

Qualitative and numerical analysis of chemical composition of selected iron alloys technique wave dispersive spectrometry (WDS) by calibration curves

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ABSTRACT

Purpose: Purpose of the dissertation was accomplish qualitative and quantitative analysis of chemical composition of selected iron alloys using wavelength-dispersive spectroscopy (WDS) by calibration curve method. In this dissertation information about X-ray microanalysis physical basis and about X-ray detection in scanning electron microscope were presented.

Design/methodology/approach: Research was execute on scanning electron microscope, on the X-ray diffraction instrument, on energy and wavelength-dispersive spectrometer. Carbon content and confidence interval at unknown steel sample were determined.

Findings: Method of calibration curves allowed the designation of the carbon content of the steel samples of unknown chemical composition, depending on a reflection intensities derived from coal. Performed tests have confirmed the possibility of using this method, even in case of depositing the carbon layer.

Originality/value: The paper presents qualitative and numerical analysis of chemical composition of selected iron alloys technique wave dispersive spectrometry (WDS) by calibration curves. Carbon content and confidence interval at unknown steel sample were determined.

Keywords: Qualitative and numerical analysis of the chemical composition; Energy dispersive spectrometer (EDS); Wave dispersive spectrometry (WDS); X-ray diffractometer

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METHODOLOGY OF RESEARCH

1. Introduction

Over the past few years there has been a rapid development of scanning electron microscopy and its accompanying X-ray spectroscopy. Scanning electron microscopy results and utilizes the phenomena of interaction with the electron beam physical objects (e.g., electrons), forming the material [1,2,7].

In a scanning electron microscope, a focused electron beam scans the surface of the sample, and generates a variety of signals, resulting from beam-matter interactions [10,16].

The method of research materials using Scanning Electron Microscopy (SEM) has become very popular due to the high efficiency of research materials in the solid state – monocrystalline, polycrystalline materials, amorphous solid (amorphous) and limited organic tissues. During the interaction of electrons with high energy beam with the material of the sample followed by emission characteristic X-ray of the chemical elements in the microregions of sample. For many years, is widely used engineering solutions that enable connection with a scanning electron microscope microanalyser (spectrometer) X-ray, so that it becomes possible to simultaneously obtain information about the surface topography, providing both to chemical composition of the research material [1-3,8,11,12,14].

Analysis of the chemical composition microregions determination based on wavelength or energy quanta characteristic X-ray with the energy emitted from the sample surface by the energy difference between the energy levels of electrons (the primary and minted) [1-3].

Analysis of the chemical composition in microregions by a scanning electron microscopy combined with X-ray microanalyser is based on using the following methods: spectrometry wavelength dispersive (WDS); energy dispersive spectrometry (EDS) [1,2,4,6].

Wavelength dispersive X-ray spectroscopy (WDS) provides the advantages of an improved spectral resolution, sensitivity and ability to detect light elements compared to energy dispersive X-ray spectroscopy (EDS). Capability to detect low concentrations (down to parts per million levels) and resolve elements with overlapping peaks in an EDS spectrum makes WDS a effective tool for microchemical analysis [9-11,13,15].

The easiest way to correct the results of the quantitative X-ray microanalysis is a method of calibration curves. Calibration curves express the dependence of the characteristic X-ray intensity in the samples containing different amounts of an chemical element, measured under the same measurement conditions, on its concentration in the material. This method is mainly used for the analysis of carbon concentration, allowing to avoid the occurrence of

the error caused on the sample surface carbon layer having a thickness of several nm. This causes the recording layer containing about 0.1% carbon, even in the absence of its presence in the material. Method of calibration curves allows to lower the detection limit of the carbon to about 0.03% [1,4-6,18].

2. Experimental

The material consisted of four samples of known chemical composition (Table 1), and one sample of unknown composition. To determine the chemical composition of the used spectrometer LECO GDS 500 A, which uses the technique of optical emission spectrometry, and glow discharge is used to determine the chemical composition of the alloys of iron and non-ferrous metal alloys.

Table 1.
The mass percentage composition of the samples used for research

	C, %	Mn, %	Si, %	Cu, %	Ta, %
Sample 1	0.063	0.580	0.164	0.383	0.628
Sample 2	0.087	0.373	0.00	0.024	0.588
Sample 3	0.028	0.209	0.00	0.014	0.620
Sample 4	0.139	0.514	0.001	0.150	0.616
Sample 5	Unknown chemical composition				

The test specimens for scanning electron microscopy were prepared by cutting the material in a grinding wheel cutter Struers. The samples were include by sinking them into the resin. This process took place at the hot under the appropriate pressure.

Then the surfaces of test samples were pre-aligned for grinding wheels with simultaneous cooling water. Further processing was carried out using abrasive papers, starting from the coarse grain paper (180, 220, 240), and ending with the smallest paper grit (1000, 1200). Grinding was carried out in a mechanical manner on the automatic rotary grinder. Next, samples were polished on a rotating disk covered with felt and dampened suspension of diamond grit from 14-0.25 μm . Polishing lead to a mirror surface, without scratches. Polished sample were washed in water and alcohol and then dried in an air stream and subjected to ultrasonic cleaning scrubber. Samples were selected for the study were characterized by a different carbon content, which ranged from 0.028 to 0.139% (Table 1).

