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ANALYSIS OF THERMAL STABILITY OF CrCN COATINGS DEPOSITED ON NITRIDED SUBSTRATES USING MODULATED TEMPERATURE THERMODILATOMETRY

The aim of the research was to investigate the influence of nitriding of the substrate made of 42CrMo4 steel on thermal stability of the antiwear CrCN coating deposited on its surface using Cathodic Arc Evaporation method. Samples of non-nitrided and nitrided substrate/CrCN coating systems were tested with Modulated Temperature Thermodilatometry, which program included system annealing in 26 h, temperature of 290°C and argon atmosphere. Recorded during tests, changes in substrate elongation in response for changes of sample temperature, enabled qualitative determination of changes in stress states in the coatings as a result of samples annealing. Annealing of the system with nitrided substrate resulted in smaller change in residual stress in coating than for the system with non-nitrided substrate, which can indicate its better thermal stability. Values of residual stresses in coatings calculated by $\sin^2\psi$ method before and after annealing on the basis of tests performed using X-Ray diffraction, agree with results of dilatometric tests.

Keywords: antiwear coatings, nitriding, residual stress, thermal stability, thoermodilatometry

1. Introduction

Increment of temperature in operating conditions of single or multi-layer antiwear coatings produced by PVD or CVD methods, activates the mechanisms leading to changes in their operational properties. It also causes phase decomposition, grain growth, the nitrogen diffusion, crystallization of the amorphous phases, phase separation, the interphase reactions and oxidation [1,2]. All these phenomena occur at a specific, different temperatures depending on coating material. The consequences of these phenomena are changes in material parameters such as: Young's modulus, Poisson's ratio, coefficients of thermal conductivity, specific heat and thermal expansion coefficient, which changes effectively contribute to the change of stress in the substrate/coating systems [3-11]. Understanding of these phenomena which determine the thermal stability of coatings, in particular knowledge of thermally activated mechanisms of micro- and macroscopic changes in the structure and composition of the coating, allows more accurate prediction of their operational durability in various applications. This mechanisms were investigated on different types of coatings, inter alia single-layer TiN, CrN, TiAlN, multilayer, nanostructural TiN/CrN, TiAlN/CrN deposited on silicon and steel substrates [12-17]. Studies by Raman spectroscopy showed that TiN, CrN, TiN/CrN, TiAlN, and TiAlN/CrN begin to oxidize at temperatures of 500, 600, 750, 800, and 900°C respectively [18]. In addition, the results indicate that multilayer coatings have much higher thermal stability than single-layer. Some of the relationships between the evolution of the mechanical properties and microstructure has been also identified. The highest thermal stability was observed for $TiN_x(B)_y$ coatings with reference to the microstructure stability, resistance to oxidation and the stability of mechanical properties [19]. Studies aimed to analyze the thermal stability of the substrate/coating system, wherein the substrate before the deposition of the coating is subjected to a process of nitriding, are also taken into account [20]. In the paper [21] is described the test for wear resistance of TiAlN ($Ti_{0.7}Al_{0.3}$) coatings deposited on the nitrided stainless steel and non-nitrided H13 steel, using ball-on-disc method at room temperature and at 600°C. It was observed that in the room temperature there are not significant differences in wear rate, but they were revealed clearly at the temperature of 600°C, in which *nitrided steel/PVD coating* system has considerably better properties than the *non-nitrided steel/PVD coating* system. Authors concluded, that this is caused by higher substrate hardness and higher H/E ratio, which corresponds to high fracture toughness.

The results of research presented in this article concern exactly this thread of analysis of the thermal stability of the substrate/PVD coating system, wherein the substrate (42CrMo4 steel) is subjected to the nitriding process. Tests were performed based on dilatometric thermomechanical method and supplemented with tests of residual stresses using XRD method. In

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the used thermomechanical method [22] is applied the concept of such methods as DL TMA (thermomechanical analysis under dynamic load) and DMA (dynamic mechanical analysis). This allow to investigate simultaneously the influence of temperature and mechanical forces on tested systems [23,24]. As a result of thermal and mechanical loads, a change in linear dimensions of the substrate/coating system is registered, which is a superposition of two components:

- component whose value is dependent on the linear thermal expansion coefficient α,
- component, which appears when in the sample thermally activated processes occur.

