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## AN ATTEMPT TO DEVELOP THE METHODOLOGY OF EXAMINING THE BORON CONTENT IN CONSTRUCTION MATERIALS WITH THE USE OF EDS METHOD

### PRÓBA OPRACOWANIA METODYKI BADAŃ ZAWARTOŚCI BORU W MATERIAŁACH KONSTRUKCYJNYCH METODĄ EDS

Borided layers are mainly produced during the process of heat-chemical treatment as a result of reactive diffusion of boron inside the material. The borided layers are particularly useful in difficult exploitation conditions. Generally, the borided layers are characterized by the increased hardness, heat resistance and good corrosion resistance. It is commonly known that the major disadvantage of X-ray microanalysis with EDS method is the difficulty in light elements analysis such as boron.

However, due to the appropriate formation of source region and taking measurements during a definite period of time, the microanalysis of boron is possible. The obtained results are characterized by relative accuracy and precision.

SEM Vega 5135 Tescan, detector of Si(Li) in Prism 2000 PGT spectrometer and the PGT software Spirit 1.06 were used. The model specimen was made from cubic boron nitride (c-BN). The estimated parameters of the analysis were verified on 42CrMo4 steel and borided Armco Iron, with satisfactory results having been obtained.

*Keywords:* borided layer, EDS method

Warstwy borowane wytwarza się głównie w procesie obróbki cieplno-chemicznej, w wyniku dyfuzji reaktywnej boru w głąb materiału. Warstwy borowane znalazły zastosowanie szczególnie w trudnych warunkach eksploatacyjnych. Ogólnie warstwy borowane charakteryzują się: zwiększoną twardością, żaroodpornością, dobrą odpornością korozyjną w wielu roztworach kwaśnych i alkaicznych. Jak wiadomo istotną wadą mikroanalizy rentgenowskiej metodą EDS jest trudność analizy pierwiastków lekkich, takich jak bor.

Jednakże w wyniku odpowiedniego ukształtowania strefy wzbudzenia i wykonania pomiaru w ciągu określonego czasu mikroanaliza boru jest możliwa. Wyniki przy tym uzyskane cechuje względna precyzja i dokładność.

Zastosowano SEM Vega 5135 firmy Tescan, detektor Si(Li) w spektrometrze Prism 2000 firmy PGT, oprogramowanie Spirit 1.06 firmy PGT. Preparat wzorcowy wykonany był z regularnego azotku boru c-BN. Ustalone parametry analizy zweryfikowano na warstwie borków utworzonych na stali 42CrMo4 i żelazie ARMCO uzyskując zadowalające rezultaty.

### 1. Introduction

X-ray microanalysis in electron microscope is a process which applies characteristic X-ray radiation generated in the micro region of a specimen by electron beam in order to define its chemical composition. It makes use of two types of spectrometers: WDS, wavelength dispersive spectrometry, namely a spectrometer which measures the wavelength of X-ray radiation, while EDS, energy dispersive spectrometry, measures the energy of X-ray radiation. A significant disadvantage of the EDS method is the difficulty in examination of light elements such as boron, carbon, nitrogen, however having selected appropriate parameters of the process the analysis of boron content is possible. SEM analysis consists in scanning of the specimen surface with electron beam, which has been previously formed by electron lenses. The electron beam, when focused on the specimen, interacts with electrons of atoms of the examined material, which, among others, provokes the

emission of secondary electrons, backscattered electrons, and X-ray radiation [1].

The result of the microanalysis is spectrum, i.e. a collection of radiation lines against the background of continuous radiation. Spectral lines, which exceed the background are called peaks [2]. Registerable signals are produced only on the surface of the specimen. Electrons of the beam penetrate the specimen to some depth and on its way may interact with the atoms of the specimen many times. Accelerating voltage defines the amount of energy transmitted by electrons of the electron beam which directly influences the size and shape, i.e. the width and height of the X-ray source region [3]. Width is an effective resolving capability of microanalysis. There are many different dependables that enable estimating the width, e.g. Anderson and Hasler equation on the basis of: value of accelerating voltage, excitation energy and average specimen density. The height of the source region according to Casting is the function of relative atomic mass and number, average

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sample density, accelerating voltage and critical excitation energy [2].