The scope of the research included a qualitative phase X-ray analysis, testing using a scanning electron microscope and X-ray spectroscopy, energy dispersive (EDS) X-ray spectroscopy and wavelength-dispersive (WDS).

2.1. X-ray phase analysis

X-ray phase analysis was performed to determine the phase composition of the samples analyzed and to identify the phase present in the material using X-ray diffractometer

X'Pert PRO PAN analytical using filtered radiation from a cobalt lamp, with a counting time of 5 s, step 0.05°.

In order to solve the diffraction pattern, first read the angular position of reflection peaks (2θ) (Figs. 1-4). Then, using the Bragg equation was calculated interplanar distance experimental:

$$d_{exp} = \frac{n \cdot \lambda}{2 \cdot \sin \theta} \quad (1)$$

where:

$$n = 1,$$

$$\lambda = 1.79 \text{ \AA}$$

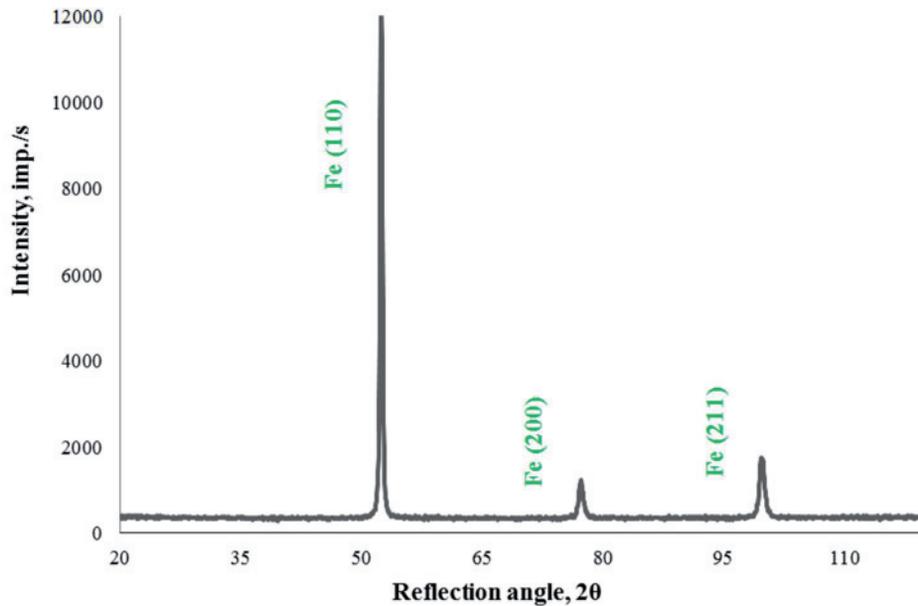


Fig. 1. The diffraction pattern of sample 1

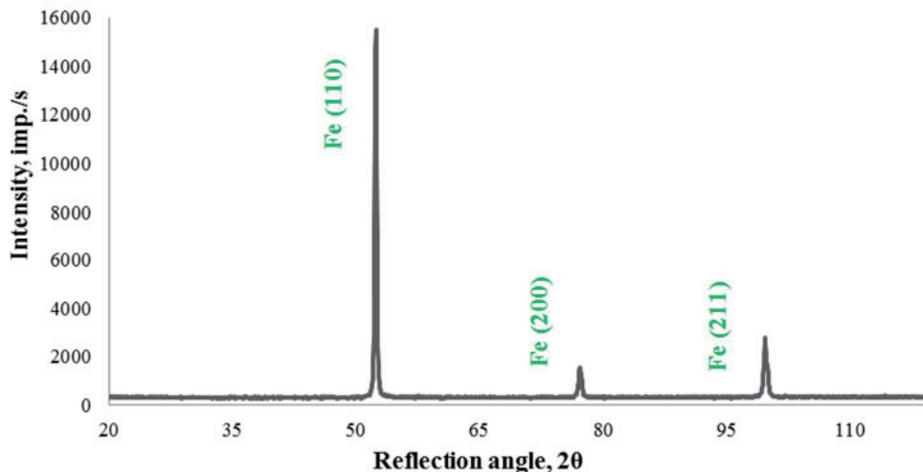


Fig. 2. The diffraction pattern of sample 2

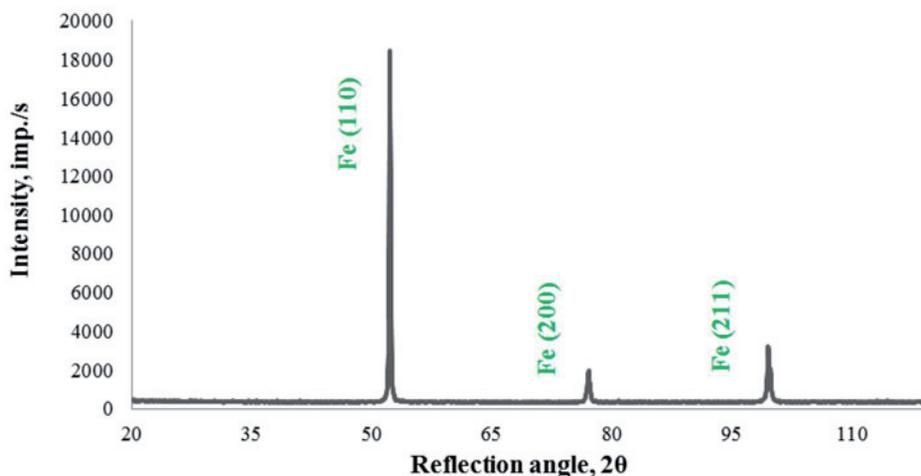


Fig. 3. The diffraction pattern of sample 3

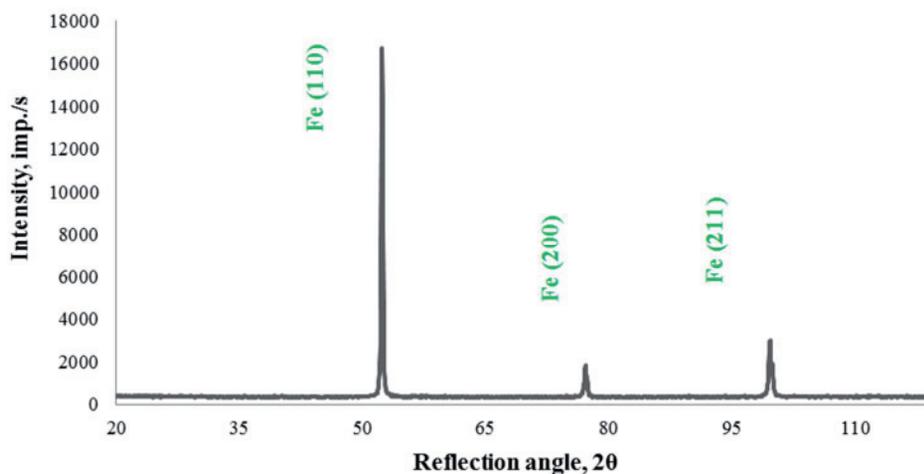


Fig. 4. The diffraction pattern of sample 4

Based on the patterns of identification JCPDS (Joint Committee for Powder Diffraction) have been traced spacings (closest experimental values) and the relative intensities of reflections, as well as indicators of reflections (hkl) (Tables 2-5).

Studies using X-ray diffractometer, which consists in determining the phase composition and identification of the phase present in the material confirmed the phase composition of the samples tested. Identified phase – iron α (Fe) (JCPDS card file: 87-0722).

2.2. Energy Dispersive Spectrometry

Research in the scanning electron microscope aimed at:

- investigate the chemical composition of microregions of the sample by means energy dispersive spectrometer (EDS) – characteristic X-ray spectrum,
