The Erosion–Corrosion Behavior of Eutectic High Chromium Cast Irons Reinforced by TiC Particles

Tian-Quan Tu 1,2,3, Shen-Lin Liu 1, Kai-Hong Zheng 2,3, Boris B. Khina 4, Artur I. Pokrovsky 4 and Zhi-Chao Luo 2,3,*

1 School of Materials Science and Engineering, Chang'an University, Xi'An 710054, China; tutianquan@163.com (T.-Q.T.); liushenglinw@163.com (S.-L.L.)
2 Institute of New Materials, Guangdong Academy of Science, Guangzhou 510070, China; zhangkaihong@gdinm.com
3 Guangdong Provincial Key Laboratory of Metal Toughening Technology and Application, Guangdong Institute of Materials and Processing, Guangzhou 510650, China
4 Physico-Technical Institute, National Academy of Sciences of Belarus, 220141 Minsk, Belarus; khina@tut.by (B.B.K); arturu@tut.by (A.I.P.)
* Correspondence: luozhichao@gdinm.com

Abstract: In this work, high chromium cast irons (HCCIs) reinforced by TiC particles are designed and fabricated to improve the erosion–corrosion and wear resistances of materials for the pumping and handling applications. The TiC particles are formed by the in situ solidification method. The experimental results show that the hardness of as-cast HCCIs is improved significantly with TiC volume fraction. It can be as high as 63 HRC when the TiC volume fraction is 9.8%. The introduction of TiC increases the abrasive wear resistance of the HCCIs in both as-cast and heat-treated states. However, it is unexpected to find that the presence of TiC significantly reduces the erosion–corrosion performance. It suggests that corrosion-enhanced erosion is the dominant mechanism that controls the mass loss of the TiC-strengthened HCCIs.

Keywords: erosion–corrosion; high chromium cast iron; TiC; composite; corrosion resistance

1. Introduction

Evaluating the influence of phase composition and microstructure on the behavior of materials in various environmental conditions is of primary importance for determining new routes for the development of advanced durable materials and coatings [1–3]. Among modern wear resistant materials, a lot of attention is currently given to high chromium cast irons (HCCIs) because of their relatively low cost and good performance [4–9]. They are widely used in mining, milling, and oil sand industries because of their excellent combination of wear and corrosion resistance [5,6,10–12]. For instance, HCCIs are extensively employed in the oil and sand pumping, handling, and processing operations. The good wear resistance of HCCI is due to a high-volume fraction of $M_7C_3$ carbide, whose hardness can be as high as 1600 HV. In addition, HCCI contains a high concentration of chromium (12–30 wt.%), which imparts both strong passivation capability and high corrosion resistance [8,13–17].

Numerous studies are devoted to improving the performance of HCCIs in different service conditions and environments [4,7–9,18]. By increasing the volume fraction of $M_7C_3$, the wear resistance can be improved. However, for the HCCIs with a hypereutectic composition, primary carbides will be formed. The large primary $M_7C_3$ particles can reduce the wear resistance due to the low fracture toughness. To date, many investigations have been conducted on refining the primary $M_7C_3$ particles in the hypereutectic HCCIs [7,19–22]. Different to the hypereutectic HCCIs, the fraction of carbides in hypoeutectic HCCIs is lower [23]. Accordingly, the eutectic HCCIs (eHCCIs) feature a good balance of hardness...
and toughness. However, the composition range of eutectic solidification is narrow for a given chromium content.

The erosion–corrosion (E–C) resistance of HCCIs is controlled by many factors such as the volume fraction of carbides and the Cr content of the matrix [8,15,17,24–28]. It has been reported that the hypoeutectic HCCIs with Cr content of 23–30 wt.% have excellent corrosion resistance, but they do not perform satisfactorily in the combined harsh erosive and corrosive environments due to the lack of sufficient carbides [13]. On the other hand, increasing the carbide fraction will consume the chromium in the matrix and hence reduce the corrosion resistance of HCCIs. M. Jone and R.J. Llewellyn examined the erosion–corrosion behavior of various materials in the resources industry [25]. They found that the near-eutectic HCCIs (28 wt.% Cr) exhibited the highest E–C resistance among all the tested materials due to the synergistic effect of high carbide fraction and high Cr content in the matrix [25]. In addition, it has also been reported that the introduction of TiC or NbC particles can significantly improve the E–C resistance of the stainless steel [29–32]. Thus, improving the E–C resistance of HCCIs without sacrificing mechanical properties seems to be an urgent problem, which is to be solved.

In connection with the above, the objective of this work is to develop a new strategy for the alloying design of hypereutectic HCCIs. To attain the goal, titanium and carbon in the mole ratio of 1:1 is introduced into molten near-eutectic HCCIs in order to obtain a high volume fraction of hard titanium carbide inclusions but avoiding the reduction of chromium content in the matrix. New eutectic HCCIs reinforced by various volume fractions of TiC are designed and fabricated by an in situ solidification method. The effect of the TiC content and heat treatments on the wear and corrosion properties of the developed HCCIs are investigated in order to evaluate a basic mechanism of the mass loss.

