Article

Wear Resistance Mechanism of ZTA<sub>p</sub>/HCCI Composites with a Honeycomb Structure

Mojin Zhou<sup>1</sup>, Yudong Sui<sup>1</sup>, Xiaoyu Chong<sup>1,2</sup> and YeHua Jiang<sup>1,*</sup>

<sup>1</sup> Faculty of Material Science and Engineering, Kunming University of Science and Technology, Kunming 650093, China; zmjkmsat@hotmail.com (M.Z.); suiyudong@126.com (Y.S.); xuc83@psu.edu (X.C.)

<sup>2</sup> Department of Materials Science and Engineering, Pennsylvania State University, University Park, PA 16802, USA

* Correspondence: jiangyehua@kmust.edu.cn; Tel.: +86-871-6513-6755

Received: 23 June 2018; Accepted: 24 July 2018; Published: 28 July 2018

Abstract: The abrasive wear resistance of zirconia toughened alumina (ZTA) ceramic particle reinforced high chromium cast iron (HCCI) composites has been systematically investigated using a moving wedge type of apparatus. The results of three-body abrasive wear show that the wear resistance of the composites with honeycomb is three times higher than that of the high chromium cast iron. The wear resistance of the composites with a honeycomb structure is close to that of the layer structure and is higher than that of the HCCI because the honeycomb wall in the cell honeycomb structure is prominent and because the honeycomb core is depressed. The wear mechanisms of the composites are mainly microcutting and fatigue fractures. The honeycomb structure forms a “macrocosmic shadow protection effect” and a “microcosmic shadow protection effect” to protect each composite and to improve the wear resistance of the composites.

Keywords: honeycomb structural composite; three-body abrasive wear; wear rate; ZTA

1. Introduction

Abrasive wear is ubiquitous in industry, agriculture, transportation and everyday life. Statistics show that 80% of material consumption is caused by the wear of parts, which not only wastes resources and causes economic losses but also reduces the product quality, affects the product efficiency, and limits the development of modern industry. Wear-resistant materials have several advantages, including light-weight, high hardness, high strength, and high performance-price ratio advantages. Ceramic particle reinforced metal matrix composites (CPRMMCs) offer several advantages, such as the elastic modulus and the strength of the matrix, as well as the hardness and the wear resistance of ceramic particles, which have been considered the most promising wear resistant materials [1–3]. Taking into account the materials’ application and production technology, the properties of ceramic particle reinforced metal matrix composites are largely dependent on the incorporated reinforcement particles and on the structure of the composites [4,5]. Cu-Cr<sub>3</sub>C<sub>2</sub> composites with interpenetrating networks were prepared by immersing the porous Cr<sub>3</sub>C<sub>2</sub> skeleton in the pure Cu solution, and the Vickers hardness is three times higher than that of the pure copper [6]. SiC-reinforced Al composites with a multi-core microstructural architecture are improved in terms of the fracture toughness and the strength [7]. Laminated metal composites can improve overall performance compared to a single layer because the brittle layer of the reinforcements and the tough layer of the metal or the alloys are superimposed on each other [8,9]. The structural architectures play an important role in the design of composites, especially of the wear resistant composites. WC or Al<sub>2</sub>O<sub>3</sub> particle reinforced iron matrix composites can improve the wear resistance, and these composites are better than the iron matrix [10,11].
Zirconia toughened alumina (ZTA) ceramics have a high hardness, better fracture toughness, and good thermal stability, and they are used as reinforcement in metal matrix composites [12,13]. V. Jeevan studied the ZTA particle reinforced A6082 alloy by the powder metallurgy process and learned that the ZTA particles can enhance the hardness of the alloy matrix and the density of the composites [14]. Lei Fan put a nickel coating on the ZTA particles by the electroless plating method, which improved the interface between the ZTA particles and the metal matrix, and they obtained the result that the interface is a non-chemical bonding between the ZTA particles and the metal matrix [15]. Zhang et al. investigated the stress–strain behaviour of ZTA/Fe45 composites by numerical simulations and found that the particle-matrix interface properties show the dominant impact for yield limit and peak stress while for the critical strain the particle volume fraction is the main factor [16]. The “Honeycomb Structure” is widely applied in the composite design, owing to its good comprehensive mechanical properties and its perfect structure [17,18]. Du J. studied the ZTA ceramic particle reinforced high chromium cast iron composites (HCCI) with a honeycomb structure obtained by infiltration casting and acquired the best casting process parameters by a finite element calculation [19]. The wear resistance results of the composites with honeycomb structure are better than that of the metal matrix [20,21].