 - imaging the sample surface using a contrast with using backscattered electrons (BSE), to check whether the material is not considered as carbide precipitates,
 - imaging the topography of the sample surface using the secondary electrons (SE).
- Materials for research consisted of five samples prepared into analysis. The tests were performed under the same measurement conditions:
- the aperture – 120 microns,
 - accelerating voltage – 10 kV and 15 kV,
 - zoom – 20 000 x.

Table 2.
The crystallographic data of sample 1

$2\theta, ^\circ$	$\text{Sin}\theta$	$d_{\text{exp}}, \text{\AA}$	I_{exp}	$d_{\text{tab}}, \text{\AA}$	I_{tab}	hkl
52.48106	0.4421	2.024	100	2.023	999	110
77.31435	0.6247	1.433	15	1.43	115	200
99.81301	0.765	1.170	20	1.168	175	211

Table 3.
The crystallographic data of sample 2

$2\theta, ^\circ$	$\text{Sin}\theta$	$d_{\text{exp}}, \text{\AA}$	I_{exp}	$d_{\text{tab}}, \text{\AA}$	I_{tab}	hkl
52.41766	0.4416	2.026721	100	2.0228	999	110
77.21773	0.624	1.434295	15	1.4303	115	200
99.73647	0.7646	1.170547	20	1.1679	175	211

Table 4.
The crystallographic data of sample 3

$2\theta, ^\circ$	$\text{Sin}\theta$	$d_{\text{exp}}, \text{\AA}$	I_{exp}	$d_{\text{tab}}, \text{\AA}$	I_{tab}	hkl
52.29645	0.4407	2.03086	100	2.0228	999	110
77.11838	0.6233	1.435906	15	1.4304	115	200
99.66375	0.7642	1.171159	20	1.1679	175	211

Table 5.
The crystallographic data of sample 4

$2\theta, ^\circ$	$\text{Sin}\theta$	$d_{\text{exp}}, \text{\AA}$	I_{exp}	$d_{\text{tab}}, \text{\AA}$	I_{tab}	hkl
52.39541	0.4415	2.02718	100	2.0228	999	110
77.19707	0.6239	1.434525	15	1.4304	115	200
99.72505	0.7645	1.1707	20	1.1679	175	211

The results of the chemical composition of the samples in microregions analyzed obtained using a scanning electron microscope using an energy dispersive spectrometer (EDS) and the surface topography images made on the basis of detection of secondary electrons (SE) and backscattered electrons (BSE) are shown in Figs. 5-10.

