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Irreversing thermal expansivity of materials coated with adhesive thin films detected by modulated-temperature dilatometry and differential thermal analysis

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Abstract

Usability of simultaneous modulated-temperature dilatometry (MT DIL) and modulated-temperature differential thermal analysis (MT DTA) for the quantitative description of degradation kinetics of wear-resistant film adhesion to the substrate as a function of temperature are presented in this work. The reversing thermal expansion coefficient of materials as a parameter sensitive to the relaxation of mechanical thermal stresses in films tested was used for this purpose. Sample experimental results allowing the process of film degradation to be described as a function of increasing temperature are quoted. Usefulness of this method considering the films deposited at diversified process parameters is also substantiated. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Modulated-temperature DIL; Modulated-temperature DTA; Thin films coating; Adhesion

1. Introduction

Thin wear-resistant ceramic films, e.g. TiN, TiCN, TiAlN are deposited on working surfaces of cutting tools or machine elements in order to improve their tribological properties. The film deposition is performed using the physical vapour deposition (PVD) or chemical vapour deposition (CVD) ionic-plasma techniques.

The author's previous works [1–3] have demonstrated the usability of the modulated-temperature dilatometry methods (MT DIL) for the quantitative description of degradation kinetics of thin film adhesion, whereas the present work presents the usability of simultaneous MT DIL and modulated-temperature differential thermal analysis (MT DTA) methods for quantitative description of the phenomena.

Stresses in films take usually a compressive form. An example of intrinsic stress pattern in the substrate/film interface [15] is presented in Fig. 1.

Considering the previous results [4–9] the thermal expansion coefficient a of materials was used to determine quantitatively the kinetics of degradation of film adhesion to the substrate using simultaneous the MT DIL and MT DTA analyses.

The studies are carried out on the basis of the formula presented in [8]:

$$\frac{dL}{dt} = \alpha\frac{dT}{dt} + f'(t, T) \quad (1)$$

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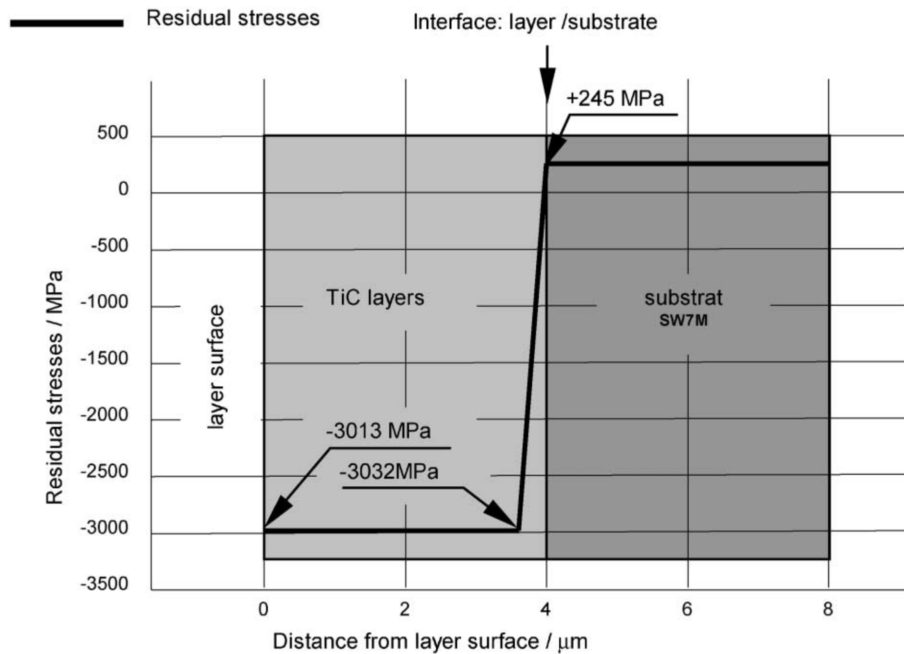

Fig. 1. Residual stress in the TiC coating and the 6-5-2 HSS substrate region near the TiC coating [15].

where L is the length of the specimen, α the coefficient of thermal expansion and $f'(t, T)$ is a certain function of time and temperature that describes irreversing changes in dimensions due to many factors, including the effects of relaxation of intrinsic stresses in the film on its adhesion.

It was assumed that under investigation conditions, the measure of degree of local degradation of substrate/film adhesion as an irreversible physical phenomenon is the change in the coefficient of thermal expansion a of the cylindrical specimen coated with a wear-resistant film.

