



# A novel approach to fabricate hybrid materials with excellent tribological properties from spray-formed ceramic

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## ABSTRACT

A novel method was introduced in this article to fabricate hybrid materials by virtue of thermal sprayed ceramic coatings as templates to improve their tribology performance. MoS<sub>2</sub> was in-situ synthesized in the pores and micro-cracks of ceramic coatings using hydrothermal method coupled with vacuum impregnation. The resultant MoS<sub>2</sub> appeared flowerlike microsphere structure and constructed with many ultrathin nanosheets, which were curly and interconnected to grow in the pores and micro-cracks of ZrO<sub>2</sub> coatings. The results of tribological test revealed that the composite coatings have excellent tribological properties due to the formation of MoS<sub>2</sub> lubricating film on frictional surfaces in comparison with pure ZrO<sub>2</sub> coatings.

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## 1. Introduction

Ceramic materials have been extensively used in industrial field due to their high hardness, excellent wear- and corrosion- resistant as well as good anti-oxidation ability [1,2]. Ceramic coatings fabricated by thermal spraying could endow metal substrates with various outstanding properties [3,4]. The high hardness of ceramic materials gives the coatings outstanding anti-wear properties but usually leads to the serious wear of metallic pairs [5], which would result in the diminution of the size or volume of metal components. Eventually, their expected functionality would be deprived. Thus, it is crucial to reduce the wear between ceramic coatings and metallic pairs. The introduction of lubrication phases in the ceramic coatings could improve the lubricating property of the coatings [6,7]. However, for thermal spraying coatings, the traditional solid lubricants (graphite, MoS<sub>2</sub>, etc.) are apt to oxidize in the presence of oxygen on account of the ultra-high temperature of plasma flame core [8]. Therefore, it is still a challenge to prepare thermal sprayed coatings including with traditional solid lubricants. Besides, pores and micro-cracks exist in the coatings inevitably due to the intrinsic characteristics of thermal sprayed technology. These defects decrease the mechanical properties, thereby affecting the friction behavior [9,10]. Thus, by means of ingenious design, introducing the solid lubricant into the micro-cracks and

pores of ceramic coatings could improve the friction and wear behavior of friction pairs.

Based on the above analysis, in the present research, the ZrO<sub>2</sub> ceramic coatings were fabricated via atmospheric plasma spraying. The lubricant MoS<sub>2</sub> was synthesized through a hydrothermal method in the pores and micro-cracks of as-sprayed ZrO<sub>2</sub> coatings. The microstructure of synthesized MoS<sub>2</sub> was studied. Afterwards, the tribological properties of the compound coatings were investigated compared with pure ZrO<sub>2</sub> coating.

## 2. Experimental section

The ZrO<sub>2</sub> ceramic coatings were deposited on 316 stainless steel substrates (φ25 × 7.8 mm) by an APS-2000A system (Institute of Aeronautical Manufacturing Technology, Beijing, China). The as-sprayed coatings were mechanically polished to a surface roughness Ra ≈ 0.21 μm, followed by ultrasonically cleaning in acetone. MoS<sub>2</sub> was in-situ synthesized by the hydrothermal method. A mixture of 1.87 g Sodium molybdate and 2.77 g thiourea were dissolved in 80 mL deionized water and magnetic stirred for 30 min. The polished specimen were immersed in the homogeneous solution and put in an ultrasonic bath for 10 min and then placed in a vacuum chamber for 10 min under 60 mmHg vacuum level. After repeating the above steps for three times, the solution with the samples was transferred into a 150 mL Teflon-lined stainless steel autoclave and was heated at 220 °C for 48 h. After that, the autoclave cooled down to room temperature naturally.

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The friction and wear tests were performed by a ball-on-disc tribometer (CSM Instrument, Switzerland) with a reciprocating mode. Metallic balls (1Cr18Ni9Ti) with a diameter of 6 mm were used as the counterpart. All experiments were conducted at room temperature of  $20 \pm 2^\circ\text{C}$ , relative humidity of  $30 \pm 5\%$ , a sliding velocity of 5 cm/s, the load of 5 N, amplitude of 2.5 mm and a total sliding distance of 100 m. The wear morphologies of coupled balls were described using a Micro-XAM-3D non-contact surface profiler (USA). The wear rates ( $W$ ) of the coatings are calculated as:  $W = V/PL$ , where  $V$  is the wear volume loss ( $\text{mm}^3$ ),  $P$  is the load (N) and  $L$  is the sliding distance (m). The maximum depth of worn track ( $h$ ) is calculated by the volume of spherical cap ( $V_1$ ) and wear volume ( $V_2$ ) of coupled ball:

$$V_1 = \pi h^2(3R - h)/3 \quad (1)$$

$$V_2 = \pi b^4/64R, \quad (2)$$

where  $b$  is the wear scar diameter and  $R$  is the radius of the ball.

