Temperature modulation in dilatometric investigation of PVD substrate-coating systems

P Myśliński¹, P Kamasa², A Gilewicz¹

¹Koszalin University of Technology, Institute for Technology and Education
75-435 Koszalin, ul. Śniadeckich 2, Poland
e-mail: piotr.myslinski@tu.koszalin.pl

²Wigner Research Centre for Physics, Research Institute for Solid State Physics and Optics
Hungarian Academy of Sciences
1125 Budapest, POB 49, Hungary

Abstract
Temperature modulation technique and phase sensitive analysis is applied for investigation the thermal stresses induced at higher temperature in the space between coating and substrate. The method applying only phase shift parameter eliminates influence of the intensity variation of measured signal. Comparison with conventional application of temperature modulation is presented. Method gives comprehensive information about the state of coating which is usually immersed using amplitude analysis.

1. Introduction

Intrinsic material properties such as hardness, strength, ductility, work hardening 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. Enhance of a wear resistance can be obtained by coating the working surface by ceramic thin films. Ceramics like TiN, TiAlN TiC, TiCN or CrN are characterized by high wear-resistance. Among other methods of deposition, the plasma assisted physical vapor deposition (PAPVD) is often used. Beside the surface properties, the resistance on a mechanical and thermal load decides 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 intrinsic stress may be generated when the layer grows [2]. Thermal stress is a result of different thermal expansion coefficient of layer and substrate when temperature is changing after the process is completed [3]. At higher temperatures the chemical and structural processes are activated and adhesive forces can be reduced and thermal stability decreased. The degradation (delamination) 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.¹

¹To whom any correspondence should be addressed.
In the field of thin wear resistance coatings the temperature stability of the adhesion is the basic parameter in the industry application. A method for the diagnosis of the state of a coatings obtained by physical vapour deposition on tools for metal and wood processing has been developed which is based on recording thermomechanical effects at changing temperatures. These thermomechanical effects reflect the mechanical stresses between substrate and coated thin layer, which depend on physical properties of the materials, mainly on thermal expansion and compressibility. These interactions can be detected by dilatometry as changes in effective thermal expansion. The effective thermal expansion of the substrate-coating system with ideal adhesion can be estimated theoretically and than verified experimentally. Any deviation from the ideal state of the deformation can be interpreted as loss of adhesion. It was recognized that a linear temperature program is not sensitive enough when the sample is massive as in case of a cylindrical rod as described in Experimental section of this paper.

A major advance in dilatometric (DIL) experiment is the application of a temperature modulation (TM), leading to temperature modulated dilatometry, TMDIL [5, 6]. In general, temperature modulation (TM) enables recording of at least two parameters of dilatometric response. Using the sinusoidal temperature modulation enables first of all recording the response as intensity of the mechanical dilatation $A_{DIL}$, independent of the phase changes of the signal. This gives increased sensitivity in detection changes of the coefficient of thermal expansion (CTE) [7]. Another experimental aspect of TM is the pure analysis of phase changes which enables to obtain additional useful information about delamination processes of wear resistance coating. A new method developed by authors brought promising experimental results and is presented here as a preliminary experimental achievement.

2. Experimental

2.1. Sample. Titanium nitride (TiN) films were deposited on pure iron (ARMCO) substrates by the PVD method using cathodic arc evaporation (CAE). The Titanium cathode was 100 mm in diameter. The arc current in the process of deposition was 80 A. The gas atmosphere in the working chamber was pure nitrogen at a pressure of 0.5 Pa and the substrate bias voltage was $-70$ V. The substrate temperature during film deposition was controlled to a value of about 400°C. The distance between the substrate and the Ti cathode surface was 18 cm. The substrate was in the shape of a cylindrical rod, 30 mm in length and 3 mm in diameter. The average film thickness was 2.4 µm and the deposited film was homogenous in thickness within ±0.3 µm. In order to get a homogeneous film the rod sample was rotated during deposition.

![Figure 1](image-url)  
**Figure 1.** Square waves obtained from sample temperature and dilatation signals, period 360 s.
2.2. Phase detection. In this work a new experimental aspect is realized, namely applying temperature modulation together with analysis of the phase shift $\phi_{\text{DIL}/T_s}$ of the $A_{\text{DIL}}$ signal with respect to the phase of the sample temperature signal, $A_{T_s}$. The method will be described in details in forthcoming paper [8]. Principles have been adopted from radiofrequency techniques using FM modulation and detection system. Briefly, analog sinusoidal signals are transformed electronically into the square waves being in phase with sinusoids: $\text{sqr}(A_{T_s})$, $\text{sqr}(A_{T_p})$, $\text{sqr}(A_{\text{DIL}})$ corresponding to sample temperature, program temperature and dilatation, respectively. Amplitude is limited to the unit and zero-transitions determine the phase shift $\phi_{\text{DIL}/T_s}$ of the $A_{\text{DIL}}$ signal versus $A_{T_s}$ (figure.1).

It is known from earlier investigations [9] that the presence of a thin layer mechanically interacts with the substrate. For the model sample in shape of rod the mechanical interactions lead to physical deformation with temperature (stretching or shrinking in length) measurable using dilatometer and easily to be analyzed numerically. Finally the effect of interest is that loosing of the sample coating adhesion appears as nonreversing axial local relocations of the coated layer versus substrate. With sinusoidal variation of the temperature the relocations of the layer change periodically their direction to the opposite (hysteresis). The effect is observed as an additional phase shift between sample temperature $A_{T_s}$ and dilatation $A_{\text{DIL}}$. When thin film has ideal adhesion to the substrate the phase shift appears as a result of heat diffusion to the sample and the resulting gradients. It should be noted that temperature modulation in spite of thermomechanical effects, enables to detect dilatometric effects associated with thermodynamical changes of the sample, i.e. reversible and irreversible transitions [10].

