Materials Physics and Mechanics 36 (2018) 92-99 Received: September 27, 2017

INVESTIGATION OF THE POSSIBILITY OF IMPROVING THE X-RAY FLUORESCENCE SPECTROMETER ANALYTICAL CHARACTERISTICS DUE TO USING THE SUPERFINE BERYLLIUM FOILS

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Abstract. Studies were made the possibilities of increasing the wave-dispersive X-ray fluorescence spectrometer analytical characteristics due to using the superfine beryllium foils 5-8 μm thick in the X-ray detector. Investigations by the example of spectrometer SPECTROSCAN MAX-GVM showed that the decrease of foil thickness can significantly increase the spectrometer analytical characteristics in the determination of light elements (sodium and magnesium). It has been established what count rate increases 8.5 times for sodium and 4.6 times for magnesium due to using the X-ray windows with thickness of 5 and 8 μm. Reducing of X-ray window thickness can be achieved by using beryllium foils obtained by severe cold plastic deformation. Such foils have increased plasticity, which allows reducing the X-ray window thickness without spectrometer reliability decreasing.

Keywords: x-ray spectroscopy analysis; spectrometer; x-ray detector; thin beryllium foils; x-rays transmission.

1. Introduction

X-ray fluorescence spectral analysis (X-ray fluorescence, XRF) is widely used to determine the chemical composition of liquids, metals, minerals, rocks, organic substances [1-5]. Its essential advantages are the simplicity and low cost of sample preparation, as well as the high accuracy and stability of chemical elements concentrations measurements in the substance [6].

The principle of the X-ray fluorescence spectrometer is based on the sample irradiation by X-ray, measuring the intensities of the secondary fluorescence radiation from the sample, and calculating on their basis the mass fractions of the chemical elements contained in the sample. Modern X-ray fluorescence spectrometers (Fig. 1) are automated universal X-ray devices that allow determining the content of chemical elements in range from sodium to uranium.

One of the spectrometer most important part is the X-ray detector (Fig. 2), which converts X-ray quanta into voltage pulses. As a rule, proportional detectors are used in X-ray fluorescence spectrometers. For example, the spectrometer SPEKTROSKAN MAX-GVM uses a two-chamber proportional detector.

http://dx.doi.org/10.18720/MPM.3612018_10

Fig. 1. Appearance of the wave dispersive X-ray fluorescence spectrometer SPEKTROSKAN MAX-GVM manufactured by Spectron.

An integral part of the detector is an X-ray window, which must pass X-rays into the detector, while performing the functions of a gas-tight barrier between the vacuum of the measuring chamber and the working gas mixture of the detector.

In the SPECTROSCAN MAX-GVM device, as standard, beryllium foil with a thickness of 15 μm is installed at X-ray detector. The entrance window of the measuring vacuum chamber is made from beryllium foil with a thickness of 12 μm.

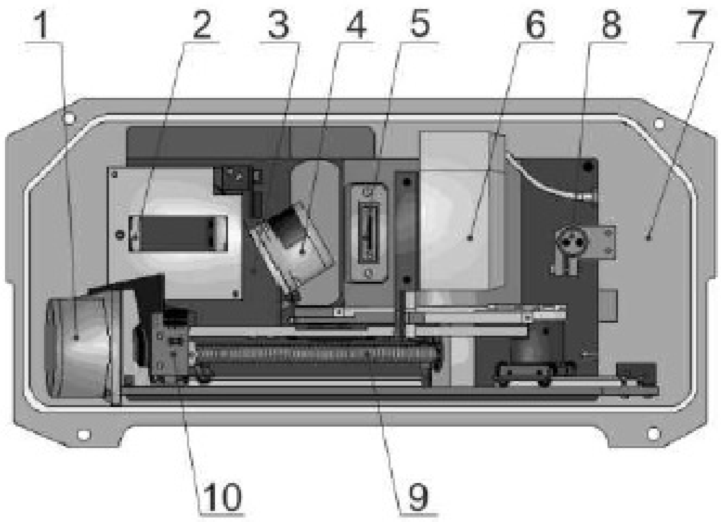

Fig. 2. Construction of the spectrometer SPECTROSCAN MAX-GV: 1 – drive of scanning mechanism; 2 – crystal-analyzer; 3 – crystals replacement mechanism; 4 – drive of crystals replacement mechanism; 5 – entrance window of beryllium; 6 – detection unit; 7 – vacuum casing; 8 – vacuum gauge; 9 – lead screw goniometer; 10 – sensor of the scanning mechanism initial position.

