Vacuum 148 (2018) 276–285

Contents lists available at ScienceDirect

Vacuum

journal homepage: www.elsevier.com/locate/vacuum

Investigations of the thermo-mechanical stability of hybrid layers for tribological applications: Nitrided layer/CrCN coating system

Piotr Myśliński [a], Łukasz Szparaga [a], Adam Gilewicz [a], Katarzyna Mydłowska [a, *], Anna Piątkowska [b]

[a] Koszalin University of Technology, Faculty of Technology and Education, ul. Śniadeckich 2, 75-453 Koszalin, Poland
[b] Institute of Electronic Materials Technology, ul. Wólczyńska 133, Warsaw PL-01-919, Poland

A R T I C L E I N F O

Article history:
Received 6 November 2017
Received in revised form
29 November 2017
Accepted 30 November 2017
Available online 5 December 2017

Keywords:
MT TMA
Anti-wear coatings
PVD
Nitriding
Thermal stability

A B S T R A C T

The paper contains a description of investigations related to an analysis of thermo-mechanical couplings in nitrided and non-nitrided steel substrate/CrCN coating systems with the use of dilatometry with temperature modulation. In this method, measured quantities are changes in the linear elongation of substrates in layered systems that occur as a result of given thermal loads. This enable i.a. to assess thermally activated changes in the states of residual stresses in the system as a result of a number of physical and chemical processes in the coating and in the substrate. Independently, results of these investigations were confronted with the results of scratch test enabling the assessment of coating adhesion and fracture toughness. On the grounds of the investigations carried out, it was found that CrCN coatings deposited on the nitrided substrates demonstrate a stronger thermo-mechanical coupling with the substrate in comparison with coatings deposited on the non-nitrided substrate and are characterized by a higher thermal stability. The results obtained explicitly confirm that systems with nitrided substrates are characterized by a higher mechanical load-bearing capacity and more favorable state of the adhesion of the coating to the substrate is observed as compared to systems with non-nitrided substrates.

1. Introduction

One of methods to improve the anti-wear properties of steel parts of machines and tools used in hot forming is to create hybrid layers on their surfaces which consist of the layer that is the result of the nitriding process and a thin PVD (Physical Vapour Deposition) coating: these are duplex type technologies. The use of these technologies leads to the production of layers that differ from the primary material (the substrate) in their chemical composition and mechanical properties, e.g.: hardness, Young's modulus E, the Poisson's ratio ν as well as in their thermal properties, such as thermal expansion coefficient α, specific heat c_p and heat transfer coefficient λ [1–3]. Taking into consideration the frequent use of this type layered system in complex tribological nodes, where mechanical and thermal loads occur simultaneously, the key question is an investigation into changes to mutual couplings between their mechanical and thermal properties. Investigations related to thermo-mechanical couplings in layered systems focus on an assessment of the impact of temperature changes on the structure of substrates and coatings and their anti-wear properties (e.g. the wear ratio, hardness, fracture toughness, coefficient of friction). However, attention needs to be drawn to the fact that so far there have been few papers related to monitoring of changes to the thermo-mechanical properties of layered systems in the function of time and temperature that identify changes in the conditions of the couplings of the temperature fields and deformation fields in anti-wear layered systems.

Monitoring of these changes can be realized with the use of dilatometry with temperature modulation MT TMA (Modulated Temperature Thermo-Mechanical Analysis) [4–6].

Changes to the linear elongation of substrates that form as a result of the given cyclic (sinusoidal) thermal loads constitute the quantity measured. Base on the above-mentioned data, what is determined is the value of the equivalent thermal expansion coefficient α_{AC} of the substrate and the value of time shift τ between the temperature changes in the sample and its dilatometric

* Corresponding author.
E-mail address: katarzyna.mydlowska@tu.koszalin.pl (K. Mydłowska).

https://doi.org/10.1016/j.vacuum.2017.11.037
0042-207X/© 2017 Elsevier Ltd. All rights reserved.

response. Furthermore, changes in the elongation of the system sample substrate ΔL_S after a given heating sequence were analyzed. This analysis enables an assessment of changes to the states of residual stresses in the system as a result of a number of physical and chemical processes that are thermally activated in the coating and in the substrate [7–9]. On the basis of the determined changes to values α_{AC}, ΔL_S and τ, an assessment is possible of the thermal stability of systems understood as the invariability of thermo-mechanical interactions between the substrate and the coating deposited, in the function of temperature, which is essential from the perspective of the diagnostics of its operational properties [10–14].