The modulated temperature program is accomplished by adding to a linear heating ramp $\langle q \rangle$ a modulating component:

$$T_s = T_0 + \langle q \rangle t + A_{T_s} \sin \omega t \tag{2}$$

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 min). The $\langle q \rangle$ indicates an average heating rate in K/min. The A_{T_s} is the amplitude of modulated temperature.

The objects of individual and simultaneous recording are the differences in elongation and the temperature differences between the specimen (substrate) coated and the specimen (substrate) uncoated as a function of temperature.

Therefore, in the first case we deal with the MT DIL and in the second case with the MT DTA.

The deconvolution procedure of relative analyses MT DIL and MT DTA and calculations made by an algorithm formulated enabled to obtain data for quantitative determination of $\mathrm{d}\Delta L/\mathrm{d}T$ values and, hence, for determination of reversible thermal-expansion coefficient $\alpha_{rev}(T)$ values for a specimen coated with TiN. It is proposed to name the coefficient α "reversible" because the value of the amplitude A_{T_s} is too small to generate any changes in the adhesion between layer and substrate.

Data sources are measuring-data sets responding to changes in values of elongation-difference amplitudes $\langle A_{\Delta L} \rangle$ and temperature-difference amplitudes $\langle A_{\Delta T} \rangle$ between substrates coated and uncoated obtained as their response to sinusoidal temperature changes in a heating unit by Eq. (2).

Algorithm constants are data on specimens' length at the ambient temperature (L_{oc}: sample with layer, L_{ouc}: substrate only) before the first process of heating and the thermal-expansion coefficient α_{uc} for substrate.

The values of the coefficient α_{rev} was derived from the following equation:

$$\alpha_{rev}(T) = [L_{ouc}\alpha_{uc}(\Delta T - \langle A_{\Delta T}\rangle) - \langle A_{\Delta L}\rangle](L_{oc}\Delta T)^{-1} \quad (3)$$

where ΔT is an increase in its temperature resulted from the effects of the heating system.

Sources of macroscopic intrinsic stresses occurring in a film are as follows [12]:

- stresses connected with the growing process itself (grown-in stresses σ_G);
- stresses due to the difference in the thermal expansion coefficients of substrate and film (thermal stresses σ_{th});
- stresses σ_p caused by precipitation or phase transformation processes in the substrate during cooling.

Thus,

$$\sigma = \sigma_G + \sigma_{th} + \sigma_p. \quad (4)$$

Within the present work, the substrate was made of a material, which allows the component to be disregarded.

In practice, it is difficult to determine exact values of individual components of intrinsic stresses in a film due to their interaction occurring under conditions of thermal activation of film/specimen system.

Only thermal stresses σ_{th}, one may determine by solving the following equation [12]:

$$\sigma_{th} = -E\,\Delta\alpha\frac{T_2 - T_1}{1 - v} \quad (5)$$

where $\Delta\alpha$ is a difference in thermal expansion coefficients between the substrate and coating; T_1 a substrate temperature while the film was deposited; T_2 a substrate temperature after its cooling down or heating up; E Young's modulus and v Poisson's ratio of the coating. The stresses σ_G resulted from conditions of the film growth are affected by the process conditions applied. For example, the value of a negative bias voltage V_s while the film is deposited has an influence on the activation energy of such processes as re-crystallisation of film deposited or changes in the concentration of point defects responsible for grown-in stresses [13,14].

Temperature characteristics of the coefficient α_{rev} are a consequence of relaxation of both types of stress occurring at given temperature.

The thermal activation of the substrate/film system described by Eq. (2) and using simultaneous the MT DIL and MT DTA analyses makes it also possible to identify relaxation of both types of stress.

2. Experimental

Substrates of sintered alloy WC–Co 6 wt.% were prepared in the form of cylinders 3 mm in diameter and 30 mm in length. The substrates were polished with abrasive paper 600, and then ultrasonic-aided cleaning was applied. Then coated with TiN films by the PVD method using an arc discharging between the cathode and the casing of the working chamber. The cathode 75 cm^2 in area was made of titanium (purity 99.9%). The arc discharge took place at current of 90 A and voltage of 20 V. A flow rate of nitrogen in the process of deposition was 260 ml/min, and a working pressure in the chamber was 5×10^{-3} Pa. Temperature of substrate while deposition was about 350 °C. A TiN film was 2.5 μm thickness.

Experiments were carried out on the thermoanalyser of own design [10,11].