The ZTA ceramic particle reinforced high chromium cast iron (ZTA_3p/HCCI) composites were obtained by the infiltration process. The honeycomb structure in the composites will affect the wear mechanism on the macroscopic and microscopic scales. This paper aimed to study the effect of the honeycomb structure on the ZTA particle reinforced high chromium cast iron composites by three-body abrasive wear in different abrasives.

2. Materials and Methods

2.1. Materials

The ZTA ceramic particles are the reinforcements in the HCCI matrix. The ZTA particles (55% Al_2O_3, 40% ZrO_2, 3% TiO_2, and 0.7% Fe_2O_3) have a coefficient of thermal expansion close to the HCCI (3.1% C, 26% Cr, 1.2% Mn, 0.5% Si, 0.5% Ni, and 0.4% Mo) [22,23]. The size of ZTA particles is 1–3 mm. The ZTA particles were uniformly mixed with the binder and were filled in a rubber mould with a honeycomb structure and the ceramic preform with honeycomb structure was obtained as shown in Figure 1a. The preformed mixture was placed into the sand mould cavity. The HCCI matrix was melted at 1500–1600 °C and was then poured into the sand mould cavity to obtain the composites was shown in Figure 1b. Figure 1b shows that the ZTA particles are evenly distributed in the metal matrix and maintain the honeycomb structure. The composite ZTA_3p/HCCI was heat-treated at 1030 °C and then tempered at 530 °C. The three-body abrasive wear specimens were cut by a diamond wire cutting machine. The wear specimens were washed with the alcohol, and the wear surface was polished by a diamond grinding disc.

![Image](image_url)

**Figure 1.** The preform (a) and the composites with honeycomb structure (b).
2.2. Characterization Methods

The microstructure was observed by an optical microscope (Leica EZ4D, OM, LEICA, Solms, Germany) (and a scanning electron microscope (Zeiss Evo18, SEM, ZEISS, Carl Zeiss, Germany) to identify the carbides. The specimen was scanned in the 2θ range of 5–90° in a step–scan mode (0.02° per step) by X-ray diffraction (XRD, Empyrean Panalytic) to identify the phases in the composites. The micro-hardness was examined by a Micro-hardness Tester with a Vickers indenter (HVS-1000A, EASTO, Qing Dao, China). The wear equipment is an MMH-5 three-body abrasive wear test machine (Ji’nan Yihua Tribology Testing Technology Co., Ltd, Ji’nan, China). The wear loss of the specimen was measured by a precision electronic balance scale (Ohaus AR423CN, New Jersey, NJ, USA). The three-dimensional micrographs of the worn surface of the composites were collected by a three-dimensional surface profiler (Nanomap 500LS, Saratoga, CA, USA).

The three-body abrasive wear detection method was used to measure the wear resistance of the composites. The density of the composites was given by the following formula [21]:

\[
\rho = \alpha \times \rho_p + (1 - \alpha) \times \rho_m
\]  

Here, \( \rho \) is the density of the composites; \( \rho_p \) is the density of the ceramic particles; \( \rho_m \) is the density of the high chromium cast iron, and \( \alpha \) is the volume fraction of ceramic particles in the composites. The volume loss of the composites was obtained according to the following formula:

\[
\Delta V_{loss} = \Delta M_{loss} / \rho
\]  

The wear rate \( \xi \) was given by the following formula:

\[
\xi = \Delta V_{loss} / (F_n s)
\]  

where \( F_n \) and \( s \) represent the load and the sliding distance, respectively. The schematic diagrams of the three-body abrasive wear test system and the wear specimen size are shown in Figure 2. Each wear cycle time was 30 min, and the abrasives were replaced after each grinding process. The worn samples were put into a beaker with the alcohol, and the beaker was sonicated for 15 min and weight afterwards. The test scheme is shown in Table 1. During the test, the wear specimens need to be pre-ground for 15 min to ensure the stability of the measurement data.