The choice of beryllium as a material for X-ray windows is due to its unique transmission capacity for both hard (with a short wavelength) and for a soft (with a longer wavelength) X-ray radiation, which is significantly higher than that of all other metals [7-10]. The transmission of beryllium foil strongly depends on its thickness [11-12], especially for soft X-ray radiation (Fig. 3). Transmission of soft X-ray radiation is significantly improved as the thickness of the beryllium window decreases. Ultrathin beryllium foils well transmit soft X-ray radiation in a wide spectrum [12].

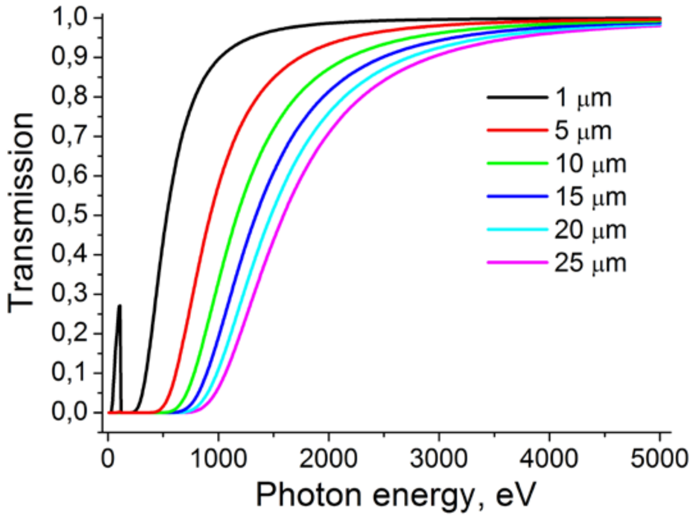

Fig. 3. Calculated X-ray transmission curves for beryllium foils with different thickness. Calculations were performed by data [11].

The main problem of using beryllium as a material for X-ray windows is its fragility [13-14]. The fragility of beryllium greatly complicates processes of both thin beryllium foils obtaining and their subsequent operation in detectors.

During operation in detector X-ray window is exposed to the load by external pressure, which creates mechanical stresses in him. The smaller the thickness of the window, the higher the stresses arise in it other things being equal, and the higher the probability of its fracture. The brittleness of beryllium forces to use relatively thick foils in the detectors, which worsens the analytical characteristics of the spectrometers.

A promising way to produce very thin beryllium foils (up to 5 μm) with high plasticity is cold rolling combined with thermal treatments in vacuum [15]. The high mechanical characteristics of the foils obtained in this way make it possible to reduce the thickness of the beryllium window, which should allow increasing the sensitivity of the detector by improving the transmission.

The goal of this paper is numerical and experimental study of the possibilities of increasing the analytical characteristics of a wave-dispersive X-ray fluorescence spectrometer due to using the superfine beryllium foils with a thickness of 5-8 μm instead of the conventionally used foils with a thickness of 12 μm. Study was performed by example of SPECTROSCAN MAX-GVM manufactured by Spectron.

2. Estimating the possibility of improving the analytical characteristics of the spectrometer

The intensity of X-ray radiation passing through a thin film of matter obeys an exponential law of decrease from the initial value due to the photoelectric effect and scattering [16]. The transmission of X-rays through an X-ray window can be described by the dependence [11]:

$$T = I/I_0 = e^{-\mu\rho t} , \quad (1)$$

where I_0 – intensity of incoming (primary) radiation;
I – intensity of radiation transmitted through the x-ray window;
μ – mass absorption coefficient (mass attenuation coefficient of radiation), characterizing the material of the window, m^2 / kg;
ρ – density of the window material, kg / m^3;
t – thickness of the window (absorption distance), m.

