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The influence of the depth of a plasma nitrided layer in tool-steel substrate on the scratch-resistant properties of PACVD TiBN coating

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Abstract

A hot-work tool steel was plasma nitrided (PN) to create a diffusion layer beneath the surface. Plasma-assisted chemical vapour deposition (PACVD) was then applied deposit a superhard nano-columnar TiBN coating to the nitrided substrate. The depth of the nitrided diffusion layer was varied to determine its influence on the cohesion and adhesion properties of the coating. Radio frequency glow discharge optical emission spectroscopy (rf-GDOES) revealed multilayers of TiBN and TiN compounds with compositional gradients across the TiBN coating layer. Microhardness measurements ($HV_{0.025}$) across the PN diffusion layer in combination with optical microstructure observation showed that an increase in the depth of the nitrided diffusion layer led to an increase in the maximum hardness at the interface between the TiBN coating and the substrate. The maximum hardness correlated linearly with the scratch-resistant properties determined from scratch tests in the progress mode, notably the critical loads corresponding to the first microcracking related to cohesive failure (L_{C1}), spallation related to adhesive failure (L_{C2}) and worn out (L_{C4}). In addition, the scratching coefficients of the TiBN coating on a thicker PN diffusion layer, determined in a scratch test along a scratch track, were all lower than those on a thinner diffusion layer in the substrate. An excessive depth of the nitrided diffusion layer however caused transverse cracking in the substrate. A nitrided layer with an optimum depth can thus improve the adhesion of the PACVD TiBN coating to the tool-steel substrate and the scratch resistance of the coating.

Keywords: PACVD; Plasma nitriding; Scratch test; TiBN

1. Introduction

Thin coatings, typically TiN, TiCN, TiBN and TiAlN coatings, may be applied to metal-forming and metal-shaping tools such as extrusion dies and die-casting moulds. The lifespan of these tools can be prolonged by a factor of up to 10 or even more due to the high hardness, low scratching and great wear resistance of these thin coatings [1–3]. The key to achieving a prolonged lifespan is the strong adhesion of the hard coating to the substrate made of a tool steel.

Previous researches by means of scratch tests have shown that the critical load, a measure of the adhesion of a hard coating to a steel substrate with a uniform cross-sectional hardness distribution, increases linearly with substrate hardness [4–7]. Nitriding prior to coating leads to the formation of a diffusion layer in the substrate with a hardness gradient (or a non-uniform hardness distribution) and it can greatly improve the scratch resistance of the coating [8–11]. Plasma nitriding (PN) is often applied as a prior treatment to form a diffusion layer at a moderately elevated temperature and to improve the adhesion of the coating to a tool-steel substrate. Then plasma assisted chemical vapour deposition (PACVD) or physical vapour deposition follows. The two-step process, customarily called duplex process, has been commercially applied to tool steels. To evaluate the influence of PN on the scratch resistance of the coating, the present authors [10] proposed the use of four critical loads corresponding to cohesion-related, adhesion-related and wear-related failure events during a scratch test.

Despite the commercial application of the PN plus PACVD duplex process to aluminium extrusion dies, the depth of the nitrided layer remains to be an ambiguous issue. A shallow nitrided layer may not provide an optimum wear resistance of the PACVD coating, as it cannot prevent the eggshell effect

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from taking place. On the other hand, a deep nitrided diffusion layer in an extrusion die with thin walls, for example, for the extrusion of multi-microport tubing, may result in premature failure due to enhanced brittleness [12]. It is therefore of paramount importance to optimise the depth of the nitrided diffusion layer with respect to a balance between the scratch resistance of the coating and the brittleness of the substrate.

In the present research, the depth of the PN diffusion layer in a hot-work tool steel was precisely controlled to create a hardness profile in the substrate prior to coating deposition. Systematic evaluation of the influence of the PN layer depth on the scratch resistance of the PACVD TiBN coating was made through scratch tests in the progressive mode. It was aimed at providing guidelines to determine an optimum PN layer depth that corresponded to a balance between the scratch resistance of the coating and the brittleness of the substrate.