![Schematic diagrams of the three-body abrasive wear system](image)

Figure 2. Schematic diagrams of the three-body abrasive wear system: (a) Wear system, (b) Wear sample.
Table 1. Test scheme.

<table>
<thead>
<tr>
<th>Scheme</th>
<th>Load (N)</th>
<th>Size (μm)</th>
<th>Abrasive</th>
<th>Materials</th>
<th>Composition</th>
<th>Micro-Hardness (HV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>30</td>
<td>380–830</td>
<td>Quartz sand</td>
<td>SiO₂</td>
<td>800~1200</td>
<td></td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>250–380</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>150–250</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>10</td>
<td>250–380</td>
<td>Quartz sand</td>
<td>SiO₂</td>
<td>800~1200</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>250–380</td>
<td></td>
<td>SiO₂</td>
<td>800~1200</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>150–250</td>
<td></td>
<td>SiO₂</td>
<td>800~1200</td>
<td></td>
</tr>
<tr>
<td></td>
<td>40</td>
<td></td>
<td></td>
<td>SiO₂</td>
<td>800~1200</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>10</td>
<td>250–380</td>
<td>Quartz sand</td>
<td>SiO₂</td>
<td>800~1200</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>250–380</td>
<td>Corundum</td>
<td>Al₂O₃</td>
<td>2100~2400</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30</td>
<td></td>
<td>Iron ore</td>
<td>Fe₂O₃</td>
<td>660~720</td>
<td></td>
</tr>
<tr>
<td></td>
<td>40</td>
<td></td>
<td>Silicon carbide</td>
<td>SiC</td>
<td>2840~3320</td>
<td></td>
</tr>
</tbody>
</table>

3. Results and Discussion

3.1. Microstructure Analysis

Figure 3a shows the SEM image of the ZTA<sub>P</sub>/HCCI composites, whereby the ZTA particles distributed evenly in the matrix. Figure 3b,d display the typical microstructure of primary carbides and eutectic carbides in the high chromium cast iron. It can also be observed that the microstructure between the ZTA particles does not change (Figure 3c), the main carbides are the primary carbides and the eutectic carbides, which can provide a better wear resistance [24].
The phases of the ZTAP/HCCI composites were identified by XRD. From the results in Figure 4, it can be known that the ZTA particles mainly consist of Al$_2$O$_3$ and ZrO$_2$ and the carbides are (Cr, Fe)$_7$C$_3$. The microstructures are mainly martensite and austenite phases [25]. The phases of Al$_2$O$_3$ and ZrO$_2$ in the ZTA particles have phase transformations ($\theta$-Al$_2$O$_3$ to $\alpha$-Al$_2$O$_3$ and $t$-ZrO$_2$ to $m$-ZrO$_2$) that will decrease the thermal stress between the ZTA particles and the metal matrix [26].

![XRD patterns of the composites and the high chromium cast iron (HCCI).](image)

**Figure 4.** XRD patterns of the composites and the high chromium cast iron (HCCI).

### 3.2. Three-Body Abrasive Wear Tests

Figure 5 shows the micro-hardness of the abrasives and the composite phases. The wear resistance of the composites has a direct relationship with the hardness, the load and the second phases [27]. It can be known that the hardness of ZTA particles is higher than that of the abrasives (Al$_2$O$_3$, SiO$_2$, and Fe$_2$O$_3$) but lower than that of the SiC. The hardness of carbides is higher than that of the quartz sand (SiO$_2$) and the iron ore (Fe$_2$O$_3$) but lower than that of the corundum (Al$_2$O$_3$), and the silicon carbide (SiC). SiC can be regarded as “Hard abrasives” (Hard abrasive: Hm/Ha < 0.8; here, Hm is the material hardness; Ha is the hardness of the abrasive particles) and Fe$_2$O$_3$, SiO$_2$ can be regarded as “Soft abrasives” (Hm/Ha > 0.8).

