Journal of Thermal Analysis and Calorimetry, Vol. 64 (2001) 1201–1207

EFFECTS OF TiN COATING OF IRON DETECTED BY TEMPERATURE MODULATED THERMO-MAGNETOMETRY AND DILATOMETRY

P. Myśliński[1], *P. Kamasa*[2] *and A. Wąsik*[1]

[1]Technical University of Koszalin, ul. Racławicka 15–17, 75-620 Koszalin, Poland
[2]Research Institute for Solid State Physics and Optics of Hungarian Academy of Sciences, 1525 Budapest, P.O. Box 49, Hungary

Abstract

The aim of the present work is to find relation between the state of ceramic coating of iron and the physical properties of coated samples as a function of temperature. The iron samples coated by plasma assisted physical vapor deposition (PA PVD) with layers of TiN were investigated with new technique – temperature modulated thermomagnetometry (TM TMAG) and thermal dilatometry (TM DIL). From the irregular behavior of the thermal dilatation and magnetic susceptibility, the process of the coating degradation can be resolved.

Keywords: dilatometry, temperature modulation, thermomagnetometry, TiN thin film coating

Introduction

The surface of modern tools for metal cutting is often modified by ceramic thin films to obtain the enhance in a wear-resistance with prolonged live-time. 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. There are many technologies of coating, which can be generally divided into several groups such as mechanical, thermomechanical, thermal, electrochemical and physical methods. In almost all cases, thin films deposited on a substrate are in the state of stress. There is a variety of mechanisms of induced stresses which depend on the technology used and adjusted parameters. Generally, the stresses can be classified as coherency, intrinsic, and thermal. The coherency stresses result when a thin film is lattice-matched to a substrate that has in-plane lattice parameter different from that of the film. Intrinsic stresses are generated during growth of the film. When technology of coating requires high temperature, the thermal stresses σ_{thermal} are generated, in case of the film and substrate have different thermal expansion coefficients due to a differential expansion between the film and the substrate when the temperature is changing after the process is completed [1]. The thermal stress component can be obtained from:

$$\sigma_{\text{thermal}} = \Delta\alpha\Delta T Y_c / (1-\nu_c) \tag{1}$$

1418–2874/2001/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

where Y_c and ν_c are the Young's modulus and Poisson's ratio, respectively. $\Delta\alpha$ is the difference in coefficient of thermal expansion between the substrate and the film, and ΔT is the temperature difference between deposition temperature and room temperature.

The degradation of the coating takes place when the adhesive forces are reduced by forces originating from all kinds of stresses, among which the thermal stresses dominate at high temperature.

Since the tools in cutting application may operate in a wide range of temperature, the knowledge about the stresses and their relaxation kinetics as a function of temperature is crucial to obtain optimal tribological properties by defining technological parameters of coating. The investigations within this scope are usually carried out using X-ray difractometers, a nanoindenters or by measuring mechanical deformation after subsequent removal part of layers [2]. If the substrate is a ferromagnetic material, the case of almost all cutting tools, the stress involved magnetostriction changes can be identified by thermomagnetometric analysis (TMAG).

This work includes results of testing stress relaxation between the TiN monolayer obtained by plasma assisted physical vapor deposition (PA PVD) and an iron substrate as a function of temperature measured by TMAG method, supplemented with simultaneous analysis by complementary technique – thermal dilatometric analysis (DIL). The measurements were carried out by means of thermoanalyser, described in detail elsewhere [3, 4]. To obtain increased response in temperature, a modulation program is added to the linear temperature increase – the technique widely used in thermal analysis [5].

The experimental examples on the magnetic and related property-changes of the coated samples observed after applying a modulated temperature technique are presented.

Experimental

Sample preparation

In the PA PVD method a layer of TiN was obtained by electric discharge sputtering in a vacuum chamber of 700×700×600 mm. Target of 75 cm^2 – titanium of purity 99.9% was sputtered with a current of 90 A and voltage of 20 V. The flow of the nitrogen gas of purity 99.995% was 6 cm^3 min^{-1}. The pressure in the chamber was kept at $5 \cdot 10^{-3}$ mbar.

