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Use of Diffraction Effects in the X-ray Fluorescence Analysis for Determination of Carbon Concentration in Steels

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The possibility of adapting the X-ray fluorescence analysis to determine the carbon content in steels is considered. The proposed method is based on the comparative analysis intensity of diffraction peaks in fluorescence spectra. The optimal geometry of the spectrum recording is determined experimentally, and it is established that in the case of unalloyed steel, this technique provides an adequate estimation of the carbon content in the sample. The restrictions and obstacles for the accurate carbon content determination in alloying steels is discussed.

Key words: X-ray fluorescence analysis, carbon steel, diffraction.

У даній статті розглядається можливість адаптації методу рентгенофлуоресцентного аналізу для визначення вмісту Карбону у крицях. Було запропоновано метод оцінки вмісту Карбону на основі інтенсивності дифракційних піків у флуоресцентних спектрах. Експериментально визначено оптимальну геометрію зйомки спектру, та встановлено, що у випадку нелегованої криці дана методика дає адекватну оцінку вмісту Карбону у зразку.

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1. INTRODUCTION

Analysis of the chemical composition of carbon steels is a widespread and critically important task in modern industry, for example, in the control of the quality of raw materials or finished products, since different grades of steel have different mechanical and physical properties [1]. Currently, the main methods for analysing the composition of carbon steels are chemical analysis and atomic emission spectroscopy, but their effectiveness is limited by their destructive nature, relative complexity of preparing samples for analysis and cost. An attractive alternative for the analysis of steels is the X-ray fluorescence analysis (XRF) method. This method is widely used for the analysis of the chemical composition of materials, due to its simplicity, express nature, and minimal need for sample preparation for measurements. However, this method has poor sensitivity to elements with low atomic number (low Z elements), due to the low yield of fluorescence from atoms of light elements, and strong scattering of low-energy X-ray radiation in the air. That's why is unsuitable for determining the concentration of carbon in samples that significantly limits its capabilities for the analysis of steels. There are different approaches to expand XRF analysis range to low Z elements. The most straightforward is creating measurement conditions that will allow fluorescence peaks of those elements to be recorded in the spectrum, mainly by elimination scatter of low energy emission in air by implementing a vacuum setup or purging air with lighter gas such as helium [2]. However, vacuum setups are not suitable for portable spectrometers, and introduction of helium only extends the analysis range to sodium, which means carbon is still undetectable by such devices. Another approach is use of neural networks to predict low atomic number element concentration [3]. Usually, this approach relies on correlation between element concentrations in natural samples, such as soils, or different types of X-ray scattering still visible in the spectrum, *e.g.* Compton scattering. While relatively new, these methods show promise at least in specific analysis tasks. This paper considers the possibility of using diffraction peaks in fluorescence spectra to adapt the X-ray fluorescence method for the analysis of carbon steels. In unalloyed and untempered steels carbon is mostly present in the form of cementite— Fe_3C compounds with iron, as the solubility of carbon in α -iron is quite low (about 0.02 wt.%). Thereby, the part of the cementite phase is directly proportional to the car-

bon content in the alloy. By choosing the geometry of the survey in such a way that the diffraction of X-ray radiation on the cementite lattice was observed, and analysing the intensity of the diffraction line in the spectrum, it is possible to estimate the carbon content in the sample. Therefore, the purpose of this work is to verify the possibility of analysing the carbon concentration in steels based on diffraction peaks in the spectra.

2. THEORETICAL BACKGROUND

The X-ray fluorescence analysis method is based on the quantification of the characteristic fluorescence spectrum that occurs during the inelastic interaction of X-ray radiation with the sample. At the same time, elastic scattering of X-rays also takes place, and if the spectrum acquisition geometry satisfies the Wolff–Bragg equation (1),

$$2d \sin \theta = m\lambda \quad (1)$$

for a certain wavelength present in the spectrum of the primary radiation beam, diffraction peaks will also be observed in the fluorescence spectra. Diffraction peaks in fluorescence spectra are considered as parasitic effect since they are not used directly in the XRF method. In certain cases, they may overlap or be falsely interpreted as characteristic fluorescence lines. Nonetheless, diffraction lines contain information about the phase structure of the sample, and therefore could be used to obtain additional information about the sample.

