



# Friction and wear properties of (WAl)C–Co ceramic composites under sea water environment

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## Abstract

In this paper, (WAl)C–Co/fluoride(CaF<sub>2</sub>, BaF<sub>2</sub>, CaF<sub>2</sub>/BaF<sub>2</sub>) self-lubricating ceramic composites were prepared by mechanical alloying and hot pressing sintering. The tribological behavior of the composite under sea water environment was evaluated. [(W0.67Al0.33)C0.67–10 wt% Co]/10 wt% CaF<sub>2</sub> composite show a coefficient of friction of 0.15 and a wear rate of  $1.3 \times 10^{-5}$  mm<sup>3</sup>/(Nm) under 60 N at 0.067 m/s. Sea water play a key role on improve the tribological behavior of the composites through form Al<sub>2</sub>O<sub>3</sub> and H<sub>2</sub>SiO<sub>3</sub> (SiO<sub>x</sub> after wear) on the worn surface.

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## 1. Introduction

Tungsten carbide/cobalt (WC–Co) cemented carbides, which characterized by high hardness and strength, are preferred to be used as materials where high wear resistance and toughness are required [1–5]. In fact, WC ceramic composites are also ideal wear resistant materials and have been widely reported [6–9]. Bonny et al. noticed that the volumetric wear rates of WC–10 wt% Co alloys were between  $7.7 \times 10^{-9}$  mm<sup>3</sup>/(Nm) and  $1.8 \times 10^{-8}$  mm<sup>3</sup>/(Nm) after a 10 km sliding distance. The addition of Cr<sub>3</sub>C<sub>2</sub>/VC during sintering can significantly enhance the wear performance of WC–10 wt% Co alloys by increasing hardness and/or reducing grain size [10]. It was demonstrated that when added a little amount of pseudo-elastic TiNi powder (around 10 wt%) to WC–60Co, the wear resistance of WC–60Co composite will increase markedly. The role of pseudo-elastic TiNi phase is helped to reinforce the Co matrix and render it tougher. While, when the added content of TiNi exceeded 10 wt%, the positive effect of TiNi can be weakened by the formation of pores [11].

Saito et al. carried out the wear tests of 13 different WC cemented carbides which have different contents of Co and grain sizes of WC coupled with carbon steel under dry condition using a block-on-cylinder type wear test machine. They found that the specific wear rate increases with the contents of Co and grain sizes of WC increase and all in the  $10^{-7}$  mm<sup>3</sup>/(Nm) range [12]. Their study also shows that binders mean free path (which is a function of WC grain size and volume fraction) of WC is a very important parameter on affects the abrasion resistance of WC coatings [13].

In recent years, the corrosion resistance of tungsten carbide based composites have caused for a lot of attentions. Zhang et al. reported that the addition of Mo can enhance the corrosion resistance of WC–TiC–Ni hard-metals though the formation of new (Ti, W, Mo) C phase based on TiC, and enhance the pitting corrosion resistance due to the formation of MoO<sub>3</sub> film [14]. The erosion–corrosion mechanism maps of WC/Co–Cr based composite coatings were given by Stack et al. [15,16]. Consequently, the corrosion resistance of the tungsten carbide based composites can be very strong.

We have reported that (WAl)C–Co/fluoride(CaF<sub>2</sub>, BaF<sub>2</sub>, CaF<sub>2</sub>/BaF<sub>2</sub>) hard materials possess good mechanical properties and self-lubricating properties under dry sliding friction and

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wear. In this paper, we focus on the corrosion resistant and wear resistant behavior of (WAl)C–Co/fluoride( $\text{CaF}_2$ ,  $\text{BaF}_2$ ,  $\text{CaF}_2/\text{BaF}_2$ ) self-lubricating ceramic materials. We hope that the composite can make use of the wear resistant and corrosion resistant of WC matrix to work as a new self-lubricating ceramic composite under sea water environment. The wear mechanism of (WAl)C–Co/fluoride( $\text{CaF}_2$ ,  $\text{BaF}_2$ ,  $\text{CaF}_2/\text{BaF}_2$ ) self-lubricating ceramic composites under sea water environment also has been investigated.

## 2. Experimental details

### 2.1. Preparation of (W0.67Al0.33)C0.67 alloy and (W0.67Al0.33)C0.67–Co/fluoride composite

Aluminum, tungsten, carbon, cobalt and fluorides ( $\text{CaF}_2$ ,  $\text{BaF}_2$ ,  $\text{CaF}_2/\text{BaF}_2$ ) were used as raw materials to prepare (WAl)C–Co/fluoride materials. The preparation method of  $\text{BaF}_2/\text{CaF}_2$  eutectic powders (which were prepared in the authors' laboratory) has been reported in [17]. The (W0.67Al0.33)C0.67 alloy was prepared by mechanical alloying and solid state reaction [18]. The (W0.67Al0.33)C0.67, cobalt and fluorides powders were put into a steel container. The ball-to-powder ratio in weight is 5:1, and argon atmosphere is used in the milling process. Then ball milled the powders with the following ratio: [(W0.67Al0.33)C0.67–10 wt% Co]/10 wt% fluorides for 10 h. The mixtures were sintered for 10 min at 1400 °C under a pressure of 40 MPa in an inductive hot-pressing vacuum furnace, with a heating rate of 10 K/min. Each specimen was cut to a size of 2 cm × 2 cm × 5 mm.

