Elastomer surface modification by means of SIAD of metal-based layers

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Abstract

The composition of Zr-based thin films on vulcanized synthetic rubber by means of self-ion-assisted deposition was investigated by utilizing the Rutherford backscattering technique and RUMP code simulation. Pin Pull Test method was applied both to measure the level of adhesion between the deposited metal (Me)-based layer and rubber and mechanical properties of modified rubber surface. Hardness measurements of the thin films on substrate were fulfilled by applying a conventional Knoop method, an ultra-low load indenter and a laser-acoustic test method. The deposited films may be soft or very hard in dependence of Me species. Deposition of Me-based coatings changes the wettability of the modified rubber to water. We observe 10% decrease and 30% increase in a contact angle of water when Mo-based and Zr-based coatings are deposited on the rubber.
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1. Introduction

Coating of articles is widely used to provide protective or decorative layers. Among the various methods, vacuum evaporation is relatively successful in many cases. However, the film adhesion is often limited and such coatings are usually under high stress [1,2] and may therefore have low lifetimes. The film adhesion and the high stress in the deposited films are special factors when the base is not a rigid material but is rubber (R).

Improved adhesion between a thin film and a substrate is provided during the growth process, for example, ion-beam assisted deposition (IBAD) techniques [1,3]. These methods have the disadvantage that the resulting coatings can contain independence on IBAD process parameters, for example, on an assisting-ion flux density up to several percent of the noble gas species which may migrate and agglomerate at the film–base interface to form even up to 10 at.% local gas concentrations [4,5]. Clearly the use of ion species which are the same as the coating material would alleviate this problem and such method has been developed [6]. Previously it was reported about the structure of rubber surface modified by self-ion-assisted deposition (SIAD) of metals-based

coatings, the adhesion between the deposited layer and rubber, the friction of rubber against steel [7]. But we are to note that due to vacuum conditions in these experiments there are contaminations (C, O, H) in the films. This work will deal with the wettability of modified rubber surface, the hardness of the coatings fabricated by means of SIAD. In addition some preliminary results of SIAD experiments will be presented.

2. Experimental

Film deposition was carried out in a vacuum chamber with a base pressure in the range of 10^{-2} Pa established by the conventional diffusion pump charged with silicon oil. SIAD experiments were performed using a resonance vacuum arc ion source, which provides in correspondence with chosen metal (Me) electrodes (Me=Cr, Zr, Mo) a mixture of neutral fraction of Me and ionized fraction of Me$^+$. A schematic diagram of the SIAD system is given in Fig. 1. Rubber is insulator, but there were no problems with charging up the insulator because of conductive properties of SIAD coatings, connected with the target holder 5 in Fig. 1.

The relative ratio of ions/neutrals (I/A) could be changed by varying the spacing of the Me source electrodes, by changing the frequency of the source supply, or by varying the target–source separation dis-

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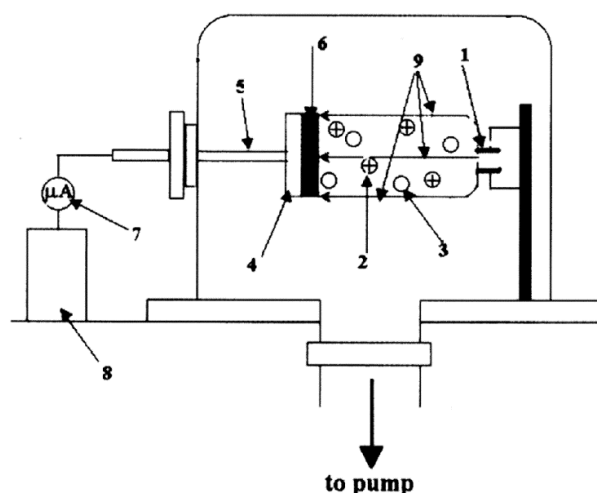*E-mail address:* root@bstu.unibel.by (I.S. Tashlykov).