The main difference of applied thermomechanical method with respect to the conventional TMA and DMA methods consists in the fact that, in these methods properties observed as a function of temperature or time refer to solid samples of a particular material. While in the thermomechanical method we are dealing with the substrate-coating system, where irreversible changes which occurs in the coating, resulting in the evolution of the stresses, causes changes in the forces affecting the substrate.

2. Experimental

2.1. Specimen preparation

The specimens for tests were made of 42CrMo4 steel. Samples for tests of residual stresses by XRD had the shape of a disc with a diameter of 30 mm and a thickness of 5 mm, and for the thermal stability tests the shape of cylinder with diameter of 3 mm and a length of 30 mm. The nominal compositions of steel are summarised in Table 1. The surface roughness of the specimens after polishing was $R_a = 0.3$ µm.

2.2. Gaseous nitriding

Nitriding of specimens was performed in a laboratory vertical quartz tube furnace, with an attached water tank (for quenching). The nitriding temperature of 813 K (540°C) was controlled within ±1°C at the position of the samples. The nitriding atmosphere was composed of ammonia (99.9 vol. % pure) and hydrogen gas (99.999 vol. % pure), which enabled the adjustment of the nitriding potential K_N. The gas flow was controlled with Bronkhorst mass-flow controllers. The linear flow rate of the gas mixture through the quartz retort was 1.4 cm/s. Nitriding potential was equal 1.5. Prior to nitriding the surfaces of the specimens were activated by preoxidation. Specimens were moved from the cool part of the retort to its working part after the atmosphere composition had stabilised. After nitriding specimens were polishing in order to remove compound layer ($Fe_{2,3}(NC)$ and γ').

2.3. Deposition of coating

The coatings were deposited in a multi-source PVD system using cathodic arc evaporation. The cathode was pure chromium. The samples were chemically degreased and ultrasonically cleaned in a hot alkaline bath for 10 min and dried in warm air. The substrates were placed on a rotational holder about 18 cm away from the chromium cathode. After the system was evacuated to the base pressure of 1 mPa it was filled with argon to about 0.5 Pa. For further cleaning the substrates were sputter etched using chromium Cr^+ and argon (Ar^+) ion bombardment with a bias voltage of –600 V for 20 min. A chromium adhesion layer of about 0.2 µm was first deposited onto the substrates. The CrCN coatings were deposited at a fixed nitrogen partial pressure of 1.8 Pa controlled by a Baratron type capacity gauge. The deposition temperature was 300°C and a negative substrate bias voltage in the range of 10÷300 V was applied. Acetylene was added at a flow rate of 10 sccm, controlled by an MKS 100 mass flow controller.

2.4. Dilatometric tests

The experimental tests were conducted with the use of a compensation dilatometer with temperature modulation. Dilatometer allows phase-sensitive registration of thermal and dilatometric responses. The technical details of the method and the conditions of the measurement of temperature and linear displacement of the systems under examination, were described in detail in [22,25-30].

2.5. The measurement of stresses

To determine the value of residual stresses in the coating before and after the annealing of the samples, was used roentgenographic indirect method, so-called $\sin^2\psi$ [31,32]. Method uses the phenomenon of shifting of diffraction lines appearing in material with crystalline structure under stress. Measurements using small angle X-ray diffraction was performed at room temperature on a coating deposited on a flat substrate (nitrided and non-nitrided) after the deposition process, and after long annealing under conditions identical to the conditions for annealing of cylindrical samples.