The iron samples used in our experiment are in shape of cylindrical rod of 30 mm length and 3 mm diameter. The material were cleaned by ultrasonically aided washing with alkaline detergent and organic solvent before placing in the vacuum chamber. The final thickness of the TiN layer was about 2.5 μm. The deposition temperature of the substrate was around 350°C. The coatings were carried out under condition with negative bias voltage of 70 V applied to the substrate. It was experimentally found that the above conditions are optimal for growth of TiN layer with minimal contaminations and unwonted phases with simultaneous good adhesion.

The layers were obtained by Cathodic Arc Plasma Deposition method (CAPD), applied in laboratory of Technical University of Koszalin. Energy dispersive X-ray method (EDX) and conventional XRD confirmed composition and stoichiometry of layers. There was not observed phase of Ti_2N, but only TiN with 50±1% atoms of Ti and 50±1% atoms of N and orientation <111> [6].

Measurement technique

The modulated temperature program is accomplished by adding to a linear heating ramp $<q>t$ a modulating component:

$$T_s = T_0 + <q>t + A_{T_s} \sin\omega t \tag{2}$$

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 reverse time, with p representing the length of one cycle in s rad^{-1}. $<q>$ indicates an average heating rate over one modulation period in K s^{-1}. The A_{T_s} is the amplitude of modulated temperature.

The stresses involved dilatometric and magnetic effects are determined against the reference sample made of the same material but without coating (reference sample) as differential signals.

The differential dilatation or contraction is measured by two sensors of linearly variable differential transformers. The signal is proportional to [7]:

$$\frac{\mathrm{d}\Delta L}{\mathrm{d}t} = \frac{\mathrm{d}(L_s - L_r)}{\mathrm{d}T}\frac{\mathrm{d}T}{\mathrm{d}t} + f(t,T) \tag{3}$$

where L_s and L_r are the length of the tested and reference specimens, $\mathrm{d}(L_s - L_r)/\mathrm{d}T$ is the difference of the thermal expansion coefficient of the two specimens, and $f(t,T)$ is the function expressing changes in the length of the specimen being tested, that are connected with irreversible changes in the mechanical stresses, occurring between the substrate and the adhesive film.

The magnetic state of the sample is detected by surrounding coil using alternating current (AC) for exciting magnetic field H. The information is taken from the induced electromotive force E, which is proportional to a complex susceptibility of the sample:

$$(E' + iE'')\mathrm{e}^{\mathrm{i}\Omega t} = \alpha\Omega H \mathrm{e}^{\mathrm{i}\Omega t}(\chi'' + i\chi') \tag{4}$$

where α is the apparatus constant, H – amplitude of magnetic field strength, Ω – angular frequency of AC magnetic field which is much higher than temperature modulation frequency ($\Omega >> \omega$). The temperature depended signal is analyzed according to [8]:

$$\mathrm{d}\Delta\underline{E}/\mathrm{d}T = E_o \eta \Delta\underline{\mu}_{sk} \mathrm{d}\Delta\underline{\mu}_r/\mathrm{d}T \tag{5}$$

where $\underline{E}$ is the differential signal of TM TMAG, E_o, η, and $\Delta\underline{\mu}_{sk}$ are the apparatus constant and $\Delta\underline{\mu}_r$ is the different in magnetic permeability between the coated samples and reference.

The measuring cell is provided to make experiment in vacuum or in atmosphere of gas. To avoid the oxidation of the surface layer at high temperature, the argon high purity gas was flowing over the measuring cell during experiment. The flow of 10 cm^3 min^{-1} was stabilized to minimize temperature fluctuations.

A computer program was developed to reveal the thermal effects of relevant analysis through the recording of changes in amplitude quantities, their components and phase shift angles of measured electrical signals.

Results and discussion

In Fig. 1a measurement is shown that resulted from a coated sample during first heating cycle. The heating rate is 2°C min^{-1} with superimposed sinusoidal temperature modulation with a period of 1 min and an amplitude of ±10°C. The curve TM DIL is the differential signal of dilatation comprising of dc component and response of temperature modulation – alternating component. The curve mean amplitude TM DIL displays changes in amplitude of the alternating component obtained from data TM DIL after deconvolution which is in direct relation to the changes of thermal expansion coefficient. Two ranges of temperature, around 300 and 570°C, where characteristic local extremes may have an origin in the degradation of TiN layer adhesion. The mean amplitude TM DIL curve has its minimum while dc component of TM DIL indicates plateau. In these two temperature regions one can observe deviation from the mean value of the vector angle TM TMAG curve.