In unalloyed and untempered steels, the main phase components are ferrite, which is a weak solid solution of carbon in α -iron (α -ferrite) with a bcc lattice or in γ -iron (γ -ferrite) with an fcc lattice, and cementite (Fe_3C) [4]. Due to the very low solubility of carbon in ferrite, most of the carbon is in the cementite phase, and the amount of this phase is directly proportional to the concentration of carbon in the sample. Having selected the geometry of the spectrum acquisition in such a way that a diffraction line from the cementite lattice is observed in the spectrum, based on its intensity, it is possible to estimate the content of the cementite phase and, accordingly, the carbon concentration in the steel. Even though in XRF a non-monochromatic bremsstrahlung emission is used as an excitation source, for the purpose of quantitative analysis it is reasonable to select a geometry that will satisfy the Wolff–Bragg equation for characteristic emission of X-ray tube anode. This choice is explained by the fact that the tube anode line is not dependent on sample composition, as is the most intensive part of the X-ray tube spectrum. Note that the relative intensity of this line to the fluorescent line of iron is meant here and hereafter. Since all iron atoms contribute to the intensity of the fluorescent line, and only those

in the cementite phase contribute to the diffraction line, their ratio will be proportional to the proportion of the cementite phase in the sample.

3. EXPERIMENTAL SETUP

The experimental setup is a model of Elvatech Prospector portable X-ray spectrometer with a moving energy-dispersive SDD detector and an X-ray tube with a titanium anode. This facility was intended to determine the optimal spectrum acquisition geometry for observing the diffraction of the K_α line of titanium ($\lambda = 2.745 \text{ \AA}$). For this wavelength, the diffraction spectrum on the lattice of cementite (Fig. 1) and ferrite (Fig. 2) was simulated using the VESTA program [5].

To find the optimal geometry, the spectra of unalloyed steels with carbon content ranging from 0.086 to 1.33 wt.% were recorded at different angles. At the recording angle $2\theta = 86^\circ$, a significant increase in the intensity of the titanium line was observed in the spectra (Fig. 3), and directly at this angle, the intensity of the titanium line exceeded even the fluorescent line of iron. This result is explained well with the simulated spectra since the most intensive cementite line $(031)e_3C$ is located at the angle $2\theta = 86^\circ$. However, no correlation between the carbon content and the intensity of the K_α line of titanium was observed (Fig. 4). Moreover, for the same sample, the intensity of the titanium line varied significantly during repeated measurements.

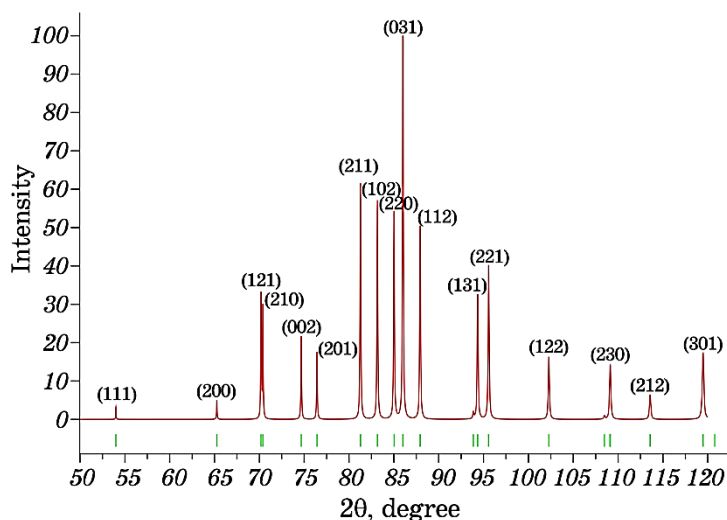


Fig. 1. The simulated diffraction spectrum of cementite for the wavelength $\lambda = 2.745 \text{ \AA}$.