The study of surface topography in SE mode and BSE confirmed the homogeneity of all samples tested. Qualitative analysis of the chemical composition of microregions were consistent with results obtained from emission spectrometer LECO GDS 500 A. Studies with the backscattered electrons (BSE) showed no precipitates in the form of carbides in the material.

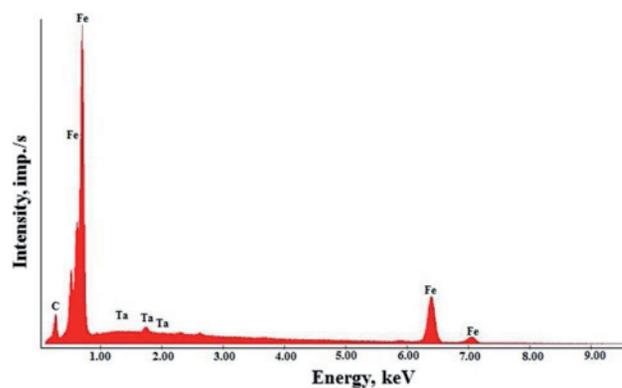


Fig. 5. Characteristic X-ray spectrum (EDS) for the sample 1

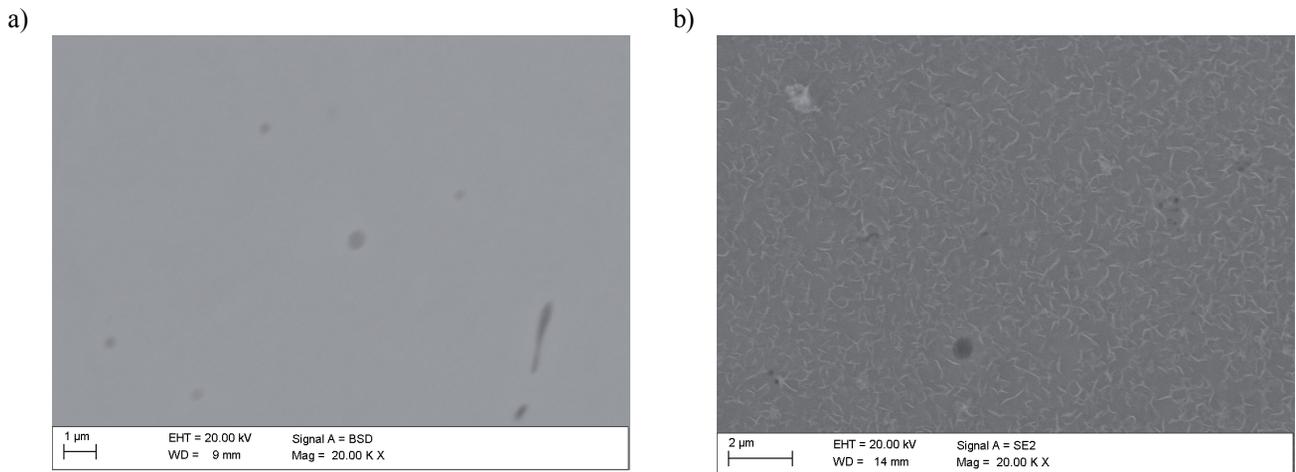


Fig. 6. Picture the surface of sample 1 obtained by means of: a) backscattered electrons (BSE), b) secondary electron (SE)

