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Characterization of the ceramic coating of iron with TiN by temperature-modulated dilatometry

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Abstract

Arc-evaporated ceramic films such as TiN, TiCN, and TiAlN find application for enhancing wear-resistance of tools for metal cutting. The wear-resistance is influenced by adhesive forces between film and substrate, which may be degraded by residual and imposed stresses, leading to delamination and damage of coating. The aim of this work was to find a relationship between physical properties of the coated iron and thermally induced stresses detected by dilatometry. Samples of iron coated with layers of TiN were investigated. In order to obtain more details about the degradation process of adhesion, the dilatometric analysis was carried out simultaneously with differential temperature and magnetometric analysis. The significant increase in thermal response was achieved by applying temperature modulation, a novel method in this field.

Keywords: Thin film coating; Adhesion; Temperature-modulated differential dilatometry

1. Introduction

The surfaces of modern tools for cutting of metals are often modified by adhesive thin films to obtain an enhanced wear-resistance with prolonged lifetime. The adhesive films comprise infusible carbon, nitrogen, or boron compounds with metals or some oxides. The most often used coatings consist of TiN, TiCN, TiAlN, or CrN obtained, among of others, by plasma-assisted physical vapor deposition (PA PVD) methods. The wear-resistance depends on the adhesive forces in the substrate/coating system which are equal to the forces necessary to separate the atoms from the substrate. The adhesion is affected by impurities, different crystallographic structure, and the degree of surface development of the substrate. It is also necessary to select proper materials for the coating by matching their physical properties. The coating is degraded when the adhesive forces are reduced by forces originating from residual and imposed stresses. In other words, empirically obtained adhesion, EA, is the difference between basis adhesion, BA, originating from atomic forces, and residual stresses, RS:

$$\mathrm{EA} = \mathrm{BA} - \mathrm{RS}$$

The residual stresses are generated during the coating process and almost all thin films deposited on a substrate are in a state of stress. There are several

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mechanisms to explain the origin of these induced stresses [1]. In general, these can all be classified as coherent, intrinsic, or thermal stresses. Coherent stresses result when a thin film is lattice-matched to a substrate that has different in-plane lattice parameters from those of the film. Intrinsic stresses are generated during growth of the films. When the temperature is changing, thermal stresses are generated if the film and substrate have different thermal expansivities. In case of the PA PVD method, the substrate is kept at higher temperature during deposition and thermal stress is generated after cooling to an ambient temperature. This stress can be given by the expression:

$$\sigma_{\text{thermal}} = \frac{\Delta\alpha \Delta T E}{1 - v}$$

where $\Delta\alpha$ is the difference in thermal expansivity between the substrate and the coating, ΔT the temperature difference between deposition and ambient temperature, E and v are Young's modulus and Poisson's ratio, respectively.

Since the tools in cutting application may reach high temperature, a knowledge about the kinetics of the stress relaxation as a function of temperature is crucial to define the tribological parameters of the film under operating conditions. The investigations within this scope are usually carried out using X-ray diffractometers, nanoindenters or by measuring mechanical deformation after subsequent removal of part of the layers [2]. To investigate the state of the coating without modifying the sample, acoustic microscopy was also used [3].