2. Experimental details

A DIN 1.2367 hot-work tool steel (X40CrMoV53) was used as the substrate material and tempered to a hardness value of about 50 HRC. Three substrate samples were subjected to controlled PN treatments in separate batches. PN was performed at a temperature of 520–530 °C in a gas mixture of 10 vol.% N_2 and 90 vol.% H_2 under a total pressure of 300–600 Pa. The duration of PN varied from 30 min to 5 h to create nitrided diffusion layers of different depths, namely 5, 15 and 80 μm. The samples are hereafter referred to as TiBN5, TiBN15 and TiBN80. The depth of the nitrided diffusion layer was defined as the distance from the sample surface to the substrate core where microhardness dropped to 700 HV [13]. For comparison purpose, one substrate sample without PN pre-treatment, denominated as TiBN0, was included in this investigation. A TiBN coating was deposited in the same batch on three substrate samples with the prior PN treatments and one substrate sample without PN, using a commercial PACVD coating system equipped with a bipolar DC voltage-controlled pulse generator. A very thin TiN layer was first deposited for the purpose of enhancing adhesion to the substrate before TiBN coating deposition started. During coating deposition, such process parameters as gas flow, wall heating, voltage, durations of pulse-on and pulse-off time and total pressure were controlled through a programmable logic controller. 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. A coating thickness in a range of 1–2 μm was targeted in deposition process control. The chemical compositions of the coating were quantitatively analysed using a Leco GDS-750A radio frequency glow discharge optical emission spectroscope (rf-GDOES) operating at a true RF power emission of 14 W.

The microstructures of the coating and the substrate with and without prior PN were examined using an optical microscope and a scanning electronic microscope (SEM). The nitrided diffusion layer in the substrate was revealed after being etched in a 5% nitric acid alcohol solution and its depth determined in the optical microscope. A microhardness profile across the nitrided layer was determined using a fully automated OmniMet MHT Microindentation Hardness Testing System. To ensure the reliability of the measurements, the readings under a loading of 25 g were calibrated in the core of the samples with those under the loadings of 100 and 1000 g. Furthermore, the microhardness profile determined was validated at other locations on the same sample twice for reproducibility.

The cohesion and adhesion properties of the coating on the four substrate samples were evaluated using a CSEM® Instruments Scratch Tester. The scratch indenter was a diamond stylus with a spherical tip having a radius of 200 μm. During the test, the load applied was progressively increased from 1 to 200 N at a rate of 10 N/min over a scratching distance of 5 mm. Scratching force, scratching coefficient, the penetration depth of the stylus and acoustic emission were registered along the scratch track. Five scratch tests were performed for each sample to obtain the average values of the critical loads. After the test, the mode of failure at a certain critical load was determined by the *post facto* observation of the scratch track using an optical microscope. The scratch resistant properties of the TiBN coating on these substrate samples were then quantified in terms of the critical loads corresponding to the failure modes as defined in Table 1.

3. Results and discussion

3.1. Chemical composition and morphology of the TiBN coating

Fig. 1 shows the compositional profiles of the coating on the TiBN5 and TiBN80 samples, determined from rf-GDOES quantitative analyses. The coating deposited had varying chemical compositions across a thickness of about 1.2 μm. Over a coating thickness range from null to 0.5 μm, the concentrations of titanium and nitrogen gradually increased from 38 to 47 at.% and from 24 to 33 at.%, respectively, whereas boron concentration kept at the same level of 7 at.%. Over another coating thickness range of 0.5–0.8 μm, titanium concentration stayed at 47 at. %, and nitrogen concentration continuously increased from 33 to 39 at.%, but boron concentration decreased to about 5 at.%. From a thickness of 0.8 μm to the interface with the substrate (at a depth of about

Table 1
Description of critical loads corresponding to different failure modes

Critical load	Description of failure mode
L_{C1}	The first cohesion-related failure event: the first appearance of microcracking, surface flaking inside/outside the track *without* any exposure of the substrate
L_{C2}	The first adhesion-related failure event: the first appearance of cracking chipping, spallation and delamination inside/outside the track *with* the exposure of the substrate
L_{C3}	The first breakthrough: the first exposure of the substrate in the scratch track resulting from wear
L_{C4}	Coating worn out in the track