Nanocomposite antifriction molybdenum disulfide (filler) – silicon oxide (matrix) coatings

S. Alexandrov1, K. Tyurikov1,*, A. Breki1, G. Kondrashkova1, V. Shashikhin1, B. Matisov1, Y. Mamaev1, A. Timofeev1, S. Burdakov1, D A Zaripova2

1Peter the Great St. Petersburg Polytechnic University, 195251, Politekhnicheskaya 29, St. Petersburg, Russia
2Kazan State Power Engineering University, Kazan, Russian Federation
*Corresponding author: kirill.tyurikov@spbstu.ru

Abstract. It was demonstrated experimentally that the spatial separation of two processes of chemical vapor deposition, one of which provides synthesis of filler (MoS2) nanoparticles and the other yields the matrix (SiO2) of the nanocomposite coating, performed in a common reactor, enables an independent control over two process rates and makes it possible to widely vary the composition of the films deposited in this way. The deposition was performed in a double-zone vertical tubular quartz reactor. Molybdenum disulfide particles were produced by pyrolysis of aerosols of ammonium thiomolybdate solutions in dimethylformamide in the upper zone of the reactor, and the plasma-chemical deposition of a nanocomposite coating occurred in the lower zone into which MoS2 nanoparticles were transported by the gas flow and tetraethoxysilane was delivered. It was shown that the nanocomposite coatings composed of molybdenum disulfide (filler) and silicon oxide (matrix) possess improved antifriction properties as compared with the matrix (SiO2 layers), these properties being determined by the relative amounts of MoS2 nanoparticles in the layer and by their average size.

1. Introduction
Nanocomposite materials have unique combinations of physical and chemical properties and therefore have attracted considerable interest [1-4]. Methods for forming coatings from nanocomposites are of particular interest, since in many practical cases it is necessary to provide only particular properties of the surface of products, which itself can be made of low cost material. Obviously, processes carried out at atmospheric pressure and allowing deposition of coatings at relatively low temperatures are the most attractive because the use of expensive vacuum equipment is not necessary and they can be employed for layer deposition on thermally unstable materials.

The results of our analysis [5] of the most common methods for depositing nanocomposite coatings at atmospheric pressure have shown that among the various processes, chemical vapor deposition (CVD) with various activation methods is one of the technologies allowing to form not only high-quality layers but also synthesize various types of nanomaterials, and even nanocomposites [6]. Only a few papers have been published on the deposition of nanocomposite coatings using CVD technologies [7-10]. Some of them are based on the use of a combination of physical methods of sputtering (PVD) targets for the formation of nanoparticles with CVD processes for coating formation [8]. It should be noted that with this approach it is necessary to provide the same total pressure in PVD and CVD reactors, which is a technically difficult task, since normally PVD processes are carried out at much lower pressures than conventional CVD processes. Nanocomposite layers can be formed by chemical deposition from the gas...
phase while simultaneously introducing into the reaction zone the reagents required for the synthesis of the filler and the matrix of the composite [9], or using reagents of complex chemical composition [10, 11]. The main disadvantage of these approaches is the serious limitations in the variation of the nanocomposite composition within a wide range. Recently, a very interesting and promising approach to the CVD technologies of nanocomposite coatings has been developed, in which the pre-synthesized nanoparticles of the filler and the reagents necessary for the formation of the matrix layer are simultaneously introduced into the reaction chamber [12, 13]. Despite the difficulties associated with storing and transporting nanoparticles, the authors succeeded in obtaining nanocomposite coatings consisting of siloxane (matrix) and carbon (nanoparticles of filler), as well as layers of siloxane - an aromatic resin [12] and films representing a glassy SixOy matrix with polytetrafluoroethylene (PTFE) nanoparticles distributed therein [13].

Obviously, the most attractive from the viewpoint of the possibility of controlled variation in the composition of the resulting composite are the CVD processes in which the nanoscale filler particles are homogeneously synthesized in one zone of the reactor and then transported by the gas stream together with additional reagents to another zone where the nanocomposite coating is heterogeneously deposited. The results of the preliminary experimental studies carried out by us for the first time [5] indicate that, in fact, the separation in the space of a single reactor of two CVD processes (i.e., the synthesis of nanoparticles and the deposition of coatings) provides an independent control of the rates of the two processes and therefore one can vary composition of deposited layers over a wide range.

