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## Rheological Behaviour and Model of Metal – Polymer - Ceramic Composite

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### ABSTRACT

In the present paper rheological behaviour of composite coating consisting of Aluminum Oxide -Polymer – Chrome Carbide was examined by using rheological models for principal Hertzian contact of a sphere and a plate. The crystallographic and morphologic texture was characterized and the fracture resistance was measured using fracture-mechanics. A rheological model of the composite coating has been proposed and confirmed by in situ experiments. Several requirements to rheological models were formulated regarding an adequate strain-deformation state of the composite coating. Load rating revealed ultimate strain-deformation rates. Analysis of the models and experimental results revealed better understanding of composite failure and degradation mechanics.

### INTRODUCTION

The fracture toughness of brittle coatings and composites are among the most important mechanical properties. Determination of fracture toughness value is a complicated process, involving preparation of specimens with well-defined sharp cracks of known length. Recent review articles [1, 2] have presented a summary of available techniques.

However, one method was conspicuously absent - that of Hertzian indentation using rheological model. In the present paper, Hertzian indentation and rheological models have been used to investigate fracture of composite coating consisting of aluminum oxide -polymer – chrome carbide. The crystallographic and morphological textures were characterized and fracture resistance of the coating was measured using fracture-mechanics and fundamentals of rheology.

### EXPERIMENTAL TECHNIQUE

Detailed study of the microstructure of the specimen was carried out by conventional TEM using selected area diffraction (SAD). The chemical composition and structure of the phases and grain boundaries were analyzed by analytical TEM and high-resolution TEM. High-resolution TEM was conducted on a 300 kV microscope (Model 3010, Nikon, Japan) with a point resolution of less than 0.16 nm. Microhardness was measured with Vickers indentation.

The metallographic analysis of the cross-sectional micro-sections of the coated samples was made with a microscope. Microhardness was measured with Vickers indentation at load on the indenter of 0.5 N for 30 s. Then a diagonal of indentation track was measured and microhardness of the layers was calculated. Porosity of the oxide hard layer was measured by the linear method

(method of secant line). The coating of texture image analysis "Leitz-TAS" (Germany) and optical microscope "Ortoplan" was used to study porosity of the oxide ceramic layers.

## RHEOLOGICAL MODELING OF NANOCOMPOSITE

To investigate mechanical properties of composites there were suggested many rheological elastic-viscous-plastic coatings described by Rudnitski et al., Shulman et al., Izraelian et al., and Reiner, [3-6]. However, despite some advantages the known models were not applied to developed composite coating and were not experimentally confirmed.

Based on recent researches of mechanical properties of aluminumoxide-based ceramics [7, 8], polymers [8-11] and its composites, a few requirements to a rheological models were formulated [19, 20]. It is expected that "chrome carbide- oxide aluminum - aluminum or its alloy" composite coating can be presented by "elastic-viscous-plastic" rheological model (model 1). The mechanical prototype of the model is shown in fig. 1a. "Steel-elastic-viscous polymer layers – aluminum – oxide aluminum layer" coating can be presented by rheological model consisting from two elastic elements and a viscous element (model 2, fig. 1b). Prototype of the model may be represented by parallel connection of the Maxwells' model and an elastic element. Final rheological equations usually depend on a level and a form of applied stress to the models. Integral deformation of sequentially joined models is calculate as follows:

$$\varepsilon = \varepsilon_1 + \varepsilon_2 \tag{1}$$

If loaded coating has strain condition  $\sigma > \sigma_0$ , than rheological equation of the composite coating (model 1 in fig. 1a) can be written by:

$$\sigma = \sigma_0 + E_1 \varepsilon_1 + \eta_1 \frac{d\varepsilon_1}{dt} \tag{2}$$

where  $\sigma_0$ ,  $\sigma$ , are strains at initial and final time of loading respectively;  $E_1$  is modulus of elasticity;  $\eta$  is coefficient of viscosity;  $\varepsilon$  is deformation.

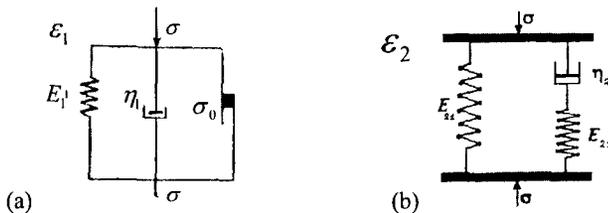


Figure 1. Rheological models of the composite coatings

For the model 2 at fig. 2b representing viscouelastic polymer-based layers, differential equation is defined by:

$$\frac{d\sigma}{dt} + \frac{E_{22}}{\eta_2} \sigma = (E_{21} + E_{22}) \frac{d\varepsilon_2}{dt} + \frac{E_{21}E_{22}}{\eta_2} \varepsilon_2 \quad (3)$$

where  $E_0, E_1$  are modulus of elasticity of materials;  $\eta$  is coefficient of viscosity.

