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Oxidation behaviour of PACVD TiBN coating at elevated temperatures

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ABSTRACT

The elevated-temperature oxidation behaviour of a TiBN coating on a plasma-nitrided hot-work tool steel (DIN 1.2367) by means of plasma-assisted chemical vapour deposition (PACVD) was investigated under the condition where a coated die would be preheated prior to being mounted on the press for aluminium extrusion. The TiBN coating was found to possess good resistance to oxidation up to 400 °C. Rapid oxidation started to occur at 450 °C. Radio frequency glow discharge optical emission spectroscopy (rf-GDOES) indicated that the oxidised layer was thickened from 100 nm to 1.0 μm, as the soaking time at 500 °C was prolonged from 2 to 16 h, which was attributed to the high temperature that promoted the penetration of oxygen into the coating. rf-GDOES also showed that boron initially in the coating vanished from the oxidised layer when the temperature was 450 °C or higher. X-ray diffractometry confirmed that the oxidised layer was composed mainly of TiO_2. SEM revealed that the TiO_2 layer was pulverised, leaving many microcracks and cavities, as a result of the losses of boron oxide and nitrogen. The rapid oxidation at above 450 °C was attributed to the pulverised TiO_2 layer that was unable to hinder the diffusion of oxygen into the coating. It is therefore recommended to apply a protective gas during the preheating of the TiBN-coated die for aluminium extrusion. Alternatively, an advanced TiBN coating with enhanced resistance to oxidation must be developed, which will be conducive to its application for aluminium extrusion dies.

1. Introduction

TiBN ternary coatings are of great industrial value, considering their prominent mechanical and tribological properties, such as super-hardness, low intrinsic stress and high wear resistance [1–3]. These coatings have been successfully applied to cutting tools, die-casting moulds, forging dies, aluminium extrusion dies, etc. Marked increases in lifespan and productivity have been achieved [4–7]. TiBN coatings developed so far have different compositions and structures in connection with a variety of processes employed, such as magnetron sputtering [8,9], physical vapour deposition (PVD), chemical vapour deposition (CVD) and plasma-assisted chemical vapour deposition (PACVD) [10–12]. For any of TiBN coatings, one of the important criteria for industrial application remains the same, i.e. thermal stability and oxidation resistance. For coated cutting tools and die-casting moulds, for example, the working temperature may reach 600–800 °C [4]. For coated aluminium extrusion dies, the preheating temperature is typically at about 500 °C, soaking time may be as long as 4–5 h, and in most cases no protective gas is applied [13,14]. Therefore, for these applications, the thermal stability and oxidation resistance of TiBN coatings will have a profound influence on the performance of the coated tools, moulds and dies during service.

In recent years, many investigations on the thermal stability of TiBN coatings have been carried out. It is known that TiBN coatings are thermally stable at a post-deposition annealing temperature higher than 900 °C and post-annealing hardness higher than that in the as-deposited condition may be achieved [15–17]. However, few research efforts have been made to evaluate the oxidation resistance of TiBN coatings at elevated temperatures. Lu et al. studied two TiBN coatings with a difference in chemical composition and found significant differences in oxidation behaviour over a temperature range of 600 to 1000 °C [8]. Héau et al. noticed that the mass gain of a $TiN_x(B)_y$ coating started at 627 °C. Over a temperature range of 727 to 977 °C, the coating was completely oxidised to TiO_2 and the mass remained almost unchanged [9]. There is a lack of understanding of the oxidation resistance of TiBN coatings at the typical temperatures to which they are exposed prior to or during service, typically at 400–550 °C where, for example, a coated die for aluminium extrusion is preheated in an air furnace.

The objective of the present research was to understand the oxidation behaviour of a PACVD TiBN coating with compositional gradients deposited on a hot-work tool steel during thermal treatments at 400–550 °C in the ambient surrounding that resembled the preheating condition of the coated die for aluminium extrusion. It was hoped that the understanding of the oxidation behaviour and oxidation mechanisms would be of use for making recommendations as to the need of applying protective atmosphere during the preheating of the coated die.

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2. Experimental details

A TiBN ternary coating with compositional gradients was deposited on a DIN 1.2367 (X40CrMoV53) hot-work tool steel substrate using a PACVD-coating system with a bipolar DC voltage-controlled pulse generator. Prior to coating deposition, the steel substrate was subjected to a tempering heat treatment to achieve a hardness value of 50 HRC. The substrate was then plasma-nitrided in the PACVD equipment to create a nitrided diffusion layer with a thickness of about 120 μm without a compound layer. Plasma nitriding was performed in a mixture of H_2, Ar and N_2 under a total pressure of 300–600 Pa. Substrate temperature was kept at 400–530 °C so as to retain the hardness of the as-tempered tool steel. During coating deposition, a very thin TiN layer was first deposited for the purpose of enhancing adhesion to the substrate before TiBN coating deposition started. During subsequent coating, the BCl_3 partial pressure was increased in order to increase the boron concentration in the coating toward the coating surface where high hardness and wear resistance were desired. Process parameters such as gas flow, wall heat, voltage, pulse-on and pulse-off times, and chamber pressure were closely controlled with a programmable logic controller (PLC). H_2, Ar, N_2, BCl_3 and $TiCl_4$ vapour were used as process gases for coating deposition. Pressure was kept at 70–150 Pa and substrate temperature at 530 °C in order to avoid exceeding the tempering temperature of the hot-work tool steel. The TiBN coating thickness was controlled at approximately 3 μm.