![Micro-hardness of the abrasives and the composite area.](image)

**Figure 5.** Micro-hardness of the abrasives and the composite area.
The wear specimens have the same volume fraction of the primary carbides. Figure 6 shows the abrasive wear resistance results of the composites and the high chromium cast iron. The structure of the wear specimens has a significant influence on the wear resistance. The wear rate increases with the abrasive size of the quartz sand (Figure 6a). Three-body abrasive wear is a special wear form in the two-body abrasion, and the wear resistance is related to the load and the hardness. In Figure 6b, the wear rate increases with the load and the hardness of the abrasives. The results are consistent with the computer simulation performed by Liang Fang that the wear resistance is related to the load and the hardness of the specimens [28]. Meanwhile, the composites with a layer structure have a better wear resistance than the composites with a honeycomb structure, and the composites have better resistance than the high chromium cast iron (Figure 6c). The trends are identical to those in the study of the Tungsten carbide (WC) particle reinforced iron matrix composites by Kaihong Zheng [21]. The wear resistance of the layer composite is close to that of the honeycomb structure, but the thickness of the metal castings infiltrating the unstructured layer (Figure 7), and the engineering of the layer composites without a structure were limited. Therefore, the following discussion focuses on the composites with a honeycomb structure.

![Figure 6](image)

**Figure 6.** Three-body abrasive wear rates of the composites: (a) In the case of different abrasive sizes in quartz sand, (b) In the case of different abrasive particles, (c) the HCCI and the composite in quartz sand, (d) Different structures of the worn surface.
Figure 7. Different structural composite results: (a) Honeycomb; (b) Layer.

The SEM morphology of the abrasives of the same load and the same size is shown in Figure 8. Figure 8a shows the results of the Hard abrasives SiC, and it can be observed that the SiC particles are not broken, and the surface of the particles is blunted. Figure 8c,d of the Soft abrasives have shown that the particles are broken, and the surface is rounder. For Figure 8b, the hardness of the abrasive particles is close to that of the composites, but the abrasive particles also change as the Soft abrasives.

Figure 8. SEM micrographs of the abrasives before and after the wear: (a) SiC, (b) Al₂O₃, (c) SiO₂, (d) Fe₂O₃.

3.3. Worn Surface and Cross Section

To learn more about the wear behaviour of the composites, the worn surfaces of the composites under an applied load of 40 N in different abrasive particles have been observed in Figure 9. The composites with a honeycomb structure have three areas, including the honeycomb wall (1), the inter-particle (2) and the honeycomb core (3). Here, area 1 represents the worn area of the honeycomb wall, area 2 represents the worn area of the metal matrix between the ZTA ceramic particles, and area 3 represents the worn area of the honeycomb core. Figure 9a shows that the SiC particles can have a cutting effect on the ZTA particles and that the metal matrix between the ZTA particles cannot provide good abrasion resistance. From Figure 9c,d, it can be seen that the ZTA particles are more prominent than the matrix. Figure 9b shows that the ZTA particles are prominent in the matrix because the hardness of the Al₂O₃ particles is higher than that of the carbides and is lower than that of the ZTA particles.

Figure 10 shows the three-dimensional colour micrographs of the worn surfaces of the composite and the high chromium cast iron. It can be seen that the ZTA particles are more prominent in the composites in the Soft abrasives (Figure 10c,d) than those in the Hard abrasives (Figure 10a). Compared with Figure 10c,e, it is known that the ZTA ceramic particles can prevent the effect of the abrasive particles on the matrix and can stop the micromutting, which goes through the entire worn surface in the high chromium cast iron. Therefore, the ZTA particles can play an important role in protecting the matrix of the composites. These morphology features conclude that the wear
resistance of the composites is better than that of the HCCI and these results agree well with the results in Figures 6 and 9.