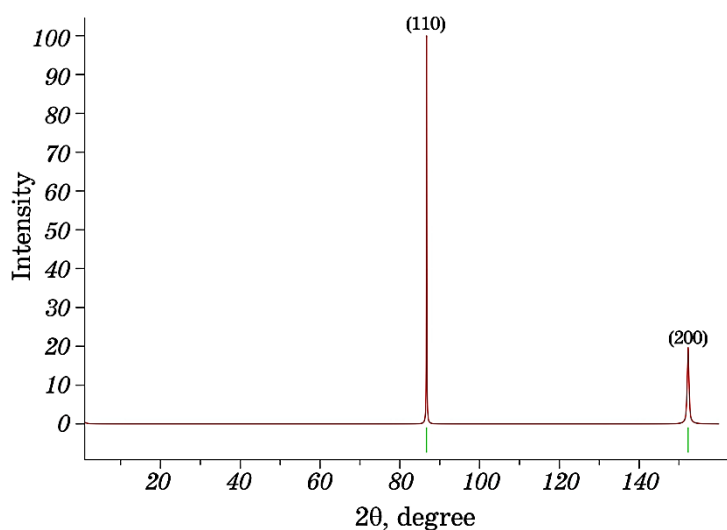


Fig. 2. Simulated diffraction spectrum of ferrite for the wavelength $\lambda = 2.745 \text{ \AA}$.

This is because, as can be seen from the simulated diffraction patterns, the most intensive peak of cementite (031) is very close to the peak of ferrite (110)-Fe. At the same time, a significant correlation was observed at the angle $2\theta = 95^\circ$ (Fig. 5), where the less intensive peaks of cementite (221) e_3C , (131) Fe_3C , and ferrite peaks are absent.

4. QUANTIFICATION OF CARBON CONTENT

A regression model built in the ElvaX program, developed by Elvatech for processing fluorescence spectra, was used to quantify the carbon content in steels. It was found that carbon concentration in steels depends linear on the normalized intensity of K_α Ti line:

$$C = aI_{K_\alpha Ti} + b \quad (2)$$

where C is the mass concentration of carbon, $I_{K_\alpha Ti}$ is the normalized intensity K_α of the titanium line, a and b are regression coefficients.

To determine the regression coefficients, measurements of unalloyed steel samples with a mass concentration of carbon ranging from 0.086 to 1.33% were carried out. To check the quality of the obtained regression, an analysis of samples that were not included in the initial set was carried out. The results are presented in Table 2. Thus, as can be seen from the results, the obtained regression allows for a fairly good estimate of the carbon content in the simple case of unalloyed and

untempered steel, while the absolute error on the tested samples did not exceed 0.05 wt.

5. DISCUSSION

In spite of good results obtained the spreading of this method to other steels is restricted, primarily due to existence of titanium in many grades of alloy steel. This problem can be solved by using another anode of the X-ray tube, or by removing an additional spectrum with a filter of soft X-ray radiation installed after the X-ray tube, to remove the anode line from the incident beam. In this case, only fluorescence of titanium, which presents in the sample, will be visible in the recorded spectrum. This will allow us to calculate the concentration of titanium in the sample, and make a corresponding correction when calculat-

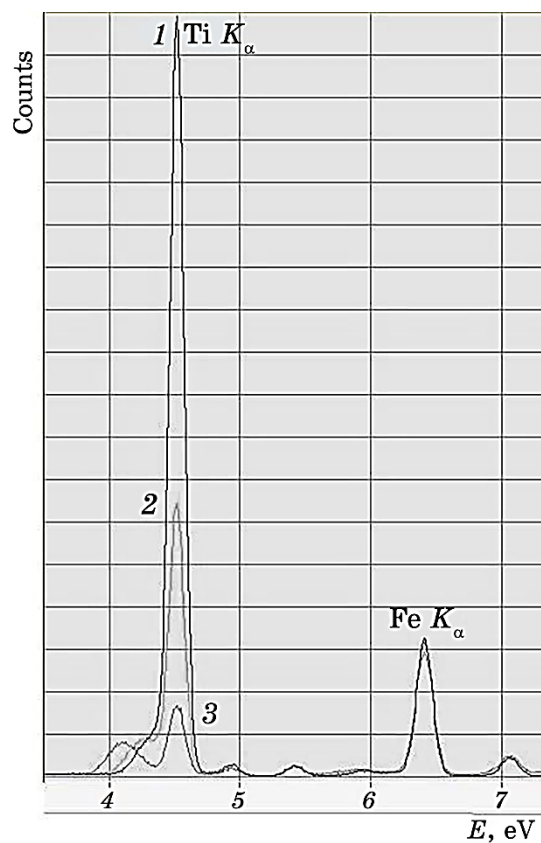


Fig. 3. The peak of titanium in the spectrum of the unalloyed steel sample at different 2θ angles. $2\theta = 86^\circ$ (1), $2\theta = 90^\circ$ (2), $2\theta = 95^\circ$ (3).