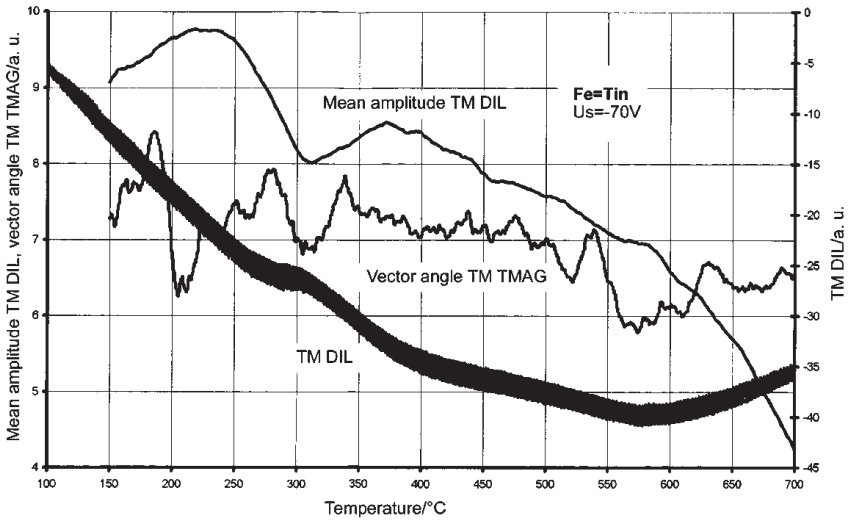

Fig. 1 Dilatometric (DIL) and magnetic (TMAG) signals recorded during first heating of the iron sample coated with TiN. The TM DIL curve contains two components: slowly changing difference in length between reference and tested sample with temperature, and response on temperature modulation. The mean amplitude TM DIL curve is the amplitude of the alternating component of TM DIL

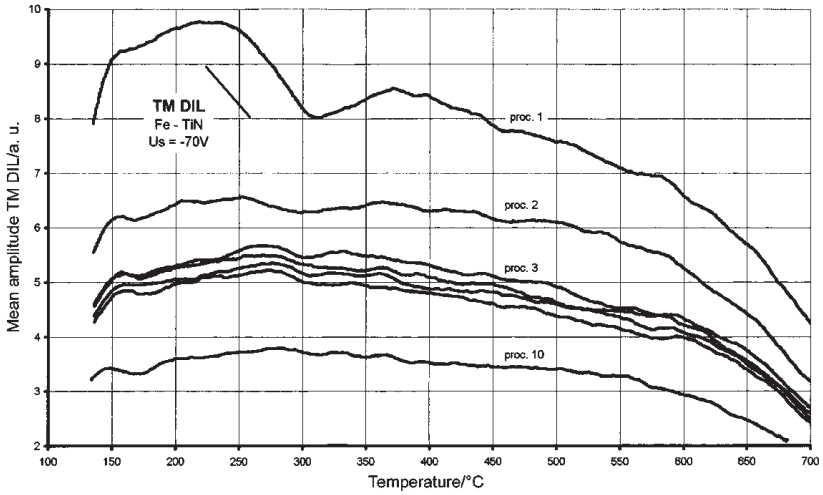

Fig. 2 The thermal stress relaxation of coating in higher temperature after subsequent heating–cooling procedures (proc.1–proc. 10). The mean amplitude of TM DIL is significantly decreasing after first heating becoming smooth

The kinetics of the degradation process of coating is observed after subsequent heating–cooling procedures as illustrated in Fig. 2. After first heating (trace proc. 2), the mean amplitude of TM DIL significantly decreased and became smooth without characteristic rapid changes of the expansion coefficient as it is seen during first procedure (trace proc. 1). During next heating the character of the mean amplitude TM DIL curve is stable with a slight constant decreasing in magnitude.

The main influence on the degradation of adhesion has thermal stresses and their relaxation as a function of temperature. In this case there is not observed contribution originating from elements of titanium diffusion from the layer to the substrate. As was reported earlier [9], the diffusion of titanium to the iron substrate is not higher than 0.5% mass at 1250°C.

The microscopic study of the surfaces, carried out after each heating process, confirms the mechanical character of the degradation observed such as surface cracks and delamination. After nitriding the mechanical failure start below the surface, depending on thermal stresses at higher temperature and surface development.