A considerable advantage of EDS technique is a relatively short time of obtaining data, due to the fact that a wide range of X-ray radiation energy is detected and analysed simultaneously. In contrast, during the WDS analysis the system analyses only one wave length and the analysis can take longer time before the required range of wavelength is analysed. Moreover, the EDS detector can be situated in a relatively close distance to the preparation (even a few millimeters), which allows to examine approximately 1% of the emitted X-ray radiation, while the crystal analyzing WDS needs large space to move around, due to which less than 1% of photons is collected. Another significant advantage of EDS is its lower price in comparison with WDS system.

The advantage of WDS when compared with EDS is the measurement range. WDS allows the analysis of elements within the range of atomic numbers from 4 to 92. In EDS technique the analysis of light elements is more difficult due to the very low energies of their radiation [1].

Light elements are the ones whose atomic number is less than 10. Among this group hydrogen and helium do not produce the characteristic X-ray radiation. The difficulty with their analysis consists in their low excitation energy values, presence of other, better detectable elements in the preparation [1]. The elements that are significant for X-ray microanalysis of light elements: coincidence with spectral lines L and M series of heavier elements, high background, method of background measurement, carbon contamination of the surface, types of the applied standards [4].

## 2. Experimental procedure

The specimen subjected to analysis was made of regular boron nitride in four variations: c-BN included in conductive adhesive bond on the basis of silver, c-BN included in the solution of water glass, c-BN galvanically included in zinc, c-BN placed directly on conductive carbon tape. From the above preparations, on the basis of preliminary research, the last variation – boron nitride on conductive carbon tape has been chosen. Boron nitride in order to identify its variation (its type) in the form of powder was subjected to X-ray analysis on PANalytical EMPYREAN diffractometer with the use of copper lamp. The X-ray microanalysis was conducted with the use of scanning microscope SEM Vega 5135 by Tescan with the Prism 2000 PGT spectrometer comprising Si (Li) detector and Spirit 1.06 PGT software. In order to work out the analysis conditions ensuring the minimum measurement error (the difference between the measured value and the real value) of boron content in construction materials with the EDS technique numerous analyses were made with the application of different measurement parameters. Firstly, the influence of accelerating voltage value in the time function on the microanalysis result was defined, the following values of accelerating voltage were assumed: 10,12,15,20 kV. Secondly, for the chosen measurement duration time amounting to 6 minutes, a number of measurements were made in the range of accelerating voltage from 5kV to 20kV with 2,5kV step. For all the measurements the dead time parameter was

established at approximately 20%. As regards the value of accelerating voltage amounting to 5 kV, the obtained dead time was as low as approximately 14%, because the low value of the voltage does not allow to obtain large electron beam. The verifying measurements offering the conditions of the analyses of borides content in constructional steels were conducted on the specimen with the borided layers produced on 42CrMo4 steel and ARMCO iron.

## 3. Results

Boron nitride powder, from which the specimens for the analysis were made, was examined by X-ray diffractometer in order to define the type of boron nitride. It was proved that the analysed material is boron nitride of regular crystallographic lattice. The influence of accelerating voltage in the function of time was defined on the basis of EDS microanalysis on the surface of one c-BN crystal in the exemplary regions shown in Fig. 1.

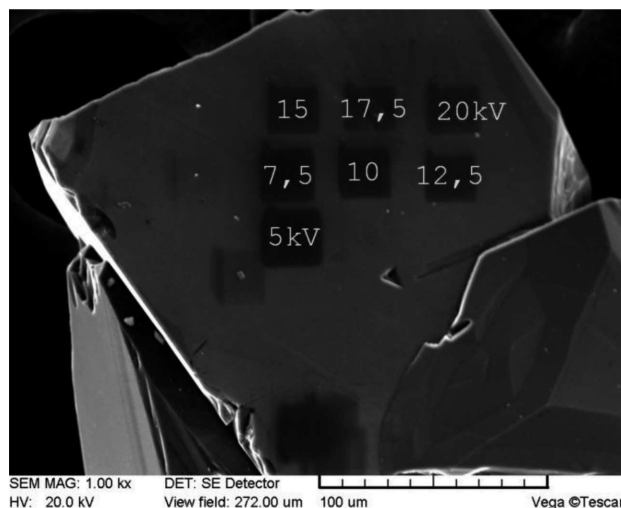


Fig. 1. Exemplary regions of EDS microanalysis on an c-BN crystal

The result of the above analyses is presented in Fig. 2 and 3. Separate analyses of the influence of accelerating voltage in time function were made for boron (Fig. 2) and nitrogen (Fig. 3) because of the difficulties connected with the deconvolution of peaks originating from boron and carbon.