Fig. 1. Schematic representation of SIAD: 1—vacuum arc ion source, 2—ionized fraction, 3—neutral fraction, 4—target, 5—target holder, 6—modified surface, 7—current integrator, 8—high voltage power supply, 9—electric field.

tance. Substrates were 2 mm plates of rubber (GOST 7-IRP-1068) floated to a negative potential with respect to the source in interval 5 and 20 kV to accelerate the ion species. The number of ions was estimated from integrated current measurements and the neutrals from measurements of film thickness on unbiased substrate over known period of time. From such measurements it was found I/A ratios were between 0.1 and 0.3 and film deposition rates were between 0.01 and 0.04 nm/s. The total coating thicknesses typically were 200–700 nm. Silicon wafers were used for a simultaneous deposition of coating on rubber and silicon in several SIAD experiments. Because of non-rigid nature of rubber we could not apply conventional techniques for thin coatings on rubber hardness measurements. Therefore hardness measurements were fulfilled on the coatings deposited on silicon substrates. Ten indents applying a conventional Knoop method were made on each sample and the average Knoop hardness was calculated. The load used in this study was 0.02 N. An indentation dwell of 60 s was used for all the samples. The hardness of the thin films was also measured using an ultra-low load indenter Fisher HP100V. When the load changes between 0.4 and 20 mN 60 measurements with 0.5 s interval between measurements are done. The laser-acoustic test method for characterizing thin films [8] was applied for measurements of Young's modulus of the coatings which is an essential parameter to correlate with hardness for film materials.

The Rutherford backscattering (RBS) technique was employed for the investigation of target composition and for depth profiling of components in prepared structures. The energy of He$^+$ ions was 2.0 MeV, and

the scattering, entry and escape angles were 168; 0; and 12°, respectively. The energy resolution of the analyzing system was 25 keV. Concentration profiles of components were evaluated using the RUMP code computer simulation [9].

Chemical analyses of coatings were conducted by X-ray photoelectron spectroscopy (XPS) in an electron spectrometer (model LHS-10, Leybold, Germany). The analysis was performed with Mg Kα X-ray radiation ($hv = 1253.6$ eV) and an applied pressure of approximately 10^{-8} Pa. Bombardment by Ar$^+$ ions at 3 keV energy and ion current density of 10 μA cm^{-2} was also carried out to obtain data about the chemical bonding states of carbon, oxygen and metal atoms at selected depths in coating. Detailed scans, for chemical state identification, from C_{1s}, O_{1s}, Zr_{3d}, W_{4f} regions were obtained. The Au_{4f} signal was used as a line position to calculate binding energies.

Water wettability data of modified rubber were achieved by measuring of the advancing and receding contact angles.

A Pin Pull Test (PPT) was employed for measuring the adhesion between the deposited film and the rubber substrate. The standard preparation and conditions of the tests were the same as those used in Ref. [10].

3. Results and discussion

3.1. Composition and chemical analysis

RBS spectrum of the initial rubber (1) and a sample upon which the Zr coating was deposited and also irradiated with Zr$^+$ ions (2) are shown in Fig. 2. It is estimated that the Zr deposition using SIAD process is accompanied by the appearance in the coating of oxy-
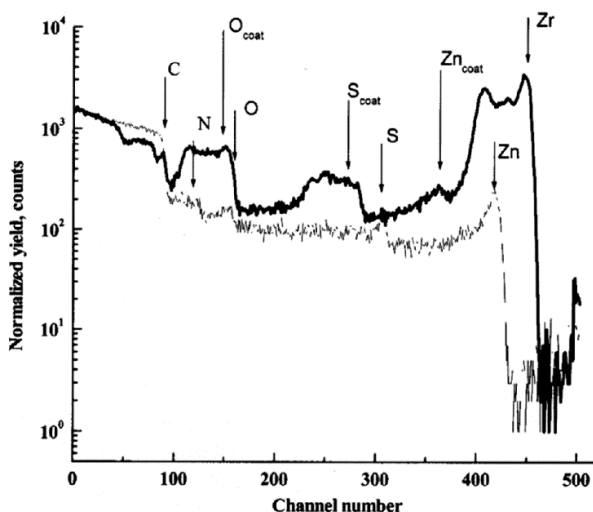