2.3. Uncoated Fe sample. Phase analysis in comparison with DIL amplitude variation for uncoated Fe sample in shape of rod is illustrated in figure 2. The result was obtained for sinusoidal modulated temperature with $5^\circ\text{C}$ of amplitude and a period of 50s. In this experiment applying temperature modulation, three values were simultaneously recorded: sample temperature $T_s$, dilatation DIL and independently the magnetic susceptibility presented as TMAG signal.

![Figure 2](image_url). Temperature modulated method applied to the Fe rod sample: The phase shift $\phi_{\text{DIL}/T_s}$ analysis by phase sensitive procedure in comparison with conventional amplitude analysis of $A_{\text{DIL}}$, $A_{T_s}$ as well as TMAG. The reader should keep in mind that the Curie point is at 770$^\circ\text{C}$. 

From traces of DIL and T, it can be concluded that changes in the DIL amplitude $A_{\text{DIL}}$ are mainly a result of temperature. The trace of temperature amplitude variation $A_{T}$ is nearly the same (besides a constant factor) as dilatation amplitude variation $A_{\text{DIL}}$. In contrast, the phase variation $\phi_{\text{DIL}/T}$ is significantly associated with changes of magnetic properties of the sample seen above the Curie temperature of iron.

3. Results

The specific behavior of a TiN layer on a pure iron (ARMCO) substrate was investigated using a model sample in shape of a cylindrical rod. Results are presented in figure 3 separately for amplitude (left column) and phase analysis (right column).

**Figure 3.** Result of phase detection (right) in comparison with traditional amplitude analysis (left). Three cases of phase analysis are available: $\text{sqr}(A_{\text{DIL}})$ phase changes in relation to the sample temperature $\text{sqr}(T)$ as reference (d), $\text{sqr}(A_{\text{DIL}})$ phase changes in relation to the program temperature $\text{sqr}(T_p)$ as reference (e), $\text{sqr}(T)$ phase changes in relation to the program temperature $\text{sqr}(T_p)$ as reference (f).

The amplitude analysis enables to obtain coefficient of thermal expansion (CTE) from the amplitude of dilatation, $A_{\text{DIL}}$, and the sample temperature, $A_{T}$, respectively. This value has an analogue meaning as direct current measurements with features for identification of the reversible and irreversible processes.

In case of phase detection there are three possibilities of analysis: (a) phase changes of $\text{sqr}(A_{\text{DIL}})$ using as a reference the sample temperature $\text{sqr}(T)$ or (b) programmed temperature $\text{sqr}(T_p)$, and (c) phase changes of $\text{sqr}(T)$ using programmed temperature $\text{sqr}(T_p)$ as a reference.

In case of periodic changes of $T$, dilatation $A_{\text{DIL}}$ changes are connected only with the sample temperature $T$, resulting in variation of the phase-shift without intensity variation (figure 3d). The influence of the amplitudes of both signals is minimized since the effect of coating can be distinguished from phys-
ical and chemical reactions. For example, in Phase column of figure 3f at temperature T \textsubscript{3} a strong effect associated with substrate being at this temperature during deposition can be seen. In the left part of figure 3 the temperature activation of chemical degradation of the thin film of TiN coating (oxidation) is seen on phase change of \( A_{DIL} \) signal at \( T_4 \) (see figure 3 d, e).

Conclusions

The applied pure phase analysis to the temperature modulation technique in the field of wear resistance coating technology is promising giving additional comprehensive information. Concluding it can be stated that this method allows not only to discriminate reversible and irreversible processes but more, the method enables to distinguish between irreversible processes like early coating delaminating and structural phase transitions. The technique used together with all previous application is a complementary one and extends the methods known as Dynamic Load Thermomechanical Analysis (DL TMA).

Reference

[1] Mittal K L, Electrocomponent Science and Technology, 3 (1976) 21.
[2] Cammarata R C, Bilello J C, Greer A L, Sieradzki K, Yalisove S M, MRS Bull. 4 (2) (1999) 34.
[3] Wendler B, Młotkowski A, Proc. 12th International Summer School Modern Plasma Surface Technology, Technical University of Koszalin, Poland, (2000) 217.
[4] Hultman L, Vacuum, 57 (2000) 1-30.
[5] Reading M, Elliot D, Hill V I, J. Therm. Anal. Cal. 40 (1993) 949.
[6] Price D M, Thermochim. Acta 315 (1998) 11.
[7] Kamasa P, Myslinski P, Pyda M: Thermal expansion coefficient determination by temperature-modulated dilatometry. In: Proc. 31st Annual NATAS (North American Thermal Analysis Society) Conference (Albuquerque, NM, USA, 2003). Ed. M.J. Rich (Michigan State University, MI, USA, 2003), on CD-ROM; published also in NATAS Notes, Fall 2003, Vol.35 No.3 pp. 17-21.
[8] Myslinski P, Kamasa P, Phase analysis in temperature modulated thermal analysis, in preparation.
[9] Myslinski P, Investigation of the thermal stability of the hard coatings by Modulated Temperature Dilatometry. Vacuum (2009) 757-760.
[10] Wunderlich B, Thermal Analysis of Polymeric Materials, Springer-Verlag, Berlin 2005, p.359.