Generally, the wear mechanism can be obtained in more detail by observing the worn subsurface. Figure 11 shows the worn subsurface in the honeycomb wall and the honeycomb core of the composites. From Figure 11a,b, it can be seen clearly that the carbides as wear resistant phases in the matrix can improve the wear resistance and the plastic deformation cannot occur under the effect of the abrasive particles. The mass of the matrix decreases mainly because the carbides are crushed, peeled off, and microcut by the abrasive particles. Therefore, grooves, debris, and chips can be observed in the cross-section of the worn surface. From Figure 11c,d, it is known that the abrasives constantly rolling on the matrix result in an impact and a compression under the load, where the carbides in the matrix of the honeycomb core are prominent. Additionally, the micro-cracks are formed in the carbides, and the matrix will be fatigue fractured, will shed and will generate chips by the microcutting of the abrasives. The results of the carbide crack propagation are consistent with the research by J. J. Penagos [29].

Figure 9. Worn surfaces of different areas of the composites in different abrasive: (a) SiC, (b) Al₂O₃, (c) SiO₂; (d) Fe₂O₃.
3.4. Wear Mechanism Analysis

To learn more about the wear mechanisms of the composites with the honeycomb structure, the corresponding sketch is shown in Figure 12. In the case of Soft abrasives (Figure 12a), the abrasive particles with sharp corners, rolling and sliding on the metal surface in the honeycomb core and between the ZTA particles, were applied to the load, which will have a microcutting. The microcutting by the abrasive particles will cause the material to be removed directly from the matrix and leave a "groove". The grooves are usually short and in different directions, because the abrasive particles are unfixed. However, the abrasive particles will indent into the worn surface repeatedly and will deform the matrix surface, which are the same conclusions as those of Yongxin Jian [30].

However, when the abrasive particles encounter the ZTA particles, the abrasives are crushed into small particles under the effect of the load. The small abrasive particles are mainly rolling and reducing the microcutting on the composites (Figure 6a). At the same time, micro-cracks start to appear in the carbides, and with repeated actions by the abrasives, the cracks expand until the carbides fall off. The carbides and the metal form debris as the abrasive particles in the wear process.

In the case of Hard abrasives (Figure 12b), the hardness of the ZTA particles is lower than that of the SiC particles, so the abrasive particles make the microcutting directly on the matrix surface and the ZTA ceramic particles. Of course, the hard particles with sharp corners will also indent into the matrix and lead to the fatigue shedding of the metal matrix.

Due to the different wear resistance between the honeycomb core and wall, the core will be concave and the wall will be standing out in the wear process (Figure 12c). The prominent wall plays the major role in the abrasion resistance and can protect the surrounding honeycomb core, called macrocosmic shadow protection effect. Similarly, for the metal matrix between the ZTA particles, the matrix has a high toughness that can hold the ZTA particles firmly. In turn, the ZTA particles can prevent the abrasive particles from cutting on the metal matrix, called microcosmic shadow protection effect [21,31]. For the ZTA P/HCCI with honeycomb structure under the condition of different hardness and different size of the abrasive, the honeycomb wall and honeycomb core are protected by macrocosmic shadow protection effect and microcosmic shadow protection effect that results in improvement of the abrasive wear resistance of the composites. When the abrasive is large and hard, the macrocosmic shadow protection effect is playing a major role; when the abrasive is small and soft, the microcosmic shadow protection effect plays the major role.
“groove”. The grooves are usually short and in different directions, because the abrasive particles are unfixed. However, the abrasive particles will indent into the worn surface repeatedly and will deform the matrix surface, which are the same conclusions as those of Yongxin Jian [30]. However, when the abrasive particles encounter the ZTA particles, the abrasives are crushed into small particles under the effect of the load. The small abrasive particles are mainly rolling and reducing the microcutting on the composites (Figure 6a). At the same time, micro-cracks start to appear in the carbides, and with repeated actions by the abrasives, the cracks expand until the carbides fall off. The carbides and the metal form debris as the abrasive particles in the wear process. In the case of Hard abrasives (Figure 12b), the hardness of the ZTA particles is lower than that of the SiC particles, so the abrasive particles make the microcutting directly on the matrix surface and the ZTA ceramic particles. Of course, the hard particles with sharp corners will also indent into the matrix and lead to the fatigue shedding of the metal matrix.