Fig. 2. RBS spectra of untreated rubber—solid curve (1); and with a deposited Zr-based thin film—curve (2).
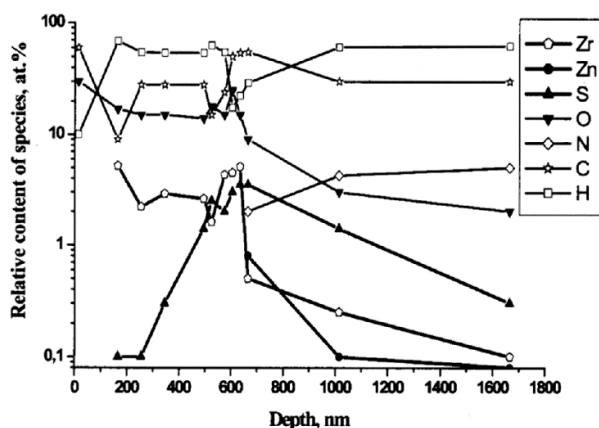
Fig. 3. Relative content of species in SIAD Zr-based thin film on rubber.

gen, carbon and other species which are diffused from the rubber.

Fig. 3 presents the depth distribution of indicated components in the same (Fig. 2, curve 2) sample. The data are obtained using the RUMP code simulation [9].

These data indicate that the Zr concentration decreases from the top surface of the coating to a value approximately 50% lower in the middle of the film and increases again near the Zr/Rubber interface. A noticeable amount of Zr (~ 0.1 at.%) is in the depth which is ~ 1000 nm deeper under interface. This means that during SIAD process the Zr atoms penetrate deeply into the rubber. The oxygen level follows qualitatively a similar trend, which suggests that there is at least some combination of oxygen with Zr to form an oxide. The carbon and hydrogen levels are approximately constant in the middle of the coating and are changed near the top surface of the sample and near the coating/rubber interface. One can observe outdiffusion of the sulphur into the coating. This is known effect for IBAD process [1]. But we do not observe any Zn diffusion from the rubber into the coating. The high O, C and H content arises, we suppose, because of the used vacuum quality which allows deposition of oxyhydrocarbons onto the growing film and accumulate them under the irradiation with the accelerated Me^+ ions. We should emphasise that presence of hydrogen in the SIAD coatings was confirmed quantitatively in the independent study (coatings on Si wafers) by means of the sharp resonance $^1H(^{15}N, \alpha\gamma)^{12}C$ nuclear reaction [11].

Chemical analysis of the Zr-based coating/rubber structures has been also conducted by means of XPS. Fig. 4 shows XPS spectra obtained from the $Zr_{3d_{1/2}}$, $Zr_{3d_{3/2}}$ region. Evaluation of the shown signal indicates qualitatively that there are fractions of metallic zirconium and zirconium in oxide form ZrO_2 presented in the coating.