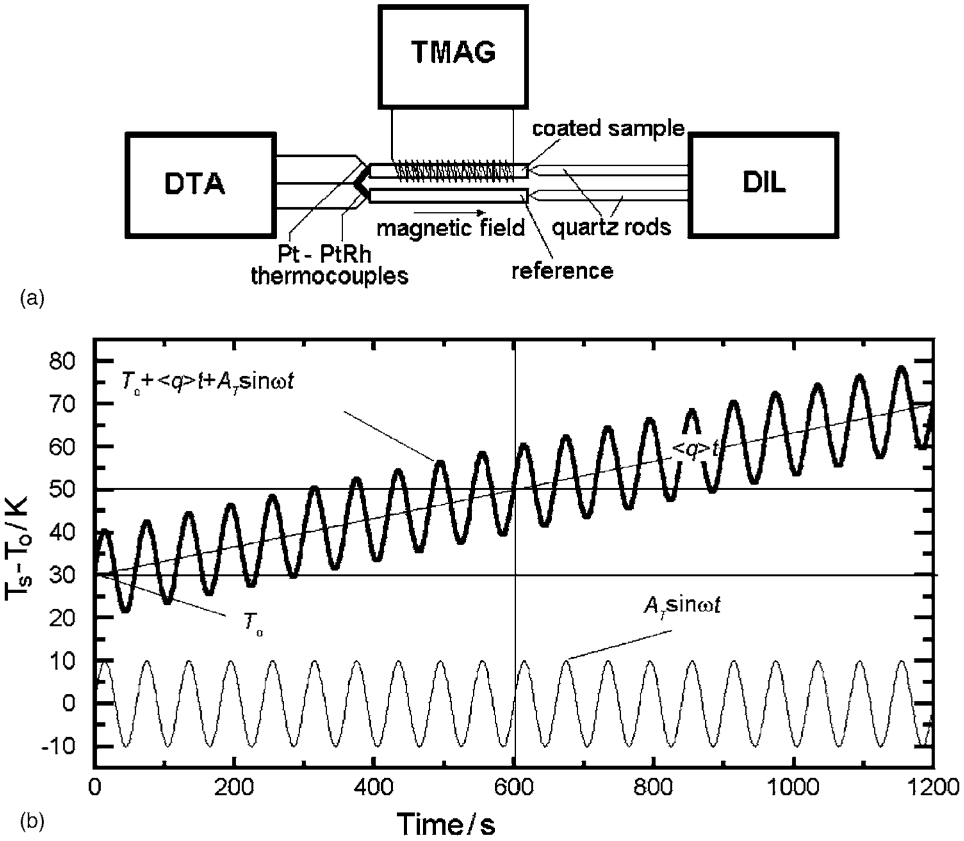

Fig. 1. (a) Schematic diagram of the experimental instrumentation for simultaneous detection of TMAG and DIL parameters in a differential system sample—reference as a function of temperature (DTA). (b) MT of the sample, $T_s - T_0$. The modulation is obtained by a sinusoidal heat/cool program $A_T \sin \omega t$, superimposed on a linear heating ramp $\langle q \rangle t$, where $p = 2\pi/\omega = 1$ min, $A_T = 10$ K, $\langle q \rangle = 2$ K min^{-1} and $T_0 = 30$ K.

This work describes an alternative research method to study the stress relaxation between a TiN ceramic film and a substrate of iron as a function of temperature. Beside the mechanical elongation measurement by differential dilatometry (DIL), differential thermal analysis (DTA) and thermal magnetometric measurement (TMAG) were simultaneously carried out on the same sample. To obtain increased response in temperature, a modulation program is added to the linear temperature increase. The influence of coating on the dilatometric behavior of tested samples and a relation between adhesion and technological parameters are presented. The advantage of adding temperature-modulated method in this field of analysis is shown.

2. Experimental

2.1. Sample preparation

Specimens were made of ARMCO type iron in the form of cylindrical rods, 30 mm in length and 3 mm in diameter. The specimens used for testing were coated by PA PVD. The plasma was obtained by electric discharge between the target of titanium in a working vacuum chamber of 700 mm × 700 mm × 600 mm. The target of 75 cm^2 was sputtered with 99.9% purity of titanium using a current of 90 A, a voltage of 20 V, and the pressure in the processing chamber equaled 0.5 Pa. The flow of the nitrogen gas of purity 99.995% was 6 $\mathrm{cm}^3\,\mathrm{min}^{-1}$. The process was carried out using different negative bias voltage U_s of the specimens (-10, -40 and -70 V). The surfaces of the specimens were polished with abrasive paper of grade 1000, then cleaned ultrasonically with an alkaline detergent and an organic solvent before placing in the vacuum chamber. Final high purity surfaces were obtained immediately before coating by argon ion cleaning with a -600 V voltage applied to the specimens for 10 min in the vacuum chamber. The specimens were coated with TiN films of 2.5 μm thickness.

2.2. Measurement

The samples were studied with a thermoanalyzer, described in detail elsewhere [4] which enables to obtain simultaneously TMAG, DIL and DTA data as a function of temperature. A schematic diagram of the thermoanalyzer is shown in Fig. 1a. The DTA and DIL tests were carried out in a differential mode using two identical iron specimens, one coated with TiN, and other not coated, as a reference. For TMAG analysis pick-up coil is used which is side placed along the sample near the surface. The adopted modulation of the constant heating rate was first applied to conventional DSC by Reading et al. [5].

Moreover, the modulated temperature (MT) program when employed, enables to separate a temperature-dependent thermal expansivity for materials without external load, which is reversible, and those irreversible due to creep involving stretching or shrinking. The technique known as temperature-modulated thermomechanical analysis (TM TMA) was introduced by Price [6] to study mechanical properties of polymers.

