Rheological Behaviour and Model of Metal-Polymer-Ceramic NanoComposite

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A possibility to develop composite coatings based on oxide aluminum, aluminum and polymer components have been investigated. The composite was produced by integration of micro arc oxidizing process/electroplating and thermal flame spraying. A nature of micro arc oxidizing processing of thermally sprayed aluminum is discussed. To understand mechanical behavior of the composite the rheological model have been developed adequate model describing stress-strain state of the nanocomposite. The composite can be presented as an elastic-tenacious-plastic rheological model. The rheological behavior of the model under localized loading and different initial stress and deformation states have been studied. Final analysis gives better understanding of nanocomposite failure and degradation mechanics. An optimal rheological model has been revealed. The rheological properties of the nanocomposite have been discussed.

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Introduction

Almost all of the companies continually seek new ways to improve their operations and cut costs, one process that manufacturers might scrutinize is product composite and layer by Shelley, (1998). An advantage that aluminum has over steel is the manufacturing cost. For many companies this means looking for better alternative in technologies that are used to coat aluminum structures and machine parts with hard alumina layer and alumina-based composites by Patel, (2000); Markov, (1992), a layer technique that is under ever-increasing pressure from an environmental-protection standpoint.

Although environmental concerns are very important, they are not the only reason that manufacturers might investigate the process alternatives or particular development of any process as well. Product designers may decide to evaluate other layer techniques because they want to extend product life cycles or improve upon specific layer characteristics. Regardless of company's reason for checking out micro arc oxidizing alternatives, some producers will need to improve the results constantly.

Materials and Technologies

The base material of the plate sample was steel. Prior to thermal flame spraying of polymer surface of base metal was prepared by grinding with water jet contained SiC, alumina particles with average size of 2 mm. In result, profile of the surface was arranged in the quincunx order with roughness of 400 μm. Apply thermally sprayed bond coating to suit the application and to facilitate good chemical and mechanical bond between coating and core. Grit blast and preheat surface. Air consumption was 0.4-0.45 m^3/min. Distance of spraying is 120-140 mm. Polymer granular powder was used to coat surface with polyamide layer of 420 μm in thickness and 6 GPa in Young's modulus. The theoretical calculations and practical approach show that aluminum layer formed by thermal flame spraying do not overheat polymer layer because temperature of Al particles do not exceed 120^0C.

Some of technologies applied to produce aluminum such as Osprey technology use special expensive equipment. In contrast to Osprey, HVOF spraying is to be used as prototype to form aluminum layers with very close desired properties. In this way, preliminary task was to compare Young's modulus of thermally sprayed Al layer and the same layers produced by Osprey technology and other processes, Wiktoreks S., (1986).

To form aluminum layer was used both aluminum cord with diameter of 2 mm or aluminum powder with granules size of 60-100 μm and purity of 99.85%. Aluminum thickness was about 3 mm. Butane was a heating gas of the system to provide temperature about 1200^0C for melting the aluminum powder. The parameters provide optimal set of mechanical properties of aluminum layer that are porosity of 1-3%, its Young's modulus of 68-72 GPa.

Then Al layer was transformed into hard oxide aluminum with micro arc oxidizing process. Micro arc oxidizing have been done by special equipment described by Kireitseu (2001) at current frequency of 50 Hz, voltage of 420 V and current density of 18-20 A/dm^2. The electrolyte was based on distilled water with KOH (NaOH) of 3 gr/l and other additives to control pH, temperature, electrical conductivity et al. The coating was formed during samples 60-90 min.

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, 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 system 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 a composite system there was suggested many rheological elastic-tenacious-plastic systems described by Rudnitski et al., (2001), Shulman et al. (1978), Izraelian et al., (1940), Reiner, (1963, 1965). However, despite of some advantages the known models was not applied to developed composite systems and was not experimentally confirmed.

Based on recent researches of mechanical properties of alumina-based ceramics by Kireytsev, (2001a,b); Basenuk and Kireitseu, (2001a-c), polymers by Bezuhov, (1968), Golberg, (1970), Gul, (1971) and its composites it is proposed requirements to a rheological model of developed systems.

The following requirements was found to be effectively used in rheological model describing behavior of the systems:

- Since the structure of the system includes hard alumina layer and the plastically deformed substrates, the irreversible deformations have to be considered as a plastic in nature. Plastic materials deform only after loading at ultimate yield strength.
- If load are smaller then yield strength, deformation increase in a step-by-step mode to a final value at constant load;
- Plastic deformation of the system is summarized under cyclic loading;
- Function of deformation vs. time has a linear segment in one of a plotted region at constant load;
- The retardation of deformations (elastic return) can be observed during unloading of the system;
- Stresses are relaxed at constant loading rate.