The purpose of this work was the experimental testing of a two-stage plasma enhanced CVD process to form nanocomposite coatings, which are a matrix layer of silicon dioxide containing nanoparticles of molybdenum disulfide, and possessing improved antifriction properties. The choice of the components of the composite was made on the basis that the silicon dioxide layers are often used as hardening coatings on the polymer surface [14], and the MoS2 nanoparticles have unique antifriction properties [15]. It was of interest to ascertain the nature of the influence of the layers deposition conditions on their antifriction properties.

2. Experimental

The design of the quartz reactor used to carry out the two-step CVD process for the deposition of nanocomposite coatings in the "MoS2 (filler) - SiO2 (matrix)" system is described in detail in [5]. The reactor consisted of two main parts: an upper zone intended for the synthesis of molybdenum disulfide nanoparticles and a lower zone used for plasma enhanced CVD of nanocomposite coatings at atmospheric pressure by maintaining a low-frequency corona discharge (27 kHz). MoS2 nanoparticles were synthesized in a gas stream by pyrolyzing the aerosol particles of a (NH4)2MoS4 solution in dimethylformamide [16] and then transported by a gas stream to a deposition zone where the substrates were placed on a grounded steel substrate holder and tetraethoxysilane (TEOS) vapor - the reagent necessary for precipitation of silicon dioxide - was injected. The upper zone of the reactor was a quartz tube equipped with two resistive heaters. The first heater designed to evaporate the solvent from aerosol particles was heated to temperatures (T1) 150-750±10°C. The second heater was used to heat the pyrolysis zone of ammonium thiomolybdate to 800±10°C (T2). The aerosol of a solution of ammonium thiomolybdate in dimethylformamide created by a piezoelectric nebulizer operating at 2.4 MHz was transported to the reactor with a carrier gas (helium of high purity) at a rate of about 0.3 slm. The concentration of the solution of ammonium thiomolybdate was in the range 0.0025-0.01 mol*L-1. The lower part of the reactor was used for plasma enhanced CVD of nanocomposite coatings by codeposition of MoS2 particles coming from the upper part of the reactor and a layer of silicon dioxide formed from tetraethoxysilane vapors. A high-voltage electrode made of a sharp tungsten rod was placed 25-30 mm above the grounded substrate holder heated to 300°C. Corona discharge at atmospheric pressure was created in this zone by means of a low frequency power supply (27 kHz, 1.8-2.2 kV). Typical values of the discharge power were 40-90W. The vapors of tetraethoxysilane were fed to the reactor from a quartz evaporator stabilized at 70°C, the design of which provided an unchanged level of the evaporated liquid. The carrier gas helium saturated with TEOS vapor was injected into the upper
part of the deposition zone approximately 30 mm downstream of the first zone through the injection nozzle. The total flow of helium through the evaporator was changed within the range 0-1 slm. The flow rate of the diluent helium was varied within the same limits so that the total flow rate was 1 slm. Substrates of silicon and polished stainless steel were placed on a grounded substrate holder.

The composition of the obtained samples and the particle size characteristics were determined using a Zeiss SUPRA 55VP scanning electron microscope (SEM) equipped with an x-ray fluorescence microanalysis unit Oxford Instruments X-Max. The structure of the samples was studied using a Jeol JEM-2100F TEM with an accelerating voltage of 200 kV and a point resolution of 0.19 nm. The composition of the layers of the nanocomposite was estimated from the images of the cross sections of composite layers obtained with the use of SEM.

To estimate the antifriction properties, the sliding friction force was measured. As a rotating counter body, a cylindrical sample (roller) was used from the bearing steel, with a diameter of 10 mm. During the tests, the counter body with its flat part pressed against the surface of the sample, which was a nanocomposite coating with thickness of about 1μm, deposited on a substrate of stainless steel with a polished surface. The clamp fixed to the bearing assembly with the help of a cable and a tensile beam in the course of the experiment was kept from the rotation imparted by the movable roller. Data on the frictional force and the acting load were transmitted from the tensile beams to the computer. In all the experiments, the load on the friction pair was 390 N, and the speed of the shaft in which the steel roller was clamped was 200 rpm.