It follows from equation (1) that, for maximum transmission of rays, the X-ray window should be as thin as possible. Equation (1) also makes it possible to perform calculation of the possible increase in the characteristics of a wave-dispersive X-ray fluorescence spectrometer by reducing the thickness of the beryllium windows used.

The standard X-ray scheme of the device (Fig. 2) includes the entrance window of a vacuum chamber with a thickness of 12 μm and the window of an X-ray detector with a thickness of 15 μm. The radiation in the device passes through the entrance window at an angle of 67 ° to the surface, through the detector window – along the normal. It should also take into account the attenuation of radiation when passing through a layer of air 3 mm thick.

Table 1 presents the calculated transmission values of beryllium foils of different thickness and air layer, calculated from the dependence (1) and the data of [11]:

Table 1. Calculated transmission values of X-ray radiation for beryllium windows of different thickness and air layer.

	The layer thickness and the angle of radiation incidence						
	Beryllium						Air
Radiant	15 μm, by normal	12 μm, 67^0	8 μm, by normal	8 μm, 67^0	5 μm, by normal	5 μm, 67^0	3 mm
Al	0,60	0,63	0,76	0,74	0,85	0,83	0,62
Mg	0,43	0,47	0,64	0,50	0,75	0,73	0,47
Na	0,23	0,27	0,45	0,42	0,61	0,58	0,28

Thus, the transmission through the "entrance window – air – detector window" system for the standard arrangement is:
For Al:
$T = 0.63 \cdot 0.6 \cdot 0.62 \approx 0.23$;
For Mg:
$T = 0.47 \cdot 0.43 \cdot 0.47 \approx 0.095$;
For Na:
$T = 0.27 \cdot 0.23 \cdot 0.28 \approx 0.017$.

Calculations show, that in the standard arrangement spectrometer has a low sensitivity to soft secondary radiation emitted by magnesium and sodium, since no more than 9.5% of the secondary radiation penetrates the detector from magnesium and 1.7% of sodium.

When the entrance window and the detector window are replaced by 8 μm thick beryllium foil, the transmission through the "entrance window – air – detector window" system will be:
For Al:
$T = 0.74 \cdot 0.76 \cdot 0.62 \approx 0.35$;
For Mg:
$T = 0.5 \cdot 0.64 \cdot 0.47 \approx 0.15$;

For Na:

$T = 0.42 \cdot 0.45 \cdot 0.28 \approx 0.053$.

It can be seen that due to use of beryllium foil 8 μm thick as the entrance window and the detector window, the recorded secondary radiation intensity should increase by 3 times for sodium, 1.7 times for magnesium, 1.5 times for aluminum in comparison with standard arrangement.

If 5 μm thick beryllium foil is used as the entrance window and 8 μm thick beryllium foil is used as the detector window, the transmission through the "entrance window – air – detector window" system will be:

For Al:

$T = 0.83 \cdot 0.76 \cdot 0.62 \approx 0.39$;

For Mg:

$T = 0.73 \cdot 0.64 \cdot 0.47 \approx 0.22$;

For Na:

$T = 0.58 \cdot 0.45 \cdot 0.28 \approx 0.073$.

Thus, when beryllium foil 5 μm thick is used as an entrance window and 8 μm thick beryllium foil is used as a detector window, the recorded intensity of secondary radiation should increase by 4.2 times for sodium, 2.3 times for magnesium, 1.7 times for aluminum in comparison with standard arrangement.

Calculations show that the foil thickness reducing can significantly increase the analytic characteristics of the device when determining light elements (sodium and magnesium).