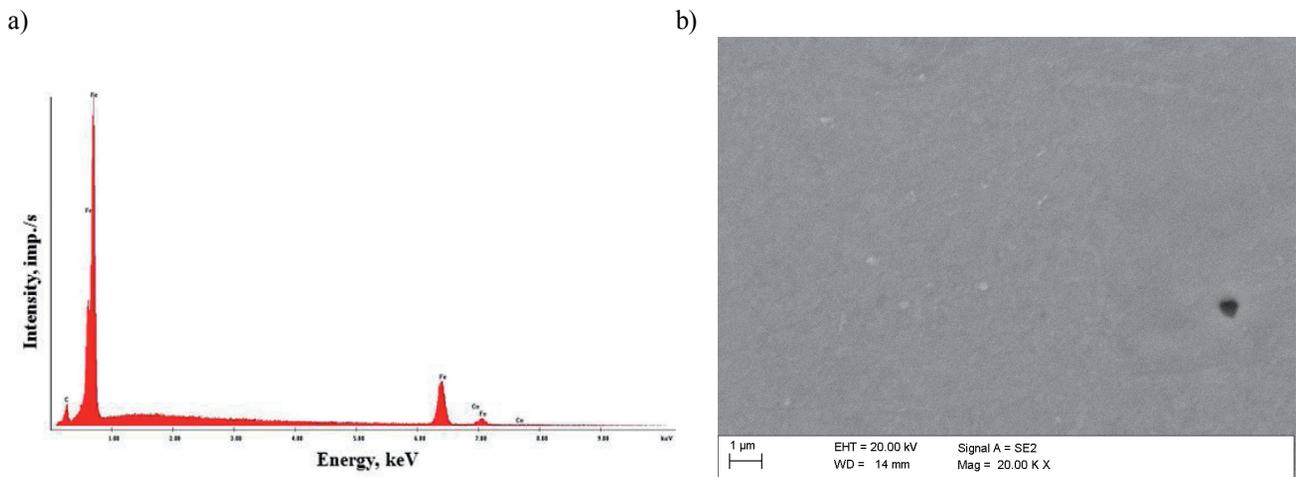


Fig. 7. Sample 2: a) the characteristic X-ray spectrum (EDS), b) image of the surface obtained using secondary electrons

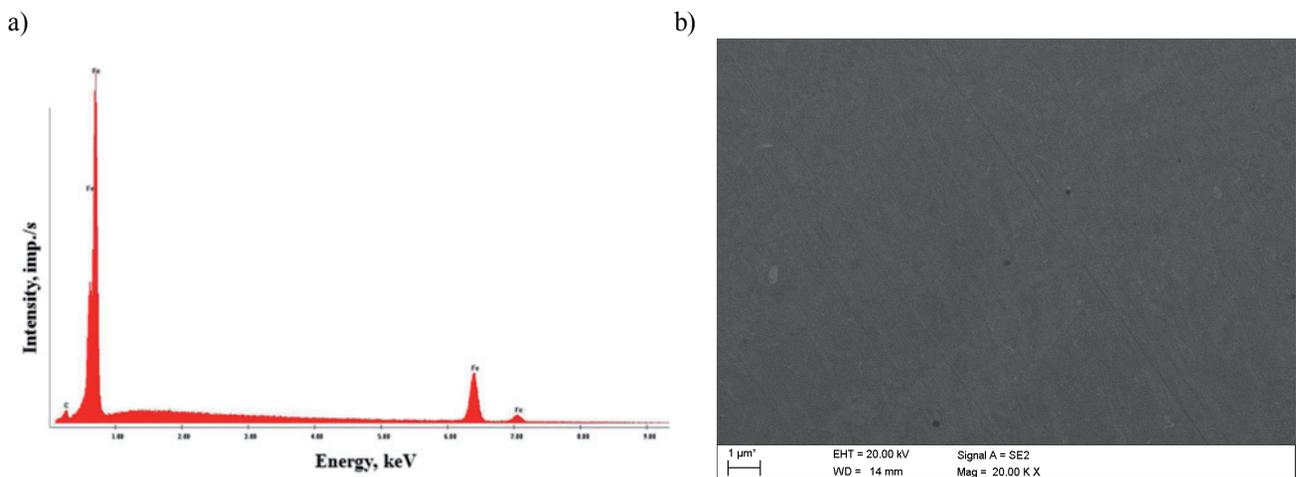


Fig. 8. Sample 3: a) the characteristic X-ray spectrum (EDS), b) image of the surface obtained using secondary electrons

