XRF AND PIXE METHOD AS TOOLS FOR THE ELEMENT ANALYSIS OF METALLIC GLASSES[1])

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The radionuclide X-ray fluorescence (XRF) and particle induced X-ray emission (PIXE) methods have been used for a rapid and nondestructive analysis of metallic glasses. The methods have been compared in accuracy and precision with atomic absorption method. Some results of analyses of $Fe_xNi_{80-x}B_{20}$ materials are briefly reviewed. The distribution of elements along the width as well as length and a qualitative analysis of the composition of material surfaces are considered.

МЕТОДЫ РЕНТГЕНОВСКОГО ФЛУОРЕСЦЕНТНОГО АНАЛИЗА КАК СРЕДСТВО ДЛЯ ЭЛЕМЕНТНОГО АНАЛИЗА МЕТАЛЛИЧЕСКИХ СТЕКОЛ

Для быстрого и недеструктивного анализа состава металлических стекол разработаны методики рентгеновского флуоресцентного анализа (РФА) радиоизотопным возбуждением, как и характеристического рентгеновского излучения (ХРИ), возбуждаемого протомами. Правильность и точность созданных методов обсуждаются на основе результатов атомной абсорбции. В работе приведены некоторые результаты анализов материалов состава $Fe_xNi_{80-x}B_{20}$. Кроме того, обсуждается распределение состава элементов по длине и по ширине материалов, в также состав поверхностных слоев этих материалов.

I. INTRODUCTION

The present research into and development of solid state physics as a technology of thin film layers produce new materials, their investigation calling for new, progressive, analytical methods. In addition to bulk analysis, there is an even greater demand for a surface analysis of both the material and the depth distribution of the element concentration. The nuclear analytical methods based on charged-particle interactions with the material seem to be very suitable. There are three principal kinds of interactions: scattering, nuclear reaction and X-ray production, which form the basis of analytical methods like the Rutherford backscattering [1], prompt gamma emission and particle induced X-ray emission (PIXE) [2, 3], respectively. Protons, deuterons, alpha particles and nitrogen ions are usually used for excitation. In the past few years amorphous materials of metal composition have been developed. Bands of the composition $Fe_xNi_{80-x}B_{20}$, for x from 40 to 70, thickness of 25 μm, width of 6 to 22 mm and a length of several meters, have been analysed. Some technological standards have been solved in international cooperation. For this purpose radioanalytical methods such as the radionuclide excited X-ray fluorescence (XRF) and the PIXE analysis have been used.

In the paper of XRF method developed for the bulk analysis of the discussed materials is presented. The results of the investigation of the length- and width-concentration changes are discussed, and the results of the surface analysis of both sides differing from the point of technology are also presented. For the latter purpose the PIXE analysis has been used.

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II. EXPERIMENTAL ARRANGEMENT

The annular ^{109}Cd nuclide of activity 37×10^6 Bq was used as an excitation source for the X-ray production in the XRF method. The characteristic radiation of the elements was detected by the semiconductor Si(Li) detector with the resolution 180 eV on the line $K_\alpha Mn$. The electric signal operated in the spectrometric tract consisting of a preamplifier, an amplifier, a 100 MHz ADC and a 4096 multichannel analyser. Separation of the peak of interest from the experimental spectra was carried out by the deconvolution method, or the Cowell method in the case of simple spectra.

In the case of the PIXE analysis protons produced on the Van de Graaff electrostatic accelerator EG-5 of JINR were used. The equipment makes possible the production of particles with an energy from 1.0 to 4.0 MeV and a flux of several nA. The experimental set up is illustrated in Fig. 1. It is possible to change the diameter of the beam from 1 to 14 mm in the measurement chamber at a chosen system of collimators. The samples are analysed in the vacuum. The sample holder makes the analyses of 11 samples possible. The total number of particles which had interacted with the sample was measured by means of the flux integrator based on a total charge collection [4]. X-rays were detected by means of the Si(Li) semiconductor detector with the resolution of 180 eV on the line $K_\alpha Mn$ and a 25 μm thickness of the Be window. The detector was placed outside the chamber (Fig. 1). The spectrometric tract consisted of a preamplifier, an amplifier, a 100 MHz ADC and a 4096 multichannel analyser. The experiment was control-

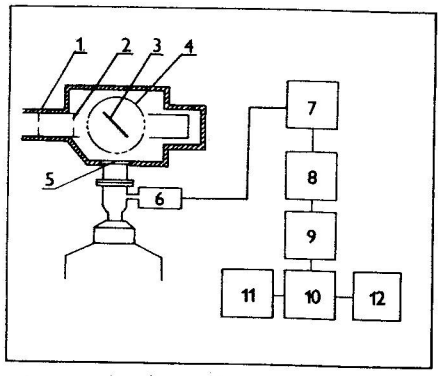

Fig. 1. Experimental set-up of the PIXE method. 1 — experimental chamber, 2 — collimator, 3 — sample, 4 — Faraday cup, 5 — Al-coated Mylar foil, 6 — preamplifier, 7 — amplifier, 8 — 100 MHz ADC, 9 — 4096 channel analyser, 10 — MERA-60 computer, 11 — screen, 12 — memory for saving spectra.

led in the CAMAC system by means of a small computer MERA-60. The program ACTIV on the PDP-11 computer was used for the deconvolution of experimental spectra.