Along with above stated conditions, of interest is the following mathematical requirements: (a) the rheological equations have to be solved to the applicable form (order of a required differential equation of a stress and a deformation should not exceed numbers of possible conditions of physical limitations); (b) the equations and formulated problems have to be solved concerning stress or strain rates. Rational choice of an adequate model will be defined by comparison of calculated and experimental results.

It is expected that "chrome carbide- alumina - aluminum or its alloy" composite system can be presented by an "elastic-tenacious-plastic" rheological model (model 1) by Shulman et al., (1977), Smolski B. and Shulman Z., (1970). The mechanical prototype of the model is shown in fig. 2a. The "steel-elastic-viscous polymer layers – aluminum – oxide aluminum layer" system can be presented by the rheological model from the two elastic elements and the tenacious element (model 2 shown in fig. 2b). The prototype of the model is parallel connection of the Maxwells' model and the elastic element. The structural equation of the sequentially joined models of the system can be written in the form: (H ‖ N ‖ St-V) - (H-N ‖ H). The type of the rheological equation usually depends on a level and a form of stress applied to the models.

The integral deformation of the sequentially joined models is calculate as follows:

$$\varepsilon = \varepsilon_1 + \varepsilon_2, \qquad (1),$$

If the loaded system has the stress condition $\sigma > \sigma 0$, then the equation of the composite system (model 1 in fig. 2a) can be written by:

$$\sigma = \sigma_0 + E_1\varepsilon_1 + \eta_1 \frac{d\varepsilon_1}{dt} \qquad (2),$$

where σo σ, are stresses at initial and final time of the loading sequentially; E1 is the modulus of elasticity of the layer; η is the coefficient of viscosity; ε is the deformation.

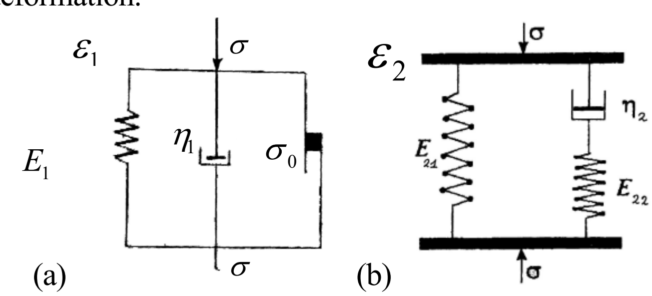

Fig. 2. Rheological models of the composite systems

For the second part of the system (model 2, fig. 2b) including elastic-viscous polymer layers, the differential equation is defined by:

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

where E_0, E_1 are modulus of elasticity of the material; η is coefficient of viscosity.

The rheological equation of the consequently connected models at the random loading conditions is given by:

$$\frac{\eta_1}{E_{22}}\frac{d^2\sigma}{dt^2}+\left(\frac{E_1}{E_{22}}+\frac{\eta_1}{\eta_2}+\beta\right)\frac{d\sigma}{dt}+\frac{E_1+E_{21}}{\eta_2}\sigma-\frac{E_{21}}{\eta_2}\sigma_0=$$
$$=\beta\eta_1\frac{d^2\varepsilon}{dt^2}+\left(\frac{\eta_1}{\eta_2}E_{21}+\beta E_1\right)\frac{d\varepsilon}{dt}+\frac{E_1E_{21}}{\eta_2}\varepsilon \quad (4)$$

The equations (1-4) describe rheological behavior of the composite systems including hard alumina-based layers, aluminum and viscous-elastic polymer layers. Below we will review the major loading conditions.

By applying the rheological models to the composite systems the stress-deformation mode of the system may be revealed. 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) described that the deformation rate and the loading rate of material surface is the function of an indentation track diameter (a) and a diameter of indenter (D). In the previous works Kireitseu, (2002) revealed that hertzian indentation technique may be effectivelly modified by rheological models to examine the streee-deformation state of composites and consolidated systems. Here we will study rheological behavior of the two proposed models.

The function of stress-deformation mode of sequentially joined models (fig. 2) is described by the equation (3-4). To perform simple mathematical transformation and application of the equation in experiments it is recommended to use special software.