This device makes it possible to perform dilatometric, thermomagnetometric and DTA studies. The temperature changes in specimens were obtained by convection–radiative heat exchange between the infrared radiator, the system of tri-elliptical mirrors and their surfaces.

The specimens were subjected to consecutive thermal processes at temperatures ranging from 20 to 800 °C. A temperature rise in a heating system proceeded at a rate $\langle q\rangle = 2$ °C/min superposition with modulation with a period of $p = 1$ min and amplitude of 10 °C, and a temperature droop proceeded at a rate $\langle q\rangle = 40$ °C/min.

Experimental data was recorded successively every 1 s. Heating processes were carried out at laminar flow of argon (purity 99.995%) through the measuring chamber.

In order to ensure complete repeatability of experimental conditions for each series of several heating and cooling processes the same set of substrates was used in this way that film residuals were removed by mechanical and chemical cleaning and then again the substrates were prepared and coated with new TiN films.

Respective couples of specimens were subjected to the same heating processes according to the above-mentioned diagrams. The number of processes included in experimental cycles depended on a degree of measurement repeatability in relation to the preceding process, and consequently on a degree of adhesion degradation between the substrate and film after each process.

Raw data from MT DIL and MT DTA analyses that were obtained as a result of the above successive temperature-modulated heating processes subject to deconvolution procedure operations by Fourier transforms.

To illustrate the potential of the present method for interpretation of adhesion degradation between the substrate and film, there are also presented the experimental results for films deposited at various values of the process parameter, i.e. the substrate bias voltage V_s.

3. Results and discussion

Fig. 2 presents the sample raw data from MT DIL and MT DTA analyses for a couple of specimens WC–Co/TiN versus WC–Co obtained during the first heating process. The bias voltage applied to the substrate in the process of film deposition was $V_s = -70$ V and the flow rate of argon through the measuring chamber was 70 ml/min. The results were then subjected to the deconvolution procedure.

Fig. 3a and b show for two different samples the graphs of elongation difference amplitudes and temperature difference amplitudes between substrates coated and uncoated WC–Co/TiN versus WC–Co obtained as a result of deconvolution of MT DIL and MT DTA analyses.

Fig. 3a illustrates the case of complete concurrency of both analysis curves, which one can interpret that there was mainly relaxation of thermals stresses σ_{th} during the first heating process, whereas Fig. 3b shows the occurrence of stress relaxation σ_G resulting from the conditions of film growth.

Fig. 4 illustrates the runs of constant components resulted from Fourier analysis of MT DIL analyses from Fig. 2 and subsequent heating processes for a couple of specimens WC–Co/TiN versus WC–Co. These results comply with the temperature characteristics

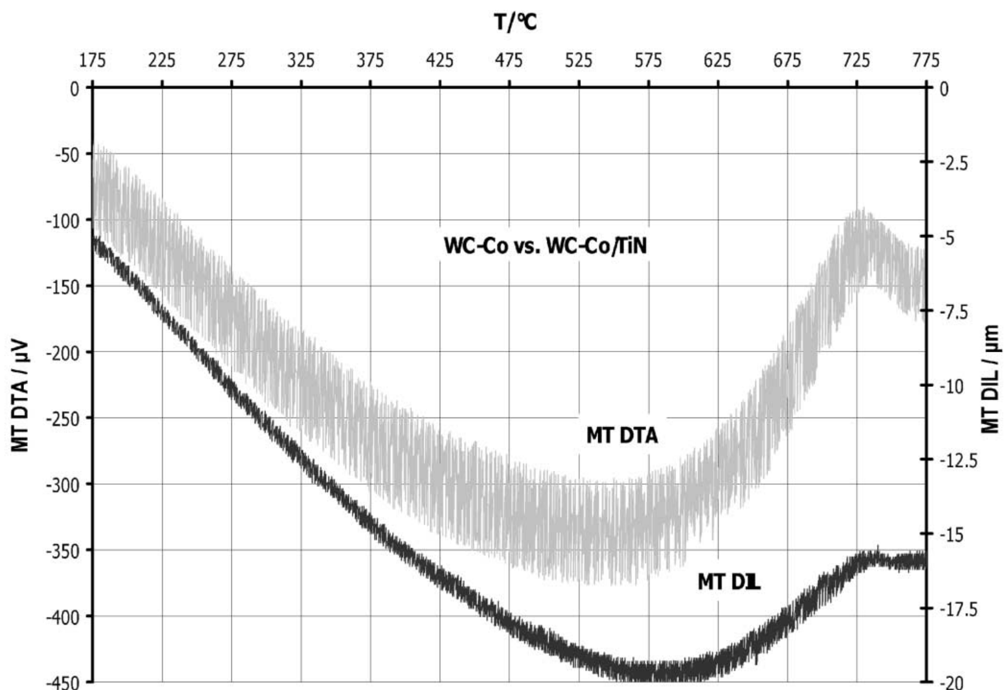

Fig. 2. Raw results from the relative MT DIL and MT DTA analyses for a couple of specimens WC–Co/TiN vs. WC–Co (measuring parameters are quoted in the text).