2. Materials and Methods

Four HCCIs reinforced with different volume fractions of TiC were prepared by the in situ solidification method in a vacuum melting furnace (ZG0.05, Boda, Shenyang, China). In the melting process, the raw materials include pure iron, titanium sponge and high-purity master alloys. Before machining, the composites were destabilized at 1323 K for 4 h. Then the samples were cooled to room temperature in air. The tempering treatment of the HCCIs was conducted at 773 K for 2 h. Table 1 displays the chemical compositions of the samples. For convenience, the as-cast and heat-treated samples are denoted hereinafter as A0–A3 and H0–H3, respectively. It is noted that the counterpart HCCI (A0) has a near-eutectic composition containing 26 wt.% Cr and 3.2 wt.% C. Basing on this composition, certain amounts of Ti and C with a mole ratio of 1:1, or mass ratio of 4:1 (see Table 1) were added to the molten HCCIs to provide in situ formation of reinforcing titanium carbide particles.

| Elemental Content Percentage (in wt.%) | As-Cast | Heat Treatment |
|----------------------------------------|---------|----------------|
| Fe-26Cr-0.8Si-1Ni-0.4Mn-3.2C           | A0      | H0             |
| Fe-26Cr-0.8Si-1Ni-0.4Mn-3.2C-(0.4C-1.6Ti)| A1      | H1             |
| Fe-26Cr-0.8Si-1Ni-0.4Mn-3.2C-(0.8C-3.2Ti)| A2      | H2             |
| Fe-26Cr-0.8Si-1Ni-0.4Mn-3.2C-(1.2C-4.8Ti)| A3      | H3             |

Before the microstructure examination, the samples were polished mechanically to obtain a mirror-like surface. Then they were ultrasonically cleaned with ethanol and dried in the air. Ethanol solution with 10% nitric acid was used to corrode the surface of the samples. The microstructure and morphology of the HCCIs were studied by scanning electron microscopy (SEM, Nova Nanosem 430, Hillsboro, OR, USA). X-ray diffraction (XRD, SmartLab, Tokyo, Japan) was used to analyze the phase composition of each samples. The XRD tests were conducted using Cu-Kα radiation at a scanning speed of 0.01°/step within the angle range from 35° to 90°. A transmission electron microscope (TEM, JEM-2100F, Tokyo, Japan) with an attached X-ray energy dispersive spectrometer (EDS) was applied to
investigate the microstructure of HCCIs. High-resolution TEM (HRTEM) and selected area diffraction (SAD) were applied to study the carbides. The TEM specimens were prepared using a focused ion beam (FIB, FEI Scios, Tokyo, Japan).

The electrochemical workstation (Gamry Interface 1000, Philadelphia, PA, USA) was used to evaluate the polarization behavior of HCCIs. A sample size of 10 mm × 10 mm × 4 mm was cold-mounted in an epoxy resin. The exposed area (10 mm × 10 mm) was carefully polished. The prepared sample was then connected to the working electrode of the electrochemical workstation. Pt and saturated calomel were used as counter electrode and reference electrode, respectively. The experiments were conducted in simulated seawater at room temperature. Table 2 shows the composition of simulated seawater used in the present investigation. The open-circuit potential (OPC) was measured first. The impedance and polarization curves were measured when the OPC was stable.

| Composition | wt.% | Composition | wt.% |
|-------------|------|-------------|------|
| NaCl        | 24.530 | MgCl₂      | 11.110 |
| Na₂SO₄      | 4.090 | CaCl₂      | 1.160 |
| KCl         | 0.685 | NaHCO₃     | 0.201 |
| KBr         | 0.101 | HBO₃       | 0.027 |
| SrCl₂       | 0.028 | NaF        | 0.003 |

Rockwell hardness tester (HR-150A, Hugong, Shanghai, China) was used to test the hardness of the samples. Ten measurements were conducted for one specimen. The wear tests were carried out on a three-body abrasive wear tester (MMH-5, Hansen, Jinan, China). Figure 1 shows the schematic diagram of the setup. White corundum with an average particle size of 0.22 mm was used as abrasive particles. Before the wear tests, the samples were pre-ground for 5 min with a load of 1 kg. The total travel distance of each sample was about 1017 m. The samples were then ultrasonically cleaned with ethanol and dried. The mass change of samples before and after the wear test was measured by a balance with a sensitivity of 0.1 mg (METTLER TOLEDO, Zurich, Switzerland). Four tests were conducted on each material. The wear rate was characterized by the ratio of the volume loss to sliding distance. The scatter bar in this work presents the standard deviation of experimental data.

Figure 1. Schematic diagram of the setup for: (a) three-body abrasive wear test, (b) erosion wear test.

