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Effect of WC/Mo_2C ratio on the erosion behavior of Ti(C,N)-based cermets

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ABSTRACT

In this paper, Ti(C,N)-based cermets of different WC/Mo_2C were prepared and the effect of WC/Mo_2C ratio on the microstructure and mechanical properties was investigated. The erosion behavior of cermets was tested in a slurry containing 5 wt.% NaCl and 5 wt.% Al_2O_3 particles. The results indicate that the changes of WC/Mo_2C ratio have no obvious effect on average grain size, but the homogeneity of hard phase, hardness and porosity decrease slightly with the increase of the ratio. The cermets with 5 wt.% WC and 5 wt.% Mo_2C exhibit the best erosion resistance, which can be attributed to the enhanced strength of rim. Additionally, excessive WC makes the rim too brittle to subject the repetitive mechanical loads. The solid solution strengthening plays an important role in the erosion resistance of the binder phase. The binder with Mo_2C addition has a better erosion resistance than that of WC.

Introduction

Petroleum fluid, containing hydrogen sulfide, carbon dioxide and different sizes of sand presents a severe degradation to the flow passage components such as rings and valves in the petrochemical field [1–4]. In the condition, the components have to withstand the corrosion of complex fluid as well as the mechanical impingement caused by solid particle and their interactions. Ti(C,N)-based cermets have high high-temperature hardness, low friction coefficient to metals, perfect chemical inertness and relatively low production costs; thus, this material is considered as an alternative to WC-Co cemented carbides and traditional metallic materials in the aggressive conditions [4–7].

The core–rim structure is commonly observed in Ti(C,N)-based cermets and results from the dissolution–precipitation process of secondary carbides addition [8,9]. Mo/Mo_2C is considered to be an important composition in the Ti(C,N)-based cermets. Mo_2C improves the wettability between binder and hard phase, resulting in enhanced mechanical properties. Besides, with the increase of molybdenum content, the microstructure becomes finer [9–11]. Irina Hussainova pointed out that the improvement in wear resistance of cermets with increasing Mo content is attributed to gain in binder hardness [12]. In literature [13], cermet materials including Mo_2C presented a finer carbonitride grain structure, as well as higher wear resistance resulting from their higher hardness and highly solution hardened binder phase. Nevertheless, Mo is a scarce resource which only reached 0.0001% of the weight of the earth crust while W shows abundant resource which reserves reach 5.2 million tons. Literatures [8,9] have indicated that WC addition to cermets was effective to improve wettability and decrease grain growth rate. And the microstructure was refined, besides, mechanical properties such as transverse rupture strength and bending strength were strengthened with the increase of WC content [7,14,15]. According to the fabrication cost and similar effect on the material improvement, WC shows great potential as a substitute for Mo_2C in Ti(C,N)-based cermets.

Some researchers [12,16] believed that Ti(C,N)-based cermets with Mo_2C addition show an excellent erosion performance, compared to the materials without molybdenum addition. However, the erosion resistance of this material would be decreased with excessive Mo_2C addition [4]. Dong reported that the debonding of particles increased with the addition of Mo_2C. Furthermore, in literature [17], the author concluded that the WC addition resulted in an increase in erosion wear resistance of cermets. The cermets containing WC have a coarser Ti(C,N) core; finally, the erosion resistance can be improved because of harder pullout of the Ti(C,N) core.

In order to establish the influence of WC/Mo_2C ratio in solid–liquid erosion conditions, the erosion behavior of cermets with different WC/Mo_2C ratio addition is studied. The slurry of saline and Al_2O_3 particles is used as the typical aggressive erosion environment.

Experimental procedures

Material preparation

All the species used in the study were prepared by conventional powder metallurgical procedures. The characteristics of the starting powders are given in Table 1. The powders were obtained commercially. Firstly, all the powders were weighed and mixed with alcohol in stainless steel lined mills for 72 h, using WC-8 wt.% Co balls with a diameter of 10 mm as milling bodies. The rotating speed of drums was

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Table 1
Characteristics of initial raw powders.

Powders	FSSS (μm)	Total carbon (wt.%)	Free carbon (wt.%)	Oxygen (wt.%)	Manufacture
$TiC_{0.7}N_{0.3}$	1.85	13.52	0.08	0.30	Changsha Wing Hing High-Tech New Materials Co., Ltd., China
Mo_2C	1.55	6.03	0.20	0.52	Changsha Wing Hing High-Tech New Materials Co., Ltd., China
WC	0.45	6.19	0.07	0.29	Changsha Wing Hing High-Tech New Materials Co., Ltd., China
Ni	2.65	0.10		0.10	Chengdu Nuclear 857 New Materials Co., Ltd., China

68 rpm, with a ratio of ball to powder of 10:1. Secondly, the slurry mixture was dried in a vacuum oven and sieved. Thirdly, rectangular-shaped specimens were pressed in a steel die at a pressure of 300 MPa and thereafter the green plates were sintered in a vacuum furnace of pilot scale at 1440 °C for 1 h, with a vacuum degree of 5 Pa. Lastly, the specimens of dimensions 20 mm × 6.5 mm × 5.25 mm were obtained.