3. Results and discussion
Taking into account the results of preliminary studies of the synthesis of MoS₂ particles by the pyrolysis of aerosols [16] and the plasma enhanced CVD of silicon dioxide layers [5], a series of experiments on the deposition of nanocomposite coatings were carried out. The main process parameters for these experiments were fixed (Table 1), except for the concentration of ammonium thiomolybdate in dimethylformamide, which varied in the range 0.0025-0.01 mol⁻¹, and the ratio of the helium-carrier and helium-diluent vapours of tetraethoxysilane.

| Parameter                                      | Value |
|------------------------------------------------|-------|
| Temperature of the first zone of the reactor, °C | 800   |
| Temperature of the second zone of the reactor, °C | 800   |
| Substrate temperature, °C                       | 300   |
| TEOS evaporator temperature, °C                 | 70    |
| Flow rate of the aerosol carrier gas, L min⁻¹   | 0.3   |
| Flow rate of the TEOS vapor diluent gas, L min⁻¹| 0.1–1 |

The results of the study of samples using SEM indicate that the deposited layers contain spherical particles characterized by a statistical distribution in the coating (Figure 1, a) and are characterized by a rough surface, probably due to the joint deposition of nanoparticles on the surface of the growing layer. The thickness of the coating was estimated from the SEM image of the cross-section of the coating (Figure 1, b).
Figure 1. Plan-view (a) and cross-sectional SEM images (b) of the nanocomposite coating constituted by silicon dioxide (matrix) and MoS$_2$ nanoparticles (filler).

The growth rate of the layers did not depend on the presence of aerosol particles in the deposition zone and was approximately the same as for plasma enhanced CVD of silica (15-20 nm*min$^{-1}$). It is interesting to note that the average nanoparticle size in the layers depends on the concentration of (NH$_4$)$_2$MoS$_4$ in the solution used to make the aerosol and decreases with the dilution of the solution (Figure 2), as in the case of aerosol synthesis of nanoparticles without simultaneous deposition of SiO$_2$.

Figure 2. Average diameter $D_{av}$ of MoS$_2$ nanoparticles (1) distributed in a nanocomposite coating and (2) collected on an electrostatic filter without deposition of SiO$_2$ vs. the (NH$_4$)$_2$MoS$_4$ concentration $c$ in solution.

The increase in the average size of nanoparticles of molybdenum disulphide in the case of nanocomposite production is due to deposition of silicon dioxide layers on them (Figure 3).

Figure 3. SEM image of MoS$_2$ nanoparticles on the surface of a nanocomposite coating, covered with a SiO$_2$ film.

The composition of the deposited composite layers was studied using Raman spectroscopy. The spectra of four samples obtained using an 1800-line per mm grid and a spectral resolution of 1 cm$^{-1}$ are shown in Figure 4.
Figure 4. (1–4) Raman spectra of nanocomposite coating samples and (0) reference spectrum of MoS$_2$. (I) Intensity and (ν) wavenumber.

Sample 1 is a layer of silicon dioxide deposited by the plasma enhanced CVD. Samples 2-4 are composite layers deposited using solutions with different (NH$_4$)$_2$MoS$_4$ concentrations in dimethylformamide (2 - 0.01M, 3 - 0.005M and 4 - 0.0025M). As can be seen, the spectra of all samples contain the Si (304, 520, 940-980 cm$^{-1}$) bands [17] due to the silicon substrate. Samples 2-4 also revealed two additional bands (384 and 409 cm$^{-1}$), which, according to the database of the Raman spectra of RRUFF [18], are due to the presence of molybdenum disulfide (MoS$_2$). The results obtained suggest that the samples of the composite layers contain MoS$_2$ particles. The bands corresponding to SiO$_2$ were not detected in the Raman spectra of all deposited coatings because of the amorphous nature of the matrix layer. However, the results of IR spectroscopy of all composite coatings show that in all spectra there are three main absorption bands with maxima of about 450, 800 and about 1075 cm$^{-1}$, corresponding to different Si-O-Si bond vibrations [19]. In addition, a relatively small peak with a maximum at 965-975 cm$^{-1}$ associated with deformation vibrations of the Si-CH$_3$ bonds was observed, with its relative normalized intensity increasing by 10-15% compared to deposition of pure silicon dioxide, probably due to higher concentrations of various hydrocarbons in the nanocomposite coating deposition zone. Thus, the analysis results of the Raman and IR spectra show that the deposited coatings are indeed a composite material consisting of MoS$_2$ nanoparticles statistically distributed in a silica matrix.

