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DETECTION OF MECHANICAL EFFECTS OF ADHESIVE THIN FILMS ON SUBSTRATE USING THE MODULATED-TEMPERATURE DILATOMETRY (MT DIL)

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The work is aimed to develop the diagnostic method for testing the state of surface coated with the wear-resistant films. Thin wear-resistant ceramic films based on titanium such as TiN, TiCN, TiAlN are deposited on working surface of cutting tools or machine elements in order to improve their tribological properties. The operation life depends mainly on the residual stresses occurring in films and the kinetics of their relaxation as a function of temperature and time. The value of the stresses is influenced by the technological conditions of film deposition and the physical and chemical properties of the substrate and film.

The paper has demonstrated the usability of the modulated-temperature dilatometry (MT DIL) for recording the changes in mechanical effects of the adhesive film on the substrate as a function of temperature and time. The substrates where in the shape of cylindrical rod, 30 mm length and 3 mm diameter and of the ribbon 30 mm in length, 2 mm in wide and 120 μm thick. The thickness of the coatings was from 2 to 3 μm. The films deposition were performed using the physical vapour deposition (PVD) technique.

Keywords: *interface layer/substrate stress, modulated-temperature DIL, wear-resistance coating*

Introduction

The material intrinsic properties such as hardness, strength, ductility etc. are very important factors for wear-resistance of the working surface. But also other factors associated with surface properties like surface finish, lubrication, load, corrosion, temperature etc. are equally important. The enhance of a wear-resistance can be obtained by coating of the working surface by ceramic thin films. The ceramics such as TiN, TiAlN TiC, TiCN or CN are characterized by high wear-resistance. Among other methods of coating, the plasma assisted physical vapor deposition (PA PVD) is often used. Beside the surface properties, the resistance on a mechanical and a thermal load decide about usability of such modification. This depends mainly on the adhesion between coating and a substrate as an intermolecular interaction. The adhesion is seriously reduced by contribution from extraneous sources [1]. These include internal stresses, which are almost always present in the layers deposited on a substrate. One sort of stress originates from the different lattice parameters of layer and substrate (coherency stresses). During process of coating the intrinsic stress is generated when the layer growths [2]. Thermal stress is a result of different thermal expansion coefficient of layer and substrate when temperature is changing after process is completed [3].

The degradation (delaminating) of the coating occurs when the adhesive forces are reduced by forces from all kind of stresses, among which the thermal stresses dominate at high temperature.

The microscopic result of stress is a variation of the lattice parameters, so the XRD method is widely used [4]. The macroscopic effect of stress is a mechanical deformation. The thermal dilatometric analysis (DIL) is a technique enabling to measure the expansivity for the sample, which depends not only on temperature but resulting on mechanical load as the stress at the interface layer/substrate is.

The modulated temperature (MT) method, first introduced by Reading *et al.* [5], was applied to the dilatometric measurement in the present work. This technique is known as modulated-temperature thermomechanical analysis (MT TMA), shown by Price [6]. Among other, the important benefit applying MT is increased sensitivity in detection the changes in thermal expansion coefficient [7].

Experimental

Sample preparation

Titanium nitride (TiN) films were deposited on substrate by the PVD method using the low voltage arc source of titanium vapours. The target plate were

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100 mm in diameter. An arc current in the process of deposition was 80 A, and pressure in a working chamber was 0.5 Pa, a bias voltage applied to the substrate was –70 or –10 V, depending on the research project. The film deposition temperature was controlled to a value of about 400°C. The distance between the substrate and Ti target surface was 18 cm. The deposited film was between 2 and 3 μm in thickness.

The substrate of ARMCO type of iron was in the shape of cylindrical rod, 30 mm length and 3 mm diameter and of a ribbon 30 mm in length, 2 mm in wide and 120 μm thick.

