

CERTIFICATION OF THE HARDSURFACED TOOLS BY THE NUCLEAR BACKSCATTERING OF THE PROTONS
ACCELERATED BY THE CYCLOTRON

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The possibilities of Nuclear Backscattering Spectrometry for the diagnostics and certification of the protective coatings on the surface of the hard alloys were studied. The elemental composition and the structure of near-surface layers of hardsurfaced tools based on the tungsten carbide were measured.

Introduction

Much of the adverse environmental impact (corrosion, friction, wear, collision, radiation, etc.) is absorbed by the surface layers of materials. To make them durable in operation, they are given various kinds of chemical and thermal treatment and covered with organic and inorganic coatings. People who monitor and certify the protective coatings and the modified surface layers seek, above all, to determine their chemical composition and thickness. Some techniques are basically aimed at measuring the content and distribution of the three light elements — carbon (C), nitrogen (N), and oxygen (O). In full measure it concerns hard alloys (HA) — ceramic-metal materials consisting of carbides of high-melting metals and plastic metal (see, for example [1]). HA are widely applicable in metal treatment.

The tungsten carbide (WC) is the matrix of the various hard alloys. Cobalt Co is widely used as a metallic binder. Carbon content can sufficiently change during HA production. There are the bounded carbon and the second phase in the form of free (unbounded) carbon in carbon enriched carbides. In this case the special determinations of both free carbon and bounded one are necessary. It is very difficult to determine and remove the oxygen admixture. Meanwhile the properties of HA strongly depend on its presence. Oxidizability of WC under warming in dry air at atmosphere pressure is higher that of metallic tungsten. The volatile oxide WO_3 is formed at the temperature $T > 700^\circ C$ and the film of WO_3 , which is not protective — at $T < 700^\circ C$.

The traditional complex of chemical and physical methods for measuring C, N, O in the surface layers provides for using ready standard samples and destroying the products during testing. For example, in measuring the depth distribution, the sample is usually shaved layer by layer, starting from the surface, and the shavings are then

dissolved in a blend of acids, or heated until they melt. So the quantity of the desired element is measured upon release in the gas form from the blend or melt [1].

The accumulated experience on non-destructive and without standard samples analysis of the concentration profiles of light elements in heavy metals and alloys [2-7] shows that Nuclear Backscattering Spectrometry (NBS) of near- and above-barrier protons is one of the most perspective technique. It is known, that NBS of the protons with energies > 2 MeV is high sensitive to measuring of concentration depth profile of light elements C, N, O due to wide overlapping resonances of elastic scattering excitation function. The depth of NBS-analysis is of several tens. It corresponds to the typical thickness of modified layers and protective coatings.

In the present paper we study the possibilities of NBS for the testing of technological process of HA production and its certification.

Experiment

The technique of the NBS-experiment was presented in [7] in detail. NBS spectra were obtained using 7.8 ± 0.1 MeV proton beam of INP MSU cyclotron. The collimated 2mm^2 cross section proton beam was directed at normal angle onto target block with the samples under investigation inside of scattering chamber. The maximum current of the protons on the samples was < 50 nA. So the samples were not heated by the proton beam. The protons backscattered at 160° were counted by Si-Li surface barrier detector with the thickness of sensitive layer of 700μ . The energy resolution of the spectrometric tract was about 25 keV. The spectra were stored by the multi-channel analyser. The statistical error of the NBS-spectra was $< 3\%$.

The plates of non-regrindable tools of various brands and types were used as the targets. The following

samples were among them: standard samples MS321 (WC +2%TaC,NbC +6%Co); the serial samples MS321, MS3210 (with the coating TiC), and MA3 (with the multi-layer coating TiN+Ti(CN)+Al₂O₃); the serial samples WC8 (WC+8%Co) as well as the serial samples WC8 subjected to the chemical-thermal treatment.

Analysis

The measured NBS spectra were analysed, and the concentration profiles of the elements were obtained using the original code NBS [8]. It serves for the determination of the best-fit concentration profiles of the target elements and the best-fit values of the energy dependencies of the differential backscattering cross sections. The code NBS allows to look over the model spectra for the each target component separately and facilitates the fitting of the adequate near-surface structure of layer. NBS has also convenient user interface for OS Windows'95.

For NBS spectrometry the energy dependencies of the differential cross sections $\sigma(E)$ for the protons scattered at $\theta=160^\circ$ on the nuclei of the elements comprising HA are necessary.

