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APPLICATION OF TEMPERATURE MODULATED RELATIVE DILATOMETRY
Temperatures of adhesion degradation

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Abstract

Application of temperature modulated dilatometry (TM DIL) to investigation on degradation of the adhesion between ceramic films and the substrate is presented. Layers of titanium nitride deposited by plasma assisted physical vapour deposition (PA PVD) methods on the Armco iron substrates were tested. This paper shows that the TM DIL method is helpful in determining the usefulness of the titanium nitride covering of the cutting tools and machine parts.

Keywords: adhesive films, temperature modulated dilatometry

Introduction

Some methods modifying the surfaces of tools and machine elements are based on the adhesion effect of the film deposited on the substrate. The main objectives of this modification are to increase the tool life and improve the qualitative and economic effects of their operational use.

The adhesive films in case of cutting tools and important machine elements comprise infusible carbon, nitrogen or boron compounds with transient metals, some oxides and lately the Me–C:H coatings deposited among others by plasma assisted physical vapour deposition (PA PVD) methods. The TiN, TiAlN, TiC, TiCN and CN coatings are the most often used adhesive films.

Adhesion is determined quantitatively as the work or the force necessary to separate the atoms from the substrate. The adhesive force in the substrate/coating system is non-uniform on the whole surface, since the interfacial zone between the coating and the substrate is often heterogeneous. The local changes in adhesion are effected by impurities, different crystallographic structure, degree of surface development of the substrate and a difference in ductility of the coating and substrate materials. Mittal [1] pointed out that practically measured adhesion consists of basic adhesion i.e. adhesion due to intermolecular interaction between the layer (coating) and the substrate plus contribution from extraneous sources.

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These extraneous sources include internal stresses in the layer which always decrease the inherent adhesion and defects or extraneous processes introduced by the measuring procedure which may increase or decrease the basic adhesion.

The coatings having the assumed values of adhesion are obtainable depending on the energy parameters and the substrate surface properties. Moreover, it is necessary to select proper materials for the coating and substrate respecting their physical properties.

In case of cutting tools, usability of specified technology and relevance to applied parameters of coating growth were also confirmed by the values of stresses obtained right in the adhesive film and in the superficial layer of the substrate. Knowledge of stress relaxation as a function of temperature or time under isothermal conditions is useful to determine the variables of coating and predict the changes in adhesion between the coating and substrate and the hardness of coating [2].

These stresses stem from: incomplete lattice coherency between the substrate and coating, a difference in thermal expansion coefficients between the substrate and coating, and residual stresses produced during the coating but not included in the above mentioned causes. The stresses resulted from the difference in the thermal expansion coefficients, specified as the thermal stresses ($\sigma_{thermal}$) can be given by the expression:

$$\sigma_{thermal} = -E\Delta\alpha\,(T_2-T_1)/(1-\nu)$$

where $\Delta\alpha$ is the difference in thermal expansion coefficients between the substrate and coating; T_1 is the substrate temperature while the film was deposited; T_2 is the substrate temperature after its cooling down or heating up; E is Young's modulus and ν is Poisson's ratio of the coating.

The thermal stress occurring in a given coating/substrate system usually has significant effects on the coating adhesion. Usually, an interlayer is formed between the substrate and coating which can compensate for the thermal stresses to a certain extent. In case of PA PVD method used for coating of cutting tools, this stress concentration can decide on tools operational properties.

The adhesive force is determined by the methods which are divided into mechanical and non-mechanical ones. One of mechanical methods is a thermal method [3].

In this paper, the results of the original application of the temperature modulated relative dilatometry [4, 5] to determine a degree and a range of thermal degradation of TiN film adhesion to the substrate made of Armco iron are presented. Tests are carried out in a relative dilatometric system using two specimens: Fe specimens and Fe specimens coated with TiN (Fe *vs*. Fe/TiN).

Experimental procedures

Sample preparation

A standard specimen and respective specimens were made of Armco iron in the form of cylindrical rods, 3 mm in diameter and 30 mm length. Each specimens used for tests were coated with TiN films by PA PVD method. Plasma was obtained by arc discharge between the target made of titanium and the working chamber of a vacuum test rig. The target is 75 cm^2 in area and purity of titanium applied was 99.9%. The coating process was carried out at an arc-discharge current of 90 A, voltage of 20 V and pressure in the processing chamber equal to 5×10^{-3} mbar.