TABLE 1

Chemical composition of the investigated material (42CrMo4) in wt-%

C	Mn	Si	P	S	Cr	Ni	Mo	W	V	Co	Cu
0,38-0,45	0,4-0,7	0,17-0,37	max 0,035	max 0,035	0,9-1,2	max 0,3	0,15-0,25	max 0,2	max 0,05	—	max 0,25

3. Results and discusion

The study of thermal stability of the *substrate/PVD coating* system was performed using the compensation dilatometer. The measurement, in accordance with the used method, is to register changes in elongation of the substrate of the system in response to the forced change in temperature of the sample. The measurement of elongation is carried out using a linear displacement sensor of LVDT type (Linear Variable Differential Transformer) with a resolution 0.01 μm. In the case of tested systems, linear dimensional change of the substrate due to temperature changes depends not only on the thermal expansion coefficients of the substrate but also depends inter alia on the thermal and mechanical properties, in particular the state of residual stress and the state of adhesive connections in the system. The measurements carried out with temperature modulation makes it possible to extract, from thermally activated processes, reversible and irreversible changes that affect the total change of stress in the coating in a direction parallel to the surface.

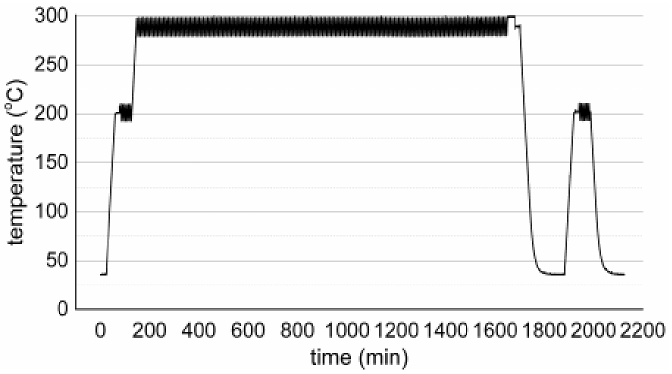

Fig. 1. The course of temperature changes of the sample during the test

Research program included the samples annealing lasting 26 hours at 290°C under an argon atmosphere. During annealing was applied sinusoidal temperature modulation with amplitude 10°C and 9 minutes of period. The period of modulation has been chosen by the optimization procedure [22]. The recorded measurement signals of elongation and temperature of the samples were then subjected to deconvolution into a constant and a variable component. This procedure enables:

- determining the values of time delay of the variable component of substrate elongation signal, relative to the signal of cycling changes of sample temperature,
- evaluation of changes in the state of stress at room temperature by determination of the ΔL_S indicator value.

ΔL_S indicator is the difference between the length of the substrate at room temperature after annealing and the length of the substrate before annealing. A negative increment of the indicator value means a decrement in the value of compressive stress occurring in the coating after the deposition process, while a positive increment of the ΔL_S value corresponds to an increment of these stresses. In addition, the results of measurement of the amplitude of the sinusoidal temperature change $<A_T>$ and elongation $<A_L>$ of the tested system are used to determine the value of the α_{AC} indicator, so-called equivalent thermal expansion coefficient according to the following formula [22]:

$$\alpha_{AC} = \frac{1}{L_{0T}} \frac{\langle A_T \rangle}{\langle A_L \rangle} \tag{1}$$

where L_{0T} is the initial length of the substrate. The measurement of the α_{AC} indicator is carried out at temperature of 200°C before and after annealing. The relative percentage increment of the indicator value is a measure of the total change in the state of stress in the coating at a temperature of 200°C as a result of annealing of the system.

Experimental studies were performed on two types of systems: *non-nitrided substrate/CrCN coating* and *nitrided substrate/CrCN coating*. As a result of nitriding, the diffusion layer was formed with specified profile of hardness changes (Fig. 2).