The function of stress-deformation mode of the composite system in fig. 2a is defined by the equation (2-4) at the linear correlation of deformation rate vs. loading time. The function of stress-deformation mode of the composite system in fig. 2b will be expressed by integrating the equation (5) at the linear correlation of deformation rate vs. loading time. The constant parameter will then read as C=0 in the equation (5), that is taken to the condition of σ(0) = 0. In result the function of stress-deformation mode of model (fig. 2b) is defined by:

$$\sigma(t)=E_{21}[\varepsilon(t)-\varepsilon_0]+\eta_2\dot{\varepsilon}(t)-\frac{3k\eta_2}{2t_1}e^{-t/\tau}+\frac{k\eta_2^2}{E_{22}t_1^2}\left(1-e^{-t/\tau}\right) \quad (5)$$

Of interest is the summarized deformation that equals to the sum of the initial deformation of rough surface layer and the deformation resulted by a loading.

The above equations define the functions of stress-deformation mode expressing rheological behavior of the composite systems. However its hand-made application could be very complex procedure due to a number of mathematical and analytical calculations to be done. Under some conditions of loading simplified rheological models (fig.2) can provide adequate results that will then well fitted to experimental base. In present work the equations (2-5) will be then used in the experiments. The function of contact stress rate can be written as:

$$P(t)=\sigma(t)\left[\pi RVt+\frac{\pi d^2(t)}{4}\right], \quad (6)$$

where R is the indenter radius, V is the velocity of indenter loading, t is the time of loading, d(t) is the function of indentation track depth vs. applied load, σ(t) is the function of stress rating at applied load.

The time of stress relaxation (τ) and Young modulus E_{22} can be defined by investigating a reaction of the polymer layer on applied load at the time (t→0). Under loading a stress will strain the composite systems, but the polymer layers will deform first. From the equation (3) it takes the form at t→0:

$$\frac{d\sigma}{dt}\mathrm{I}_{t\to 0}=\dot{\varepsilon}_0(E_{21}+E_{22}) \quad (7)$$

The equation (7) defines relation between Young's moduluses of the model (fig. 2b). Then it will modified to E=E21+E22. Contact Young modulus is calculated by:

$$\frac{dP}{dt}\mathrm{I}_{e\to 0}=\dot{\varepsilon}_0(E_{21}+E_{22})\frac{\pi d_0^2}{4} \quad (8)$$

The Young modulus of the composite system is expressed by the initial angle of plotted curve - "contact load vs. depth of indentation track" as it follows:

$$\frac{dP}{d\alpha} = \frac{1}{V}\frac{dP}{dt} = \frac{3k}{V}\frac{V}{D}(E_{21}+E_{22})\frac{\pi d_0^2}{4} = \frac{3\pi k}{4}(E_{21}+E_{22})\frac{d_0^2}{D} \quad (9)$$

Results of Pelhica et al., (1983), Dorner, (1992), Basenuk et al. (2001 a) 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 and it was found that for the viscous-elastic polymer layers of the system the initial angle is calculated by:

$$tg\gamma = \frac{dP}{d\alpha} = 0{,}8 - 1{,}3 \quad (10)$$

The tgγ depends on thickness of the polymer layers. In present work it was found that tgγ=0,8 for the system with the polymer layer of 1,5 mm.

The Young modulus E21 is defined by:

$$E_{21} = \frac{3P}{4\sqrt{R}\,\alpha^{3/2}} \quad (11)$$

Therefore, based on experiments on stress relaxation by the polymer layers it was calculated that E21 = 80 MPa, given by Reiner M., (1963) value of η2 = 8 MPa·s, and then it was found E22=2 MPa (τ = η2/E22= 4 s).

To confirm the proposed rheological models Hertzian spherical indentations were done by the indentation techniques at five points on the following samples. Size of the samples was 25×10×5 mm coated by "steel base – damping viscous-elastic polymer – aluminum alloy – Al2O3 layer" composite system.

The indentation was done by the spherical steel balls with the diameters of 3.978 mm and 7.978 mm. Five sets of load-unload data were obtained at each point, with the maximum load being increased from P1=1 N to P2=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 (σ(t)) versus indentation track depth (α, mm) was obtained and plotted at fig. 3. According to Hertz theory these two parameters should show a linear relationship within the zone.

A transition from elastic to fully plastic deformation was observed in the load range investigated. A first order approximate value of the radius of the contact circle at each maximum load was calculated, with the plastic depth determined by differentiating the first part of the unloading curve. A plot of (P) vs. (α) was produced for all five-indentation sets. The "pile up" correction parameter (actual contact radius) was found to be disproportional changed in contrast to load rate, thus indicating different types of deformation.