The films were deposited under different operating conditions. The process was modified using different negative bias voltages of the specimens in the course of coating: 10, 40 and 70 V respectively. Surfaces of specimens before coating were polished with abrasive paper in a grade of 1000, ultrasonically cleaned in alkali detergents and then etched with highly excited argon ions in the processing chamber. The specimens were coated with TiN films of 2.5 μm thickness.

Measurement technique

Experiments were carried out on thermoanalyser constructed in our laboratory [6]. A characteristic feature of this device is the ability to carry out simultaneous thermal investigation tests by the following methods:

- differential thermal analysis (DTA),
- relative or absolute dilatometry (DIL),
- relative or absolute thermomagnetometric analysis (TMAG).

Owing to the radiative-convectional heat exchanging system and the computer controlled system of electric power supply to an infrared radiator it was possible to carry out experiments in the wide range from the ambient temperature up to 1000°C in accordance with standards specified by ICTAC. The system also enables to make tests with the application of modulated temperature programming. The computer program developed for temperature modulated tests enables to perform digital filtration of measuring signals from a given thermal analysis. In this way an additional data source essential for this type of thermal tests was provided.

The temperature modulated relative dilatometric tests were carried out in the relative system of Fe *vs*. Fe/TiN specimens. Temperature was increased at a rate of 2°C min^{-1}, whereas sinusoidal modulated temperature programming was carried out according to the following parameters: the heating amplitude ±10°C and a period of 1 min.

Results and discussion

Figure 1 shows the recorded selected result of temperature modulated relative dilatometric tests on a couple of specimens Fe *vs*. Fe/TiN. The plot marked by TM DIL is an input signal encompassing changes in elongation difference at a given temperature $d\Delta L/dT$ forced by sinusoidal changes in temperature of the heating system. The 'mean amplitude TM DIL' curve results from computer processing of the input signal and shows changes in its amplitudes as a function of temperature. Within the range of temperatures from 350 to 400°C and from 450 to 500°C there is a rapid change in the difference of thermal expansion coefficients between the tested and the standard specimens. The above changes in the coefficients provide the relaxation of thermal stresses in the surface of the specimen tested as a result of partial adhesion degradation between the film and the surface.

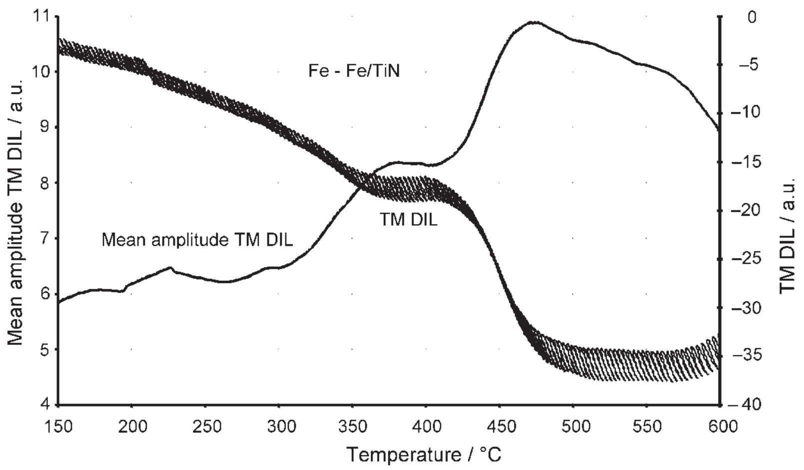

Fig. 1 Result of temperature modulated relative dilatometric tests of two specimens Fe *vs*. Fe/TiN. 'TM DIL' original signal, 'mean amplitude DIL' variation of signal amplitudes in dilatometric analysis