The NBS spectra for stoichiometry oxides WO₃ and Al₂O₃ were measured in order to determine $\sigma_O(E)$ and $\sigma_{Al}(E)$ at $\theta=160^\circ$. The comparison of the simulated NBS spectrum of WO₃ with the experimental one, taking into account the Rutherford proton cross section for W, allowed to determine $\sigma_O(E)$ (see Fig.1). We measured also $\sigma_O(E)$ at the same angles θ as in [9]. The obtained data were in good agreement with $\sigma_O(E)$ [9]. We used the cross sections $\sigma_O(E)$

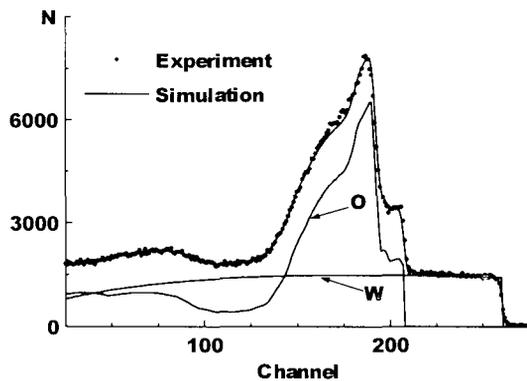


Fig. 1. 7.7 MeV H⁺ NBS spectrum for WO₃. Spectra for W and O deconvolution of simulated spectrum for WO₃.

for the measurements of $\sigma_{Al}(E)$ from NBS-spectra of Al₂O₃. The detailed data on the excitation function of the proton elastic scattering on ¹²C are presented in [10,11]. We profited by the $\sigma_C(E)$ [10] at $\theta=160^\circ$ because the model NBS-spectrum of the graphite target simulated with the use of this cross section gave a good fit to the measured one. The data on $\sigma_{N,Ti}(E)$ were taken from [6].

The wide resonances of the excitation function of the proton elastic scattering provide the increased sensitivity of NBS to the C, N, O in wide energy range and,

consequently, at high depth. At energy from 6.8 to 7.7 MeV the cross section of the proton backscattering on C, N and O are of 130-200 mb/str, that is 100 times over than one calculated according to the Rutherford law and only 2 times less than Rutherford cross section on W. Cross section $\sigma_{Al}(E)$ is 2 times over than the Rutherford one, and $\sigma(E)$ for the medium weight elements, for example Ti, Co etc., is close to the $\sigma_{Ruth}(E)$.

The simulated NBS-spectra of the samples under investigation were fitted to the experimental data within the statistical error by the variations of elemental composition, the quantity and the thickness of the model near-surface structure layers. The thickness of the simulated layers was determined in units of 10¹⁵ at/cm². We converted the thickness from these units into the metric scale, taking into account the density of corresponding structural phases and chemical compounds.

Results

The measured NBS-spectrum of the standard sample MS321 is in good agreement with the model spectrum of the homogeneous alloy with the standard element composition (Fig.2). The model spectrum of the stoichiometry tungsten monocarbide WC is presented in Fig.2 also. We deduce there is not the exceeding free carbon in this sample. The high-energy step in NBS-spectrum is due to presence of Co in HA. The qualitative data on Co

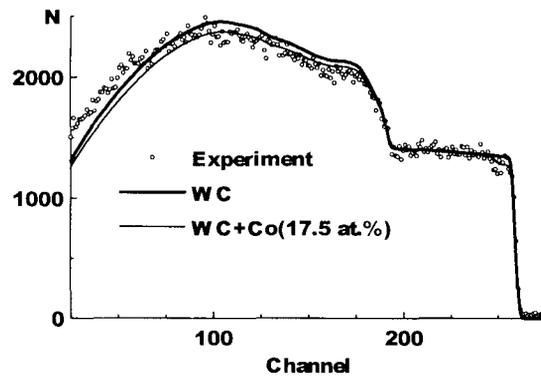


Fig. 2. 7.7 MeV H⁺ NBS spectrum for MS321 and simulated spectra for monocarbide WC and MS321.

content were obtained due to not high sensitivity of NBS to it. The NBS-spectra of the heated samples WC8 were measured to study the dynamics of the Co near-surface concentration conditioned by this treatment. In particular, we observed that the near-surface concentration of Co in the serial samples WC8 strongly decreased after the process of vacuum heating during 30-60 min at the temperature >150°C. The heating of the cutters made of WC8 like mentioned above usually accompany its working.

The high sensitivity of NBS to oxygen allowed to observe it in the NBS-spectrum of one of the serial samples WC8 (Fig.3). Near-surface layer with the thickness of 2.4 μ

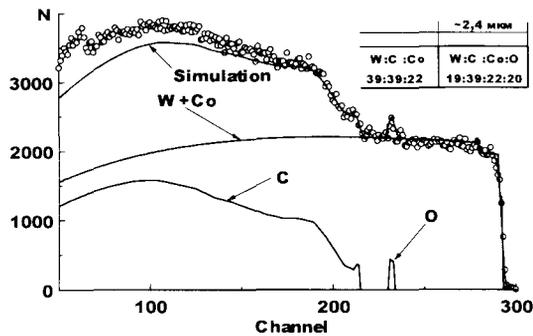


Fig. 3. 7.7 MeV H⁺ NBS spectrum for WC8. Spectra for W+Co, C and O deconvolution of simulated spectrum for WC8.

contains the oxides, and the concentration of carbon is unacceptably high. This sample was found to be not satisfying the standard. So the violation of technology of the thermal treatment and deposition of the coatings for some HA samples was observed. It led to the presence of the oxides in the surface layers of HA. For example, the NBS-spectrum of the sample MS3210 (MS321 with the coating TiC) is presented in Fig.4. The oxygen (obviously, in the form of the oxides of titanium) was observed.

