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Response of a molybdenum alloy to plasma nitriding

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ABSTRACT

A molybdenum alloy (TZM: 0.50 wt% titanium, 0.08 wt% zirconium and 0.02 wt% carbon with balanced molybdenum) was used to investigate its response to plasma nitriding in terms of layer formation and hardening at temperatures between 500 and 760 °C using various times. A thin hard nitride case plus a shallow diffusion zone was formed after plasma nitriding. The thickness of nitride layer increased with the treatment temperature and time. The nitrided surface of molybdenum alloy had a low coefficient of friction against the Al_2O_3 counterpart ball at ambient atmosphere and elevated temperatures, and the wear resistance of the surface was greatly improved. Molybdenum had a tendency to react with nitrogen to form a mixed nitride phases at the tested temperature range, and the TZM alloy had an activation energy of 330 kJ/mol.

1. Introduction

When sintering high-strength materials at high temperatures, the major technical problems associated with traditional graphite dies in an electric-field-activated sintering technology (FAST) process, are their premature failure or short lifespan related to the low mechanical strength at elevated temperatures. Therefore tools (dies/punches) have to be made from superalloys, refractory metal alloys or even ceramics [1]. Titanium-Zirconium-Molybdenum (TZM) alloy is a great choice due to its stability and strength at elevated temperatures up to 1500 °C. In addition, TZM exhibits good thermal conductivity, high electrical conductivity and low coefficient of thermal expansion which make the materials resistant to thermal shock and cracking arisen when the tool surface experiencing cycles of rapid heating and cooling [2]. After sintering, the ceramic micro-parts need to be pushed to slide out the mould off-site or on-site depending on the production system setup and throughput. However, when the size of the tools and components is scaled down to millimetre-scale, soldering due to severe adhesion between the mould and the working material would occur and thus demoulding becomes a major challenge for Micro-FAST process.

In our earlier work on the sliding test between TZM and the ceramic materials (i.e. Al_2O_3 and Si_3N_4), it was found that the friction was high and had an adhesive character between TZM and Al_2O_3 counterpart ball which was not beneficial for a smooth demoulding, and thus some surface modifications or coatings were needed to improve the surface tribological properties [3]. Many attempts have been made to improve hot-working tools, such as surface welding, thermal spraying, electrodepositing, diffusion treatments and thermal chemical treatment like nitriding and carburising etc. Nagae and his colleagues nitrided pure molybdenum at 1100 °C in NH_3 gas for 16 h, and reported a molybdenum nitride surface layer formation which consists of a γ-Mo_2N outer layer and a β-Mo_2N inner layer [4]. However, Martinez's work found that no nitrogen absorption could happen under 800 °C in molybdenum and the reaction started between 800 and 1500 °C in a gas nitriding with forming gases (N_2 + H_2). He attributed the slow nitriding of TZM to the existence of titanium, which is a strong nitride forming element [5]. It is widely known that the titanium alloys also need a high temperature (700–1000 °C) to be effectively nitrided [6]. High-temperature treatments generally led to recrystallization of the deformed molybdenum, and the forming gases, i.e. ammonia, embrittled the material [5], therefore the research on nitriding of molybdenum stalled for a long time. Recently, it was reported that molybdenum can be nitrided at a much lower temperature with the help of plasma. Jauberteau and his colleagues found that a deposited molybdenum layer could be nitrided at 600 °C in a gas mixture of argon, nitrogen and hydrogen by using an expanding microwave plasma reactor for an exposure time of 20 min [7]. They also claimed that Mo–N phases could be formed in molybdenum films even at a temperature as low as 400 °C, although the electron beam evaporation deposited molybdenum layer was very thin (400–600 nm) [8]. Their researches shed some light on plasma nitriding of molybdenum-based alloys at lower temperature, which has been widely reported to increase the surface hardness as well as the wear and corrosion resistance of hot-working tools [9]. Therefore it necessitates this research on plasma nitriding the molybdenum alloy at a lower temperature (< 800 °C) to challenge the previous high temperature gas nitriding.

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In the current research, DC plasma nitriding of TZM alloy between 500 and 760 °C was designed to investigate the response of molybdenum-based TZM alloy to the treatment temperature and time. The friction and wear behaviour of the nitrided and untreated TZM samples were compared by reciprocating sliding tests against Al_2O_3 at room temperature and unidirectional sliding at elevated temperature to simulate the demoulding of micro-ceramic sintering parts off-site or on-site.

2. Experimental

2.1. Design of the plasma nitriding processes

A molybdenum-based TZM alloy bar provided by *Edfagan Europe Inc.* was used in this study. It has a density of 10.22 $g{\cdot}cm^{-3}$ and chemical compositions of 0.50% titanium, 0.08% zirconium and 0.02% carbon (in wt%) with balanced molybdenum. Coupons of $\Phi 25 \times 4.5$ mm were sectioned and wet ground with SiC paper down to 1200 grit, followed by progressive polishing with 9, 6 and 1 μm diamond paste to generate a mirror-like finish.