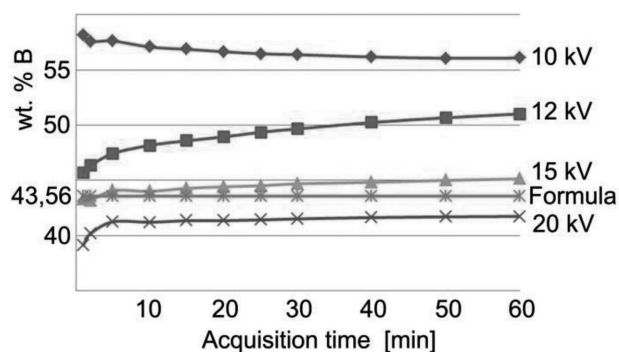


Fig. 2. Analysis of the boron content in a material for different accelerating voltages and times

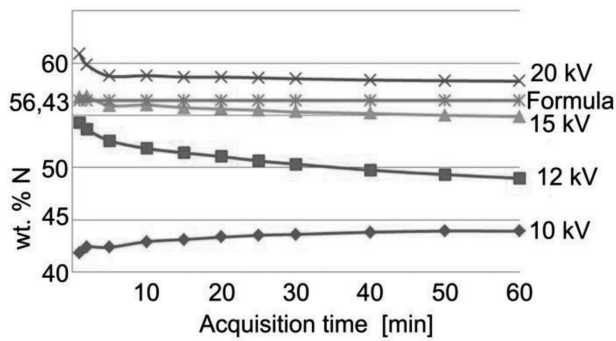


Fig. 3. Analysis of nitrogen content in a material for different accelerating voltages and times

Estimated on the basis of atomic masses weight content of boron and nitrogen in c-BN amounts to accordingly : 43,56% for B and 56,44% for N (on the charts these values were marked as “formula”)

The results of the smallest compliance with the model content of boron and nitrogen were obtained for the voltage of 10kV. It results from the fact of appearance after 10 minutes of the proceeding analysis (Fig. 4) a peak originating from carbon, which grew higher as the analysis continued. After 45 min, the peak of carbon was higher than the boron one, subsequently after 48 min, it was higher than the nitrogen peak (Fig. 5). The appearance of such a conspicuous and ever growing carbon peak is connected with the phenomenon of carbon contamination from the atmosphere of the specimen chamber.

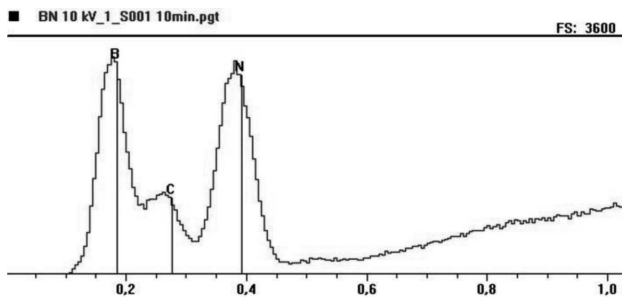


Fig. 4. EDS analysis of boron nitride on carbon tape; accelerating voltage 10kV; measurement duration time 10 min. The appearance of carbon peak

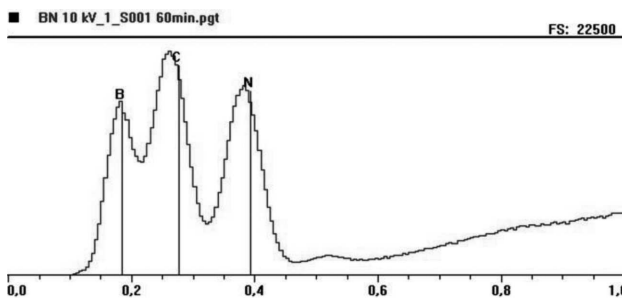


Fig. 5. EDS analysis of boron nitride on carbon tape.; accelerating voltage 10kV; measurement duration time 60 min. Carbon peak exceeds nitrogen and boron