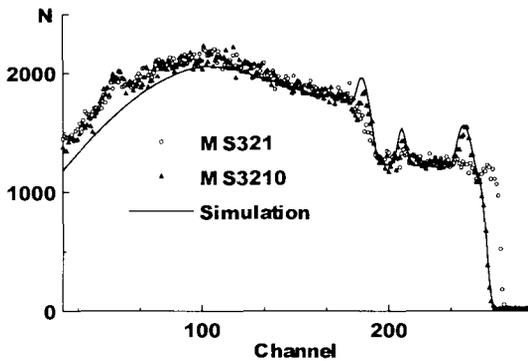


Fig. 4. 7.7 MeV H⁺ NBS spectrum for MS3210, standard sample MS321 and the best-fit composition for MS3210 ($300 \cdot 10^{16} \text{ cm}^{-2}$ Ti(34 at.%) + O(66 at.%), $5000 \cdot 10^{16} \text{ cm}^{-2}$ Ti(50 at.%) + C(50 at.%), WC + Co(17.5 at.%)

The possibilities of NBS for the testing of multi-layer coatings are shown in Fig.5. The peaks for the elements comprising the coating MA3 are pronounced. So the study of the coating structure become possible. The NBS-spectra of MA3 clearly demonstrate the advantage of the Nuclear Backscattering Spectrometry for the diagnostics and certification of such coatings.

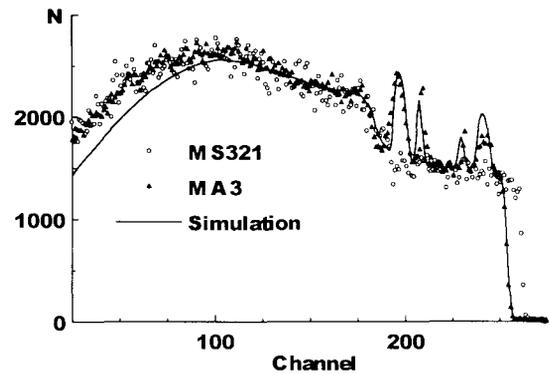


Fig. 5. 7.7 MeV H⁺ NBS spectrum for MA3, standard sample MS321 and the best-fit composition for MA3 ($500 \cdot 10^{16} \text{ cm}^{-2}$ Al(40 at.%) + O(60 at.%), $3800 \cdot 10^{16} \text{ cm}^{-2}$ Ti(65at.%) + C(15at.%) + N(20 at.%), WC + Co(17.5 at.%)

In conclusion, Nuclear Backscattering Spectrometry allows to diagnose and certify products made of hard alloys based on tungsten carbide with or without protective coatings. The oxygen admixtures which can affect on the properties of such tools become determinable. The thickness and stoichiometry of the coatings TiC_xN_y were measured by NBS.

References

- [1] L.E.Toth. Transition metal carbides and nitrides. (Academic Press, New York, London, 1971).
- [2] B.I.Kuznetsov, I.P.Chernov, G.Ya.Starodub, A.A.Yatis. Atomnaya energiya., 35, 439 (1973) (in Russian).
- [3] Treatise on materials science and technology, ed. J.K.Hirvonen (Academic Press.N-Y, London.V18. 1980).
- [4] E.Rauhala, Nucl.Instr.Meth. B40-41, 790 (1989).
- [5] A.M.Borisov, N.G.Goryaga, E.A.Romanovsky, et. al. Bulletin of the Russian Acad. of Sciences. Physics, 56, 964 (1992).
- [6] E.A.Romanovsky, A.M.Borisov, N.G.Goryaga et. al. Bulletin of the Russian Acad. of Sciences. Physics, 58, 666 (1994).
- [7] E.A.Romanovsky, Yu.K.Evseev, N.G.Goryaga et. al. Poverkhnost. Physics, Chemistry, Mechanics, 8-9, 123 (1994).
- [8] A.M.Borisov, S.Luntsov, V.G.Sukharev.Unpublished.
- [9] Salisbury S.R., Hardie G., Oppliger L., Dangle R. Phys. Rev. 126, 2143 (1962).
- [10] S.J.Moss, W.Heaberli, Nucl. Phys. 72, 417 (1965).
- [11] J.B.Swint, A.C.L.Barlard, T.B.Clegg, J.L.Weil, Nucl. Phys. 86, 2143 (1966).