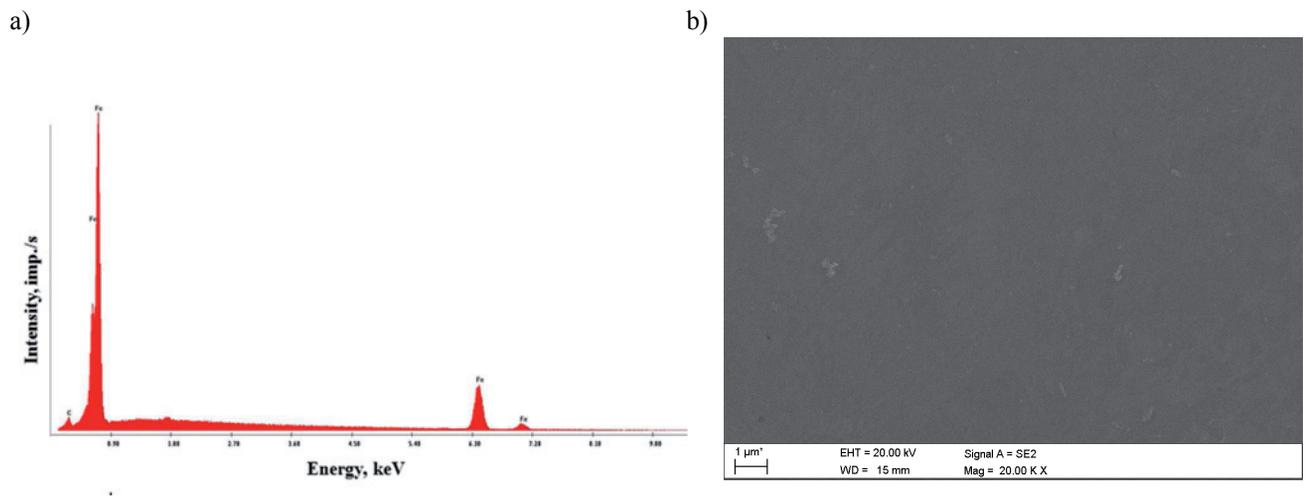


Fig. 9. Sample 4: a) the characteristic X-ray spectrum (EDS), b) image of the surface obtained using secondary electrons

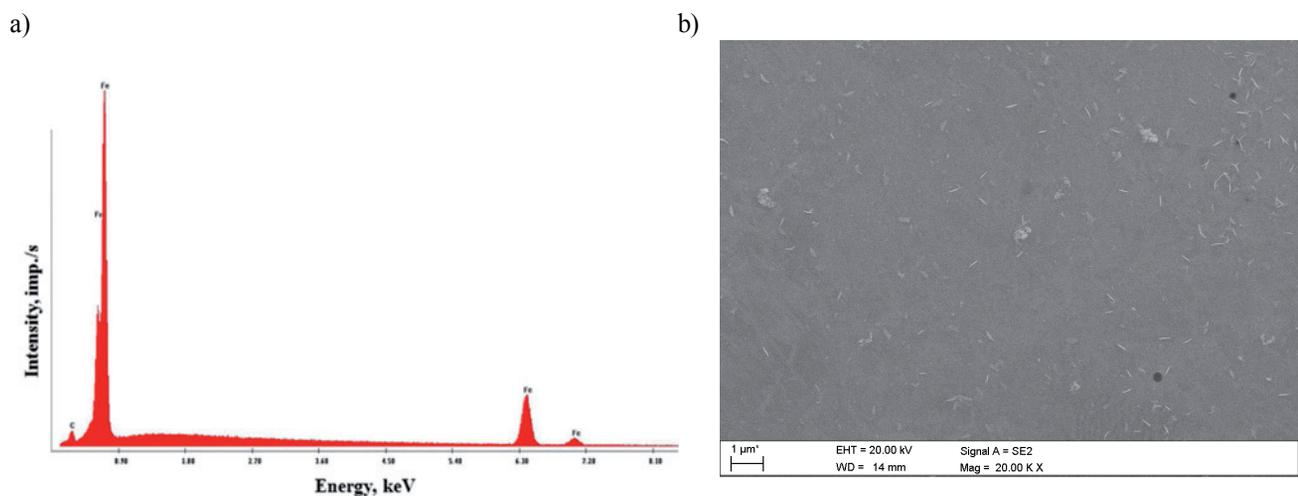


Fig. 10. Sample 5: a) the characteristic X-ray spectrum (EDS), b) image of the surface obtained using secondary electrons

2.3. Dispersive Spectrometry Wavelength

The scope of research using a spectrometer wavelength dispersive (WDS) included the five series of measurements for each sample of known carbon content at a value equal to the acceleration voltage of 10 kV and 15 kV. The measurement results for the acceleration voltage of 10 kV are equal as shown in Table 6, while the acceleration voltage of 15 kV in Table 7.

For an accelerating voltage of 10 kV equal to the average intensity value for each of the four test samples did not differ significantly from each other. The probable

reason for this result was the deposition of carbon layer on the surface of the sample during the measurement.

Due to the smaller penetration depth of electrons at an accelerating voltage of 10 kV, the measurement errors due to the presence of contamination is greater than the value of 15 kV, so the use of a higher acceleration voltage value.

For measurement series at an accelerating voltage of 15 kV was performed one measurement X-ray for each sample. By the measuring determined the intensity of counts (cps), the background in the direction of higher and lower energy and standard deviation (%).

Table 6.
The results for a series of measurements at an accelerating voltage of equal 10 kV

Sample	Measurement	The intensity (height) of reflexes originating from carbon	The intensity of mean \pm average error
Sample 1	1	29.83	23.2 \pm 2.1
	2	24.23	
	3	22.68	
	4	20.09	
	5	19.06	
Sample 2	1	32.51	28.3 \pm 1.5
	2	28.67	
	3	25.55	
	4	26.46	
	5	24.33	
Sample 3	1	21.02	22.2 \pm 0.7
	2	21.75	
	3	21.74	
	4	22.02	
	5	24.47	
Sample 4	1	24.12	21.8 \pm 1.7
	2	18.12	
	3	21.24	
	4	19.13	
	5	26.4	

Table 7.
The results for a series of measurements at an accelerating voltage of equal 15 kV

