWCI C</td>
<td>795</td>
<td>0.70</td>
<td>0.293</td>
<td>0.0014</td>
<td>0.95 E-8</td>
</tr>
</tbody>
</table>

Figure 7. Comparison of microstructural refinement between HEWCI alloys and HCCI alloys.

Figure 8. (a) Wear volume and specific wear rate of the HEWCI alloys, (b) Cross-section profiles of the wear track, and (c) Three-dimensional profilometry image used for the calculation of wear volume.
4. Conclusion

New abrasion-resistant white cast iron alloys were developed, combining the concepts of high entropy alloys with the conventional metallurgy of high chromium cast iron (HCCI). Three modified alloys were successfully produced, containing more than five alloying elements and exhibiting a configuration entropy greater than 1.5R. The base hypoeutectic (HCCI) alloy was enhanced by adding carbide-forming elements such as V, Mo, and the non-carbide-forming element Ni. The incorporation of these carbide-forming elements resulted in the refinement of $\text{M}_\text{C}$ eutectic carbides and the formation of new, finer carbides, including $\text{M}_\text{C}$, $\text{M}_\text{C}$, and $\text{M}_\text{C}$. The high-entropy wear-resistant cast irons (HEWCI) exhibited improved resistance to wear and mechanical properties, which can be attributed to its refined microstructure and the presence of various types of fine carbides, including $\text{M}_\text{C}$ (V-rich), $\text{M}_\text{C}$ (Mo-rich), $\text{M}_\text{C}$, and $\text{M}_\text{C}$. The addition of alloying elements led to an average increase in tensile strength of 34.5%. Notably, the average strain to fracture in HEWCI showed a significant improvement, increasing by approximately 3.5 times compared to HCCI. Regarding the specific wear rate, HEWCI demonstrated an average response of approximately 40% better than the base alloy.

5. Acknowledgments

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6. References