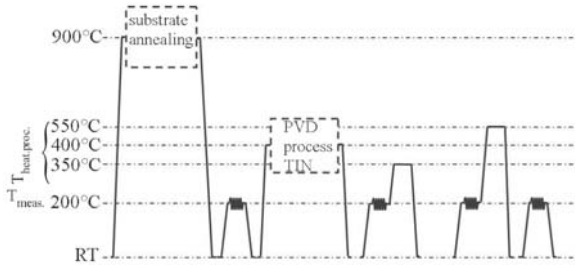

Fig. 1 Schematic diagram of the temperature program: T_{meas} – measurement temperature, $T_{heat.proc.}$ – temperature/time of annealing

Methods

Instrumentation

The thermal expansion of the sample was investigated using a thermoanalyzer, described in detail elsewhere [8]. Originally the instrument was provided for testing the sample in the shape of rod, max. 30 mm in length and 3 mm in diameter. In order to enable the investigation of the elongation of ribbon samples, a special sample holder was constructed which is described in [9]. The sample holder consists of two semicylindrical platinum rods, between which the ribbon sample is placed preventing lateral deformation. The sample was slightly longer than the holder so that the push-rod and back of dilatometer tube could only contact the ends of the sample. The free ends of the sample (about 100 μm) were stiff enough to sustain the tracking force of the push-rod.

The sufficient resolution of the dilatometric measurement (0.01 μm) for such experiment was achieved by applying the linear variable displacement transducer type of sensor (LVDT) with modification described in [10].

Measurement procedure

The experiment was carried out applying temperature program as illustrated in Fig. 1, which is combination of isothermal measurement cycles at lower temperature (200°C) separated with annealing cycles at higher temperatures, above 300°C. Transitions between lower and higher temperatures were carried out with rate of 2 K min^{-1}.

The modulated temperature program is applied during isothermal measurement cycles. From the thermal response of the sample, the dilatation and temperature amplitudes, $<A_{DIL}>$ and $<A_T>$, respectively, was obtained similarly as in [11]. These values then can be used to obtain temperature dependent the thermal expansion coefficient in modulated temperature mode, α_{AC} [12, 13].

In the present work we have made an investigations using a special procedure for eliminating an experimental errors, so the effects resulting from interaction between coating and substrate was detected. Two frequencies were applied separately during isothermal measurement cycle. From ten periods of each frequency the dilatation and temperature amplitudes were obtained. The relative change in respect to lower frequency was calculated as:

$$W_{DIL} = \frac{A_{DIL}(\nu_1) - A_{DIL}(\nu_2)}{A_{DIL}(\nu_1)} \text{ and}$$
$$W_T = \frac{A_T(\nu_1) - A_T(\nu_2)}{A_T(\nu_1)} \quad (1)$$

where ν_1 and ν_2 are two frequencies of modulated temperature.

The choice of frequency for modulation of the temperature was made after experiments with the wide range frequencies from 0.025 down to 0.005 s^{-1}, having periods of 40 to 180 s.

Then the correlation between dilatometric and temperature relative changes, W_{DIL} and W_T, was found as a ratio:

$$F_C = \frac{W_{DIL}}{W_T} \quad (2)$$

The correlation factor, F_C, is determined after deposition and after every annealing process. Their values are normalized dividing by $F_{C_{substrate}}$ for sample before deposition:

$$F_{C_{normalized}} = \frac{F_C}{F_{C_{substrate}}} \quad (3)$$

It was experimentally found that the variation of correlation factor is sensitive on stress resulting from the state of the coating. As results, the examples from the series of measurement are presented obtained for two conditions of the deposition and two different sample shapes.

Results and discussion

The changes of correlation factor for cylindrical sample in comparison with values of residual stress obtained by XRD is depicted in Fig. 2. The experiment was carried out using sinusoidal MT having periods 120 and 60 s, and amplitude 5°C. Changes of the correlation factor after annealing at 450°C have the same tendency as stresses determined by XRD. After annealing at 650°C the observed effect is in discrepancy with the previous from lower temperature. This effect is probably due to increased adhesion with stress remained at the same value.