### 2.2. Characterization

The densities of the sintered specimens were tested using the Archimedes' method. The theoretical density of (W0.67Al0.33)C0.67 solid solution is reported as 11.56 g/cm<sup>−3</sup>, which is lower than that of WC (15.63 g/cm<sup>−3</sup>) [5].

The microhardness of specimens was tested using a MH-5 tester by normal loads of 0.3 kg and 1 kg respectively, with a dwell time of 15 s. The measurement for each sample was carried out at least ten times, and the data of each specimen given in the Table 1 [5] is the average value. The compositions and properties of (W0.67Al0.33)C0.67–10 wt%Co/10 wt% fluoride materials are given in Table 1. The tribological tests were evaluated on a HSR-2M pin-on-disk tribometer (Zhong Ke Kai Hua Corporation, China) under sea water lubrication.

Fig. 1 gives the configuration of HSR-2M pin-on-disk tribometer. The sea water was prepared according to the standard of ASTM 1141-98 (Table 2). The PH value of sea water was adjusted to 8.2 by using 0.1 mol/L NaOH solution. Before test the specimens were polished by diamond disks until the roughness (Ra) of polished surfaces was about 0.3–0.5 mm (Ra). The counterpart is commercial SiC ceramic ball with a diameter of 6.43 mm. The selected loads and speeds are 20 N, 40 N, 60 N and 0.033 m/s, 0.067 m/s, 0.100 m/s, respectively. The coefficient of friction (CoF) was recorded automatically, and the values at the steady-state sliding were reported herein. The wear rate ( $W$ ) is defined as wear volume ( $V$ ) divided by total sliding distance ( $S$ ) and applied load ( $N$ ). The wear volume was defined as  $V=AL$ , in which  $A$  is the cross-section area of wear track, and  $L$  is the circumference of the worn track. The cross-section profile of the worn surface was measured by a surface profilometer.

The specimens were examined by JSM-5600LV scanning electron microscope (SEM). The phase compositions were analyzed using X-ray diffraction (XRD, Philips X'Pert-MRD X-ray diffractometer, 40 kV, 30 mA and  $\text{CuK}\alpha$ ). The chemical states of elements on the worn surface were examined using a PHI-5702 multifunctional X-ray photoelectron spectroscope (XPS). The XPS analysis used Al  $\text{K}\alpha$  radiation as the exciting source and the binding energy of carbon contaminant (C1s-284.8 eV) as the reference. Before observations, samples were cleaned with acetone and then dried in hot air.

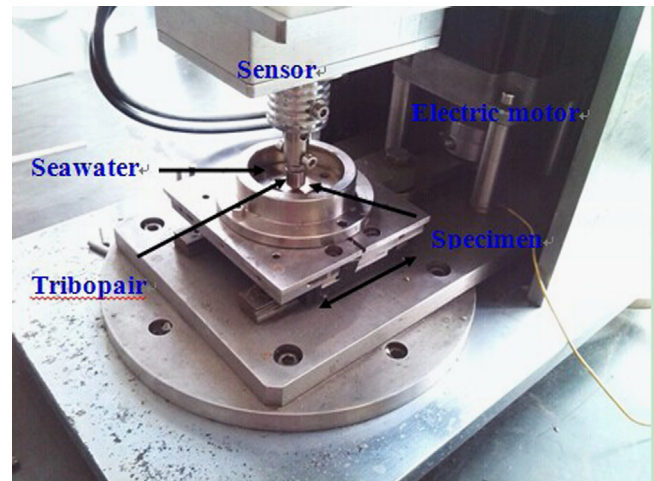


Fig. 1. The configuration of HSR-2M pin-on-disk tribometer.

Table 1

The densities and hardness of the (W0.67Al0.33)C0.67–Co/fluoride materials prepared by hot-pressing sintering.

Nr	Composite materials (mol%)	Theoretical Density (cm <sup>3</sup> )	Experimental Density (cm <sup>3</sup> )	HV0.3 GPa	HV1 GPa
WA1	[(W0.67Al0.33)C0.67–10 wt% Co]–10 wt% $\text{CaF}_2$	8.95	9.03	12.5 ± 1.0	9.6 ± 1.1
WA2	[(W0.67Al0.33)C0.67–10 wt% Co]–10 wt% $\text{BaF}_2$	9.93	10.97	15.8 ± 1.1	13.1 ± 1.3
WA3	[(W0.67Al0.33)C0.67–10 wt% Ni]–10 wt% ( $\text{CaF}_2$ – $\text{BaF}_2$ )	9.50	10.70	12.2 ± 1.0	9.8 ± 1.1

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