Figure 3 shows indentation depth vs. load curve. It was plotted as mechanical response of the systems under Hertzian indentation at constant rate with sintered alumina ball of 4 mm diameter. Experimental data are shown by solid lines 1 and 2 and are compared with calculated data in dotted line in fig. 3.

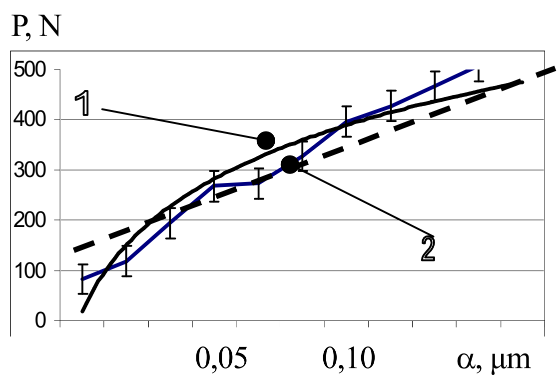

Figure 3: Stress-deformation rating of the rheological systems

At unloading the system showed the retardation of deformations (elastic return) because of damping viscous-elastic 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 "alumina-aluminum- viscous-elastic material (polymer) – steel" composite systems.

It was revealed that experimental results on stress-deformation test well correlate with calculated data. It was found that elastic polymer layers (the thickness of above 500 μm) of the system showed effect of stress relaxation.

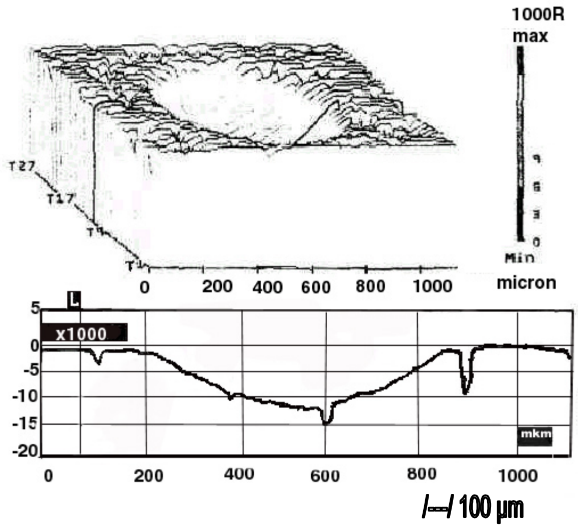

Figure: 4. Indentation track profile

Figure 4 shows indentation track obtained on the surface of the top Al2O3 of the composite system. The diffuse damage, the traditional cone and ring cracks (fig. 4) have been observed in both systems, but the fracture features have different impact on the system. The stresses are distributed through top CrC and/or alumina layers. It was found that stresses concentrate in the zones of pores, internal voids and micro-defects. In result, it could initiate cracks and fracture of the systems.

The oxide aluminum layer is generally characterized by numerous microfailures and microcracking in the structure. On the other hand, the boundary line of the indentation track on the surface views uniform and smooth. Of interest is the fact that the microhardness near the interface between alumina and CrC layer, which was found to be 20.0 GPa, is higher than that of the uncoated one (about 17 GPa) by Mott, (1956).

By loading the specimen it is found that tensile stress result in localized deformation that is generally the elastic-plastic in nature. The deformation is resulted from the radial spreading of the contact zone under the indenter with initiating of the local cracks (fig. 4). An effect of material flow result in both stresses distribution and residual deformation.

Shear stresses described by Lawn B., (1998) act in the top ceramic layers at depth of about 200 μm that is about a half of the thickness of the layers. The stresses result in crack initiation and its propagation in the layers. The form and the depth of maximum stress distribution revealed that overall load rating of the system under localized indentation does not depend strongly on hardness of base substrate. However it could be stressed under high stresses too rapidly.

The ultimate contact stress for the composite system with polymer layers was about 1.5 GPa. In fact, polymer layers significantly decrease strength and stiffness of the systems.

Conclusion

The work revealed rheological behavior and fatigue of advanced composite systems like «steel – polymer – aluminum - alumina». Rheological models have been proposed with several requirements to modeling of the systems. The models been confirmed by in-situ experiments using Hertzian theory for spherical indentation. Applying the rheological models in analysis of rheological behavior of the composite systems it is possible to investigate correlation between rheological properties (plasticity, elasticity and tenacious), microstructure and composition of the systems. Rheological models give reliable explanation of contact mechanics and rheological behavior of the systems at loading up to 500 N. It could be used for analysis of its strength and load rating characteristics.

It was discovered that the ultimate contact stress of the system 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 alumina ceramics and new composites strengthen by ultra hard nanoparticles such as diamonds.

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