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Protective over-layer coating preventing cracking of thin films deposited on flexible substrates

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ABSTRACT

The article reports on a special over-layer which protects brittle coatings deposited on flexible substrates against cracking during bending. It is shown that the over-layer with (i) the low effective Young's modulus $E^* = E/(1 - \nu^2)$ resulting in a high ratio $H/E^* \geq 0.1$, (ii) the high elastic recovery $W_e \geq 60\%$ and (iii) the compressive macrostress ($\sigma < 0$) deposited on a brittle coating can prevent its cracking during bending; ν is the Poison's ratio and H is the hardness of the over-layer. The possibility of how to prevent cracking of the brittle coatings is demonstrated experimentally. The over-layer was deposited on the brittle coating which easily cracks when the flexible substrate is bended. In this experiment the Zr–Si–O coating with low ratio $H/E^* < 0.1$, low value of $W_e \approx 50\%$ and tensile macrostress ($\sigma > 0$) was used as the brittle coating and the highly elastic Zr–Si–O coating with high ratio $H/E^* \approx 0.1$, high value of $W_e \approx 70\%$ and compressive macrostress ($\sigma < 0$) was used as the over-layer. Both the brittle coating and the over-layer were prepared by the reactive magnetron sputtering using a dual magnetron. Besides, the mechanical behavior of the coating composed of three and four layers is described in detail. Obtained results can be used in the development of flexible coatings, strengthening of the surface of brittle materials, elimination of cracking of functional coatings and cracking at surfaces of bended materials.

1. Introduction

In recent years, new hard coatings based on nanocomposite materials were successfully developed. The hard nanocomposite coatings exhibit an enhanced hardness and thus they represent a new generation of nanocomposite coatings ([1–16] and references therein). However, up to recently, the main attention was concentrated only on the hardness H of the nanocomposite coating, on methods of the hardness enhancement and on the achievement of the hardness H approaching or even exceeding that of the diamond. Generally, the hardness H is considered as one of the most important mechanical properties of the material but the absolute value of hardness is, however, an insufficient condition to select correctly the nanocomposite material of coating for a given application.

Hard materials are brittle and their brittleness increases with increasing hardness H. The high brittleness of very hard coatings strongly limits their practical utilization due to their cracking under loading. The cracking of brittle materials and coatings during bending and/or loading is well known fact. This undesirable phenomenon, however, results in catastrophic consequences such as is, for instance, the interruption of (i) the protection of substrates by protective coatings and (ii) the function of functional coatings deposited on flexible substrates, the breaking of brittle materials such as the glass, etc. It means that good coatings should exhibit not only the high hardness H but also a sufficient toughness because the coating toughness is in many applications more important than its hardness H [16–23]. Therefore, in the development of new advanced materials and hard coatings it is vitally important to find and master a way how to prevent their cracking or at least to enhance their resistance to cracking. This is the main reason why now many labs over all world try to develop new advanced ceramics with enhanced resistance to cracking, and simultaneously with a sufficiently high (≥20 GPa) hardness. Recently, great attention has been devoted to the development of flexible hard thin films and coatings [24–32].

This article reports on one possible way how the cracking of coatings and the cracking at surfaces of brittle materials can be prevented. This method is based on the deposition of a special over-layer on the brittle coatings. Properties of this special over-layer are described in detail.

2. Principle of prevention of cracking of brittle coatings and at surface of bended brittle materials

It is well known that brittle materials easily crack. During bending of the brittle material, e.g. the brittle strip (foil), on its surface cracks are formed, see Fig. 1. These surface cracks are due to the tension stress $\sigma > 0$ generated in the upper part of brittle strip during bending. On the other hand, the bottom part of brittle strip is in a compression ($\sigma < 0$). In the case of an isotropic material the zero stress $\sigma = 0$ is in the half thickness of the strip. The surface cracks are initiators of

