

APPLICATION OF MÖSSBAUER SPECTROSCOPY TO CHARACTERIZE IRON-CONTAINING OXIDE COATINGS FORMED ON TITANIUM BY PLASMA ELECTROLYTIC OXIDATION

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Abstract. In this work, we report the application of the Mössbauer spectroscopy technique to the study of Fe-containing oxide coatings formed on titanium by plasma electrolytic oxidation (PEO). Several models were used to process the Mössbauer spectrum, and the most suitable model was selected. The results of the Mössbauer spectrum processing showed the presence of both Fe(II) and Fe(III) high-spin states of iron in the samples.

1. Introduction

One of the promising methods of surface engineering of valve metals and their alloys is the technology of plasma electrolytic (microarc) oxidation (PEO), which allows obtaining surface oxide layers with a unique set of properties on objects of almost any geometric shape [1].

Iron-containing oxide PEO coatings on metals can have ferromagnetic properties and make it possible to obtain magnetic materials, including constructional ones, for example, 'metal/magnetic film' systems, which can be used as electromagnetic screens, structures absorbing electromagnetic radiation and etc. [2].

The magnetic properties of coatings depend on the valence state, the nearest environment of atoms located not only on the surface, but also in the bulk of the coatings.

Mössbauer spectroscopy is a highly informative method to obtain qualitative and quantitative information about the valence states and the nearest environment of iron. The values of isomeric shifts can indicate the presence of both Fe(II) and Fe(III) and their spin states. Due to the high selectivity of this method, it seems possible to determine the nature of the bonds formed during PEO coatings doping with 3d elements, that which are responsible for ferro- and ferrimagnetism. Similar studies have not yet been carried out for PEO coatings. For the correct interpretation of the Mössbauer spectra, it is necessary to choose the correct model for their processing, which was the task of this study.

2. Experiment

Titanium plates of the grade VT1-0 of a size of 2.0×2.0×cm were used in plasma electrolytic oxidation. Prior to anodizing, the samples were mechanically and chemically polished in a mixture of concentrated acids HF:HNO₃ (1:3) at 60–80 °C for 2–3 s and then rinsed in distilled water and dried in air.

PEO process was carried out in polypropylene glass of 1000 mL in volume using thyristor unit TER4-63/460H (Russia) with unipolar pulse current.

The Fe-containing coating on titanium was formed at effective current density 0.1 A/cm² for 10 min in an aqueous electrolyte containing 0.05 M Na₃PO₄ + 0.05 M EDTA + 0.05 M Fe₂C₂O₄. After PEO treatment, the PEO-coated sample was rinsed with water and air-dried at 70 °C.

To obtain Mössbauer spectra Fe-containing PEO coating was removed from the titanium surface and powdered. Mössbauer spectrum of Fe-containing PEO coating (hereinafter, the Fe-containing sample) was obtained at room temperature in transmission geometry on a Wissel spectrometer (Germany). The ⁵⁷Co isotope in a rhodium matrix (RITVERZ JSC, Russia) was used as a source of γ-radiation. The velocity scale was calibrated using the spectrum of sodium nitroprusside with further conversion to metallic iron (α-Fe).

3. Results and discussion

The Mössbauer spectrum of Fe-containing sample is a wide asymmetric doublet. The broadening and asymmetry of the absorption lines of the Mössbauer spectrum indicate the presence of several different positions of the iron environment in the sample under study, which differ from each other in the type of symmetry.

The value of the isomeric shift of the Mössbauer spectrum indicates the presence of the positions of the iron nuclei in the bivalent high-spin state in the sample under study.

For correct processing of Mössbauer spectrum, it is necessary to determine the processing model. To do this, three models were used, consisting of two, three or four subspectra describing the bivalent high-spin states of iron, Figure 1.

The types of the theoretical spectrum, the distribution curve of the fitting error, and the χ^2 values for different processing models were compared to find the best model. It was established that the model with two subspectra (Figure 1, model A) was not suitable for describing the experimental spectrum ($\chi^2 = 2.11$), the model of three subspectra (Figure 1, model B) had a better value of $\chi^2 = 1.68$. However, the distribution of the error suggested that introduction of one more subspectrum is required for good description of the experimental spectrum. The four-subspectrum model (Figure 1, model C) for describing the divalent high-spin states of iron nuclei had $\chi^2 = 1.55$, but did not completely coincide with the experimental spectrum. The error distribution curve showed that it was necessary to use the subspectrum corresponding to the high-spin trivalent state of iron nuclei (Figure 2, model D). Parameters of processing by different models of the Mössbauer spectrum presented in Table I.