III. RESULTS AND DISCUSSION

The development of the radionuclide XRF analysis method for a simultaneous analysis of metallic glasses of the composition $Fe_xNi_{80-x}B_{20}$ is based on the measurements of the $K_\alpha Fe$ ($E=6.4$ keV) as well as the $K_\alpha Ni$ ($E=7.4$ keV) line yields. The typical accumulated X-ray spectrum of the discussed samples is illustrated in Fig. 2. The concentrations of iron c_{Fe} and nickel c_{Ni} are proportional to

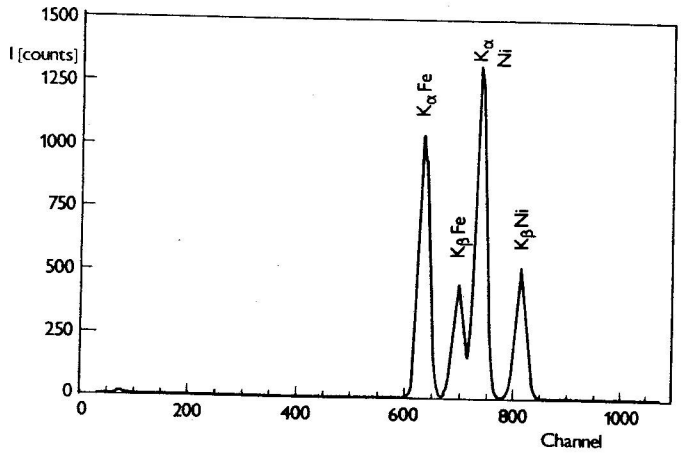

Fig. 2. Typical X-ray spectrum of metallic glasses of composition $Fe_xNi_{80-x}B_{20}$.

the measured signal Y_{Fe} and Y_{Ni}, respectively. Elimination of matrix effects in the sample has been considered to improve the results of the analysis. The Lachance-Trail equations [5] proved to be suitable for solving this problem [6]:

$$c_{Fe}=\frac{Y_{Fe}}{\alpha_{11}}(1+\alpha_{12}c_{Ni}) \tag{1}$$

$$c_{Ni}=\frac{Y_{Ni}}{\alpha_{21}}(1+\alpha_{22}c_{Fe}). \tag{2}$$

The coefficients $\alpha_{11}, \ldots, \alpha_{22}$ have been calculated from experimental data measured on the standard samples. Precision and accuracy of the Fe and the Ni analysis were tested and compared with results of the atomic absorption AA method, and the boron content was analysed by the acidometric titration method. The results are given in Table 1 where c_{XRF} and c_{AA} are concentrations obtained by the XRF method and atomic absorption, respectively. In the ideal case $c_{XRF}=c_{AA}$, but according to the obtained results we have considered the relation:

Table 1

Results of XRF analysis, c_{teor} — calculated concentration from chemical formula, c_{AA} — concentration determined by atomic absorption for iron and nickel and acidometric titration method for boron, respectively, c_{XRF} — concentration determined by means of the XRF method

sample	element	concentration weight %		
		c_{teor}	c_{AA}	c_{XRF}
$Fe_{40}Ni_{40}B_{20}$	Fe	46.53	46.9 ± 0.4	46.2 ± 0.9
	Ni	48.95	48.7 ± 0.2	49.7 ± 0.9
	B	4.52	4.7 ± 0.1	—
$Fe_{50}Ni_{30}B_{20}$	Fe	58.53	58.8 ± 0.2	58.1 ± 1.1
	Ni	36.94	36.5 ± 0.2	35.8 ± 0.7
	B	4.53	4.8 ± 0.1	—
$Fe_{60}Ni_{20}B_{20}$	Fe	70.66	69.6 ± 0.3	68.8 ± 1.3
	Ni	24.78	25.8 ± 0.3	25.7 ± 0.6
	B	4.56	4.6 ± 0.1	—
$Fe_{70}Ni_{10}B_{20}$	Fe	82.95	83.1 ± 0.4	82.7 ± 1.6
	Ni	12.46	12.4 ± 0.1	13.1 ± 0.4
	B	4.59	4.4 ± 0.1	—

$$c_{XRF}=a_0+a_1c_{AA} \tag{3}$$

with the following statistical tests of the hypotheses $H_0: a_0=0$ and $H_0: a_1=1$, respectively. After the evaluation of the t- and the F-statistics both hypotheses

have been accepted at the 95 % confidence level both for iron and nickel. They yield a suitable accuracy and precision of the XRF method for the Fe and the Ni determination in metallic glasses.