For the voltage of 12kV the initial results seemed promising, however with the passing time they began to differ considerably from the model ones. The boron content was increasing

with the measurement duration time, it resulted from the fact that after 16 min, there appeared a carbon peak, which was included by the Spirit 1.06 software into the boron peak analysis. After 45 min, carbon peak equaled the boron one, however until the end of the analysis it did not exceed nitrogen peak, which occurred at the voltage of 10kV. For the voltage of 20kV it was observed that parallel to the lengthening of the measurement duration time the nitrogen content decreased, while the boron content was increasing. After 30 min the obtained results started to change once again approaching the model results. After the 60 min measurement duration time 41,73%B and 58,27% of N was obtained, which falls within the measurement error of 1,83%. At the voltage of 20kV an evident carbon peak appeared only after 25 min of EDS analysis, however it did not increase rapidly, as in the case of voltages of 10kV and 12kV. After 60 minutes analysis and accomplishment of this series of the analysis, carbon peak did not exceed boron peak, nor the nitrogen one. For the accelerating voltage of 15kV and duration time range from 1 min to 25 min the measurement error was less than 1%. For the duration time of 1 min: 43,27% B and 56,73% N ( Fig. 6); the difference from the model content amounted to 0,29%. After 2 minutes of analysis the values changed, while for 5 and 10 minutes they remained at the same level and with the lengthening of measurement duration time the content of nitrogen began to decrease linearly and the boron content increased. After the accomplishment of the analysis the obtained values amounted to 45,12% B and 54,88% N (Fig. 7).

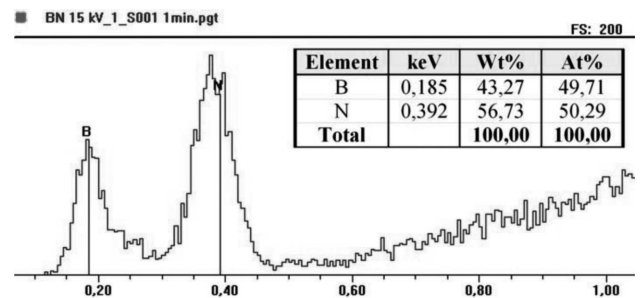


Fig. 6. EDS analysis of boron nitrogen on carbon band, accelerating voltage 15kV, measurement duration time 1 minutes

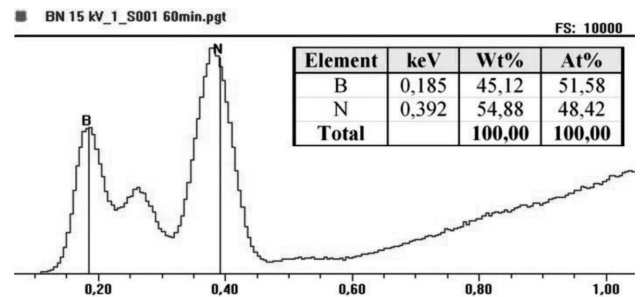


Fig. 7. EDS analysis of boron nitrogen on carbon band, accelerating voltage 15kV, measurement duration time 60 minutes

Carbon, originating from the contamination phenomenon, in this case did not considerably influence the results. Carbon peak was not evidently clear enough and did not increase rapidly. Its intensity after 60 min analysis was comparable with the height of carbon peak obtained for beam energy of 20kV within 30 min.

On the basis of the above results it was assumed that the characteristic measurement duration time is 6 minutes and for that value a subsequent series of analyses was conducted, with the accelerating voltage from 5kV to 20kV. In Fig. 8 the dependence between the number of counts within 6 minute signal processing from Si(Li) counts detector for nitrogen, boron and carbon and the applied accelerating voltage.

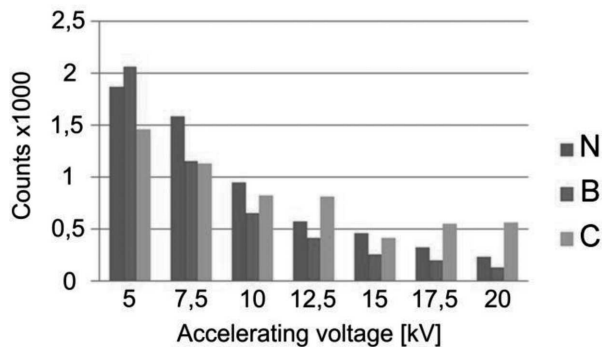


Fig. 8. Influence of beam energy on the number of counts within 6 minutes

On the basis of Fig. 8 it was observed that the number of registered counts decreases with the increase of accelerating voltage. It results from the diminished counting capacity of the equipment as the number of channels into which a spectrum will be digitized increases. For 17,5kV and 20kV the number of counts for carbon is considerably higher than for boron and nitrogen, while for the voltage 5 and 7,5kV relatively smaller number of counts for carbon in comparison with boron and nitrogen was obtained. After calculating by the analyzing software the number of counts for the content of a particular element in a given specimen the chart presented in Fig. 9 was produced.