Table I. Parameters of processing by different models of the Mössbauer spectrum*

Model	δ (mm/s)	Δ (mm/s)	Relative area (%)	χ^2
A	1.13	1.97	58	2.11
	1.18	2.53	42	
B	0.99	2.04	25	1.68
	1.18	2.71	17	
C	1.22	2.13	58	1.55
	0.96	1.98	22	
	1.19	2.26	33	
	1.19	2.74	21	
D	1.21	1.85	24	1.19
	0.93	1.98	10	
	1.10	2.04	31	
	1.16	2.68	33	
	1.29	2.01	21	
	0.36	0.62	5	

*Isomer shift (δ), quadrupole splitting (Δ). Values of δ are reported relative to α -Fe. Fitting error in the values of δ , Δ remained below 0.01 mm/s.

4. Conclusions

A comparison of three models for processing the Mössbauer spectrum of titanium-free Fe-containing PEO coating has enabled one to find the number of subspectra required to describe the bivalent high-spin states of iron in the sample. It was also figured out that addition of subspectrum corresponding to the positions of iron in the trivalent high-spin state was necessary to fit experi-

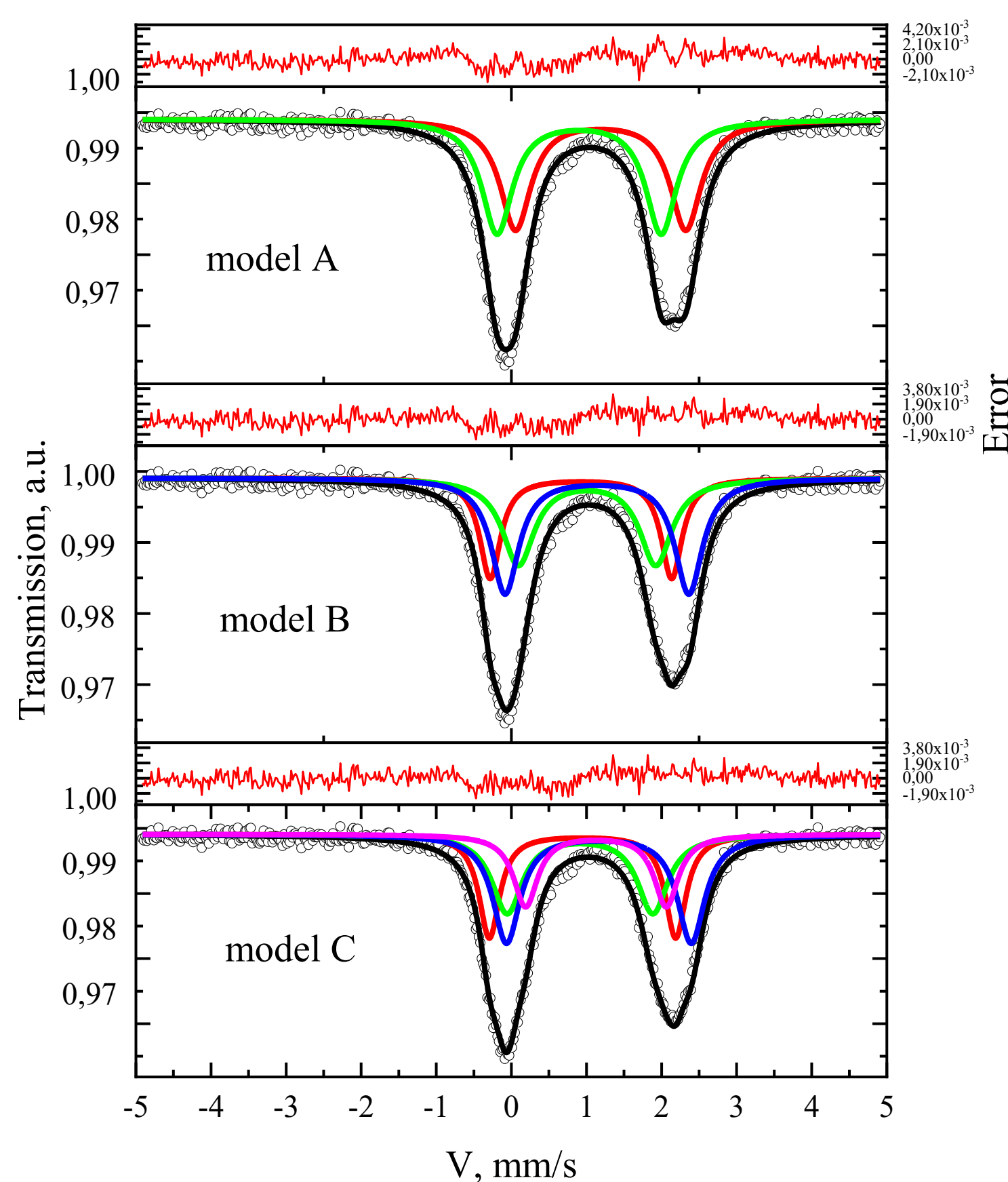


Fig. 1. Models for processing two valence high-spin states in the Mössbauer spectrum of Fe-containing sample and the values of the fitting errors. The models A, B, and C consist of two, three, and four doublets, respectively.