The concentration variations along the length and the width of the band sample $Fe_{40}NiB_{20}$ have been studied. As no significant differences of the boron concentration along the length have been observed, the ratio of the K_α yields of iron and nickel Y_{Fe}/Y_{Ni} has been chosen as the criterium of homogneity. Y_{Fe} and Y_{Ni} have been measured with a relative error less than 3 %. The ratio Y_{Fe}/Y_{Ni} has been checked by testing a_1 parameter in a linear dependence of Y_{Fe}/Y_{Ni} on the length coordinate x by means of the following equation:

$$Y_{Fe}/Y_{Ni} = a_0 + a_1 x \tag{4}$$

$H_0: a_1 = 0$ against $H_1: a_1 \neq 0$ has been tested by the evaluation of F-statistics and the analysis of the variance method. H_0 was accepted at the confidence level 95 %, which is not a significantly increasing trend of the Y_{Fe}/Y_{Ni} ratio along the longth of the material. No significant variations or trends were also observed in the case the width distribution of elements.

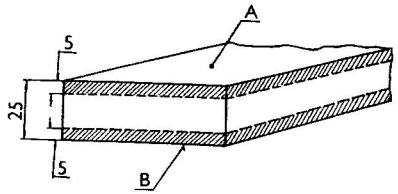

Fig. 3. The metallic glass progile — 25 μm thick. A — cooled side, B — opposite side. Dashed mark the 5 μm depth of the PIXE analysis.

The question whether there is any concentration difference of iron or nickel between the two surfaces of a metallic band (Fig. 3) has been a matter of subsequent experiments. The PIXE analysis as a nondestructive method has been chosen for this purpose. Samples of the composition $Fe_xNi_{80-x}B_{20}$ have been analysed with protons of an energy 1.4 MeV in the geometry 45°. These conditions made the analysis from a depth of only about 5 μm possible. It follows from the fact that the range R of protons ($E = 1.4$ MeV) is about 12 μm and practically equal for all examined samples due to very close values of dE/dx of iron and nickel in the used energy interval (see Table 2). Values in Table 2 have been calculated according to the following equation [7]:

$$R(E) = R(0.1) + \int_{0.1}^{E} \frac{dE}{\sum_i c_i \left(\frac{dE}{dx}\right)_i} \tag{5}$$

R (0.1) is the range for the energy $E = 0.1$ MeV, $(dE/dx)_i$ is a stopping power of the ith element and c_i its concentration. The values of dE/dx have been taken from the tables of Janni [8].

Table 2
Range of 1.4 MeV protons in metallic glasses

sample	R [μm]
$Fe_{40}Ni_{40}B_{20}$	11.68
$Fe_{50}Ni_{30}B_{20}$	11.75
$Fe_{60}Ni_{20}B_{20}$	11.83
$Fe_{60}Ni_{20}B_{20}$	11.93

About 95 % of information in the PIXE analysis come from the depth of 0.6 R, which follows from the analysis of an integral in the following equation describing the dependence of the X-ray yield on the depth l:

$$Y(l) = c\, k \int_0^l \sigma(E(x)) e^{-\mu x}\, dx \tag{6}$$

c is the concentration of the element, k is a geometrical factor, l — the depth, σ — the ionization cross section of the K-shell, μ — a linear absorption coef. for X-ray. Values of $\sigma(E)$ for equation (6) have been obtained by fitting the experimental data for Fe and Ni published during the past 15 years. The linear abs. coef. has been taken from the Montenegro tables [9].

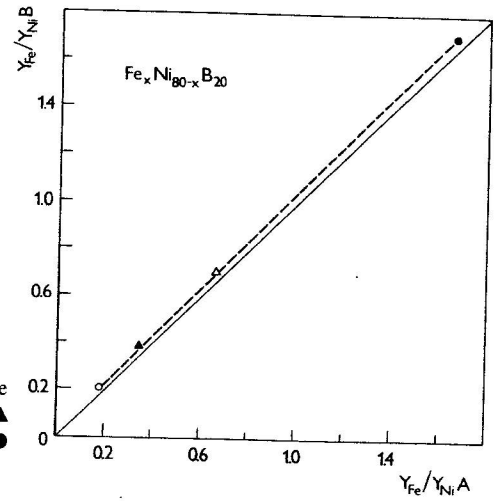

Fig. 4. Dependence of the Y_{Fe}/Y_{Ni} ratio of side B versus side A. ○ — $Fe_{40}Ni_{40}B_{20}$, ▲ — $Fe_{50}Ni_{30}B_{20}$, △ — $Fe_{60}Ni_{20}B_{20}$, ● — $Fe_{70}Ni_{10}B_{20}$.

Experimental data of Y_{Fe} and Y_{Ni} of the K_α lines for samples $Fe_xNi_{80-x}B_{20}$ are illustrated in Fig. 4, where the ratio Y_{Fe}/Y_{Ni} for side B versus side A are plotted. In the case of equivalence all data could be placed on the diagrams diagonal. Statistical tests for coefficients of the linear equations $Y_B^{Fe/Ni} = f(Y_A^{Fe/Ni})$ have shown

a significant difference between sides A and B for the iron and nickel composition. These conclusions are in correlation with the results of the boron surface analysis [10]. All the conclusions profide a possibility to improve the technology of preparation of metallic glasses.

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