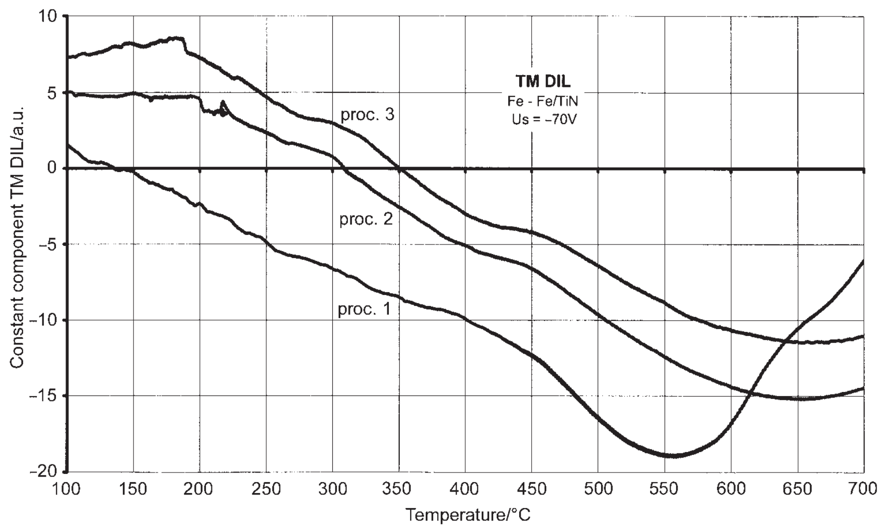

Fig. 2 Variations of constant components of TM DIL signal for respective thermal processes proc. 1, proc. 2 and proc. 3 for the same couple of Fe *vs*. Fe/TiN specimens

Occurrence of the above phenomena is confirmed by the plot of curves shown in Fig. 2, where the curves represent runs of component values of original runs dΔL/dT of successive heating cycles marked by proc. 1, proc. 2 and proc. 3 respectively. Runs of proc. 2 and proc. 3 curves show that during the first heating cycle at the temperature of about 550°C there is dramatic adhesion degradation between the film and substrate. This degradation results from liberation of thermal stresses $\sigma_{thermal}$ occurring between the film and substrate. A decrease in amplitudes of proc. 2 and proc. 3 signals in relation to the first heating cycle proc. 1 proves the gradual loss of adhesion in successive heating cycles.

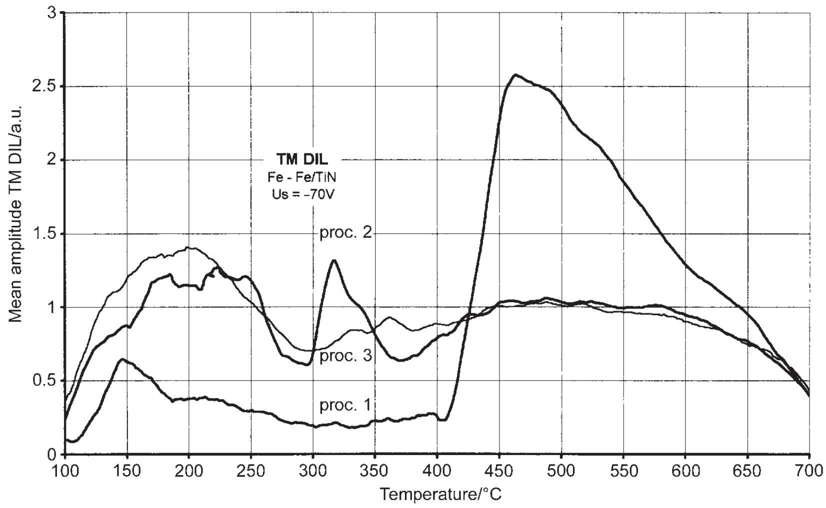

Fig. 3 Examples of experimental results obtained by TM DIL methods for a couple of Fe *vs*. Fe/TiN specimens when the degradation effect on adhesion of TiN film to the substrate occurred during the first thermal process (proc. 1)

The above interpretation of results obtained is confirmed by microscopic observations of specimen surfaces after successive heating cycles.

A similar run of adhesion degradation between the film and substrate is illustrated in Fig. 3 where the runs of changes in amplitudes of elongation differences during each heating cycle for the above-described couple of Fe *vs*. Fe/TiN specimens are visible. A run of proc. 1 curve reconfirms the temperature range of adhesion degradation between the film and substrate whereas proc. 2 and proc. 3 curves confirm successive phases of its loss.

On the other hand, Fig. 4 presents the runs of changes in amplitudes of elongation differences for the specimen tested where the film reveal no changes in adhesion degradation between the film and substrate. The conclusion is drawn that both operational conditions of film growth and preparation of upper surface of the substrate are correct. Then, proc. 2÷proc. 3 curves of changes in amplitudes recorded in the course of consecutive heating processes can be used as a source of fundamental digital data for determination of the relaxation kinetics of thermal stresses within the temperature range applied to the tests.

