

RBS Depth Profiling of Metal Coatings on Elastomer

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Received February 10, 1995; in final form February 16, 1995

The surface composition of an elastomer upon vulcanization and modification by ion-beam-assisted deposition of bronze or titanium coatings was studied by Rutherford backscattering spectroscopy (RBS). After vulcanization, the near-surface layers of the elastomer contain 98.5% carbon, 1% sulfur, and 0.4% zinc. Oxygen and nitrogen were identified only in a thin (a few atomic monolayers) superficial layer, rather than in the whole modified layer. The ion-beam-assisted deposition of metals onto elastomers is accompanied by active processes of mass transfer at the phase boundaries of the modified structure.

The use of elastomer (vulcanized synthetic rubber) articles is frequently related with the necessity to control the friction properties of their surfaces in contact with other parts, involved in the rotating or reciprocating motion. Methods are known that allow the friction characteristics of elastomers to be modified by introducing additives in the elastomer composition [1]. In order to reduce the consumption of modifiers (by approximately half [1]) and obtain reproducible parameters of the elastomer surface, it is possible to employ certain physical methods providing the application of coatings to modify the desired properties of elastomers.

EXPERIMENTAL

In our experiment, thin metal coatings were applied to elastomer samples under conditions of irradiation with 20-keV ions of the same metal ions (ion-beam-assisted deposition, IBAD). The ions were produced by a resonance source of electric-arc plasma in vacuum [2]. The elastomer samples were made of a rubber mixture (grade 7-IRP-1068-24 according to the State Standard GOST 8752-79) with the composition (parts by weight): synthetic nitrile rubber (100), thiuram (0.6), sulfenamide (2),

dithiodimorpholone (2.2), zinc oxide(5), diaphene (1), naphthame-2 (1), technical carbon grade P-234 (30), technical carbon grade P-803 (95), dibutyl phthlate (5), aldol-naphthylamine (2), synthetic fatty acids C₂₁-C₂₅ (2), and rosin (3), to a total of 248.8 parts. Thus elastomers contain the following elements: hydrogen, carbon, nitrogen, oxygen, sulfur, and zinc.

Electrodes of the ion source were made of bronze or titanium. Therefore, the elastomer samples were treated by the IBAD method to obtain thin films comprising titanium or the components of bronze.

The elemental depth profiling of metal-elastomer structures was performed by Rutherford backscattering spectroscopy (RBS) using helium ions with the energy $E_0 = 1.5$ and 2.5 MeV. Depending on the task of the experiment (optimum elemental sensitivity against high-resolution depth profiling), the experiments were performed in various geometries: (i) $\theta_1 = 0^\circ$, $\theta_2 = 10^\circ$, $\theta = 170^\circ$; (ii) $\theta_1 = 45^\circ$, $\theta_2 = 55^\circ$, $\theta = 170^\circ$; (iii) $\theta_1 = 60^\circ$, $\theta_2 = 70^\circ$, $\theta = 170^\circ$. The energy resolution of the detecting system was 15 keV.

RESULTS AND DISCUSSION

Figure 1 shows the experimental RBS spectra of He ions from elastomer samples in the initial state (1) and from beryllium samples coated with a thin bronze film (2). The latter sample was used as a reference that allowed elements with $M_2 > 9$ to be identified the spectra from modified elastomer targets. Arrows indicate the positions of signals from identified elements entering into the elastomer composition and the modified beryllium sample.

The elemental compositions, surface concentrations, and the bulk contents of components were calculated by conventional methods [3]. The character of spectrum 1 (Fig. 1) suggests that modified surface layers of elastomer contain only three elements of the total set identified. The shape of the signals due to nitrogen and oxygen (a peak rather than a step) indicates that these elements are present only in a superficial (a few atomic monolayers) surface layer, rather than in the whole IBAD-modified layer. In addition to the above elements, the RBS spectra of elastomer also showed the presence of trace amounts of lead (about 10^{13} cm^{-3}), as indicated by a small peak in the region of channel 215 (Fig. 1, spectrum 1).

A comparison of the signal observed in the region of steps H_O , H_S , and H_{Zn} (Fig. 1, spectrum 1), with an allowance for the scattering cross-sections of He ions on these elements, allows the elastomer composition with respect to the identified elements to be described as $C_{0.985}S_{0.01}Zn_{0.004}$. Thus, the elastomer is composed of 98.5% carbon, 1% sulfur, and 0.4% zinc.

Table 1 gives data on the variation of the concentrations of oxygen and nitrogen in the sample, obtained by integrating signal areas under the corresponding peaks and by modeling the RBS spectra. For the comparison, also given are the values of component concentrations in a bronze film on beryllium and a titanium film on elastomer. In the Table (and in the text below), data refer to the total contents of copper and zinc, because the proximity of atomic masses (64 and 65, respectively) does not allow their RBS signals to be resolved.