3. Experimental evaluation of improving the analytical characteristics of the spectrometer using the superfine beryllium foils

To carry out experimental studies, thin beryllium foils with 5 and 8 μm thickness were produced by the method of severe cold plastic deformation [17, 18] in combination with heat treatment in high vacuum [15,19]. The chemical composition of obtained thin beryllium foils is presented in Table 2. Composition was determined by scanning electron microscope (SEM) SUPRA55VP WDS / WDX with the microanalysis systems INCAWAVE, AZTECENERGY.

Table 2. The chemical composition of beryllium foils used in the study.

Element	Be	Al	P	S	Cl	Ca	Cr	Mn	Fe	Ni	Cu	W
Weight %	99.82	0.02	0.02	0.01	0.02	0.03	0.01	0.01	0.02	0.02	0.01	0.01

The complex of mechanical tests performed in [15, 19] showed that foils samples obtained by the method of severe cold plastic deformation in combination with heat treatment in high vacuum have a higher level of strength and plastic characteristics compared to samples after hot and warm rolling. Fig. 4 compares the tensile test results for cold-rolled foil samples and foils samples obtained by hot rolling.

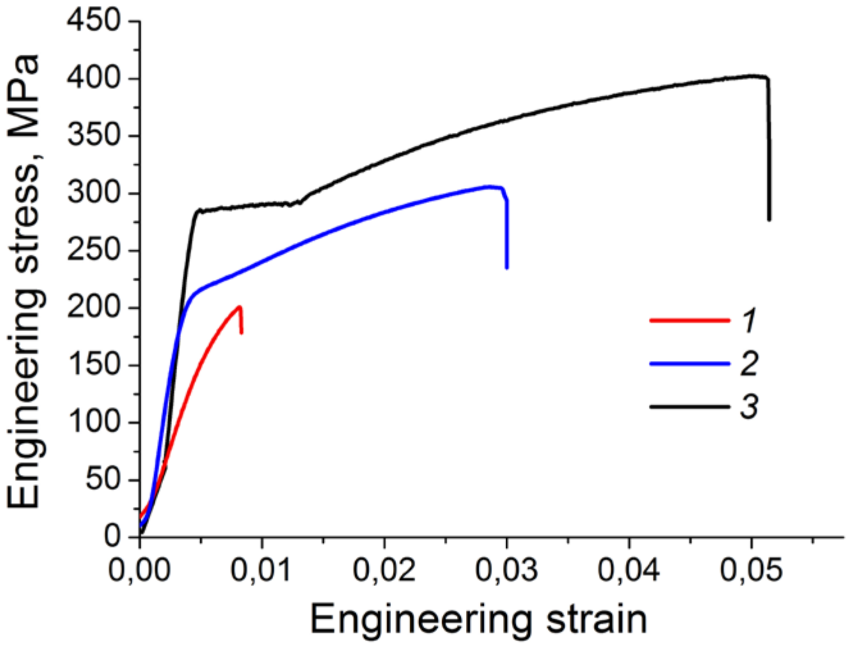

Fig. 4. Stress - strain curves, obtained by tensile tests of beryllium foil samples according to the data of [19]: 1 – foil thickness of 250 μm, after hot rolling; 2 – foil thickness of 200 μm, after cold rolling (logarithmic strain is 0.61) and annealing; 3 – foil thickness of 45 μm, after cold rolling (logarithmic strain is 2.10) and annealing.

The mechanical properties of thin foils (the thickness of which is 100 or more times smaller than the width of the sample) during tensile tests can significantly differ from the mechanical properties obtained when testing full-size samples from the same material (the so-called "scale factor") [20-23]. Tests for loading by external pressure for thin beryllium foils 5-10 μm thick, obtained by several cold deformation, were performed in [19]. The tests showed (Table 3) that the ultimate plastic strain at the time of fracture under external loading is significantly higher than the ultimate stain established in the tensile tests (Fig. 4).

Foils with thicknesses of 5-10 μm, obtained by method of several cold deformation, withstand pressure up to 6 atmospheres without fracture signs [19]. Thus, the use of cold-rolled beryllium foils having enhanced plastic properties makes it possible to reduce the thickness of the X-ray windows without increasing the probability of premature fracture.