To simulate the preheating condition of PACVD coated aluminium extrusion dies physically, TiBN-coated samples with a cubic shape and sizes of 8×8×8 mm were subjected to thermal treatments at 400–550 °C for 2–16 h in the ambient atmosphere in a chamber furnace, followed by air cooling. The samples were cleaned using ethanol in an ultrasonic bath, prior to microstructure examination and chemical analysis.

The surface morphology and cross-section microstructure of the TiBN coating in the as-deposited state were determined by using a Jeol JSM 6500F scanning electron microscope (SEM) for comparison with those after the thermal treatments. The phases and crystallographic structures of the as-deposited and as-oxidised coating were examined by means of a Bragg–Brentano X-ray diffractometer (XRD) where the Co *Kα* line at 0.179026 nm was used as the source for diffraction. Chemical composition profiles on the cross section of the coating in both the as-deposited and as-oxidised states were quantitatively analysed using LECO's GDS-750A radio frequency glow discharge optical emission spectroscopy (rf-GDOES). The sputtering diameter on the sample was 4 mm. RF-mode was run at 700 V plus 14 W as the true power and Ar pressure was typically 9 Torr (120 Pa). The sputter rate was 4–5 μg/s. Spectral wavelengths were as follows: Ti: 365.350, N: 149.262, B: 182.641, O: 130.217, C: 165.701, Cl: 134.724, Cr: 2425.433, and Fe: 2371.994 nm.

3. Results

3.1. Colour change

The PACVD TiBN coating in the as-deposited condition was silver-golden in colour (Fig. 1a). After thermal treatment at 400 °C for 4 h, the colour remained essentially unchanged. However, after thermal

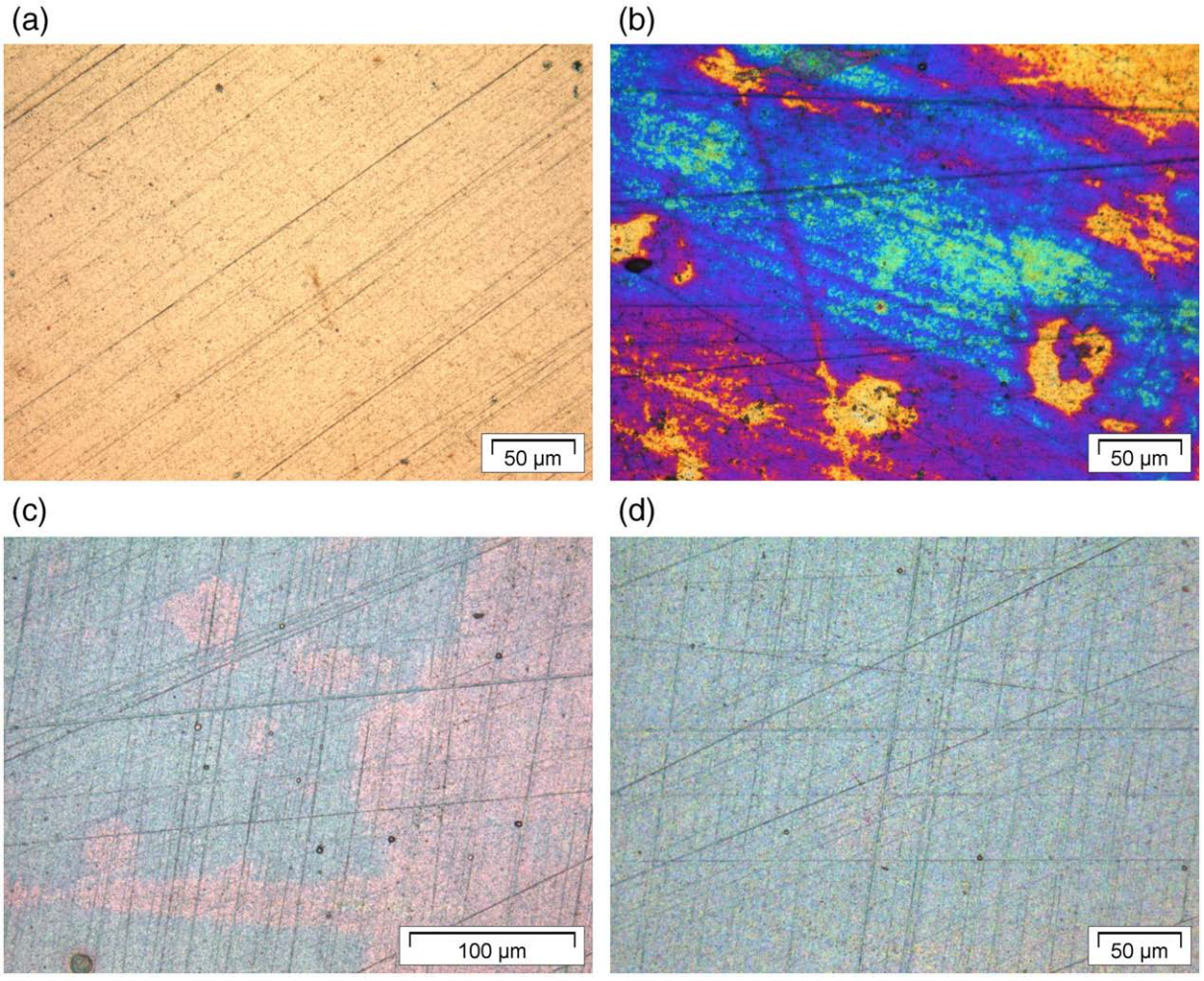

Fig. 1. Colour changes of the TiBN coating surface from (a) the initial as-deposited state as a result of thermal treatments at (b) 450, (c) 500 and (d) 550 °C for 4 h.