This paper includes a description of investigations into the thermal stability of steel substrate (non-nitrided or nitrided) - the CrCN coating with the use of the dilatometric method with temperature modulation MT TMA. The research results were compared with the results of standard tribological investigations, i.e. critical loads (correlated with the state of adhesion and crack resistance) determined in the so-called scratch test and the results of assessment of residual stresses state via deflection curvature measuring method.

2. Material and methods

2.1. Preparation of substrates

The investigations were carried out for 4 and 8 μm thick CrCN layers deposited on nitrided and non-nitrided substrates from 42CrMo4 steel. Their chemical composition is presented in Table 1.

The substrates to be used in dilatometric investigations had the shape of a cylinder with the diameter of 3 mm and the length of 30 mm. They were mechanically grinded and polished to the roughness of Ra ~0.05 μm. In order to perform investigations into the tribological properties of substrate/coating systems, rectangular substrates sized 5 × 20 mm and 3 mm thick were also prepared. To minimize residual stresses that form in the material of the substrate as a result of machining (i.e. cutting, grinding and polishing) before the nitriding process and deposition of coatings, they were annealed two times in vacuum in the temperature of 500 °C. Within the framework of the present work, substrates from monocrystalline silicon sized 10 × 40 × 0.5 mm were additionally prepared for the needs of the assessment of the state of residual stresses in the coating with the use of the so-called deflection curvature measuring method. Both the thermo-mechanical and tribological tests were carried out on 5 samples of each of the investigated systems (cylindrical nitrided and non-nitrided substrates with 4 and 8 μm CrCN coatings as well as flat rectangular samples).

2.2. Gaseous nitriding

Nitriding of samples [15,16] 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. After nitriding, samples were polishing in order to remove compound layer (ε - $Fe_{2,3}(NC)$ and γ') to the roughness of Ra ~0.1 μm. Analysis of the nitrided layer phase composition by XRD method confirmed the lack of ε phase on the surface of samples after polishing.

2.3. Deposition of coatings

CrCN layers were deposited with the PVD method, with the technique of cathodic arc evaporation in a TINA 900 M technological device. In the deposition process, two arc sources were used with chromium cathodes with 99.8% purity and a diameter of 100 mm. As a reactive gases, nitrogen and acetylene were used. The control of the pressure and of the flow rate of gases was carried out with the use of a Baratron type capacitive head and mass flow controllers manufactured by MKS company. The coating deposition process was preceded with the ion cleaning of the surface of the substrates in a working chamber under the pressure of 0.5 Pa with the substrate bias polarization equal to −600 V by 10 min. The CrCN coating was produced in a nitrogen atmosphere under the pressure of 1.8 Pa and acetylene flow rate of 10 sccm with the substrate bias polarization of −70 V and the source current of 80 A in the temperature of ca. 300 °C [17–19].

2.4. Modulated temperature dilatometry

The investigations into the thermal stability of non-nitrided or nitrided substrate/CrCN coating systems were carried out with the use of a compensation dilatometer designed and created in the Koszalin University of Technology. It enables a simultaneous measurement of the temperature of the sample and linear elongation of the systems substrates that form as a result of given cyclic (e.g. sinusoidal) thermal loads.

The use of temperature modulation makes it possible to identify the reversible and irreversible component of the dilatometric response of the substrate of system [5]. The reversible component represents the thermally induced linear elongation (expansion) of substrates that is proportional to temperature variations. The irreversible component is connected with the thermal activation of irreversible processes in the substrate and coating (e.g. creeping, relaxation of residual stresses, induced diffusion of crystalline defects, growth of grains, recrystallization). This is manifested by the lack of coincidence between signals of dilatometric response and thermal forcing. For example, a change may occur to the amplitude of the elongation of the substrate with the unchanged amplitude of thermal forcing. The reason for this is the above-mentioned consumption of heat energy used for the activation and progress of irreversible processes [20,21].

In the dilatometer constructed, changes to the elongations of the substrates of the system are measured with the use of a linear variable displacement transformer (LVDT) manufactured by TESA company.

The measurements were performed based on the thermogram shown in Fig. 1. It includes four sequences of annealing: three first ones are carried out in argon atmosphere, and the fourth in air. Annealing carried out in argon atmosphere limited to considerable

Table 1
Chemical composition of 42CrMo4 steel, %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