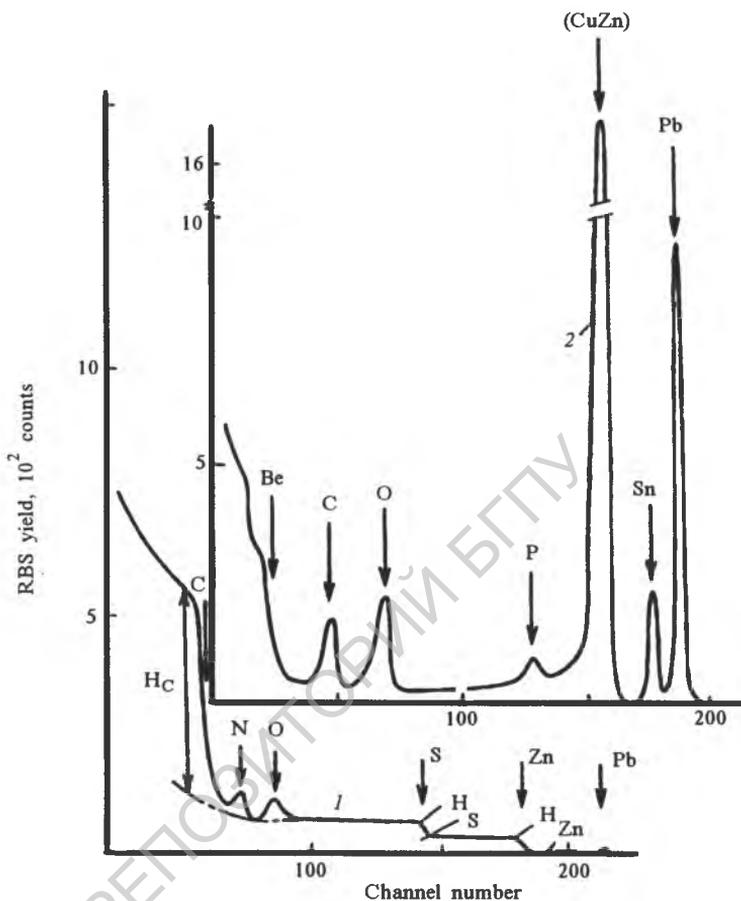


Figure 1. Helium RBS spectra: (1) initial elastomer ($E = 1.5$ MeV, $\theta_1 = 60^\circ$, $\theta_2 = 70^\circ$, $\theta = 170^\circ$); (2) beryllium IBAD-modified with bronze ($E = 2.5$ MeV, $\theta_1 = 50^\circ$, $\theta_2 = 70^\circ$, $\theta = 160^\circ$).

Table 1. RBS data on the variation of element concentrations in IBAD-modified structures

Sample	Concentration, 10^{16} cm $^{-2}$						
	C	N	O	CuZn	Sn	Pb	Ti
Initial elastomer	—	2.1	2.7	—	—	0.001	—
Bronze on beryllium	3.4	—	2.2	3.8	0.07	0.23	—
Titanium on elastomer	17.2	—	44.0	—	—	—	39.0

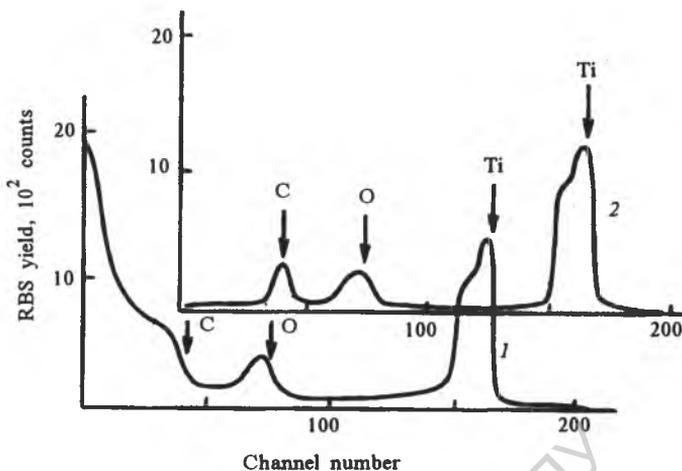


Figure 2. Helium RBS spectra: (1) experimental spectrum from the elastomer IBAD-modified with titanium ($E = 1.5$ MeV, $\theta_1 = 0^\circ$, $\theta_2 = 10^\circ$, $\theta = 170^\circ$); (2) computer-simulated spectrum from a titanium film with impurities.

An analysis of the elemental composition, note that the surface of samples is enriched, besides metals, by carbon and oxygen, which are probably supplied to the surface from the residual atmosphere. This effect is well known and observed during the ion irradiation of solids and the ion-assisted deposition of coatings [4].

The RBS spectrum from a beryllium sample shows a quite long "tail" due to Cu + Zn, which can be explained by deep (to 100 nm and above) penetration of these elements into beryllium (for the comparison, Cu^+ ions with $E = 20$ keV have a projected range of $R_p = 12$ nm). A similar deep penetration is observed for titanium in the IBAD-modified elastomer carrying a thin titanium coating (Fig. 2). This fact is indicative of the active mass transfer processes occurring in both the elastomer and beryllium irradiated with heavy ions at relatively low energies employed in this work. Note that the character of RBS signals from O and C (Figs. 1 and 2) suggests that these impurities are distributed through the entire thickness of metal coatings. The same conclusion follows from the comparison of computer modeling (spectrum 2, Fig. 2) of the experimental RBS curve (spectrum 1, Fig. 2).

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