The MT program consists of a sinusoidal oscillation added to a linear heating ramp $\langle q\rangle t$:

$$T_s + T_0 + \langle q\rangle t + A_{T_s}\sin\omega t$$

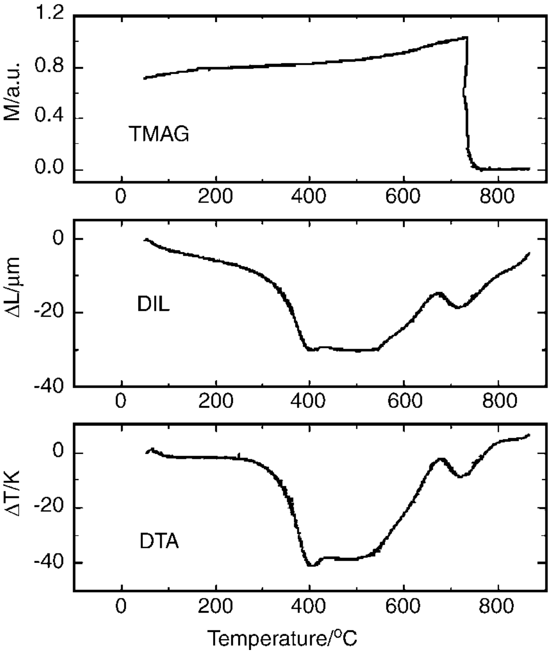

Fig. 2. Experimental results with linear temperature control ($\langle q\rangle = 40\ \mathrm{K\,min}^{-1}$) without modulation. The TMAG, DIL and DTA curves were recorded in the same run. A direct relation can be seen between temperature (DTA) and thermal expansion (DIL). The Curie temperature of the ferro-paramagnetic transition for iron is at 761 °C (T_c).

with T_0 representing the isotherm at the beginning of the scanning. The modulation frequency ω is equal to $2\pi/p$ in units of rad min^{-1}, with p representing the length of one cycle (min). The expression $\langle q \rangle$ indicates an average heating rate over one modulation period (K min^{-1}). The amplitude of the MT is A_{T_s}. Results presented in this work are obtained by experiments with $p = 1$ min, $A_T = 10$ K, $\langle q \rangle = 2$ K min^{-1} as illustrated in Fig. 1b.

3. Results

The results obtained for a linear temperature control (heating rate 40 K min^{-1}) without modulation are shown in Fig. 2. The TMAG curve has the same shape as in the case of the not coated sample, i.e. there is no detectable influence of coating. From the variation of the temperature difference and corresponding differential dilatation (curves DTA and DIL in Fig. 2, e.g. the region between 300 and 400 °C), one can obtain the thermal expansivity of 15×10^{-6} K $^{-1}$, which is the same as known for iron. There are several available descriptions of temperature variation in the DTA technique, which are the key to obtain thermal quantities such as heat capacity and thermal conductivity [7]. The most reasonable explanation of the observed changes in temperature difference in Fig. 2 is a variation of the radiation/absorption properties of the coated sample during heating.

The result from an experiment with MT is shown in Fig. 3. In this case $A_{\Delta T}$ and $A_{\Delta L}$ refer to the amplitude of MT difference and difference in length due to temperature modulation, respectively, measured as difference signals by the sensors attached to the sample and reference. The MT DTA curve is similar to the one obtained from linear temperature control (Fig. 2). The temperature-modulated DIL curve as a function of temperature, in contrast, has a significant rise in amplitude starting at about 500 °C. Above this temperature