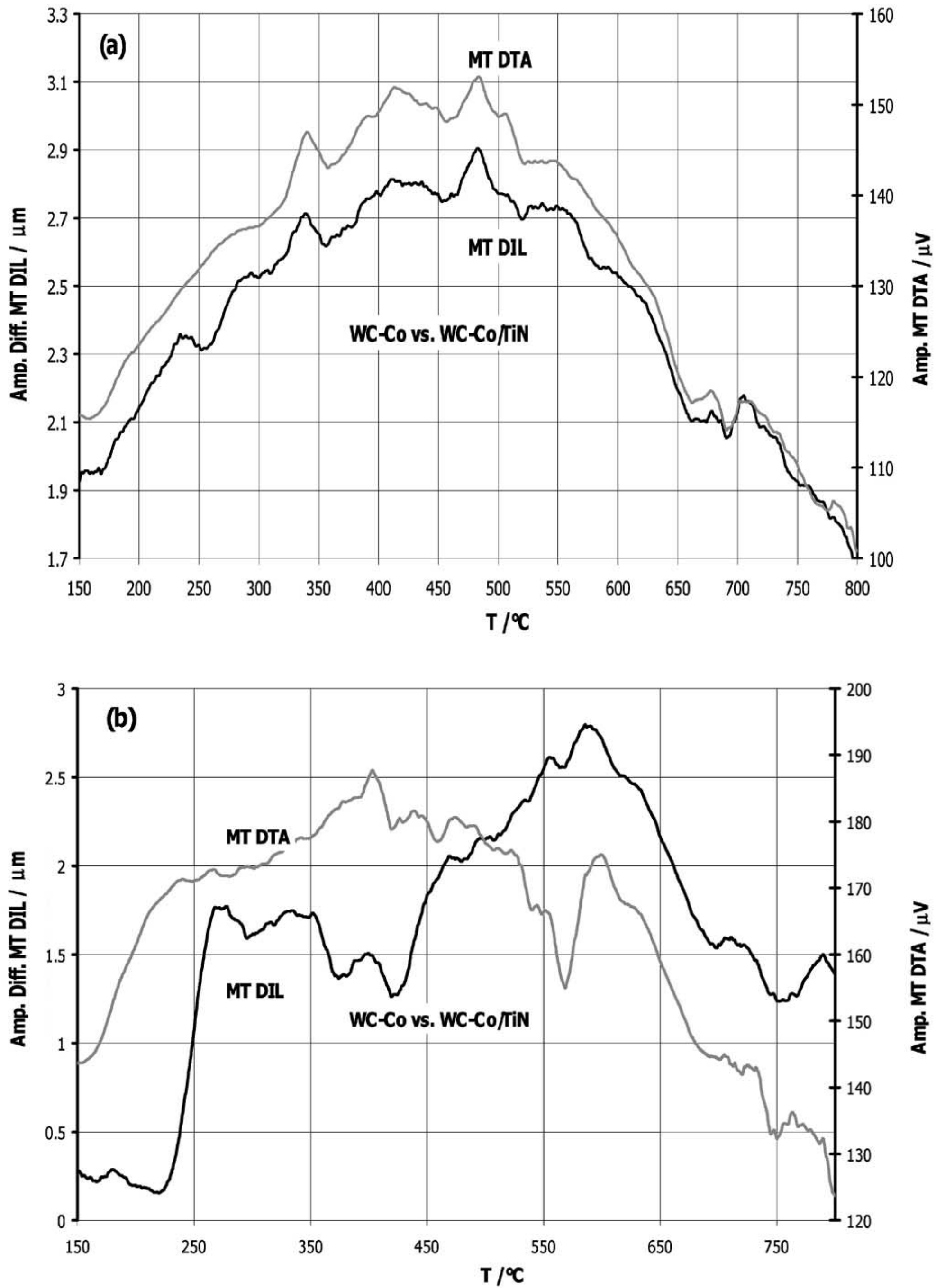

Fig. 3. Sample graphs of elongation difference amplitudes and temperature difference amplitudes between specimens WC–Co/TiN vs. WC–Co in the course of the first heating processes obtained as a result of deconvolution of the MT DIL and MT DTA analyses (description in the text).