Principal rheological equation of sequentially joined models at randomly driven loading is given by:

$$\frac{\eta_1}{E_{22}} \frac{d^2\sigma}{dt^2} + \left( \frac{E_1}{E_{22}} + \frac{\eta_1}{\eta_2} + \beta \right) \frac{d\sigma}{dt} + \frac{E_1 + E_{21}}{\eta_2} \sigma - \frac{E_{21}}{\eta_2} \sigma_0 = \beta \eta_1 \frac{d^2\varepsilon}{dt^2} + \left( \frac{\eta_1}{\eta_2} E_{21} + \beta E_1 \right) \frac{d\varepsilon}{dt} + \frac{E_1 E_{21}}{\eta_2} \varepsilon \quad (4)$$

Equations from 1 to 4 describe rheological behavior of the composite coating including hard aluminum oxide -based layer, aluminum and viscouelastic polymer layers. By applying the rheological models to the composite coatings the strain-deformation mode of the coating may be studied. It should correlate with rheological and mechanical properties (plasticity, elasticity and viscosity), microstructure and composition of the coatings. Adequate rheological model should be confirmed by experimental results.

## MODELLING OF INDENTATION TECHNIQUE

Lawn, (1993, 1998), Frank and Lawn, (1967), Collins, (1993), Pharr et al., (1993) [12-17] described that a deformation rate and a loading rate of materials is a function of indentation track diameter ( $a$ ) and diameter of indenter ( $D$ ). Previous works [7, 8, 19, 20] revealed that hertzian indentation technique may be effectively modified by rheological models to examine a stress - deformation state of composites and consolidated coatings. Here we will study rheological behavior by proposed models.

The function of stress-deformation mode of the composite coating in fig. 1a is defined by equation (2) at linear correlation of deformation rate vs. loading time. Therefore, the function of strain-deformation mode of model is defined by:

$$\sigma(t) = \sigma_0 + E_1 \varepsilon_0 + \eta_1 \dot{\varepsilon}(0) + E_1 \dot{\varepsilon}(0) \cdot t \quad (5)$$

The rheological function (5) uses  $E_1, \sigma_0$  and  $\eta_1$  parameters that characterize mechanical properties of the coating. Function of strain-deformation mode of the composite coating in fig. 1b will be expressed by integrating the equation (3) at the linear correlation of deformation rate vs. loading time. The function of stress-deformation mode of model (fig. 1b) is defined by:

$$\sigma(t) = E_{21} [\varepsilon(t) - \varepsilon_0] + \eta_2 \dot{\varepsilon}(t) - \frac{3k\eta_2}{2t_1} e^{-t/\tau} + \frac{k\eta_2^2}{E_{22}t_1^2} (1 - e^{-t/\tau}) \quad (6)$$

where  $\tau = \eta_2/E_{22}$ ,  $t_1 = R/V$ ;  $k = 4/(3\pi \cdot (1 - \mu^2))$ .

Principal Hertzian equation for a contact of spherical indenter and a sample can be written as the following function:

$$P(t) = \sigma(t) \left[ \pi R V t + \frac{\pi d^2(t)}{4} \right] \quad (7)$$

where R is indenter radius, V is velocity of loading, t is time of loading, d(t) is function of indentation track depth vs. applied load,  $\sigma(t)$  is rheological function (1-6).

Recent results [8] revealed that the initial angle depends on Young modulus of a polymer layer and initial diameter of the track d0 resulted from a roughness of the layer. Therefore, based on experiments on stress relaxation by polymer layers it was calculated that  $E_{21} = 80$  MPa, given value  $\eta_2 = 8$  MPa-s, and then it was found that  $E_{22} = 2$  MPa ( $\tau = \eta_2/E_{22} = 4$  s).