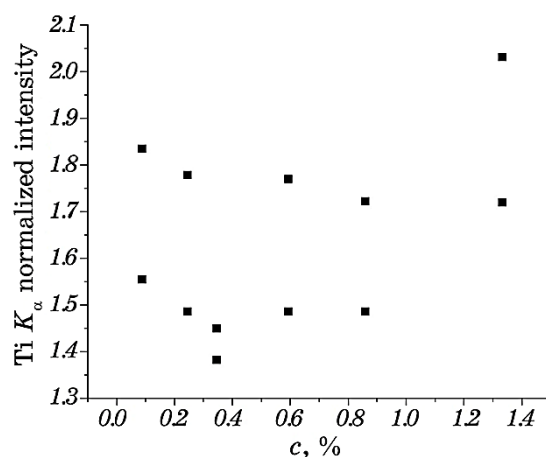


Fig. 4. Dependence between the carbon content and the intensity of the titanium line at $2\theta = 85^\circ$.

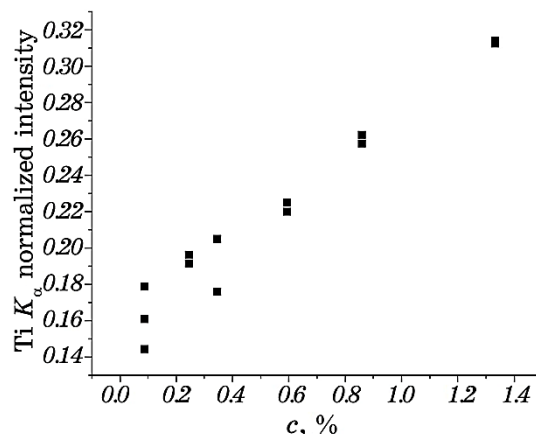


Fig. 5. Dependence between the carbon content and the intensity of the titanium line at $2\theta = 95^\circ$.

ing the concentration of carbon. It will be more difficult to solve problems related to the presence of other phases containing carbon, namely austenitic in alloyed steels and martensitic in hardened steels since in this case carbon will be partially or completely in other phases [6, 7], and therefore there will be no direct relationship between the proportion of the cementite phase, and accordingly the intensity of the diffraction peak, and the carbon content in the sample.

From the obtained experimental results, it can be concluded that

TABLE 1. Certified and calculated according to the regression parameters carbon content in the samples was used to construct the regression.

Sample name	c_{cert} , wt. %	c_{calc} , wt. %	Absolute regres- sion error, wt. %
138-1		0.11	0.011
138-1	0.086	0.088	0.011
138-1		0.105	0.012
138-2		0.23	0.012
138-2	0.243	0.214	0.012
138-2		0.236	0.012
138-3		0.295	0.012
138-3	0.343	0.327	0.012
138-3		0.323	0.012
138-4		0.563	0.013
138-4	0.592	0.623	0.014
138-4		0.611	0.013
138-5		0.852	0.015
138-5	0.857	0.874	0.014
138-5		0.863	0.015
ug0		1.31	0.02
ug 0	1.33	1.33	0.02
ug 0		1.34	0.02

with the correct selection of the spectrum acquisition geometry, a simple linear regression based on the intensity of the tube line diffracting on the cementite lattice allows to estimate the carbon content in unalloyed steel. However, when this technique is applied to alloy steels, a number of problems are expected, primarily related to the formation of carbides of alloying elements. In general, alloyed steels are quite complex systems to describe, and usually their description is limited to tertiary phase diagrams, but even from them, a number of problems that arise when the proposed method is extended to alloyed steels can be outlined.

Such alloying elements as Cr, Ni, Mn in small concentrations form carbides of the cementite type M_3C , however, when their concentrations increase, carbides of the types M_7C_3 , $M_{23}C_7$ are formed in the case of chromium [8], M_7C_3 , M_5C_2 , in the case of Mn [9]. Mo, Ti and V at suf-

TABLE 2. Certified and calculated according to regression parameters carbon content in test samples.