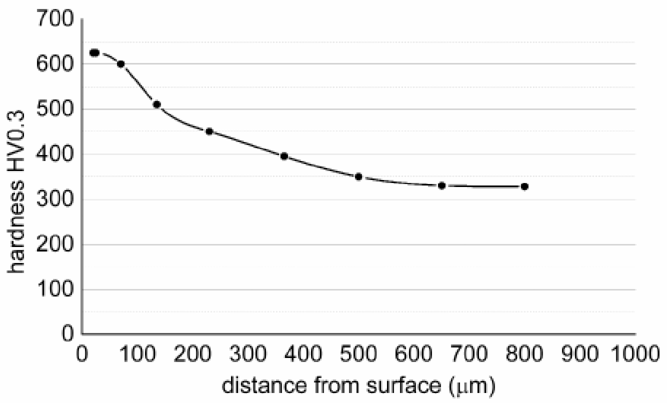

Fig. 2. Hardness measurements over the cross section of nitrided samples

Dilatometric tests of substrate – PVD coating systems were also preceded by thermomechanical studies of steel substrates both before and after the nitriding process. The results of these studies are presented in the publication [33]. On the surfaces of both types (cylinder and disc) of nitrided and non-nitrided substrates, during one process was deposited CrCN coating with 8 μm of thickness using cathodic arc evaporation method. The graph (Fig. 3) shows the change in value of the ΔL_S indicator for both types of tested systems (*nitrided and non-nitrided substrate/coating*) arising as a result of the applied annealing. It can be seen that annealing of the system with non-nitrided substrate caused the change in value of the indicator by 0.23 μm, while the decline in the value of ΔL_S for a system with nitrided substrate is negligibly small.

These results shows, that the annealing resulted in a reduction of compressive stresses in the coating and this change was significantly higher in the case of a non-nitrided substrate. Residual stresses in the CrCN coatings determined using X-ray diffraction on flat samples (disc) corresponds with the test results obtained by thermomechanical analysis. The values of residual stress in the coating deposited on the nitrided and non-nitrided substrate measured after the deposition process, and after 26 hours of system annealing are summarized in the Table 2.

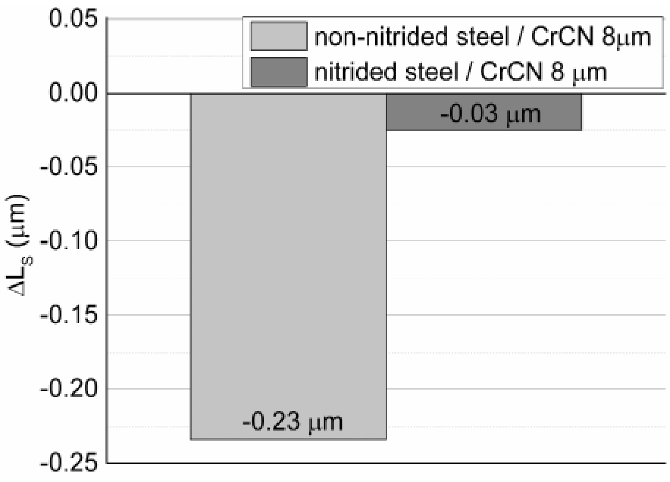

Fig. 3. Changes in ΔL_S indicator after annealing of tested substrate/PVD coating systems

TABLE 2

The values of residual stresses in the coating after the deposition process and the annealing of the systems in 290°C measured by XRD

System	**Residual stresses in coating (MPa)**	
	After deposition	**After annealing**
non-nitrided 42CrMo4 steel / CrCN	–7974	–7283
nitrided 42CrMo4 steel / CrCN	–7543	–7019

Measurements have shown, that the coating deposited on the nitrided substrate is characterized by a smaller compressive stresses after the deposition process as compared to a coating deposited on the non-nitrided substrate. Annealing of the samples resulted in a decrement of stresses in the coatings of both systems. In the coating deposited on the non-nitrided substrate this decrement was approximately 700 MPa, while in the coating deposited on the nitrided substrate residual stresses decreased by 523 MPa.