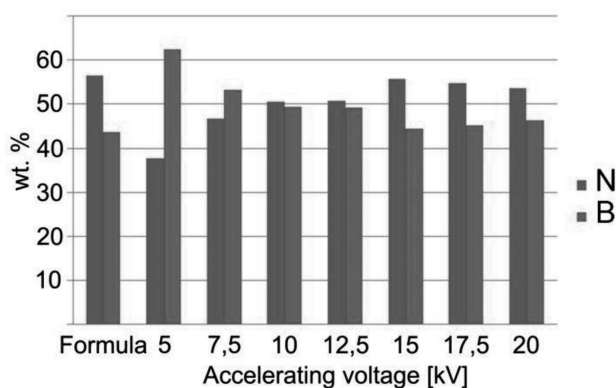


Fig. 9. The influence of accelerating voltage on the results of BN crystal analysis

On the basis of Fig. 9 it was observed that despite a smaller number of counts, prevalence of impulses originating from carbon contamination, as well as the coincidence of boron peaks with carbon, the results most closely approaching the model ones, i.e. the ones with the smallest measurement error, were obtained for beam energy of 15kV and 17,5kV. The elements content was accordingly: 44,36%B and 55,64% N for 15kV (error 0,8%) and 45,15%B and 54,85%N for 17,5kV (error 1,59). In the applied analyzing software there is a possibility to define the value of ADC Resolution parameter. This

parameter determines the number of channels into which a spectrum will be digitized., e.g. for beam energy 20kV and resolution 4096 channels means that one channel will analyze a signal of the 'width' of 5eV.

The influence of ADC Resolution parameter on the measurement result at the accelerating voltage of 15kV and counting duration time of 10 minutes is presented in Fig. 10.

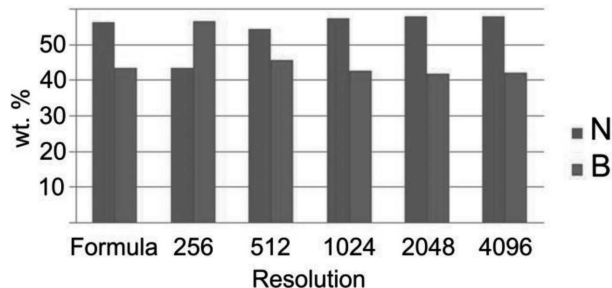


Fig. 10. The influence of ADC resolution parameter on the results of c-BN crystal microanalysis

On the basis of the dependence in Fig. 10 it was observed that the results obtained for the resolution 512, 1024, 2048 and 4096 are similar. The difference between the most extreme resolutions in this group, namely for 512 and 2048 amounted to 3,65%. For the resolution 256 the result least compatible with the model was obtained. Moreover, the shape and quality of the obtained spectrum constituted a considerable difficulty in its identification and interpretation.

Verification of the assumed parameters for boride microanalysis.

The established, believed to be the optimum, parameters of microanalysis i.e. beam energy 15kV, duration time 10 minutes were subjected to verification for the specimen: borided steel 42CrMo4 (Fig. 11) and borided ARMCO iron (Fig. 12).

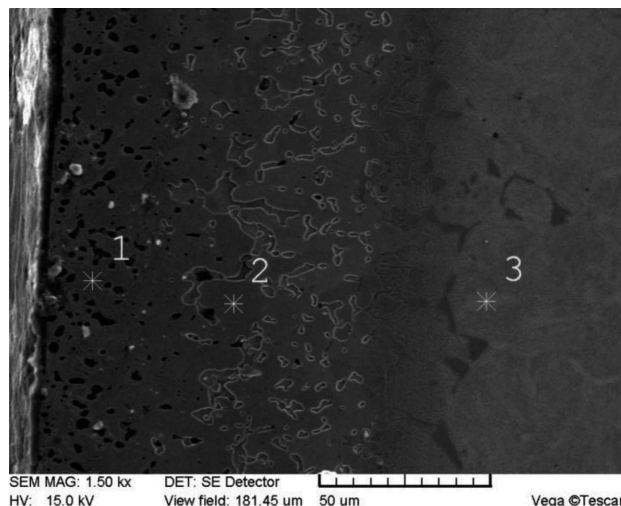


Fig. 11. SEM picture of specimen: borided steel 42CrMo4; 1,2,3 – areas subjected to EDS analysis