The erosion–corrosion resistance of HCCIs was examined by a laboratory instrument (MF-20, Hansen, Jinan, China). Figure 1b shows the schematic diagram of the test setup. Four specimens were clamped in the molds, which were fixed during the experiment. Three impingement angles (0°, 45°, 60°) were used for each material. The geometries of the specimen were 12 × 12 × 30 mm³. Before the tests, the samples were ground using abrasive paper up to 2000 grit to obtain a mirror-like working surface. The erosion and corrosion medium contains simulated seawater and white corundum particles (mean diameter 0.22 mm) with the volume ratio of 5:4. During the tests, the specimens were
immersed in a mixture of simulated seawater and abrasive particles. The rotor in the center rotates at a speed of 1200 rpm to drive the motion of the fluid and abrasive particles. The test period is 3 h. Two tests were conducted for each material.

3. Results

Phase composition of the HCCIs in the as-cast and heat-treated states was determined by XRD. Figure 2 shows the XRD patterns of different HCCI samples. It can be seen that the as-cast HCCIs contain austenite matrix and carbides. Two categories of carbides, M$_7$C$_3$ and TiC, are observed in the microstructure. For comparison, the heat-treated HCCIs are composed of martensite, M$_7$C$_3$ carbide, TiC, and a small amount of retained austenite. The increase in the content of carbon and titanium promoted the formation of TiC as shown in Figure 2.

![Figure 2. X-ray diffraction profiles of the as-cast (a) and heat-treated HCCIs (b).](image)

The microstructure of HCCIs in both as-cast and heat-treated states were investigated as shown in Figure 3. The morphology combined with EDS results demonstrate that the microstructure consists of two categories of carbides. The TiC particles are grey and polygonal, while the rod-like particles are eutectic M$_7$C$_3$ carbides. No coarse primary M$_7$C$_3$ grains are observed in all the HCCI specimens. After heat treatment, the matrix can obviously be corroded due to the formation of martensite as shown in Figure 3e–h.

The Image-Pro Plus (Version 6.0, MEDIA CYBERNETICS, Houston, TX, USA) was used to obtain the volume fraction of carbides in the HCCIs. The results are shown in Figure 4a. For the as-cast HCCIs, it is seen that the volume fraction of M$_7$C$_3$ carbide decreases slightly with increasing the TiC content. Specifically, the volume fraction of M$_7$C$_3$ is about 34.1% in A0 specimen while A3 contains 27.2% M$_7$C$_3$ and 9.8% TiC. It has been reported that M$_{23}$C$_6$ carbide is formed after heat treatment of HCCI [33].

![Figure 4a](image)

Figure 4b shows the hardness of the specimens. With increasing the TiC content, the hardness of as-cast HCCI increases significantly, from 56.2 to 62.5 HRC, as shown in Figure 4b. Improvement of the HCCI hardness can be due to an increased amount of hard TiC grains, refinement of M$_7$C$_3$, and increased total volume fraction of carbides. Furthermore, after heat treatment, the hardness of HCCIs was significantly improved due to the formation of a martensite-dominant matrix. In addition, it was found that the hardness of heat-treated HCCIs increases first and then decreases with the introduction of TiC particles. The reduction in hardness of H3 specimen may be caused by the fracture of martensite matrix.

Three-body abrasive wear tests was used to investigate the wear resistance of TiC-strengthened eutectic HCCIs. Figure 5 shows experimental results. It can be seen that the wear rate of HCCIs decreases with increasing TiC fraction in both as-cast and heat-treated state. Specifically, for the as-cast HCCIs, the wear rate decreases from 2.6 to 2.2 cm$^3$/cm·10$^{-8}$ with the addition of 9.8 vol.% TiC. After heat treatment, the wear rate was further reduced to 1.8 cm$^3$/cm·10$^{-8}$ as shown in Figure 5. If the wear resistance was presented by the reciprocal of wear rate, the improvement of wear resistance by the heat
treatment and the TiC addition can be as high as 50%. The abrasive properties of the HCCIs are consistent with the hardness, as shown in Figure 4b.

Figure 3. Microstructure of HCCIs: (a–d) correspond to A0-A3 and (e–h) correspond to H0–H3, respectively.

Figure 4. Carbide volume fraction (a) and hardness (b) of the HCCIs.