Plasma nitriding was carried out in a 60 kW Klöchner DC plasma furnace at a pressure of 4 mbar. A DC voltage from 300 to 1000 V was applied between the sample (cathode) and the wall of the furnace (anode) during the process. The treatment temperature was measured with a thermocouple inserted in a hole in the jig. Temperature and duration increased gradually until a clear nitriding layer was observed (660/25). 13 batches of samples were plasma nitrided with a gas mixture of 25%N_2 and 75%H_2 at temperatures ranging from 500 to 760 °C for varied times. Detailed treatment conditions and the corresponding sample codes are listed in Table 1.

2.2. Characterization of the surface layers

The surface morphologies and microstructure of the plasma nitrided specimens were observed under scanning electron microscopy (JEOL 7000 SEM). The surface roughness was assessed by a XP-200 Plus Stylus 3D-profilometer. The phase constitution of the plasma nitrided layers was identified by X-ray diffraction (Philips X'pert X-Ray diffractometer) using a Cu-K_α radiation ($\lambda = 0.154$ nm). The chemical compositions of the layers were analysed using a glow discharge spectroscopy (GDS, LECO GDS-750 QDP), which allowed for continuous depth profiling for Mo and N. Metallographically prepared cross-section samples without etching were used for nano-hardness profiling using a nano-indenter (Micro Materials Ltd.) under a load of 20 mN. The surface microhardness was measured by a Vickers microhardness tester (Mitutoyo MVK-H1) under a load of 25 gf. Specimens were electrically etched in a phosphate solution for layer structure observation by JEOL 7000 SEM equipped with an Energy Dispersion X-ray (EDX) for the localised composition analysis. An X-ray photoelectron spectroscopy (XPS) was used to analyse the elemental valences on the nitrided surface.

Table 1
Detailed plasma nitriding conditions and the corresponding sample codes.

Sample code	Temperature (°C)	Duration (hour)
500/5	500	5
550/10	550	10
600/20	600	20
660/25	660	25
720/12.5	720	12.5
720/25		25
720/37.5		37.5
720/50		50
720/62.5		62.5
720/75		75
760/8	760	8.33 (500 min)
760/16		16.67 (1000 min)
760/25		25 (1500 min)
Untreated	–	–

2.3. Evaluation of the friction and wear properties of the surface layers

Friction and wear properties of the untreated and treated samples were assessed via a TE79 multi-axis tribology machine (Compend 2000 Version 2.3.1) in reciprocating mode at room temperature with a 8 mm in diameter Al_2O_3 ball as the counterpart under the loads of 2, 5, 10 and 20 N respectively. The whole tribo-tester was enclosed in a chamber with transparent walls to avoid dust and air turbulence. The reciprocating sliding wear tests were conducted in air, in nitrogen by nitrogen purging, in distilled water and in simulated seawater containing 3% NaCl by filling the liquid into the container. The reciprocating sliding distance was set to 5 mm, the sliding speed was 10 mm/s, and the coefficient of friction (CoF) was recorded for 1000 cycles. Each reciprocating test was repeated 2–3 times until a stable curve was obtained, and only the positive side (one direction) was plotted as the value of CoF was symmetrical.

Unidirectional sliding wear tests were conducted using the CSM HT pin-on-disc tribo-tester under a load of 2 N with an Al_2O_3 ball of 6 mm in diameter at a unidirectional sliding speed of 10 cm/s for 5000 cycles at three different temperatures: room temperature (20 °C), 300 °C and 600 °C.

The wear tracks of the samples were measured utilising a XP-Plus Stylus Profilometer and the wear volumes were calculated accordingly. The morphology of the wear tracks was observed under SEM and the composition of the tracks was analysed by EDX.

3. Results

3.1. Surface morphology and roughness

The original shining metallic colour of the specimens was changed to varying bands of greyish after plasma nitriding treatments at 720 °C or under, and a typical one is shown in Fig. 1a (720/25). The surface colour turned into dark grey with extended treatment time like 720/50 and 720/75. At 760 °C, the specimen surfaces were dark and grey and lack of metal lustre after 8.3-hour treatment and turned totally brownish after 25-hour treatment (Fig. 1a right & Fig. 1b).

The surface roughness was measured across a 0.5 mm length and the typical Ra value of a polished untreated TZM surface is about 0.01 μm. The Ra value was about 0.05 μm after plasma nitriding treatment of 660/25 and 720/25 as seen in Fig. 2. The surface roughness was rapidly increased for treatment time longer than 37.5 h at 720 °C. When treated at 760 °C for 25 h (760/25), the surface became very rough with a Ra value of 0.1933. Generally, longer treatment time and higher treatment temperature led to a rougher surface.

3.2. Surface layer structures

Cross-sectional SEM observations on all the nitrided samples revealed that a dense surface layer with some spikes along certain directions was formed (Fig. 3a&b). There hardly any diffusion zone can be discerned under the hardened layer. For the samples treated at the higher temperature (760/25), three layers in the nitride case can be distinguished under backscattering electron image as denoted by dashed lines in Fig. 3c. The superficial layer is very thin and irregular, and the second and third layers are interlocked each other but with dark and light contrast respectively.

3.3. Nitrogen distribution after plasma nitriding treatment

The typical elemental distribution trends of nitrogen of the samples treated at 720 °C against treatment time are shown in Fig. 4. The depth of the nitrogen rich layer increased with the progress of the treatment

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