The effect of the degradation of coating has an influence on magnetic properties detected by TM TMAG as shown in Fig. 3. The rough changes in magnetic induction observed by vector angle TM TMAG during first heating (proc. 1), are not observed during the next processes (proc. 2, proc. 3) [10].

The correlation between dilatometric and magnetic effects is evidence and data can be used for further numerical analysis of the stress relaxation.

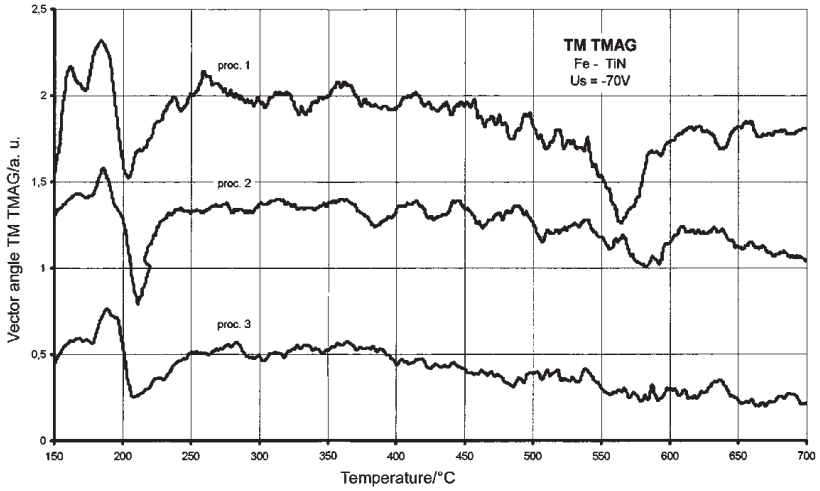

Fig. 3 The effect of the thermal stress relaxation of the coating in high temperature detected by TM TMAG. The rough changes in magnetic induction detected by vector angle TM TMAG disappear after first heating (proc. 1)

Conclusions

The temperature modulation added to the linear heating program in thermomagnetometry and dilatometry allows to determine the temperature regions of stress relaxation between TiN thin layer and the iron substrate. The modulation technique allows a more comprehensive analysis having amplitude, phase, and vector values to be analyzed, in many cases more sensitive for physical changes in tested specimen. A relation was found between mechanical and magnetic changes in tested samples.

The results from subsequent heating processes were compared with results from similar processes without applied modulation. It was found that during a single linear heating the kinetic of stress relaxation is not observed. The last one shows only the temperature range where total degradation takes place.

The method, in contrast to basically used X-ray diffraction and nanoindentometry, allows continuous monitoring of the stress relaxation as a function of temperature or time.

The development of this new measurement technique, including thermomodulated differential thermal analysis (TM DTA), is still developed, and will be reported in more detail in the next future.

References

1 B. Wendler and A. Młotkowski, Proc. 12th International Summer School Modern Plasma Surface Technology, Technical University of Koszalin, Poland, (2000) 217.
2 I. A. Waisman and A. Philips, Proc. of the Society Experimental Stress Analysis, (1954) t.XI, 29.

3 P. Myśliński, W. Precht and J. Staśkiewicz, J. Thermal Anal., 35 (1989) 193.
4 P. Myśliński, P. Kamasa and J. Vandlik, J. Therm. Anal. Cal., 56 (1999) 233.
5 B. Wunderlich, Y. Jin and A. Boller, Thermochim. Acta, 238 (1994) 277.
6 A. Zawada-Tomkiewicz and M. Pancielejko, Proc. 12th International Summer School 'Modern Plasma Surface Technology', Technical University of Koszalin, Poland, (2000) 393.
7 D. M. Price and G. M. Foster, J. Therm. Anal. Cal., 56 (1999) 649.
8 F. Förster, Z. Metallkd., 45 (1954) 44.
9 G. V. Samsonov, G. S. Opadhaja and V. S. Nieszpor, Fizyczniskoje Matweriałowjedienii, Edition: Naukowaja Dumka Kijev (1974) 378.
10 P. Myśliński, J. Staśkiewicz, A. Czyżniewski and P. Kamasa, Conf. Abstract, 14th Soft Magnetic Materials, Balatonfured, (1999) P2/6.