The worn surface after abrasive wear tests were examined to investigate the mass loss mechanisms of the HCCIs. Figure 6 shows the worn surface morphology. The intense plastic deformation and fracture of the samples were reflected by the pits, grooves, and scars in the worn surface as shown in Figure 6. The dominant grooves and scars features indicate that the microcutting and fracture are the major mass loss mechanisms. For comparison, the bright zones in the worn surface were caused by the accumulation of material due to severe plastic deformation. The heat-treated samples exhibit the abrasive wear behavior that is similar to the as-cast samples, as shown in Figure 6e–h.
For pure corrosion resistance, the dynamic polarization curves of the HCCIs in simulated seawater are presented in Figure 7. The open-circuit potential ($E_{\text{corr}}$) of the HCCIs was obtained as shown in Table 3. It reveals that the addition of TiC to the material results in a reduced $E_{\text{corr}}$. Furthermore, the corrosion current density ($I_{\text{corr}}$) of the system was measured from Tafel extrapolation. Statistical analysis was performed to measure the accuracy of the fit which is at 95% confidence level. The corrosion rate in the absence of erosion was calculated from $I_{\text{corr}}$ using Equation (1):

$$w_{co} = \frac{kI_{\text{corr}}A}{np} = \frac{kA}{np} \cdot i_{\text{corr}}$$  \hspace{1cm} (1)
where \( k \) is a constant, \( A \) is atomic weight, \( n \) is the number of electrons gained and lost, \( \rho \) is density, \( i_{\text{corr}} \) is the corrosion current, and \( S \) is sample area. Table 3 presents the \( i_{\text{corr}} \) and the calculated \( w_{\text{co}} \) values for the studied HCCls. It is noted that for the as-cast HCCls, the corrosion rate increased from 98.33 to 586.03 \( \mu \text{m/a} \) when the volume fraction of TiC is 9.8\%, the increment being as high as five times. Furthermore, the heat treatment can significantly reduce the corrosion rate for these HCCls. Specifically, the corrosion rates of heat-treated HCCls were lower than 19.92 \( \mu \text{m/a} \) as shown in Table 3. In addition, for the heat-treated HCCls, the introduction of TiC particles had a minor effect on the corrosion rate.

![Figure 7. Polarization curves of the HCCls: (a) as-cast, (b) after heat treatment.](image)

**Table 3.** \( i_{\text{corr}} \) and \( E_{\text{corr}} \) values for different HCCI samples.

| Sample | \( i_{\text{corr}} \) (\( \mu \text{A/cm}^2 \)) | \( w_{\text{co}} \) (\( \mu \text{m/a} \)) | \( E_{\text{corr}} \) (V) |
|--------|-----------------|-----------------|-----------------|
| A0     | 8.28            | 98.33           | −0.598          |
| A1     | 5.75            | 69.36           | −0.625          |
| A2     | 10.60           | 126.87          | −0.665          |
| A3     | 47.30           | 586.03          | −0.690          |
| H0     | 2.13            | 26.11           | −0.456          |
| H1     | 2.55            | 31.13           | −0.502          |
| H2     | 1.61            | 19.92           | −0.533          |
| H3     | 1.85            | 23.46           | −0.556          |

The slurry erosion tests were performed in the sand-containing simulated seawater as described in Section 2. In this work, three impingement angles (0\(^\circ\), 45\(^\circ\), 60\(^\circ\)) were used. However, it should be noted that the effect of attack angles on the E–C behavior of HCCls was not considered in the present work. Though the rotation rate of rotor was set at 1200 rpm for all the tests, the relative rate of the fluid against the specimen was affected by the geometry of holder. It suggests that the attack rates of fluid were not identical due to the geometrical change of sample holder. Nonetheless, for a given impingement angle, the E–C behaviors of different HCCls were comparable. The effect of the TiC addition and matrix microstructure on the E–C resistance of HCCls was investigated. Furthermore, the dominant mass loss mechanism is supposed to be changed by varying the impingement angle of the fluid.

The wear rate of HCCls under E–C condition is shown in Figure 8. The E–C wear rate (\( w_{\text{EC}} \)) was determined by the following formula:

\[
w_{\text{EC}} = \frac{W}{A \cdot t}
\]

where \( W \) is the mass loss of the specimen, \( A \) is the working surface area, \( t \) is the test time. It turns out that the E–C wear rate is about one or two orders of magnitude higher than the rate of pure corrosion (\( w_{\text{co}} \)). The results showed that the E–C resistance of HCCls is improved by the heat treatment. With increasing the TiC content, the E–C wear rate of both as-cast and heat-treated HCCls increases. Specifically, the E–C wear rate of as-cast TiC-free HCCls is about 6 g/m\(^2\)-h when the impingement angle is 0\(^\circ\). The addition of 9.8\% TiC leads to a significant increment of the E–C wear rate, to 12.5 g/m\(^2\)-h under the same conditions. Furthermore, the detrimental effect of the introduction of TiC particles was observed to intensify with increasing the attack angle. For instance, the wear rate of A3
specimen was by the factor of 2 larger than that of A0 when the test angle is $0^\circ$. For the test angle of $60^\circ$, it was found that the wear rate of A3 was 3 times larger than that of A0. Similar trends can also be observed in the heat-treated HCCIs.