Prior to testing, the microstructure was observed by using an S-4800 scanning electron microscope (Hitachi company, Japan), and the energy dispersive spectroscopy (EDS) model OX-FORD IE-250 attached to the SEM was used to analyze the chemical compositions of surfaces. The porosity was performed by the NEOPHOT (Zeiss, Germany) metallographic microscope. Hardness was tested on the HV-50 Vickers hardness tester, and the WE-100B Universal Material Testing Machine (Changchun testing machine plant, China) was used to test the transverse rupture strength.

Erosion test

The samples presented for this experiment were surface ground and polished to 1 μm surface finish using diamond paste. Before testing, the square area of the working surface and the weight of specimen were measured, and all the parameters were obtained at room temperature (25 °C). In this study, the erosion test was carried out in a slurry with aluminum oxide sand at a concentration of 5 wt.% on the rotating cylinder system. The Al_2O_3 particles were used in this study because of its high hardness (2200–2500 HV), strengthening the erosion effect. The experimental apparatus is illustrated in literature [4,6], and the slurry components used for this study are listed in Table 2. The slurry was prepared in the cylindrical container. Once the engine was started, the specimens were rotating with 360 rpm. Two specimens were placed by the distance of 20 cm. The experimental time of each group was kept constant. After erosion test, the mass of specimens was weighed with a precision electron balance model BSA124S (Beijing Sartorius Co., Ltd., China) with an error of 0.1 mg. The erosion morphology of specimen was examined, using SEM.

Results and discussion

Microstructure and properties of Ti(C,N)-based cermets

The microstructure of cermets is shown in Fig. 1. All cermets show a typical core/rim structure which consists of black core and gray rim [4–10]. The formation of the rim phase is related to the dissolution–precipitation mechanism, and the rim phase is divided into relative bright inner rim and grayish outer rim [5,18,19]. The inner rim is formed in the liquid phase sintering stage while the outer rim formed during the solid phase sintering stage. The inner rim contains much W and Mo, and the outer rim enriches Ti element but poor in Mo, W.

Table 2
Slurry concentration of the erosion test.

Velocity (r/s)	Salt concentration (wt.%)	Particle concentration (wt.%)	Erosion time (min)	Particle size (mesh)
360	5	5	60, 120, 180	80–120

It can be seen from Fig. 1 that the mean grain size is not changed obviously, which is in the range of 1.1–1.5 μm. With Mo_2C and WC dissolving in the binder phase, these hard carbides precipitate around undissolved Ti(C,N) to form (Ti,M)(C,N) (M = Mo,W) rim and the solid solution finally prevents further contact with each other of Ti(C,N) [20]. Literatures [4,10,12,18] reported that molybdenum or/and tungsten addition refines the microstructure of cermets, and in this study, results indicate that WC and Mo_2C have a similar and comparable effect on grain refinement in Ti(C,N)-based cermets, as listed in Table 3. Meanwhile, with the increase of WC addition, the rim thickens and the size and shape of undissolved Ti(C,N) core become more inhomogeneous. This phenomenon results from the following explanations. On the one hand, the different dissolution rate of Mo_2C and WC in Ni binder can be taken into consideration. In the sintering process, the dissolution rate depends on chemical affinity between the metal element in the carbide and nitrogen. And the chemical affinity reduces with the increase of metal atomic number. The smaller chemical affinity, the higher formation energy, and the freedom to formation energy of WC are higher than Mo_2C [21]. As a result, the higher relative dissolution rate of WC leads to the thicker rim with the increase of WC content. On the other hand, as the solubility of Mo_2C and WC in the Ni phase is 36 wt.% and 27 wt.% at 1440 °C, respectively [22]. It is reasonable to assume that the solubility of WC is smaller than Mo_2C at room temperature. That is to say, with the same amount of carbide addition, more (Ti,W)(C,N) solid solution precipitates around the undissolved Ti(C,N) core, when compared to Mo_2C. Additionally, the formation of irregular of Ti(C,N) core is due to the following factors. With the Mo_2C content decreasing (et. WC addition increasing), the dissolution in the Ni phase of carbides decreases and the Ti(C,N) content dissolved in the binder phase increases, and finally the size of cores is reduced.

The property of Ti(C,N)-based cermets is listed in Table 3. It can be clearly seen that the porosity increases with the increase of WC addition. An explanation is due to the decrease of the wettability of the metal phase to rim phase with Mo_2C addition decreasing. The hardness of cermets decreases slightly with the increase of WC content. This result can be attributed to the increase of porosity. As shown in Table 3, there are some gradual changes in the bending strength with variation in WC content; the thickening of rim phase can be taken into consideration. With the increase of WC content, the rim phase becomes much brittler. That is why the bending strength decreases.

Erosion behavior

The weight loss of cermets is presented in Fig. 2. It is clearly seen that the weight loss of cermets increases remarkably with the accumulation of time from 1 h to 3 h. And it is much smaller at the beginning of the erosion process. As erosion occurs initially by the initiation and propagation of microcracks, the extent of material-removal is relatively small. When the impingement time increases, the detachment of small pieces is caused by the continuous impact of erodent. Furthermore, the weight loss has a trend to decrease from cermets T1 to T3, and then increase remarkably with further increase of WC addition. It is clearly demonstrated that cermet T3 has the best erosion resistance.

Fig. 3 shows the eroded morphology of Ti(C,N)-based cermets. It is evident that different molybdenum and tungsten addition affects the erosion behavior of materials remarkably. In Fig. 3(a), fragmented