	Sample 1	Sample 2	Sample 3	Sample 4
The intensity of counts (cps) after background subtraction	118.3	139.2	78.7	271.7
Background level towards lower energy	100.4	117.4	91.2	119.6
The background level towards higher energy	146.6	175.2	145.0	197.4
Standard deviation, %	2.55	2.36	3.56	1.41
The carbon content (mass fraction, %), analysis of the model taking into account the ZAF correction	0.59	0.70	0.39	1.36
The carbon content (atomic percentage, %), analysis of the model taking into account the ZAF correction	2.66	3.11	1.77	5.88

The results obtained were used to prepare the calibration curve shown in Fig. 11 is shown on the graph the relationship between the intensity counts and the concentration of carbon in four samples of known chemical composition, described a simple equation. The graph has also highlighted the confidence interval for the expected carbon content in the sample, at a confidence level equal to 68%.

In Table 8 shown measurement results of characteristic X-ray intensity of a sample with unknown chemical composition. Measurement parameters were the same as in the determination of the calibration curve based on the results obtained for samples of known chemical composition.

Based on the results perform a calibration curve, and then read from it the concentration of carbon in the sample. Carbon concentration in the sample was determined

amounting to 0.076% of the point where a straight line described by the equation $y = x + 1741.7$ 13.946 dashed lines. External lines define the range of the confidence interval with a confidence level equal to 68% (Fig. 12).

3. Conclusions

The study presents methodology for measuring the spectral dispersion wavelength using a spectrometer LEXS of EDAX company, which is a part of a scanning electron microscope Zeiss Supra 35. Also described methodology allows the determination of the calibration curve for determining the carbon content in the steel samples, on the basis of the depending intensity of reflections originating from the carbon designated in tested samples of known concentration of the chemical element.

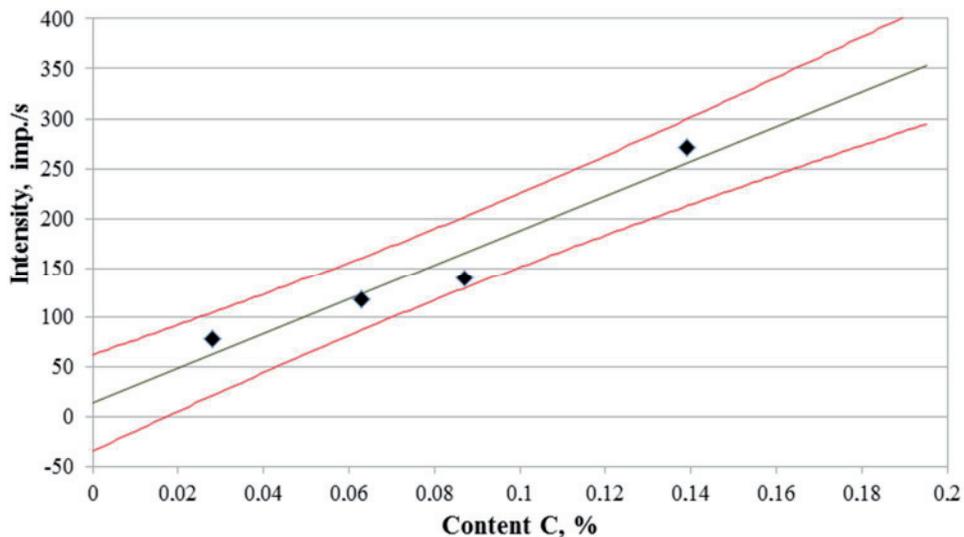


Fig. 11. The calibration curve (EHT = 15 kV)

Table 8.

Measurement results of characteristic X-ray intensity of a sample with unknown chemical composition (Sample 5)

	Sample 5
The intensity of counts (cps) after background subtraction	145.4
Background level towards lower energy	104.4
The background level towards higher energy	163.6
Standard deviation, %	2.21
The carbon content (mass fraction, %), analysis of the model taking into account the ZAF correction	0.727
The carbon content (atomic percentage, %), analysis of the model taking into account the ZAF correction	3.233