![Figure 8. The erosion–corrosion wear rate of HCCIs.](image)

Figure 8 shows the wear surface morphology of different HCCIs. It can be seen that the wear surface exhibits mainly corrosion pits and shallow furrows. The sample was corroded by solution and worn by the abrasive particles (corundum) during the erosion–corrosion process. Therefore, the mass loss of the sample was caused by the synergistic effect of these two factors. As shown in Figure 9, the number of corrosion pits for the as-cast and heat-treated specimens both increase with raising the TiC content. Thus, increasing the TiC content makes the cast iron more susceptible to pitting corrosion. This is consistent with the electrochemical results that the corrosion rate of HCCIs was increased by the introduction of TiC particles. Furthermore, shallow furrows were observed in all the worn surface (Figure 9).

![Figure 9. Surface morphology of HCCIs after erosion at $60^\circ$: (a–d) correspond to A0–A3 and (e–h) correspond to H0–H3, respectively.](image)
4. Discussion

In this work, various volume fractions of TiC were obtained in the Fe-26Cr-3.2C (in wt.%) near-eutectic HCCI matrix by adding a certain amount of titanium and carbon at the molar ratio corresponding to stoichiometry TiC₁₀. It was anticipated that in the liquid phase containing Ti and C, refractory phase TiC whose melting temperature is about 3070 °C was formed because of the highly negative Gibbs energy of reaction Ti + C → TiC, and this was confirmed by XRD (see Figure 2). At a temperature around 1573 K, the eutectic reaction occurs where the liquid phase transforms to austenite and M₇C₃. It appears that the presence of TiC has a minor effect on the phase constitution of matrix and the morphology of M₇C₃ carbide, as shown in Figures 2 and 3.

It should be noted that recently, particle-reinforced steel matrix composites (SMC) produced by solidification method were intensively investigated due to their exceptional combination of lower density, high strength, and high Young’s modulus [34–36]. Compared with the traditional SMCs produced by the powder metallurgy method, these new composites exhibit a much better ductility because the interfaces between the matrix and ceramic particles are semi-coherent and can undergo considerable interfacial plasticity prior to the interface debonding [37,38].

Thus, it seems necessary to study the phase boundaries in more detail. Figure 10 displays the carbides in specimen H3 after heat treatment. Three phases, namely TiC, M₇C₃ and ferrite, were determined by SAD as shown in Figure 10b–d. Furthermore, HRTEM images reveals that the interphase boundaries M₇C₃/Fe and M₇C₃/TiC are very clean. It is believed that such clean interfaces should have a positive effect on the wear and corrosion resistance of HCCIs.

During the abrasive wear process, the interaction micro-mechanisms between the samples and hard particles can be separated as: (i) abrasion, (ii) deformation, (iii) fatigue, and (iv) fracture [39,40]. For the steels or irons, it has been reported that materials with combined high hardness and sufficient fracture toughness exhibit the best abrasive wear resistance [40]. The composites, which incorporate hard ceramic particles into a softer and ductile matrix, can offer a new route to achieve good abrasive wear resistance [39]. Many microstructural factors, such as the mechanical properties of ceramic particles, volume fraction and size of ceramic phase, the interface properties, have a strong effect on the abrasive wear resistance of the composites. For the present TiC-reinforced HCCIs, the
The hardness of TiC phase can be as high as 3000 HV, which is much higher than that of the abrasive particles. Therefore, it is expected the hardness and abrasive wear resistance can both significantly improved by the introduction of TiC particles, which is consistent with the experimental results as shown in Figures 4 and 5.

Corrosion is one of the key factors that control the wear loss mechanism of HCCIs in the erosion-corrosion condition. The corrosion potential of carbides in HCCI is believed to be nobler than that of the matrix. Therefore, the \( E_{\text{corr}} \) of HCCIs becomes more negative with increasing carbide content. On the other hand, the total corrosion resistance of HCCIs mainly depends on the corrosion behavior of the matrix and hence the content of Cr dissolved in the matrix. It has been reported that with increasing the Cr content in the matrix, the polarization resistance increases and the open-circuit potentials move to the noble direction, indicating an improvement of corrosion stability [41]. The relationship between the polarization resistance \( (R_P) \) and chromium content of the matrix \( (\text{Cr}_M) \) can be empirically expressed as [41]:

\[
R_P = R_0^P \exp(\beta \cdot \text{Cr}_M)
\]

where \( R_0^P \) and \( \beta \) are empirical constants depending on test conditions. It is well known that Cr has a stronger affinity to form carbides than Fe. For conventional HCCIs, the amount of carbides will increase with raising the carbon content, and it will inevitably reduce the content of Cr dissolved in the matrix, thus resulting in poorer corrosion resistance. However, it should be noted that Ti is a stronger carbide former than Cr. Then carbon will be consumed by the formation of TiC. Therefore, the Cr content of the matrix should be identical for the HCCIs in the present study. As a result, the increment of Ti and C should not reduce the corrosion resistance of the HCCIs. However, it is found that corrosion current density of HCCIs increases significantly with the TiC addition as shown in Table 3. It is believed that the increased corrosion rate of HCCIs by TiC addition was not caused by the decreased content of Cr dissolved in the matrix.