For detailed determination of the structure of composite coatings they were investigated using high resolution transmission electron microscopy. For this purpose, the coatings were deposited on a monocrystalline NaCl, which was then removed by dissolution in water. In Figure 5 shows an image of a fragment of a small area of coverage and a map of the distribution of the main elements (Mo, Si, S and O) obtained with the help of a XRD analysis.
The presented results give a direct proof of the nanocompositional nature of deposited coatings consisting of MoS$_2$ nanoparticles statistically distributed in a matrix of silicon dioxide.

The evaluation of the antifriction properties was carried out based on the results of the measurement of the frictional force produced by the contact of the rotating counter body with the surface of the coatings deposited to the polished stainless steel substrates, the selected loading regimes were corresponding to the most severe operating conditions of friction pairs in various equipment. In Figure 6 is a plot of the frictional force versus the test time of a sample on which a silica layer and a nanocomposite coating containing nanoparticles of molybdenum disulfide were applied.

As can be seen from the presented data, the coefficient of friction for the nanocomposite coating was significantly lower over the whole range of the test time (almost twice at the initial stage). It should be noted that the frictional force measured on a sample with a SiO$_2$ layer has always been characterized by a large scatter of values compared to samples with deposited nanocomposite layers. The nature of the time dependence of the frictional force is due to the complex influence of several factors, the main of which are the following: the formation of wear products of the counter body, the destruction of the coating layer, which, on the one hand, is accompanied by the entry of friction particles of SiO$_2$ into the friction region and the other hand by the parts of antifriction particles MoS$_2$, and heating of the friction area. It is possible that these phenomena are more important for a silicon dioxide layer, and in the case of a nanocomposite coating, judging by the smooth nature of the dependence, they play a smaller role. In connection with these reasons, for a more objective comparative evaluation of the frictional force of the samples of nanocomposite coatings obtained under different conditions, the values of the frictional force were chosen in the steady-state part of the time dependence, which corresponds to test times exceeding 200 s.
In the first series of experiments, the effect of ammonium thiomolybdate concentration in a solution of dimethylformamide, used to create aerosols, on the antifriction properties of coatings was investigated. Figure 7 shows the data characterizing the effect of this factor on the frictional force of rotation.

As can be seen, for all samples of nanocomposite coatings the frictional force has lower values than for SiO2 layers. Reduction of the frictional force with increasing concentration (NH4)2MoS4 to 0.005 mol*l-1, is most likely due to an increase in the relative amount of MoS2 nanoparticles in the coating, as evidenced indirectly by an increase in their surface density determined by SEM. With increasing thiomolybdate concentration, the average size of synthesized molybdenum disulfide nanoparticles increases, and bearing in mind the fact [20-27] that an increase in the size of the nanoparticles of the lubricant material leads to a deterioration in its antifriction properties, this circumstance apparently causes an increase in the frictional force with a further increase in concentration.

The results of the investigation of the effect of the partial pressure of tetraethoxysilane, varied due to a change in the ratio of carrier gas and TEOS vapor dilution gas, showed that the sliding frictional force increased insignificantly in the range of 10-15% with an increase in the amount of reagent. Most likely, an increase in the partial pressure of the reagent leads to an increase in the deposition rate of silicon dioxide and at a constant intensity of the nanoparticle intake to the substrate, a smooth decrease in their relative amount in the coating, and accordingly an increase in the frictional force.

4. Conclusions
It has been demonstrated experimentally that the separation of two chemical vapor deposition processes in the space, one of which provides the synthesis of the nanoparticles of the filler (MoS2), and the other, the formation of the nanocomposite coating matrix (SiO2) in one reactor, provides independent control of the two process speeds and allows to vary the composition of deposited films within a wide range.

It is shown that the nanocomposite coatings of molybdenum disulphide (filler)-silicon (matrix) have improved antifriction properties in comparison with the matrix (SiO2 layers), which are determined by the relative amount of MoS2 nanoparticles in the layer and their average size.

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