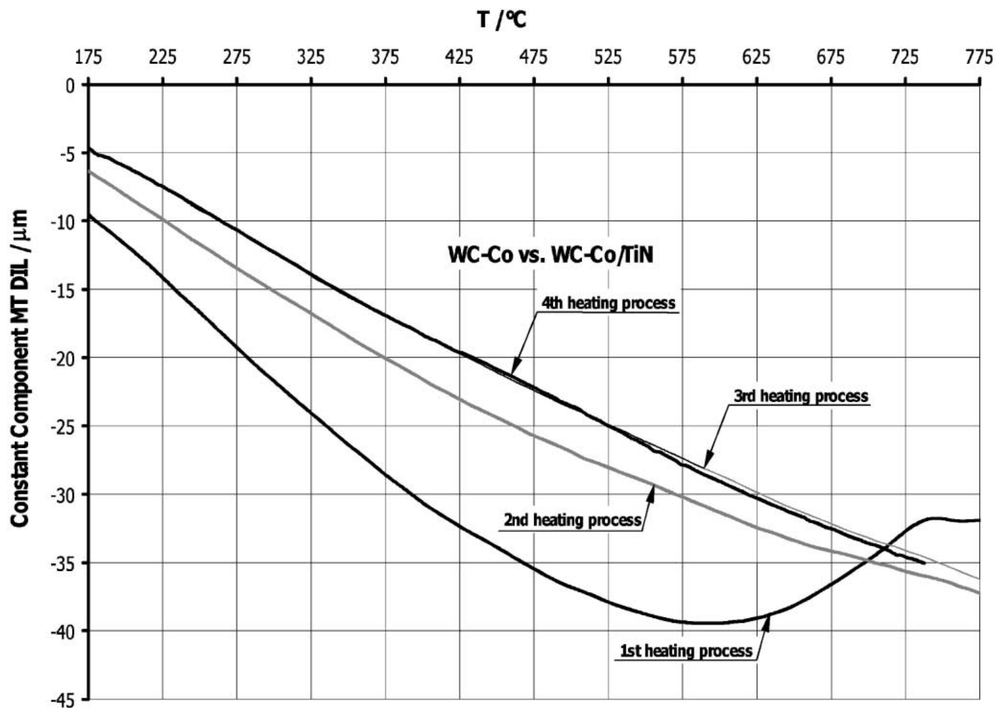

Fig. 4. Graphs of measuring-signal dc components from the MT DIL analysis obtained as a result of deconvolution of results presented in Fig. 2.

of elongation differences in specimens and can be used for determination of the effective thermal expansion coefficient of specimens coated. The curve of the first heating process distinctly discloses the significant change in the thermal expansion coefficient of specimens becoming uncoated at the temperature of approximately 550 °C, which one can interpret as the adhesion degradation between the substrate and film occurring intensively at that temperature.

Fig. 5a and b present the graphs of elongation difference amplitudes for a couple of specimens WC–Co/TiN versus WC–Co recorded during four successive heating processes under conditions applied to the MT DIL analysis. The specimens coated were prepared under different bias voltages $V_s = -70$ V and -10 V, respectively.

Due to the graph for the first heating process of the substrate with a film deposited at $V_s = -70$ V, it is possible to determine the range of temperature where adhesion is subject to rapid changes.

Differences in characteristics responding to the second heating processes indicate that the fundamental change in adhesion degradation has already occurred after the first heating process only when $V_s = -10$ V.

Furthermore, it is possible to carry out comparative quantitative assessments of these and any other phenomena for various types of films, substrates and different operational conditions on the basis of temperature value analyses of the thermal reversing coefficients α_{rev} for substrates coated.

Fig. 6a and b show the sample graphs of coefficients α_{rev} for the first and the fourth heating process for a couple of specimens WC–Co/TiN versus WC–Co. Changes in coefficients α_{rev} during the fourth heating process in relation to the first process showed that the fundamental degradation of film adhesion to the substrate had occurred. This effect was confirmed by macroscopic examination.