Sample name	c_{cert} , wt.%	c_{calc} , wt.%	Absolute regres- sion error, wt.%
C01	0.004	0.051	0.012
C01		0.001	0.014
C03	0.029	0.028	0.013
C03		0.034	0.013
C04	0.155	0.18	0.013
C04		0.185	0.014
C06	0.395	0.351	0.013
C06		0.354	0.015

ficient concentrations in turn form carbides Mo_2C , TiC and VC , respectively [10–12].

It is worth noting that even elements that do not form their own carbides can significantly change the phase diagram of alloy steel. For example, Si acts as an inhibitor of cementite phase formation, greatly slowing down its formation at relatively low firing temperatures [13].

In part, these problems could be solved by taking into account the correction for the content of carbide-forming elements in the regression, but this implies the requirement for the same steel production technology, since the temperature and duration of annealing of the alloy largely determine its composition. This is especially true for alloy steels. For example, in the Fe–Cr–Mo–V–C system, cementite is a metastable phase relative to carbides M_7C_3 , M_{23}C_6 , M_6C , MC , and is observed only under conditions of low temperature and duration of annealing [14].

In general, the problems described above make this method poorly suited for the analysis of alloyed steels, since if the content of alloying elements can be obtained by the XRF method, and potentially make a correction for the content of carbide-forming elements, the conditions of steel production are generally unknown, it makes it possible to estimate the distribution of phases in the studied sample without additional heat treatment or preliminary information about the sample manufacturing method.

6. CONCLUSIONS

The possibility of using parasitic diffraction effects of the X-ray fluorescence analysis for determining the carbon content in unalloyed

steels is confirmed.

It was found the correlation between the carbon content in unalloyed steels and the intensity of the peak of diffraction of the characteristic TiK_{α} line of X-ray tube on cementite phase with correctly chosen geometry of the spectrum recording.

Linear regression that used to relates the mass concentration of carbon to the intensity $Ti K_{\alpha}$ diffracted line allowing us determines the mass fraction of carbon with the absolute error less than 0.05 mass% in the samples with a carbon content ranging from 0.086 to 1.33 wt.%.

Despite the good results for unalloyed steels, some difficulties are foreseen when applying this method to the analysis of alloyed steels: presence of other metal carbides, austenitic and martensitic phases as well as interfering the method by the Ti alloying in many grade of steels.

REFERENCES

1. A. El-Sesy and Z. M. El-Baradie, *Mater. Lett.*, **57**, No. 3: 585 (2002).
2. A. Migliori, P. Bonanni, L. Carraresi, N. Grassi, and P. A. Mandò, *X-Ray Spectrom.*, **40**, No. 2: 112 (2011).
3. J. Shao, R. Li, Q. Pan, and L. Cheng, *Spectrochim. Acta, Part B*, **196**: 106518 (2022).
4. M. J. Q. Hernandez, J. A. Pero-Sanz, and L. Verdeja, *Solidification and Solid-State Transformations of Metals and Alloys* (Elsevier: 2017).
5. K. Momma and F. Izumi, *J. Appl. Crystallogr.*, **44**, No. 6: 1276 (2011).
6. I. Harding, I. Mouton, B. Gault, D. Raabe, and K. S. Kumar, *Scr. Mater.*, **172**: 42 (2019).
7. B. Denand, V. A. Esin, M. Dehmas, G. Geandier, S. Denis, T. Sourmail, and E. Aeby-Gautier, *Materialia*, **10**: 100664 (2020).
8. A. V. Khvan, B. Hallstedt, and C. Broeckmann, *Calphad*, **46**: 33 (2014).
9. D. Djurovic, B. Hallstedt, J. Von Appen, and R. Dronskowski, *Calphad*, **35**, No. 4: 491 (2011).
10. N. Fujita and H. K. D. H. Bhadeshia, *Mater. Sci. Technol.*, **15**, No. 6: 627 (1999).
11. M. Kawalec, *Arch. Metall. Mater.*, **59**, No. 3: 1054 (2014).
12. C.-C. Hsieh, Y.-C. Liu, J.-S. Wang, and W. Wu, *Met. Mater. Int.*, **20**, No. 4: 712 (2014).
13. T. Suzuki, S. Teramoto, and Y. Neishi, *ISIJ Int.*, **64**, No. 2: 276 (2024).
14. A. Kroupa, J. Havránková, M. Svoboda, M. Coufalová, and J. Vřešťál, *J. Phase Equilib.*, **22**, No. 3: 323 (2001).