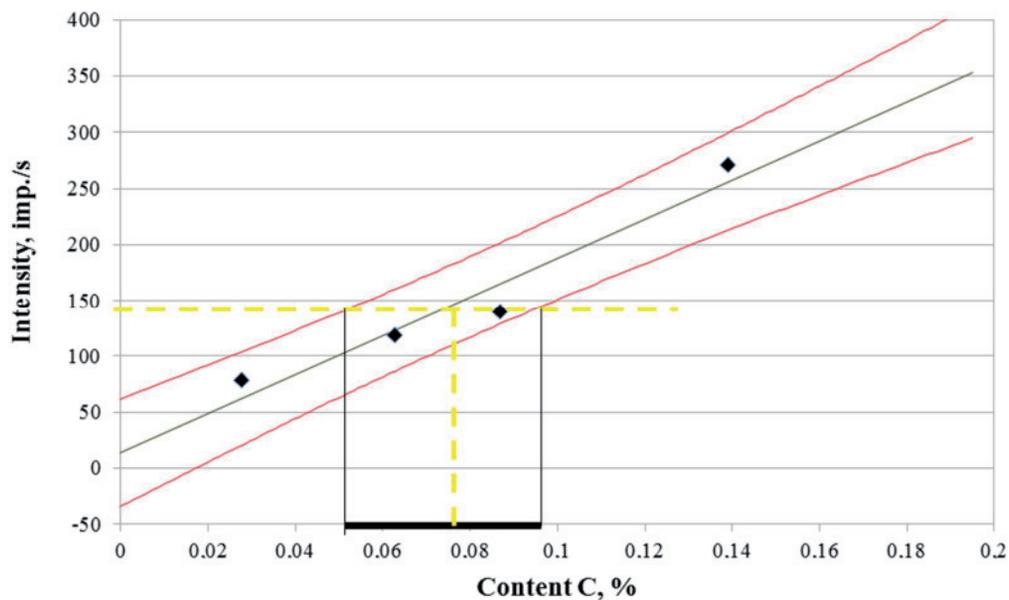


Fig. 12. Methodology for the determination of the carbon content and the designation confidence interval of the calibration curve

Performed investigation were confirmed the possibility of using the calibration curve method to determine the concentration of carbon in the steel, even in the event of carbon layer.

Determine the carbon content and the determined confidence interval in steel sample of unknown composition.

References

- [1] A. Szummer (Ed.), K. Sikorski, Ł. Kaczynski, J. Paduch, K. Caretaker, *Foundations of Quantitative X-Ray Microanalysis*, WNT, Warsaw, 1994 (in Polish).
- [2] Z. Bojarski, *X-ray microanalyzer, Chemical analysis method in microareas*, Silesia, Katowice, 1971 (in Polish).
- [3] M. Żelechower, *Introduction to X-ray microanalysis*, Silesian University of Technology Publishing House, Gliwice, 2007 (in Polish).
- [4] M. Krzysztof, *Signal detection and imaging technique in a scanning electron microscope in the low vacuum range*, PhD thesis, Wrocław, 2010 (in Polish).
- [5] B.L. Thiel, *Imaging and Microanalysis in Environmental Scanning Electron Microscopy*, *Microchimica Acta* 155 (2006) 39-44.
- [6] A. Barbacki, *Electron Microscopy*, Poznan University of Technology Publishing House, Poznan, 2007 (in Polish).
- [7] M. Terauchi, M. Koike, K. Fukushima, A. Kimura, Development of wavelength-dispersive soft X-ray emission spectrometers for transmission electron microscopes - an introduction of valence electron spectroscopy for transmission electron microscopy, *Journal of Electron Microscopy* 59/4 (2010) 251-261.
- [8] D.A. Wollman, K.D. Irwin, G.C. Hilton, L.L. Dulcie, D.E. Newbury, J.M. Martins, High-resolution, energy-dispersive microcalorimeter spectrometer for X-ray microanalysis, *Journal of Microscopy* 188/3 (1997) 196-223.
- [9] A. Ul-Hamid, H.M. Tawancy, A.I. Mohammed, S.S. Al-Jaroudi, N.M. Abbas, Quantitative WDS analysis using electron probe microanalyzer, *Materials Characterization* 56 (2006) 192-199.
- [10] A.J. Laigo, F. Christien, R. Le Gall, F. Tancret, J. Furtado, SEM, EDS, EPMA-WDS and EBSD characterization of carbides in HP type heat resistant alloys, *Materials Characterization* 59 (2008) 1580-1586.
- [11] P. Nowakowski, F. Christien, M. Allart, Y. Borjon-Piron, R. Le Gall, Measuring grain boundary segregation using Wavelength Dispersive X-ray Spectroscopy: Further developments, *Surface Science* 605 (2011) 848-858 (in Polish).
- [12] K.D. Vernon-Parry, *Scanning electron microscopy: an Introduction*, *III-Vs Review* 13/4 (2000) 40-44.

- [13] N.W.M. Ritchie, D.E. Newbury, J.M. Davis, EDS Measurements of X-ray Intensity at WDS Precision and Accuracy Using a Silicon Drift Detector, *Microscopy and Microanalysis* 18 (2012) 892-904.
- [14] R.A. Aulrata, Double detector system for BSE and SE imaging, *Scanning* 6 (1984) 174-182.
- [15] R. Aulrata, Backscattered electron imaging using single crystal scintillator detectors, *Scanning Microscopy* 3 (1989) 739-763.
- [16] L.A. Dobrzanski, E. Hajduczek, *Light and electron microscopy*, WNT, Warsaw, 1987 (in Polish).
- [17] D. Kaczmarek, *Reconstruction of a surface image of the sample in the scanning electron microscope using backscattered electrons*, Wroclaw University of Technology, Wroclaw, 1999 (in Polish).
- [18] M. Głowacka (Ed.), *The science of metals*, Publishing House Gdansk University of Technical, Gdansk, 1996 (in Polish).