Along with the Cr content, microstructure has also a strong effect on the corrosion resistance of HCCIs [41]. For instance, segregation of elements often exists in HCCIs owing to their complex compositions. The segregation can result in a significant reduction in corrosion resistance of HCCIs. The presence of TiC particles will increase the electrochemical heterogeneity of the material and hence reduce the corrosion resistance. Therefore, the introduction of TiC particles has a negative effect on the corrosion rate as shown in Table 3. Furthermore, during the destabilization treatment at a temperature as high as 1323 K, the element segregation may be eliminated, which will result in the improvement of corrosion resistance.

The erosion-corrosion of metallic materials is a complex phenomenon that covers all aspects of tribologically (mainly mechanically) induced damage due to relative motion of abrasives in conjunction with electrochemical corrosion processes [15,24,26,42]. It has been reported that the erosion-corrosion wear rate can be expressed by the following relationships [28]:

\[
T = E + C + S
\]

where \( T \) is the material loss under erosion-corrosion, \( E \) is the material loss by pure mechanical erosion process, \( C \) is the material loss caused by electrochemical corrosion process and synergy term \( S \) is the combined interaction between erosion and corrosion process. In addition, the synergistic term can further be subdivided into two additional components:

\[
S = \Delta C + \Delta E
\]

where \( \Delta C \) is the erosion-enhanced corrosion part, and \( \Delta E \) is the corrosion-enhanced erosion part. In general, the corrosion resistance of metals relies on the formation of a relatively thin passive film. However, for the fluid flow where solid particles have been entrained, this passive film will be attacked by mechanical wear. When the film is damaged or removed, corrosion can occur at substantially higher rates than those observed under static conditions [42]. In turn, corrosion can accelerate the erosion process by the formation of
soft and brittle corrosion products, which can be removed easily by hard abrasive particles. Furthermore, as a metallic phase around hard second-phase particles is corroded and removed, the second-phase particle edges are hit and fractured by the consecutive erosive fluids. Structural damages are generated which cause a mass loss.

For the present HCCIs, the materials loss rate under erosion–corrosion condition is 1–2 orders of magnitude higher than that of pure corrosion as shown in Figure 9 and Table 3. Therefore, the $C$ term in Equation (4) is negligible. The pure erosive term ($E$) can be related to the abrasive wear properties as shown in Figure 5. Therefore, it suggests that the $E$ part decreases with the addition of TiC particles. However, it is seen that the erosion–corrosion rate of the HCCIs increases significantly with TiC addition in both as-cast and heat-treated states as shown in Figure 9. Therefore, it is the synergistic term ($S$) that dominates the erosion–corrosion wear mass loss mechanism of the studied TiC-strengthened HCCIs.

Figure 11 shows the schematic diagram of the erosion–corrosion wear mechanism of the TiC-strengthened HCCIs. During the erosion–corrosion process, the TiC/matrix interface is corroded and the metallic phase dissolves in the fluid (Figure 11a). Then the particles are exposed to the flow and abrasive agents, and strong interactions between corundum particles and TiC can result in either fracture or pullout of the TiC particles (Figure 11b). Subsequently, the surface holes form and the interaction between abrasive particle and metallic matrix is promoted (Figure 11c), which leads to the increased mass loss rate. Therefore, the corrosion-enhanced erosion wear should be the dominant mechanism that controls the mass loss of TiC-strengthened HCCIs.

5. Conclusions

Investigation of the wear and corrosion resistance of TiC-strengthened HCCIs permits drawing the following conclusions on the structure, properties and erosion–corrosion wear behavior of the produced material:

- The as-cast HCCIs consist of TiC, $M_7C_3$, and austenite. After heat treatment, the HCCIs are composed of TiC, $M_7C_3$, martensite, and residual austenite. The hardness of as-cast HCCIs increases with raising the TiC content and can be as high as 63 HRC and the total carbide volume fraction can reach 37.5%.
- The introduction of TiC and heat treatment had a positive effect on the three-body abrasive wear resistance of eutectic HCCIs. With the addition of 9.8 vol.% TiC, the
wear rate of the as-cast HCCI decreases from 2.6 to 2.2 cm$^3$/cm$^2$·min$^{-1}$. After heat treatment, the wear rate was further reduced to 1.8 cm$^3$/cm$^2$·min$^{-1}$;

- The TiC has a negative effect on the corrosion resistance of as-cast HCCIs: their corrosion rate increased from 0.083 to 0.48 g/m$^2$·h when the volume fraction of TiC was 9.8%. The increased corrosion rate by the addition of TiC can be caused by the raise of electrochemical heterogeneity. Furthermore, the heat treatment can reduce the corrosion rate for the studied HCCIs;

- It is unexpected to find that the introduction of TiC significantly reduces the erosion–corrosion resistance of present eutectic HCCIs in both as-cast and heat-treated states. It is also found that the heat treatment can also reduce the erosion–corrosion wear rate for investigated HCCIs. The corrosion-enhanced erosion wear should be the dominant mechanism that controls the mass loss of TiC-strengthened HCCIs.