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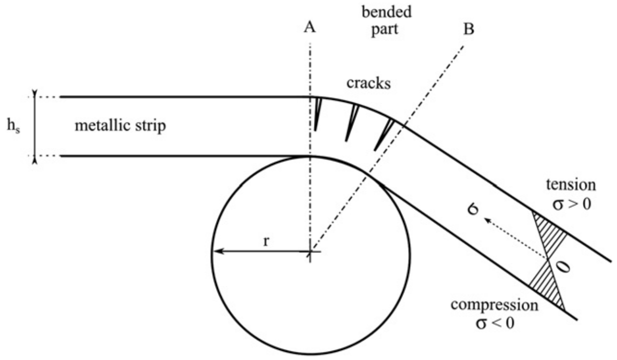

Fig. 1. Schematic illustration of cracks generated at the surface of metallic strip during its bending along the fixed cylinder of radius r and a distribution of stress generated inside the strip. The stress is generated inside the bended part of metallic strip only.

breaking of the brittle materials or coatings. When the coating cracks, its function is interrupted, for instance, the passage of the electric current, the protection of the substrate surface against oxidation, corrosion, erosion, etc. These are serious reasons why the formation of cracks at bended surfaces of brittle materials and coatings should be avoided.

One way, how to avoid cracking of brittle coatings and at surface of bended brittle material is to overcoat the surface by a special over-layer coating. The principle of this method is based on the conversion of the tensile stress at the interface between the bended material and the over-layer coating to the compressive stress. It means that the interface stress $\sigma_{\mathrm{interface}} = \sigma_m + \sigma_c < 0$ must be negative; here σ_m is the macrostress at the surface of bended material and σ_c is the macrostress of the over-layer coating. The interface stress $\sigma_{\mathrm{interface}}$ can be compressive ($\sigma_{\mathrm{interface}} < 0$) only in the case when the macrostress σ_c of over-layer coating is compressive, and its absolute value $|\sigma_c| > |\sigma_m|$ because the macrostress σ_m is tensile ($\sigma_m > 0$), see Fig. 2. In the case when the macrostress σ_c of the over-layer coating is tensile ($\sigma_c > 0$) the formation of cracks is not avoided but, on the contrary, the cracking at the surface of bended material is enhanced. The verification of this hypothesis is the main goal of this paper.

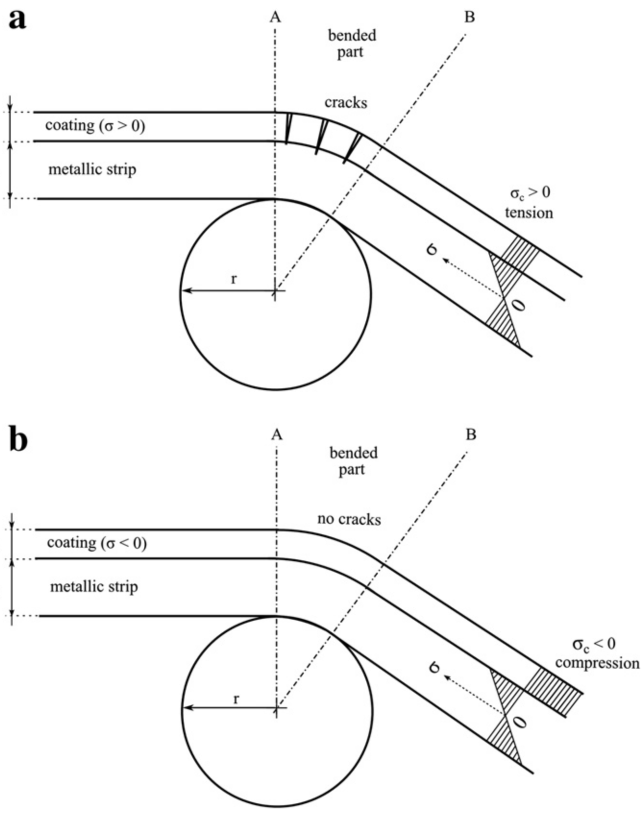

Fig. 2. Schematic illustration of bended metallic strip covered by (a) the coating in tension ($\sigma > 0$) and (b) the coating in compression ($\sigma < 0$).