3.2. Adhesion

The knowledge of the properties of the Me/elastomer interface is important, particularly to enhance the control of the force of the adhesion. It is found that the formation of metal atoms complexes with the oxygen at the interface promotes a subsequent increase in the adhesion [12]. The authors of Ref. [13] consider that the adhesion between the rubber and the base depends on both the composition of the elastomer and the material of the base. It should be noted here that in all cases we used elastomer with identical composition, which is indicated in Ref. [7]. The maximum possible level of adhesion is necessary in metallization of elastomers that are commonly used for the electronic devices, in the packing industry. But sometimes it is more important to achieve a consistent adhesion in a more modest level. For example, in a process of the moulding when the adhesion between a mould surface and a rubber surface has been wished to be eliminated. For measuring of the level of the coating adhesion PPT method was applied. It was previously shown that the critical pool-off force (the force when coating–rubber construction is destroyed) depends strongly on the chemical nature of metal in coating on rubber. The new data of PPT measurements are presented in Fig. 5. The shown curves provide evidence, suggesting that the SIAD process may control the level of adhesion. Compared with peel force (per mm^2) of the pin from the virgin rubber the Zr-, Cr- and Mo-based coatings indicate improved adhesion. After delamination, islands of the rubber are left on every pin, which was fixed at the Zr-, Cr- and Mo-modified rubber plates. Obviously there is no direct correlation of the degree of interface mixing, e.g. Me content in the rubber and adhesion. For example, the authors of Ref. [13] consider that interfacial layers formed during the moulding have a thickness that
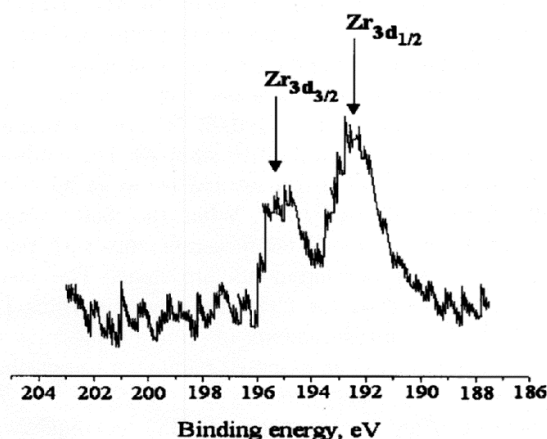

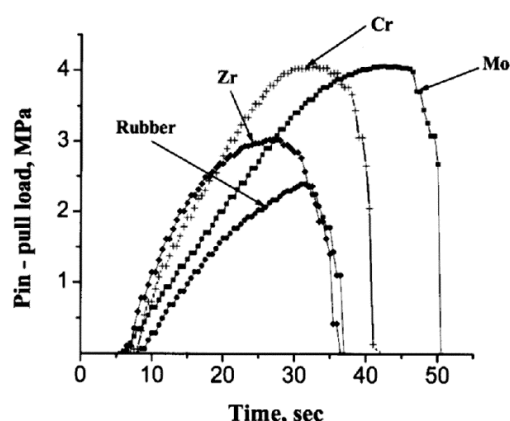Fig. 4. XPS-spectra of SIAD Zr-based thin film in region Zr_{3d} signal at depth 30 nm.

Fig. 5. PPT-curves for SIAD Me-based coatings on rubber. R-pin fixed on virgin rubber.

depends on the compound, but 6 nm can be taken as an indicative figure. Indeed, reactions, accompanying SIAD process are very complex and complicated, involving substitution, replacement, interdiffusion, new phase formation and so on. Their mechanisms are additionally interfered by oxidation, taking place simultaneously [12]. All this may make the surface layer of the coated rubber stiffer. We consider that, as observed in Fig. 5, different slope of the curves at beginning of PPT experiment quoted in Table 1 is consistent with this conclusion.

3.3. Film hardness

It is known that there are always difficulties in hardness measurements of thin films. This is because of the processed state of microstructure, residual stress, defects, adhesion and the properties of the substrate are all critical in determining the overall system responses [10,14]. Additionally in our system coating–rubber the substrate is non-rigid material. That is the point of measuring hardness of coatings on the coating–Si system. Obviously there is no guarantee that the hardness information could be directly used for the coating–rubber system, however, we suppose that a certain degree of coating hardness on rubber can be tolerated. In this investigation we applied three different techniques for studying of hardness of the same coatings prepared by SIAD. The achieved data are presented in

Table 1
Speed of pin-pull load, peel force (stress) and relative change of Young's modulus of modified rubber

Me-based thin film	Virgin rubber	Cr	Zr	Mo
$\Delta\sigma/\Delta t$, MPa/s	0.15	0.45	0.45	0.20
σ_{peel}, MPa	2.4	4.1	3.0	4.1
$E_{\text{Me/R}}/E_{\text{R}}$	–	2.9	3.0	1.4