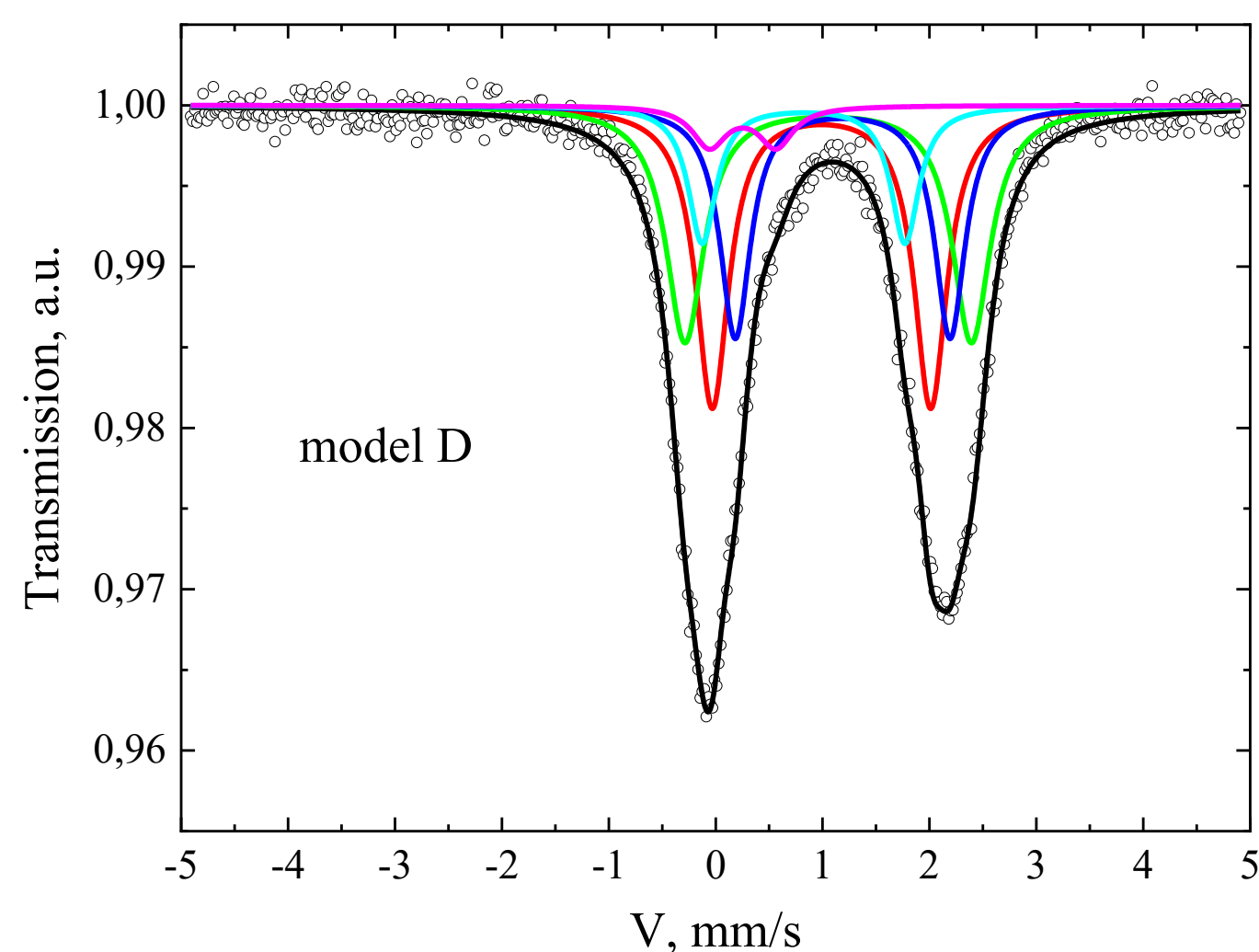


Fig. 2. Model for processing two and three valence high-spin states consisting of five doublets in the Mössbauer spectrum of Fe-containing sample.

References

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