![Figure 12](image_url)

**Figure 12.** Two conditions of the failure of the honeycomb structural composite on the worn surface: (a) Soft abrasives; (b) Hard abrasives; (c) Shadow protected effect.

Due to the different wear resistance between the honeycomb core and wall, the core will be concave and the wall will be standing out in the wear process (Figure 12c). The prominent wall plays the major role in the abrasion resistance and can protect the surrounding honeycomb core, called macrocosmic shadow protection effect. Similarly, for the metal matrix between the ZTA particles, the matrix has a high toughness that can hold the ZTA particles firmly. In turn, the ZTA particles
can prevent the abrasive particles from cutting on the metal matrix, called microcosmic shadow protection effect [21,31]. For the ZTA_{P}/HCCI with honeycomb structure under the condition of different hardness and different size of the abrasive, the honeycomb wall and honeycomb core are protected by macrocosmic shadow protection effect and microcosmic shadow protection effect that results in improvement of the abrasive wear resistance of the composites. When the abrasive is large and hard, the macrocosmic shadow protection effect is playing a major role; when the abrasive is small and soft, the microcosmic shadow protection effect plays the major role.

4. Conclusions

1. The wear rate of ZTA_{P}/HCCI composites with a honeycomb structure increases with the load, hardness, and size of the abrasive particles. When the abrasive is quartz sand, the size is 150–250 µm and the load is 30 N (40 N) that the composites wear rate is 0.30 (0.32) mm^3/N·m. With the size of the abrasive increasing to 380–830 µm, the wear rate is 0.63 (0.67) mm^3/N·m. When at the same load (10 N, 20 N, 30 N, and 40 N) and the same abrasive size (250–380 µm) was applied the composites wear rate was found to be 0.26 (0.35, 0.39, and 0.66) mm^3/N·m for Fe_{2}O_{3} abrasive (660–720 HV). With increasing hardness of the abrasive, the composites wear rate is 1.12 (1.35, 1.82, and 3.54) mm^3/N·m using SiC abrasive. At the same time, the wear resistance of the composites with honeycomb structure was found to be three times higher than that of high chromium cast iron.

2. The wear mechanism of ZTA_{P}/HCCI composites with honeycomb structure consisted of two parts: The macroscopic wear of the honeycomb structure and the wear between the ZTA ceramic particles in the composites area. Accordingly, the wear mechanism of the composites is characterised predominantly by micrcutting and fatigue fracture.

3. The effect of ZTA_{P}/HCCI with honeycomb structure on the wear protection mechanisms can be described preferentially by the macrocosmic shadow protection effect, whereby the honeycomb wall protect the honeycomb core as well as the microcosmic shadow protection effect, according to which the ZTA particles protect the metal matrix.

Author Contributions: Y.J. and M.Z. designed most experiments, analyzed the results and wrote this manuscript. Y.S. and M.Z. performed most experiments. X.C. helped analyze the experiment data and gave some constructive suggestions about how to write this manuscript.

Funding: This work was funded by the National Natural Science Foundation of China (No. 51571103), China Postdoctoral Science Foundation (No. 2018T110999).

Acknowledgments: This work is supported by National-local Joint Engineering Laboratory of metal Advanced Solidification Forming and Equipment Technology of China.

Conflicts of Interest: The authors declare no conflicts of interest.

References


10. Li, Y.; Gao, Y. Three-body abrasive wear behavior of CC/high-Cr WCI composite and its interfacial characteristics. Wear 2010, 268, 511–518. [CrossRef]
17. Tao, Y.; Chen, M.; Chen, H.; Pei, Y.; Fang, D. Strain rate effect on the out-of-plane dynamic compressive behavior of metallic honeycombs: Experiment and theory. Compos. Struct. 2015, 132, 644–651. [CrossRef]
18. Ivañez, I.; Fernandez-Cañadas, L.M.; Sanchez-Saez, S. Compressive deformation and energy-absorption capability of aluminium honeycomb core. Compos. Struct. 2017, 174, 123–133. [CrossRef]


© 2018 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).