Whereas Fig. 5 illustrates changes in dΔL/dT amplitudes during the successive heating cycles where surface of the specimen tested was intentionally mechanically defected in a few places, that leads to local differences in a degree of surface development and stresses in the upper surface of the substrate. Successive heating cycles, ac-

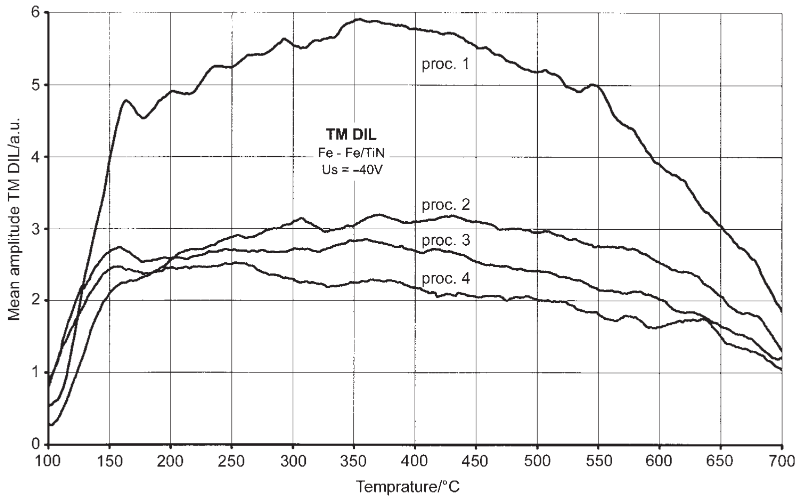

Fig. 4 Examples of experimental results obtained by TM DIL methods for a couple of Fe *vs*. Fe/TiN specimens when the degradation effect on TiN film adhesion did not occur but only the thermal stress relaxation in successive processes were found (proc. 1÷proc. 4)

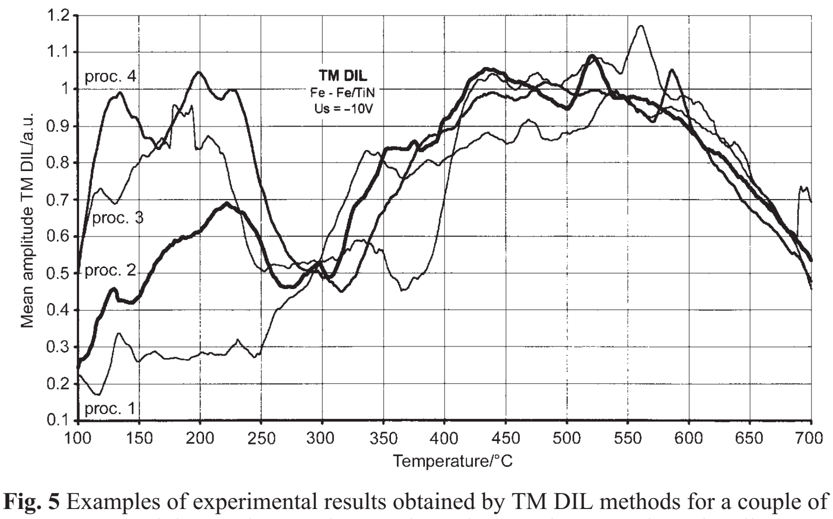

Fig. 5 Examples of experimental results obtained by TM DIL methods for a couple of Fe *vs*. Fe/TiN specimens where surface of Armco iron were intentionally mechanically defected

cording to runs of respective curves, did not lead to the total relaxation of thermal stresses. The above experiment confirms suitability of the method developed for observation of an influence of the thermal-stress relaxation of the film-substrate system on adhesion of the film to the substrate.

Conclusions

The temperature modulated relative dilatometric measurements with the aid of the computer filtration program of measured signals, provide a qualitative presentation of the thermal stresses affecting the adhesion of TiN film to the Armco-iron substrate. It is possible to determine the optimal operational variables of coating process for cutting tools in particular where this types of coating act as an anti-abrasive layer. Regarding an unfavourable influence of many factors on stability of properties obtained by PA PVD methods, the method presented in this paper can be used for diagnosis.

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