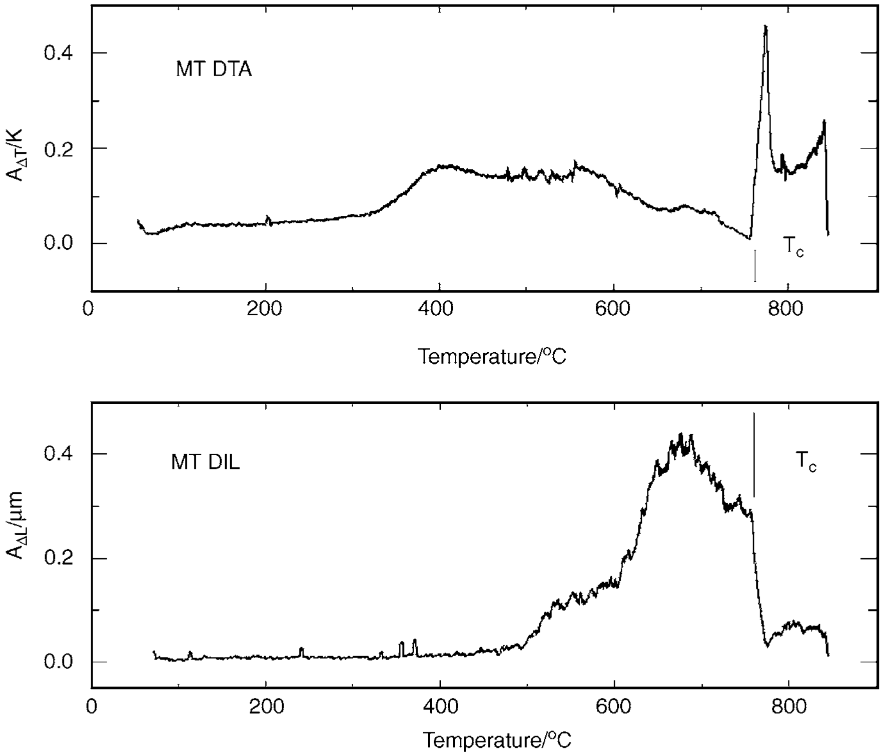

Fig. 3. MT experiment with $p = 1$ min, $A_T = 10$ K, $\langle q \rangle = 2$ K min^{-1}. The MT DTA curve (upper) displays an amplitude difference between sample and reference. The character of MT DTA is comparable to the standard DTA (Fig. 2) if considering extremes at certain temperatures. In contrast, the MT DIL indicates an additional factor in dilatation at about 500 °C.

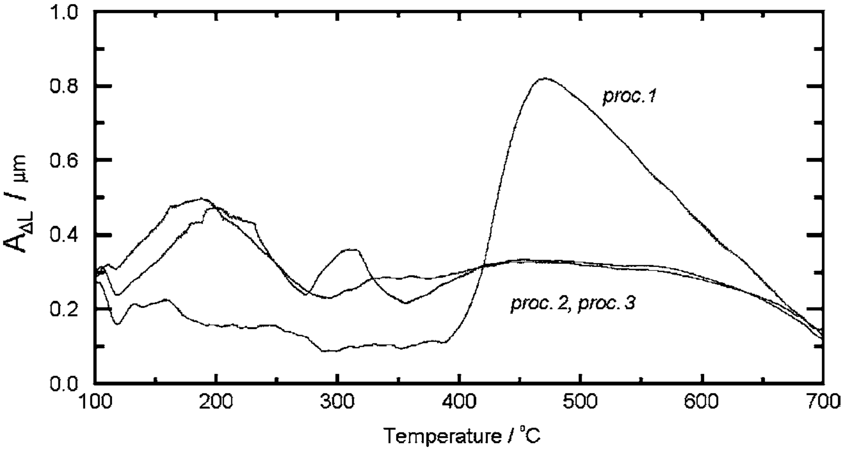

Fig. 4. Experimental result obtained by the TM DIL method for a Fe vs. Fe/TiN specimens (coating process using $U_s = -70$ V). The degradation effect of TiN film adhesion occurs during the first heating cycle. It cause a significant rise of the $A_{\Delta L}$ (curve proc. 1) which is not observed during subsequent heating cycles (proc. 2 and proc. 3).

the thermal expansion is not related to the MT amplitude. The effect is much larger than the thermal expansivity of 15×10^{-6} K^{-1}, indicating an additional factor in dilatation. The above changes in the expansivity prove the relaxation of thermal stresses in the surface of the specimen tested as a result of the local displacements between the film and the surface.

The occurrence of the effect of degradation of the adhesion is confirmed by the family of plots in Fig. 4, where the curves marked by proc. 1, proc. 2 and proc. 3 represent amplitudes of modulated dilatation $A_{\Delta L}$ obtained during subsequent heating cycles. A disappearance of the rise in modulated dilatation, visible during first heating cycle (proc. 1), proves the complete loss of adhesion seen on the first cycle, not retrieved on cooling (proc. 1 and proc. 3).