Owing to application of statistical processing of the above α_{rev} data it is possible to determine the basic parameters of degradation kinetics of film adhesion to the substrate in selected ranges of temperature. For example, Table 1 comprises summarised digital values

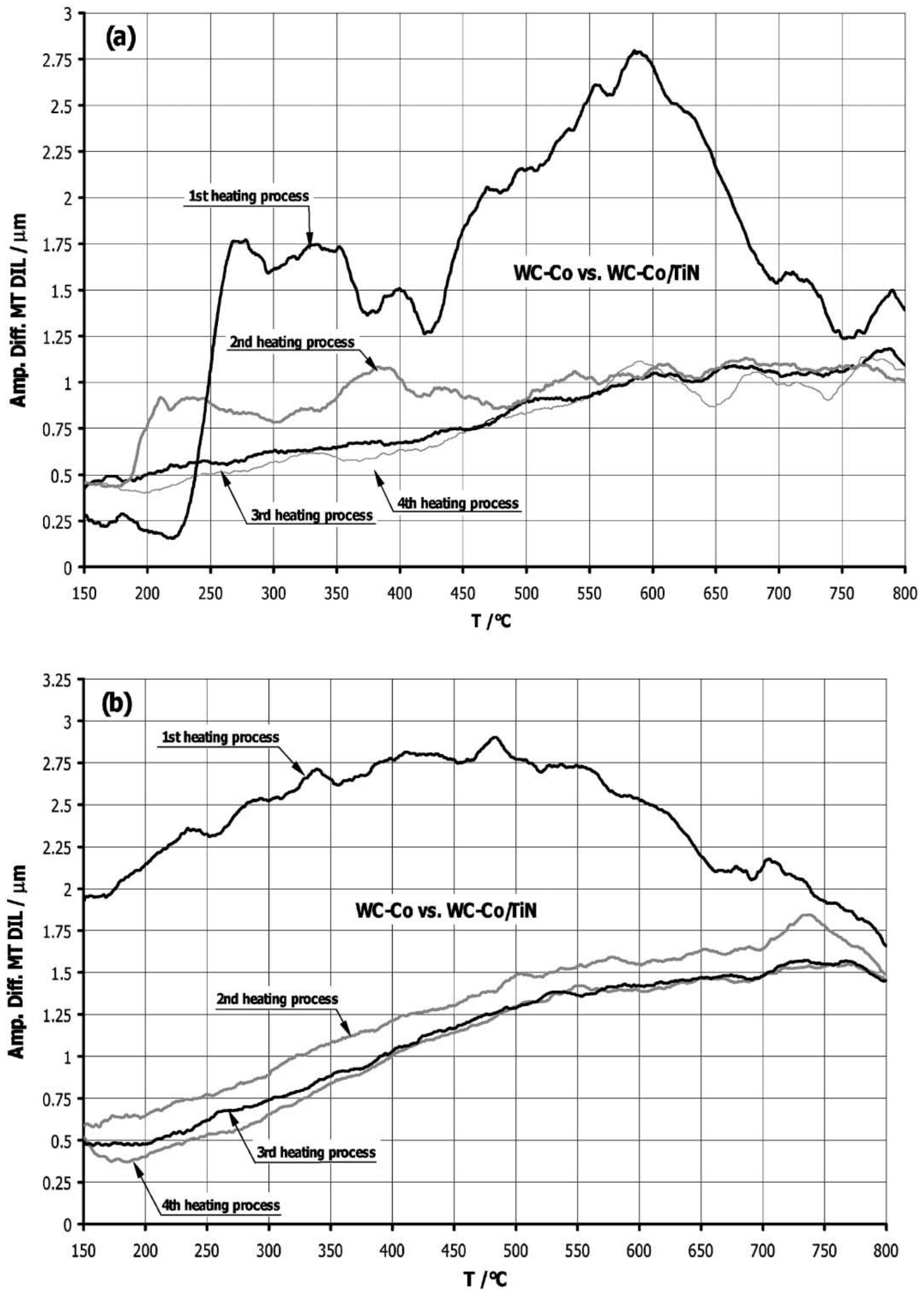

Fig. 5. Graphs of elongation difference amplitudes between specimens WC–Co/TiN vs. WC–Co for successive heating processes. Values of bias voltages applied to substrates in the process of film deposition: (a) $V_s = -70$ V; (b) $V_s = -10$ V.