Table 2. The hardness values at a depth of 100 nm (from nanoindenter tests) and those at 0.02 N load (from Knoop tests) are shown in Table 2. Thicknesses of the coatings have been taken in experimental measurements. The Knoop microhardness of a Cr-based coating is considerably lower than that of the other coatings in spite of the highest value of Young's modulus of the Cr-bulk. This result agrees well with the nanoindenter hardness values for Cr and Zr. It should be noted, that the hardness of Zr-based coatings reaches values 13–15 GPa, in Table 2, which is comparable with the hardness of coatings [15] and is suitable for many applications. Zr-based coatings are approximately twice harder than the bulks.

3.4. Wetting behavior

As it was shown above the properties of SIAD produced Me-based coatings sensitively depend on the metal species. Obviously there are considerable differences according to the chemical nature of the proved several metals such as Cr, Zr, Mo and their oxides and carbides. If incorporation of metal atoms in coatings is somehow different, their influence on the surface energy is very noticeable in the wetting behavior of liquids. Fig. 5 shows the change in the contact angle of water (change in wettability), when different Me-based coatings are deposited on rubber. It is clear that depending on the Me species in coatings they could be deposited with desirable wetting behavior. For example, in Fig. 6 we observe 10% increase of wettability of the Mo-based coating modified rubber compared with the untreated rubber. On the contrary, the Zr-, Cr-based coatings on rubber are characterized by an increased contact angle of water. The most pronounced effect (30% decrease in wettability) takes place when rubber is modified by Zr-based coating deposition. Some authors [15] have shown that wetting behavior of coatings strongly depends on

Table 2
Hardness of the coatings deposited by means of SIAD

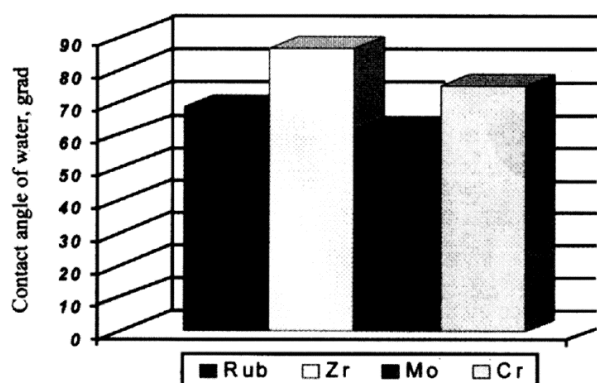| Me-based	Thickness of the coating, nm	Energy of ion assisting, keV	Knoop microhardness, HK	Nanoindenter hardness at 100 nm depth, N/mm²	Young's modulus, GPa	
					Experimental	Me-bulk
Cr	620	10	536	4300	–	280.0
Zr	600	10	829	13 500	170	68

Fig. 6. Contact angle of water to Me-based SIAD coatings on rubber.

elements such as F, Si, O and N incorporated in coating. They consider that reduction in the surface energy resulted mainly from reduction in the polar part of the surface energy. Therefore we are going to conduct further experiments in respect of the surface energy of modified rubber measurements.

4. Conclusions

In this study it was shown that the Zr-based coatings produced by means of SIAD have a complicated composition. Thin films deposited on rubber consist of Zr, C, O, H and S. The last one appears in the coatings due to out-diffusion of sulphur from rubber. The SIAD process of the Me-based coatings causes strong modification of the rubber surface. The thin films deposited on substrate may be soft or very hard. It was measured that the hardness of Zr-based coatings reaches values 13–15 GPa. Deposition of Zr-, Cr- and Mo-based coatings improves mechanical properties of the rubber surface. PPT experiments reveal a considerable increase in quasi Young's modulus of the modified rubber surface.

Deposition of Me-based coatings changes the wettability of the modified rubber. We observe 10% decrease in the contact angle of water when the Mo-based thin film is deposited on rubber and 30% decrease of wettability takes place when the rubber is modified by Zr-based coating deposition. These results seem to be important with respect to commercial application of the modified rubber articles.

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