**Author Contributions:** Conceptualization, Z.-C.L. and A.I.P.; methodology, K.-H.Z. and B.B.K.; validation, S.-L.L., Z.-C.L. and T.-Q.T. formal analysis, T.-Q.T. investigation and writing original draft preparation, Z.-C.L. and B.B.K. writing—review and editing. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by the support from Guangdong provincial Science and Technology Project (2020B0101340004, 2020B1515130007, 2018A050506055, Jiangke2020182), Guangdong Academy of Science (2020GDASYL-2020010314, 2021GDASYL-20210102002), National Natural Science Foundation of China (51901049), Guangzhou Municipal Science and Technology Project (202007020007 and 201907010026).

**Data Availability Statement:** Data presented in this article are available at request from the corresponding author.

**Conflicts of Interest:** The authors declare no conflict of interest.

**References**

1. Zum Gahr, K.-H. Microstructure and Wear of Materials; Elsevier: Amsterdam, The Netherlands, 1987.
2. Hutchings, I.; Shipway, P. Tribology: Friction and Wear of Engineering Materials; Butterworth-Heinemann: Oxford, UK, 2017.
3. Budinski, K.G. Friction, Wear, and Erosion Atlas; CRC Press: Boca Raton, FL, USA, 2013.
4. Kim, Y.-J.; Kim, S.-W.; Kim, H.-B.; Park, C.-N.; Choi, Y.-I.; Park, C.-J. Effects of the precipitation of secondary phases on the erosion-corrosion of 25% Cr duplex stainless steel. *Corros. Sci.* 2019, 152, 202–210. [CrossRef]
5. Fordyce, I.; Annasamy, M.; Sun, S.D.; Fabijanic, D.; Gallo, S.C.; Leary, M.; Easton, M.; Brandt, M. The effect of heat treatment on the abrasive and erosive wear behaviour of laser metal deposited Fe–28Cr–2.7C alloy. *Wear* 2020, 458–459, 203410. [CrossRef]
6. de Silva, A.E.; de Melo, I.N.R.; Pinheiro, I.P.; da Silva, L.R. Characterisation and machinability of high chromium hardened white cast iron with and without the addition of niobium. *Wear* 2020, 460–461, 203463. [CrossRef]
7. Zheng, Y.; Song, R.; Pei, Y.; Wen, E.; Zhao, Z. The formation of TiC–NbC core-shell structure in hypereutectic high chromium cast iron leads to significant refinement of primary M7C3. *J. Alloys Compd.* 2020, 824, 153806. [CrossRef]
8. Giourntas, L.; Brownlie, F.; Hodgkiess, T.; Galloway, A. Influence of metallic matrix on erosion-corrosion behaviour of high chromium cast irons under slurry impingement conditions. *Wear* 2021, 477, 203834. [CrossRef]
9. Purbak, R.H.; Shimizu, K.; Kusumoto, K.; Todaka, T.; Shirai, M.; Hara, H.; Ito, J. Erosive wear characteristics of high-chromium based multi-component white cast irons. *Tribol. Int.* 2021, 159, 106982. [CrossRef]
10. Penaglos, J.J.; Pereira, J.I.; Machado, P.C.; Albertin, E.; Sinatoa, A. Synergetic effect of niobium and molybdenum on abrasion resistance of high chromium cast irons. *Wear* 2017, 376, 983–992. [CrossRef]
11. Tozetti, K.D.; Albertin, E.; Scandian, C. Abrasive size and load effects on the wear of a 19.9% chromium and 2.9% carbon cast iron. *Wear* 2017, 376, 46–53. [CrossRef]
12. Chong, X.; Hu, M.; Wu, P.; Shan, Q.; Jiang, Y.H.; Li, Z.L.; Feng, J. Tailoring the anisotropic mechanical properties of hexagonal M7X3 (M=Fe, Cr, W, Mo; X=C) by multialloying. *Acta Mater.* 2019, 169, 193–208. [CrossRef]
13. Wiengmoon, A.; Pearce, J.T.H.; Chairuangsi, T. Relationship between microstructure, hardness and corrosion resistance in 20 wt.% Cr, 27 wt.% Cr and 36 wt.% Cr high chromium cast irons. *Mater. Chem. Phys.* 2011, 125, 739–748. [CrossRef]
14. Tang, X.H.; Chung, R.; Pang, C.J.; Li, D.Y.; Hinckley, B.; Dolman, K. Microstructure of high (45 wt.%) chromium cast irons and their resistances to wear and corrosion. *Wear* 2011, 271, 1426–1431. [CrossRef]
15. Tian, H.; Addie, G.; Visintainer, R. Erosion–corrosion performance of high-Cr cast iron alloys in flowing liquid–Solid slurries. *Wear* 2009, 267, 2039–2047. [CrossRef]