3. Experimental details

The Zr–Si–O coatings of different physical and mechanical properties were deposited on the Si(100) substrate and the Mo strip ($60 \times 10 \times 0.1$ mm^3) by reactive magnetron sputtering using a dual magnetron equipped with targets of 50 mm in diameter. The dual magnetron was operated in ac pulsed bipolar mode generated by a pulsed power supply DORA MSS-10 with a maximum output power 10 kW. The repetition frequency f_r of pulses was 2 kHz and ac frequency of pulses was 56 kHz. More details on the deposition system are given in references [27].

The deposition of coatings was carried out in two steps. In the first step, only the layer 1 and only the layer 2 were deposited on Si and Mo substrate to determine their physical and mechanical properties and to test their resistance to cracking. The layer 1 is a brittle layer with low ratio $H/E^* < 0.1$, low elastic recovery $W_e < 60\%$ and tensile macrostress $\sigma > 0$. On the other hand, the layer 2 with high ratio $H/E^* \geq 0.1$, high elastic recovery $W_e \geq 60\%$ and compressive macrostress $\sigma < 0$ is the layer with enhanced resistance to cracking. The coatings deposited on Si (100) substrates were used for measurement of their structure, physical and mechanical properties and those deposited on Mo strip for assessment of their cracking by bending test. In the second step, three coatings composed of alternating layers always with the brittle layer 1 on the substrates – (1) layer 1/layer 2, (2) layer 1/layer 2/layer 1 and (3) layer 1/layer 2/layer 1/layer 2 – were deposited on Si and Mo substrates. All layers in the multilayer coating were deposited without exposure to the atmosphere.

The coatings were sputtered under the following conditions: discharge current $I_{da} = 1$ A averaged over the pulse period $T = 1/f_r$, target power density $S_d = P_d/S \approx 25$ W/cm^2, substrate bias $U_s = U_{fl}$, the substrate temperature $T_s = 500$ °C, substrate-to-target distance $d_{s\text{-}t} = 80$ mm, partial pressure of oxygen $p_{O2} = 0.04$ and 0.15 Pa for the layer 1 and 2, respectively, and total pressure $p_T = p_{Ar} + p_{O2} = 1$ Pa; here S is the area of magnetron target and U_{fl} is the floating potential. Physical and mechanical properties of both sputter deposited layers and their elemental composition are given in Table 1.

The structure of the layer 1 and the layer 2 deposited on Si(100) substrate was characterized by X-ray diffraction using an XRD diffractometer PANalytical X'pert PRO in Bragg–Brentano configuration with CuKα radiation. The elemental composition was determined by X-ray Fluorescence (XRF) spectroscopy with PANalytical XRF Spectrometer MagiX PRO. Mechanical properties were determined from load vs. displacement curves measured by a microhardness tester Fisherscope H100 with Vicker's diamond indenter at a load $L = 20$ mN. For all sputtered films the ratio d/h of diamond depth impression d to the film thickness h was less than 0.1. It indicates that the measured hardness H of sputtered films is not influenced by the substrate [33,34]. The macrostress and the thickness of the films were measured using a stylus profilometer DEKTAT 8. The macrostress was determined from the thickness and curvature of the films deposited on Si (100) strips ($35 \times 5 \times 0.64$ mm^3) using a Stoney's formula. The resistance of the film to cracking was tested by a bending test. The coating was deposited on a Mo strip ($60 \times 10 \times 0.1$ mm^3) and the coated Mo strip was bended along a fixed cylinder of diameter r up to the occurrence of cracks in the coating surface. More details are given in Refs [16,27]. The transparency of Zr–Si–O layers was measured in the range from 300 to 800 nm using a spectrometer Specord M400.