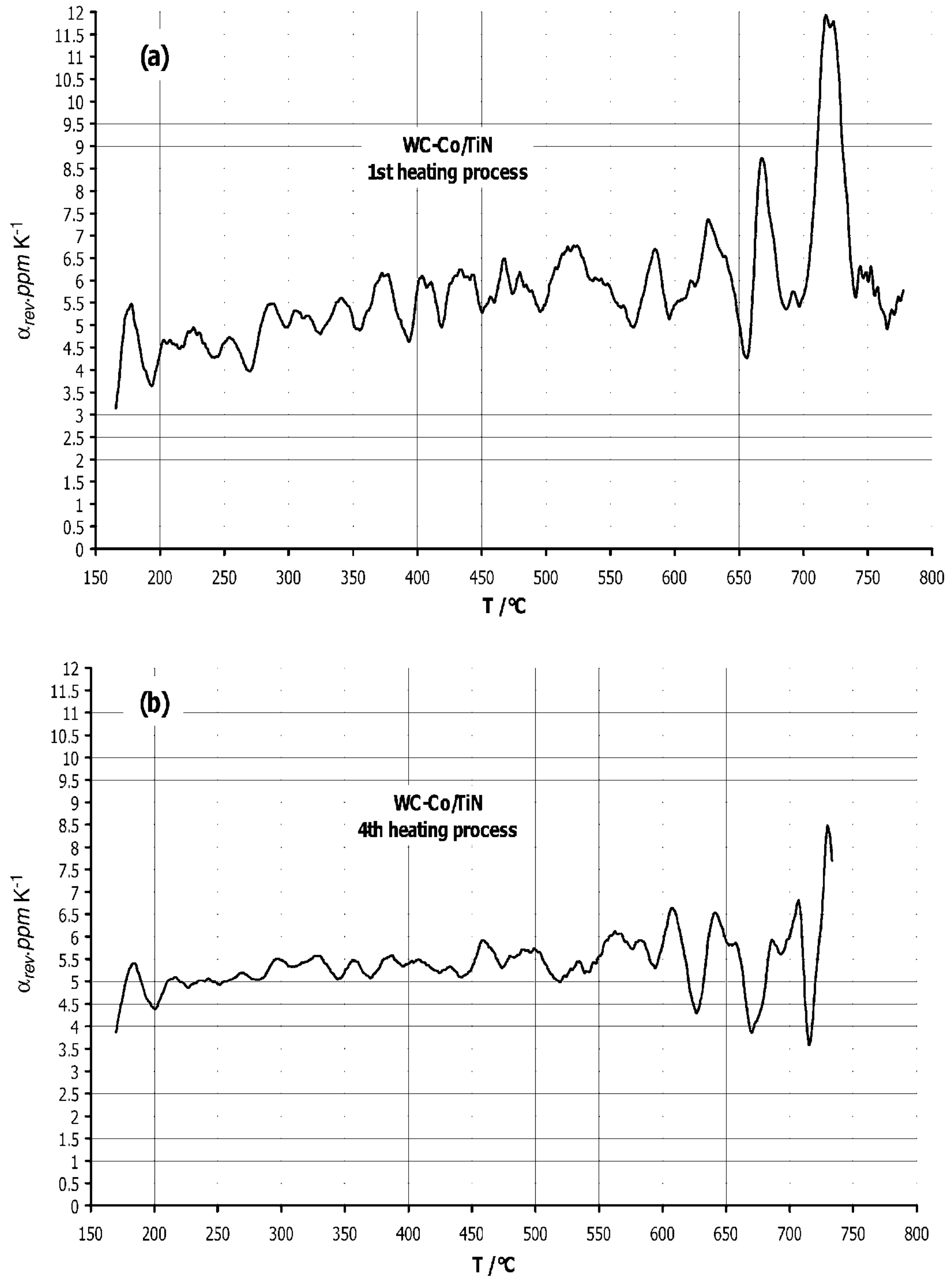

Fig. 6. Graphs of the reversing thermal expansion coefficient $\alpha_{rev}(T)$ for specimens coated with TiN for the first (a) worked out on the basis of the results obtained from the deconvolution procedure of the results presented in Fig. 2 and the fourth (b) heating processes.

Table 1
Coefficients α_{rev} for specimens WC–Co/TiN with TiN films deposited at different bias voltages V_s

V_s (V)	Heating process	220–300 °C			320–400 °C		
		α_{rev} (ppm/K)	Deviation α_{rev}		α_{rev} (ppm/K)	Deviation α_{rev}	
			ppm/K	Percentage		ppm/K	Percentage
−10	First	5.5724	0.0202	0.36	5.5753	0.0326	0.58
	Second	5.5777	0.0110	0.19	5.5794	0.0130	0.23
−70	First	5.5235	0.0831	1.50	5.5895	0.0411	0.74
	Second	5.5865	0.0145	0.25	5.5829	0.0178	0.32

of α_{rev} for specimens with TiN films deposited at diversified voltages V_s (Fig. 5a and b) in two temperature intervals. Specified data of the reversing thermal expansion coefficient $\alpha_{rev}(T)$ concern their average values. "Deviation α_{rev}" data determines the average value of maximum deviation from the average value α_{rev} in the same range of temperature specified as absolute numbers or percents in relation to the value of α_{rev}.