16. Stevenson, A.; Hutchings, I. Wear of hardfacing white cast irons by solid particle erosion. *Wear* 1995, 186, 150–158. [CrossRef]
17. Neville, A.; Hodgkiess, T.; Dallas, J. A study of the erosion-corrosion behaviour of engineering steels for marine pumping applications. *Wear* **1995**, *186*, 497–507. [CrossRef]
18. Karafyllas, G.; Galloway, A.; Humphries, E. The effect of low pH in erosion-corrosion resistance of high chromium cast irons and stainless steels. *Wear* **2019**, *420*, 79–86. [CrossRef]
19. Chung, R.J.; Tang, X.; Li, D.Y.; Hinckley, B.; Dolman, K. Microstructure refinement of hypereutectic high Cr cast irons using hard carbide-forming elements for improved wear resistance. *Wear* **2013**, *301*, 695–706. [CrossRef]
20. Chung, R.J.; Tang, X.; Li, D.Y.; Hinckley, B.; Dolman, K. Effects of titanium addition on microstructure and wear resistance of hypereutectic high chromium cast iron Fe–25 wt.% Cr–4 wt.% C. *Wear* **2009**, *267*, 356–361. [CrossRef]
21. Huang, Z.; Xing, J.; Zhang, A. Microstructure and Property of Hypereutectic High Chromium Cast Iron Prepared by Slope Cooling Body-Centrifugal Casting Method. *J. Mater. Sci. Technol.* **2006**, *22*, 775–778.
22. Buytoz, S. Microstructural properties of M7C3 eutectic carbides in a Fe–Cr–C alloy. *Mater. Lett.* **2006**, *60*, 605–608. [CrossRef]
23. Geng, Y.; Tan, H.; Cheng, J.; Chen, J.; Sun, Q.; Zhu, S.; Yang, J. Microstructure, mechanical and vacuum high temperature tribological properties of AlCoCrFeNi high entropy alloy based solid-lubricating composites. *Tribol. Int.* **2020**, *151*, 106444. [CrossRef]
24. Rajahram, S.; Harvey, T.; Wood, R. Evaluation of a semi-empirical model in predicting erosion–corrosion. *Wear* **2009**, *267*, 244–254. [CrossRef]
25. Jones, M.; Llewellyn, R. Erosion–Corrosion assessment of materials for use in the resources industry. *Wear* **2009**, *267*, 2003–2009. [CrossRef]
26. Wood, R.J. Erosion–Corrosion interactions and their effect on marine and offshore materials. *Wear* **2006**, *261*, 1012–1023. [CrossRef]
27. Sapate, S.; RamaRao, A. Erosive wear behaviour of weld hard-facing high chromium cast iron after different heat treatments. *Vacuum* **2019**, *149*, 149–162. [CrossRef]
28. Buytoz, S. Microstructural properties of M7C3 eutectic carbides in a Fe–Cr–C alloy. *Mater. Lett.* **2006**, *60*, 605–608. [CrossRef]
29. AlMangour, B.; Grzesiak, D.; Yang, J.-M. In situ formation of TiC-particle-reinforced stainless steel matrix nanocomposites during solidification. *Wear* **2009**, *267*, 695–706. [CrossRef]
30. Duraiselvam, M.; Galun, R.; Wesling, V.; Mordike, B.L.; Reiter, R.; Oligmüller, J. Cavitation erosion resistance of AISI 420 martensitic stainless steel laser-clad with nickel aluminide intermetallic composites and matrix composites with TiC reinforcement. *Surf. Coat. Technol.* **2006**, *201*, 1289–1295. [CrossRef]
31. Gahr, K.H. Wear by Hard Particles. *Tribology International*. **1998**, *31*, 587–596. [CrossRef]
32. Fischer, A. Well-founded selection of materials for improved wear resistance. *Wear* **1996**, *194*, 238–245. [CrossRef]
33. Lu, B.; Luo, J.; Chiovelli, S. Corrosion and wear resistance of chrome white irons—A correlation to their composition and microstructure. *Metall. Mater. Trans. A* **2006**, *37*, 3029–3038. [CrossRef]
34. Kan, W.H.; Yu, Z.; Lucey, T.; Chang, L.; Proust, G.; Cairney, J.M. The effect of NbC morphology on the slurry erosion performance of a 15Cr-8.5Ni-1.5Mo-0.5Nb-0.5Ti-0.5Si-0.5Al stainless steel. *Tribol. Int.* **2019**, *126*, 99–108. [CrossRef]
35. Barik, R.C.; Wharton, J.A.; Wood, R.J.K.; Stokes, K.R. Electro-mechanical interactions during erosion-corrosion. *Wear* **2009**, *267*, 1900–1908. [CrossRef]