In point 1, Fig. 11 the presence of FeB was confirmed with the measurement error of 0,8% and in point 2, the presence of Fe<sub>2</sub>B was confirmed with the measurement error of 0,12%. The next test parameter was borided ARMCO iron (Fig. 12). The analysis was conducted for the counting dura-



tion times: 1 and 10 minutes. It was observed that point 1 Fig. 12 is situated in the area of FeB borides, with the minimum measurement error 0,1% obtained for the counting duration time of 10 min: 83,88%Fe and 16,12%B. It was observed that point 2 Fig. 12 belongs to the range of borides Fe<sub>2</sub>B. After 1 minute counting the error amounted to 0,57%, while for 5 min – 1,99%.

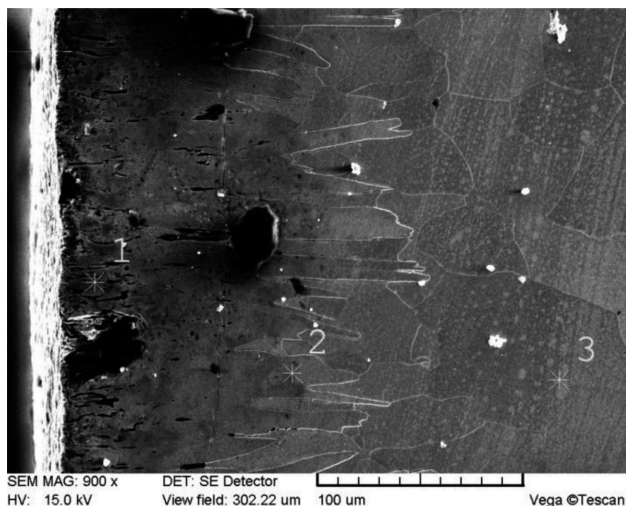


Fig. 12. SEM picture of specimen: borided ARMCO iron; 1,2,3 – areas subjected to EDS analysis

#### 4. Summary

On the basis of the conducted analyses it was noticed that for the accelerating voltage values of 10kV and 12kV, irrelevantly of the measurement duration time, the phenomenon of carbon contamination considerably increased the measurement error.

The most precise and accurate result was obtained for accelerating voltage of 15kV and counting duration time of 1 minute. Moreover, it was observed that the duration time lengthening to 25 minutes (accelerating voltage 15kV) does not considerably influence the result of microanalysis (the error below 1%). Owing to the verification of the optimum microanalysis parameters on the borided steel 42CrMo4 and borided ARMCO iron it was noticed that the microanalysis conditions defined by the c-BN model can be applied for the measurement of boron also in other materials. In future the authors intend to conduct further analyses with the use of various types of borides.

#### 5. Conclusions

EDS microanalysis of materials containing boron when applying appropriate analysis parameters provides results of low measurement error.

The biggest intensity of boron K $\alpha$  lines was obtained for the accelerating voltage of 15kV. At this voltage value the obtained results represented the smallest measurement error.

The duration time of the microanalysis is one of the most important parameters which considerably influences the results. The most effective duration time of the microanalysis falls within the range from 1 min to 10 min.

Appropriate value of accelerating voltage and counting time results in minimizing the influence of carbon contamination of the specimen surface from the atmosphere of the specimen chamber, which gradually can effectively obscure the presence of boron due to the peaks coincidence. Appropriate value of beam energy directly influences the shape of X-ray source region, enabling, to some extent, bypassing the surface layer of carbon.

The higher value of beam energy diminishes the effectiveness of the computer process of the microanalysis because the number of channels in which a spectrum will be digitized increases. Nevertheless, the results with the smallest measurement error were obtained for the beam energy of 15kV and 17,5kV.

The value of microanalysis resolution influences the shape of the peaks; the higher it is the more easily adjacent peaks can be distinguished. However, higher resolution results in the fact that the signal is analyzed by more channels, which entails a considerable increase of dead time parameter.

Optimum parameters for a model specimen (boron nitride on a conductive carbon tape) are as follows: accelerating voltage – 15kV, ADC resolution – 4096, duration time 1-10 min.

The application of the analysis parameters established for c-BN on other specimen showed that they can be successfully applied because the differences in contents between the calculated data and the obtained ones constituted less than 2%. In order to provide for experimental procedure standardization it seems advisable to conduct similar analyses in future for other boron compounds.

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