### 3. Results and discussion

The XRD pattern of the powders synthesized via hydrothermal reaction is shown in Fig. 1(a). It can be observed that all the diffraction peaks are in good agreement with that of hexagonal  $\text{MoS}_2$  (JCPDS No. 73-1508, molybdenite). Besides, no characteristic peaks of other impurities are detected, demonstrating that the sample fabricated by hydrothermal reaction is highly pure. The morphology and size of  $\text{MoS}_2$  are elucidated by SEM (Fig. 1(b)) and TEM (Fig. 1(c)). From Fig. 1(b), the samples exhibit microsphere structure composed of many lamellae. High-magnification SEM image of region "A" and TEM indicate that the size of lamellae is very thin with a thickness of about 10 nm, which interweaved together and formed the microsphere structure.

As shown in Fig. 2(a), the  $\text{ZrO}_2$  coatings with a thickness of about  $345 \mu\text{m}$  are uniformly deposited on the substrate. The pores and micro-cracks display on the fracture surface of pure  $\text{ZrO}_2$  coating, and the fracture surface is relatively smooth (Fig. 2(b)). However, the fracture surface of the composite coating (Fig. 2(c)) is

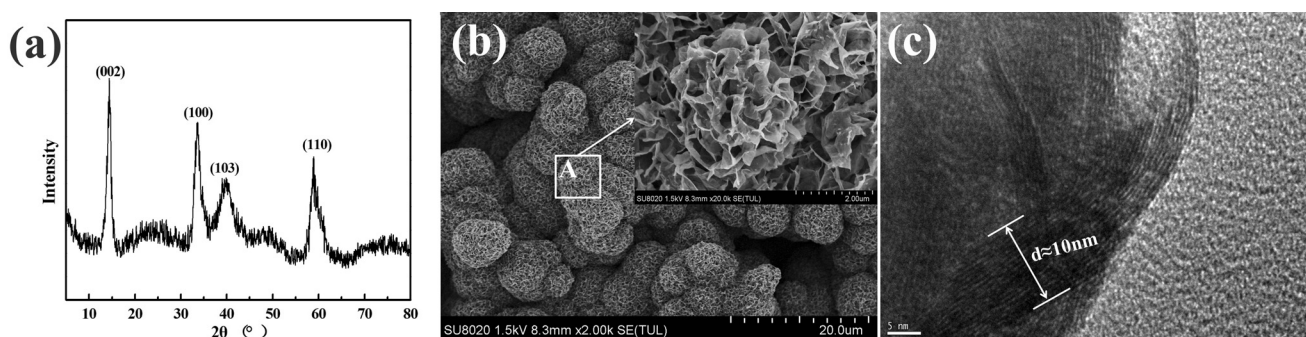


Fig. 1. The XRD pattern (a), SEM (b) and TEM (c) images of the resultant  $\text{MoS}_2$ .

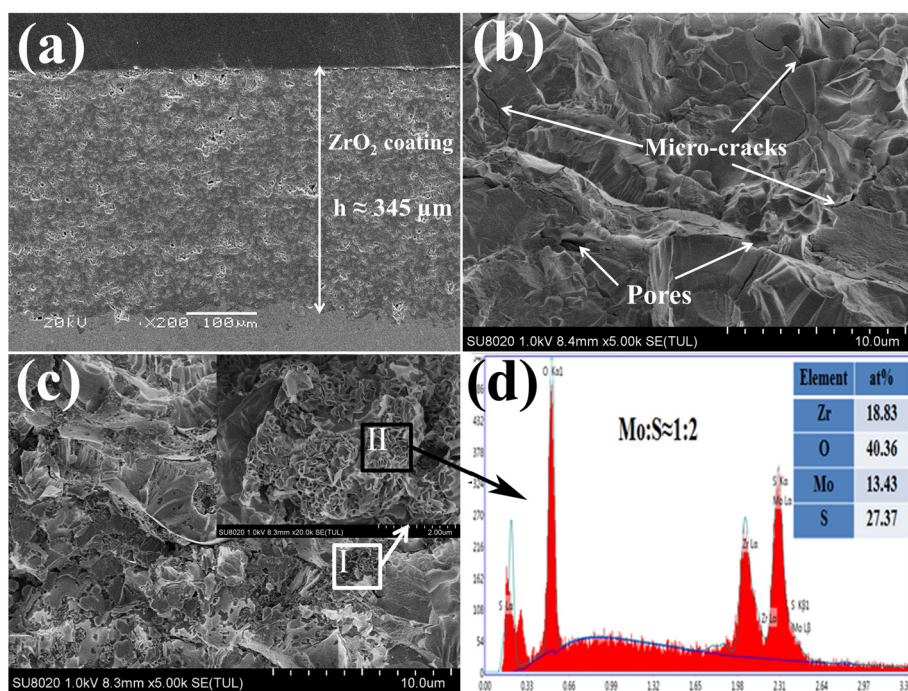


Fig. 2. The SEM images of cross-section (a) and fracture surface (b) of  $\text{ZrO}_2$  coating and the fracture surface (c) of composite coating and EDS analyses (d).

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