Analysis of the processes occurring in the studied systems during the annealing at temperature of 290°C was performed based on changes in: α_{AC} indicator, amplitude of dimensional changes (length) of the system $<A_L>$ (function of annealing time) and changes in the time delay τ between the change in length of the system and the temperature of the sample.

As can be seen from the graphs presented in the Fig. 4, the course of changes in the value of the α_{AC} indicator in the case of a system with non-nitrided substrate is characterized by greater time variability, mainly in the initial stage of annealing (5 h) compared to the second of the tested systems (nitrided substrate).

Moreover, time dependence of the α_{AC} indicator (Fig. 4a) for system with non-nitrided substrate is correlated with time evolution of the amplitude of dimensional changes (length) of the system $<A_L>$ (Fig. 4b). Such result indicates the possible presence of coating degradation processes or changes in adhesion of the coating to the substrate. On the other hand, changes of the elongation amplitude $<A_L>$ for the sample with nitrided substrate (Fig. 4b) shows no correlation with the evolution of the α_{AC} in the marked range in Fig. 4a. Additionally, no essential change in elongation of the system (in this range) was observed. It follows that the characteristic changes in α_{AC} indicator (Fig. 4a) are associated mainly with thermally induced processes in nitrided substrate/CrCN coating system.

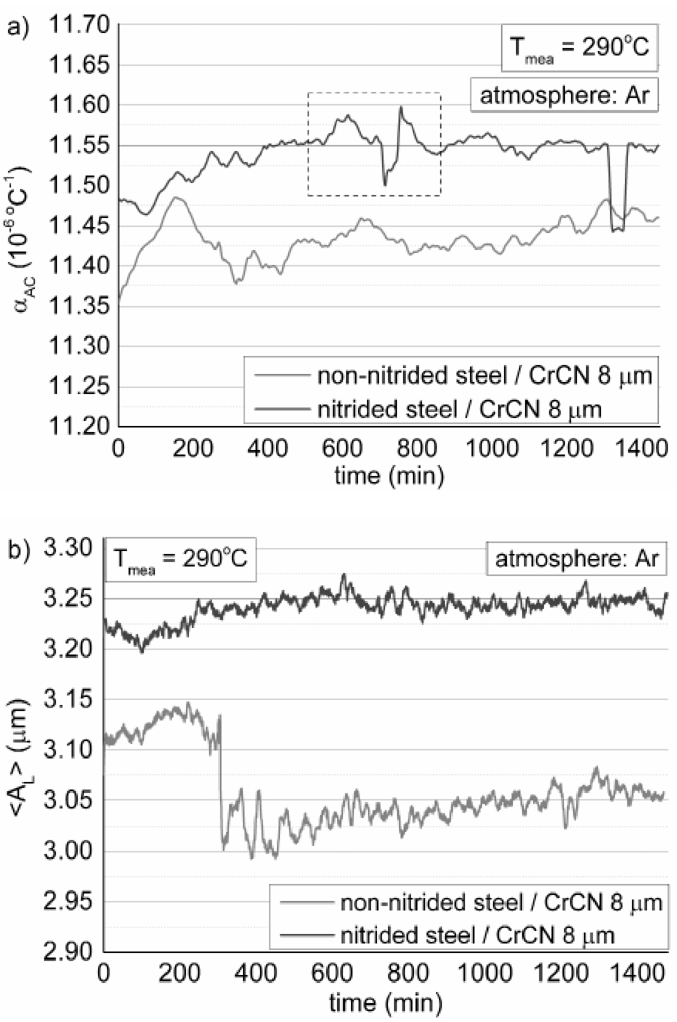

Fig. 4. Variations in the a) α_{AC} indicator, b) amplitudes $<A_L>$ of the non-nitrided substrate/CrCN coating and nitrided substrate/CrCN coating systems in the function of the annealing time in the temperature of 290°C

The obtained results indicate that processes occurring during annealing in CrCN coating deposited on the non-nitrided substrate, affect value of equivalent coefficient of thermal expansion α_{AC} correlated with the amplitude of system elongation $<A_L>$ and affect change in substrate elongation ΔL_S. It was not observed high thermo-mechanical interactions between the coating and the substrate in the case of nitrided substrate. It follows that the *nitrided substrate/CrCN coating* systems are characterized by a higher thermal stability than systems with non-nitrided substrate.