Figure 3 illustrates the different in correlation coefficient F_c obtained for coated sample under different bias voltage Vs. It is known from the coating technology that bias voltage applied to the substrate under deposition has result in the adhesion and residual stresses. White and shadowed bars represents bias voltage Vs equal –10 and –70 V, respectively. The measure numbered by 1 is obtained for deposited

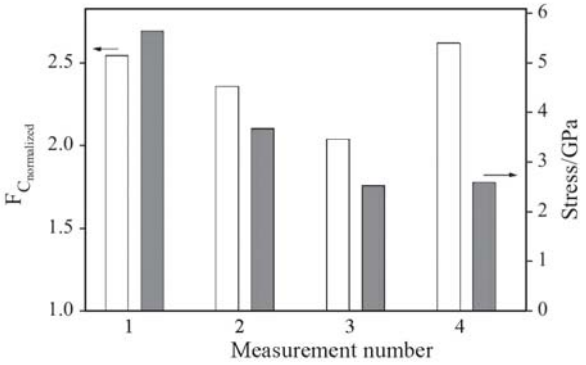

Fig. 2 The residual stresses in comparison with values of normalized correlation factor F_C in subsequent stage of annealing process in TiN layer in the system Fe/TiN: 1 – after deposition, 2, 3 – after annealing at 450°C/2 h, 4 – after annealing at 650°C/2 h. Bias voltage V_s= –70 V

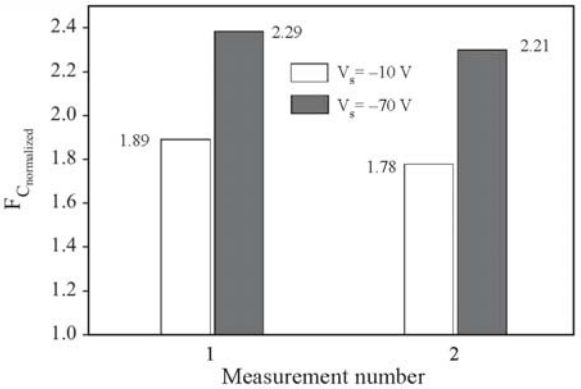

Fig. 3 The correlation factor F_c 1 – before and 2 – after annealing at 450°C/9 h in the Fe/TiN system obtained for two polarization voltage of the substrate: V_s= –10 V and V_s= –70 V

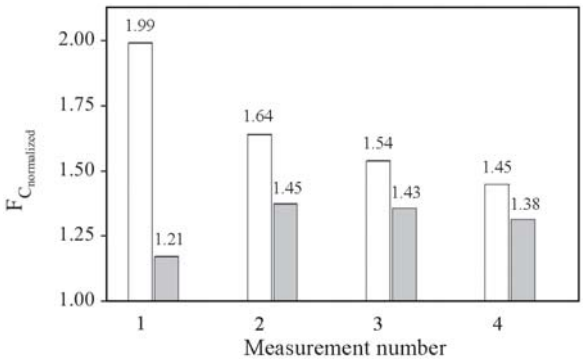

Fig. 4 The correlation factor F_c after subsequent stage of annealing process of TiN layer deposited on thin ribbon of Fe. Bias voltage V_s= –70 V

sample before any heat treatment. Number 2 data are obtained after annealing at 450°C by 9 h.

The result for the sample in the shape of thin ribbon is illustrated in Fig. 4. The values of the F_c correspond to the changes of adhesion layer TiN to the substrate Fe after subsequent, long time heating processes. White bars in figure numbered 2, 3, 4 illustrate relative changes of the adhesion after 20 h of heating for each step at 200°C. The white bar numbered by 1 represents the sample after deposition without any heat treatment. The second series represented by shadowed bars was obtained after annealing at 350°C by 2 h.

Conclusions

The applied procedure gains detection of the effects associated with mechanical interaction between coating and substrate. It had been shown correlation between stress determined by XRD and those obtained by proposed algorithm from dilatometric data is qualitatively in agreement. Moreover, F_c factor is very sensitive on the value of bias voltage V_c, what is very important, between other, for processing of PVD technology. The method allows the continuous monitoring of the stress relaxation as a function of temperature or time during experiment, similar to TMA application enabling to study thermal stability of complex system [14].

The thermal dilatometric analysis (DIL) is a technique enabling to measure the expansivity for the sample as a function of temperature with negligible external mechanical load. When the stress at the interface layer/substrate appears, this technique becomes more close to the thermomechanical analysis (TMA) enabling to study thermal stability and relaxation [5].

The correlation factor F_c is constant if the properties of the system layer/substrate do not change.

The developed method can be useful in the macroscopic diagnostic of the thermal stability of the adhesive wear-resistance thin films.

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