To confirm the proposed rheological models Hertzian spherical indentations were done by indentation techniques at five points on the following samples. Size of the sample was  $25 \times 10 \times 5$  mm coated by "steel base – damping viscoelastic polymer – aluminum alloy –  $Al_2O_3$  layer – chrome carbide layer" composite coating. The indentation was done by the spherical steel balls with diameter of 3.978 mm. Five sets of load-unload data were obtained at each point, with the maximum load being increased from  $P_1 = 1$  N to  $P_2 = 1000$  N. For each indentation, unloading was continued to up to 5% of the maximum load. After each indentation, the contact radius (a) was measured from the residual contact trace on the top layer. Then, the plot of indentation stress ( $\sigma(t)$ ) versus indentation track depth ( $\alpha$ , mm) was obtained and plotted at fig. 2a. According to Hertz theory these two parameters should show a linear relationship within the zone.

Figure 2a shows indentation depth vs. load curve. The measured values plotted in line 1 in fig. 2a are convex down because of uncounted effects in the experiments such as roughness, structural defects etc.; however, the deviation of the results is unexpectedly little. It should be noted that loading conditions, geometry of contacted surfaces and its mechanical properties may be included in rheological equations to be used in particular case or trial tests. However, the equations may take difficult mathematical forms and their handmade and quick application in practice would be hard. The calculated curve in line 2 is concave down that resulted from accepted conditions in the rheological equations and applied technique of its approximation. Ultimate contact stress for the composite coating with polymer layers was about 1.5 GPa. Polymer layers significantly decreased strength and stiffness of the coatings.

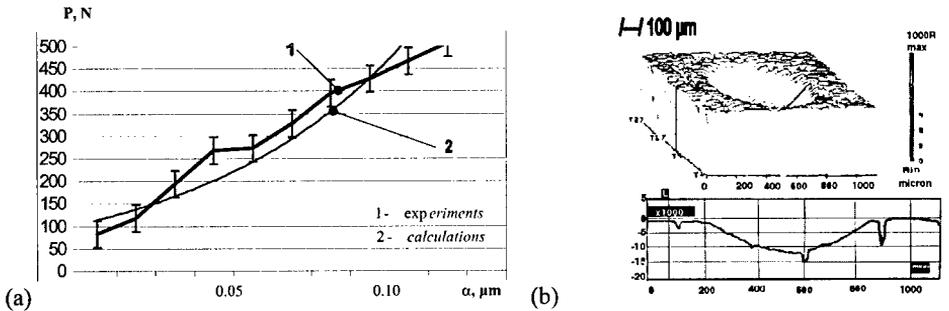


Figure 2. Stress-deformation rating and indentation track

At unloading the coating may show an effect of retardation of deformations (so-called elastic return) because of damping properties of viscous-elastic polymer material. It could be shown in a figure as a downfall curve. The plotted relations of experimental data and calculated data with the equations (2, 5, 6) are shown good agreement of developed rheological model and mechanical behavior of the composite. Deviation from this line indicates the onset of irreversible deformation. The above stated conditions are found to be used in investigations of mechanical and rheological properties of "oxide aluminum-aluminum- viscous-elastic material (polymer) – steel" composite coatings.

Figure 2b shows indentation track obtained on surface of the composite coating. Diffuse damage, traditional cone and ring cracks have been observed, but fracture features have different impact on the coating. Strains may distribute not only through top CrC and/or oxide aluminum layers, but also relaxed by undernear polymer layer. It was found that strains principally concentrate around porous zones, internal voids and micro-defects of the coating resulted from its structural mismatches. In addition, strains may initiate crack propagation and fracture of the coatings. However, CrC layer naturally strengthened aluminum oxide-based coating.

## CONCLUSION

The present work revealed rheological behavior and fatigue of advanced composite coatings like «steel – polymer – aluminum - oxide aluminum». Rheological models have been proposed with several requirements to modeling of the coatings. The models been confirmed by in-situ experiments using Hertzian theory for spherical indentation. Hertzian indentation technique effectively modified by rheological models is a powerful approach to investigate fracture mechanics of the coatings. The rheological analysis can consider not only elastic properties of materials, but also plastic and viscous properties of the composite heterogeneous coating. In addition, it may be possible to investigate correlation between rheological properties (plasticity, elasticity and viscous), microstructure and composition of the coatings. Rheological models may give reliable explanation of contact mechanics and rheological behavior of the coatings at loading up to 500 N. They could be used for analysis of its strength and load rating characteristics. It was discovered that ultimate contact stress of the coating included elastic-viscous polymer layers depreciate the ultimate stress to as low as 1.5 GPa. In future it is expected that upcoming investigations on this research will concentrate on smart nanostructured composites based on oxide aluminum ceramics and new composites strengthened by ultra hard nanoparticles such as diamonds.

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