The sharp degradation of the adhesion between the film of TiN and iron substrate was observed only for coating processes using the negative bias voltage $U_s = -70$ V as seen in Fig. 4. Fig. 5 displays the

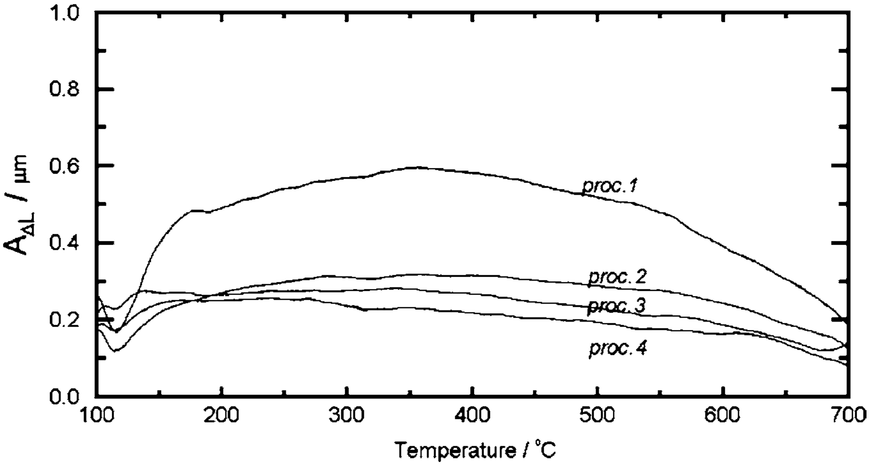

Fig. 5. Experimental result obtained by TM DIL method for a Fe vs. Fe/TiN specimens (coating process using $U_s = -40$ V) when degradation of TiN the film adhesion did not occur. Only thermal stress relaxation is observed after successive heating processes.

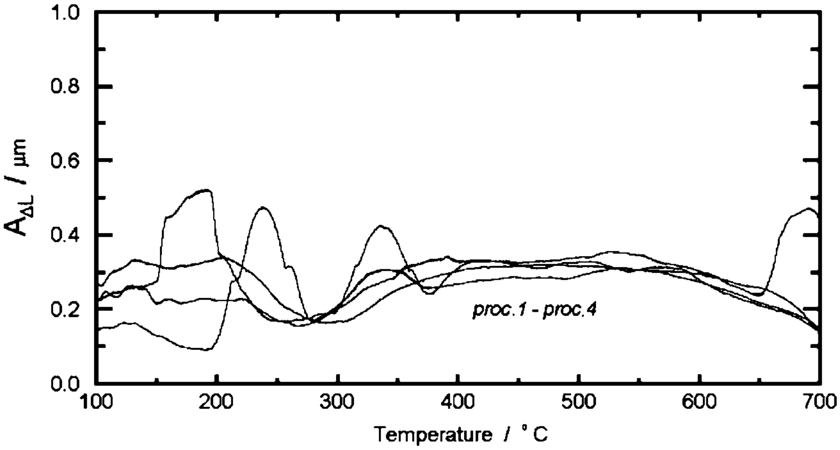

Fig. 6. Experimental result obtained by TM DIL method for a Fe vs. Fe/TiN specimens (coating process using $U_s = -10$ V) where low adhesion has no influence on the thermal dilatation. It can be seen that the effect is reproducible and is similar to that observed after first heating for the specimen from Fig. 4 (proc. 2 and proc. 3).

changes in amplitude of dilatation differences for specimen with a film obtained using $U_s = -40$ V bias voltages. In contrast to Fig. 4, the specimen does not reveal any sharp changes in the modulated dilatation. The much higher amplitudes of the signal indicates a strong adhesion involving a permanent stress. The decrease in amplitude recorded in the consecutive heating processes indicates a thermal stress relaxation within the temperature range applied to the tests.

When the process of coating was carried out with a bias voltage $U_s = -10$ V (Fig. 6), the coating has relatively little influence on the thermal dilatation. It can be seen that the effect is constant and is similar to that observed after the first heating for the specimen shown in Fig. 4 after the adhesion was completely degraded (proc. 2 and proc. 3).

4. Conclusions

From the experimental results presented in this work, it is evident that the influence of technological parameters during coating is crucial for the quality of adhesion. This is a well known fact, but was never directly observed. In the example of a thin ceramic coating of TiN on the iron substrate, it was demonstrated here that the introduction of the temperature-modulated DIL allows to detect adhesive forces by their anomalous behavior of expansivity. This was shown for three cases of coating obtained by the PA PVD method with different negative bias voltages U_s. The method allows to separate effects of the state of coating (hard or soft) and the identification of the temperature regions where damage of the coating occurs. There is very little influence of stress on the magnetic property, perhaps due to the sample geometry.

One can discuss the effect of the increasing dilatation signal only with measurements carried out with temperature modulation. The effect may originate from small irreversible replacements between film and substrate, leading to a relaxation of the stress. The work is still in progress and is focussed on the described problem as well as on the quantitative determination of the stress and magnetic properties.

Acknowledgements

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