Thermodilatometric study also revealed the influence of substrate nitriding on the dynamics of thermally-activated processes occurring in the tested substrate/PVD coating system, which is shown in the graph (Fig. 5). On the basis of Fig. 5 it can be concluded that during annealing in both *substrate/PVD coating* systems, occurring processes leading to the appearance of the time delay τ of the substrate elongation DIL with respect to change in the sample temperature T. The average value of the time delay in the case of the system with nitrided substrate is larger in comparison to *non-nitrided substrate/PVD coating*, however, decreases with increasing annealing time. This shows the gradual disappearance of the processes occurring in the sample and stabilization of the system. In the second tested sample increment of the delay values is observed.

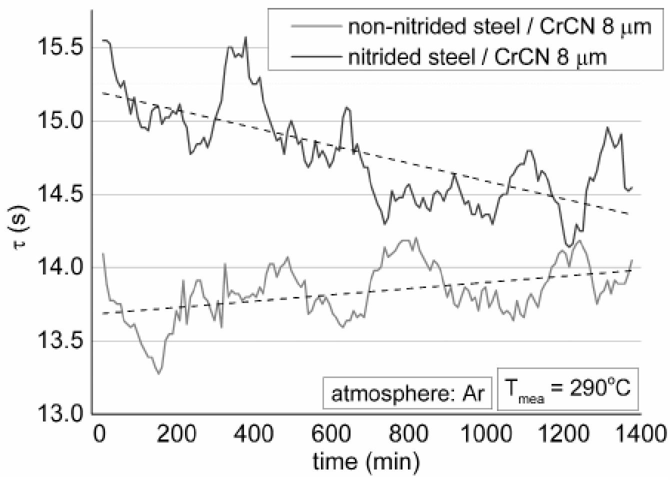

Fig. 5. Courses of time delays τ between elongation of the substrate and the temperature of the sample during annealing of substrate/coating systems

4. Conclusions

The aim of this study was to identify the influence of nitriding of a substrate made of 42CrMo4 steel on thermal stability of deposited on its surface antiwear CrCN coatings. Samples of systems with non-nitrided and nitrided substrate were tested using thermomechanical method during which was applied isothermal annealing lasted for 26 h at temperature 290°C and under atmosphere of argon. By determination of changes in elongation of the substrate (after annealing at room temperature) relative to the length after deposition of the coating, it is possible to qualitative assessment of the residual stresses changes. Systems with nitrided substrate was characterized by a much lower value of the elongation of the substrate ΔL_S after annealing relative to the non-nitrided substrate. This result indicates that annealing of a system with non-nitrided substrate resulted in a significant reduction in compressive stresses in the coating, but does not result in significant changes of stresses in the other system (nitrided surface) what may suggest its better thermal stability. Examination of the residual stresses in the coatings using X-ray diffraction confirmed the results of thermomechanical tests. CrCN coating deposited on nitrided substrate was characterized by a smaller compressive stresses after the deposition process with respect to the coating on non-nitrided substrate. Annealing resulted in a reduction of compressive stresses in the coatings of both systems: in the system with nitrided substrate of 523 MPa, whereas in the case of non-nitrided system of 691 MPa.

The applied thermomechanical testing method also allowed the monitoring of the heat-induced processes in the system during annealing by determination of changes in the value of α_{AC} indicator and the time delay τ. The gradual decrease in the value of the time delay τ with annealing time indicates a stabilization of thermally-activated processes occurring in the system with nitrided substrate.

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