Table 2 shows a breakdown of numerical values of α_{rev} for substrate specimens with a TiN film deposited using a bias voltage of the same value, i.e. $V_s = -70$ V, however, measurements were carried out at diversified values of argon flow rates through the measuring chamber. Under uncontrolled air access to the chamber while the measurements were taken the diversified conditions of TiN-film oxidation were created.

An influence of the bias voltage V_s on the degradation kinetics of film adhesion to the substrate my be determined by evaluation of the numerical value of the thermal reversing coefficients α_{rev} for variable operational conditions of film deposition.

On the basis of data from Table 1 it is possible to confirm that runs of film adhesion to the substrate as result of stress relaxation occurring in the substrates coated during the first thermal processes are different, depending on values of bias voltages. For a bias voltage of $V_s = -70$ V while the film was deposited the essential change in the adhesion occurred at temperatures close to the range of 220–300 °C, whereas for $V_s = -10$ V it occurred at the range of 320–400 °C. The interrelations of coefficients α_{rev} applied to these temperature ranges (2.0219 for $V_s = -70$ V and 0.6135 for $V_s = -10$ V) showed that progression of adhesion degradation in films deposited at $V_s = -70$ V was more than three times higher than in films deposited at $V_s = -10$ V.

The conclusions drawn from the analysis of adhesion degradation progress after the first thermal process for the predetermined test temperature range are useful when the stability of machining properties of cutting tools are taken into consideration. The results of α_{rev} obtained for the second thermal process are assumed as the reference data for calculations. It results from the above data of α_{rev} that the degradation

Table 2
Coefficients α_{rev} for specimens WC–Co/TiN measured under diversified conditions of TiN-film oxidation

Flow rate of Ar (ml/min)	Heating process	220–300 °C			320–400 °C		
		α_{rev} (ppm/K)	Deviation α_{rev}		α_{rev} (ppm/K)	Deviation α_{rev}	
			ppm/K	Percentage		ppm/K	Percentage
70	First	4.7311	0.7249	15.32	5.4721	0.8914	16.29
	Second	5.0393	0.4092	8.12	5.3344	0.3414	6.40
600	First	5.5235	0.0831	1.50	5.5895	0.0411	0.74
	Second	5.5865	0.0145	0.25	5.5829	0.0178	0.32

progression for the test temperature range of 20–800 °C was 2.78 times higher in case of films deposited at a voltage $V_s = -70$ V than at a voltage $V_s = -10$ V if the tool approaches the temperature close to the range of 220–300 °C.

To illustrate the one of possible applications of the present thermal analysis a series of thermal processes were carried out at the diversified conditions of TiN-film oxidation. The data of α_{rev} presented in Table 2 confirm that under favourable conditions for the film oxidation (the measuring chamber is supplied with argon at a rate of 70 ml/min) the degradation progression is 8.72 times higher with reference to less favourable oxidation conditions (argon flow rate 700 ml/min).

4. Conclusions

Results of measuring-signal deconvolution obtained by simultaneous analyses: the MT DIL and MT DTA for a couple of specimens WC–Co/TiN versus WC–Co show that the method discussed in the paper could be used for the macroscopic monitoring of the process of adhesion degradation between the substrate and film as a function of temperature. Thermal activation of the substrate/film system according to respective thermo-modulated experiments enables to reveal the non-reversing changes in its thermo-physical properties.

The process description of degradation can include an influence of respective components of intrinsic stresses on resultant stresses in a film at given temperature or a degree of adhesion degradation advance after a successive thermal process.

Characteristics obtained of the reversing thermal expansion coefficient α_{rev} as a function of temperature enabled to quantify the processes of adhesion degradation between the substrate and film. Application of mathematical data processing enables to obtain the basic parameters for description of the degradation kinetics of film adhesion to the substrate as a function of temperature or time for variable operational conditions of film deposition.

Experiments of this kind can be used for determination of optimum parameters of film deposition on metal and ceramic substrates, which is of great importance in case of cutting tools.

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