Table 3. Parameters and results of bulge tests for thin beryllium foils [19].

Foil thickness, μm	Foil area, mm^2	Pressure at fracture, atm	Ultimate strain
9	80	5.1	0.18
8.5	20	5.9	0.2
5	38	4.1	0.154

To assess the change in the analytical characteristics of the spectrometer, changes were made to its construction – the thickness of the entrance window was reduced from 12 μm to 8 and 5 μm and in the detector from 15 to 8 μm (Table 4).

Measurements have shown that when using beryllium foil 8 μm thick as an entrance window and as a detector window, the count rate for sodium increases 4 times, for magnesium – 3 times (Fig. 5). When beryllium foil 5 μm thick is used as the entrance window and 8 μm thick beryllium foil as the detector window, the count rate for sodium increases 8.5 times, for magnesium 4.6 times (Fig. 5). The increased count rate allows to collect more reliable statistic and to increase the accuracy of determination of the concentration of light elements in the substances.

Table 4. Parameters (width, height and thickness) of beryllium windows used to estimate the change in the analytical characteristics of the spectrometer SPECTROSCAN MAX-GVM.

Device scheme	Entrance window parameters	Detector window parameters
Standard	5.5x15 mm –12 μm	10x33 mm – 15 μm
Changed №1	5.5x15 mm – 8 μm	10x33 mm – 8 μm
Changed №2	5.5x15 mm – 5 μm	10x33 mm – 8 μm

a) *b)*

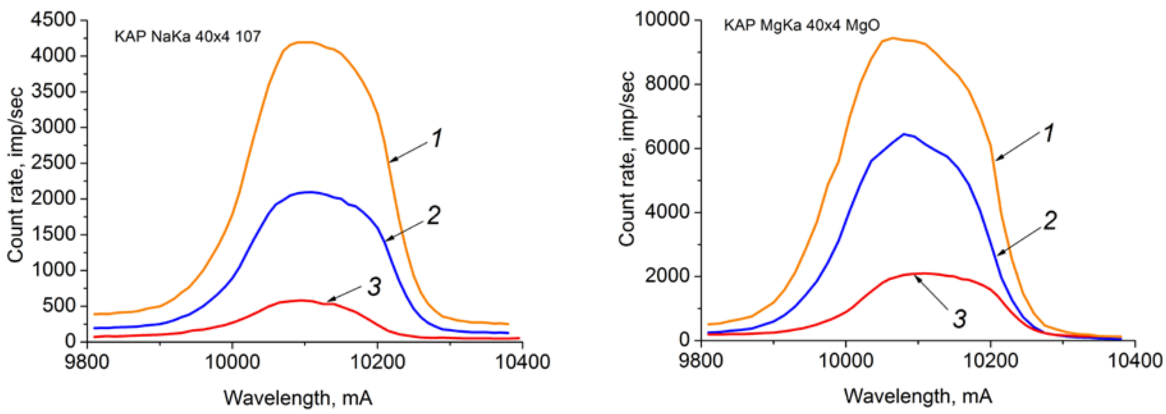

Fig. 5. Dependence of the count rate on the wavelength of radiation when determining sodium (*a*) and magnesium (*b*): 1 – foil thickness of 5 μm in the entrance window and 8 μm in the detector; 2 – foil thickness of 8 μm in the entrance window and 8 μm in the detector; 3 – foil thickness of 12 μm in the entrance window and 15 μm in the detector.

4. Conclusions

1. The analytical characteristics of the X-ray fluorescence spectrometer in determining the concentration of light elements in the substances can be significantly increased by using ultrafine beryllium foils as X-ray windows. With reduction of entrance window thickness from 12 μm to 5 μm and the detector window thickness from 15 μm to 8 μm, count rate for sodium increases 8.5 times, for magnesium 4.6 times.

2. A promising method for obtaining the beryllium foils is several cold deformation in combination with heat treatments in high-vacuum. The foils obtained in this way have an increased plasticity, which makes it possible to reduce the thickness of the X-ray window without reducing device reliability.

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