X-RAY BASED TECHNIQUES USED IN MATERIALS ANALYSIS AND CONTROL

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Abstract: *This work provides some results obtained by application of X-ray based techniques for the characterization of various industrial, environmental and new synthesized materials with regard of micro-composition and structure. The employed techniques are X-Ray Fluorescence (XRF) with energy dispersion (ED-XRF) and coupled with scanning electron microscopy (SEM-EDX), and X-ray Diffraction (XRD). Aspects concerning the limit of detection, the number of elements analyzed, matrix effects and spectral interferences in XRF, and its complementarity with other micro-analytical techniques are highlighted.*

Keywords: *X-ray microanalysis, XRF, XRD, SEM-EDX.*

1. Introduction

Knowledge of trace element content and microstructure of industrial materials is important for engineers and technologists working in various branches due to the fact that these parameters influence the properties of the final product. Many analytical techniques have been developed to investigate the micro-composition of materials with different uses and much attention has been paid to atomic and nuclear spectroscopic techniques which have the advantage of being multi-elemental and very sensitive for a large range of chemical elements. Among these techniques, X-Ray Fluorescence (XRF) with energy (ED-XRF) and wavelength-dispersion (WD-XRF) has been widely used in industrial and research laboratories for the analysis of a large variety of solid and liquid materials – raw and auxiliary materials, final products, by-products, environmental materials, nano-materials, etc. [1,2]. In this work are presented some applications of X-ray based methods XRF: X-ray diffraction (XRD) and scanning electron microscopy (SEM) with energy-dispersive X-ray microanalysis (EDX).

2. Experimental methods

The metallurgical samples have been taken from the technological flux of Iron and Steel Works (ISW) of Galati, Romania.

For ED-XRF analyses, a ^{238}Pu (3×36 mCi) radioactive source was used as primary excitation source and a detection geometry at 1.5 cm, the detection of X-rays being done with a Ge detector placed at 180° with respect to the incident beam, having an area of 1 cm^2 and a thickness of 7 mm, a beryllium window of 0.127 mm and the energetic efficiency of 220 eV at 6.4 keV. The calibration of the XRF spectrometer was done using a standard containing Cu, Ag, Pb and Au.

The SEM images of the investigated samples and the electron beam induced X-ray spectra have been obtained using the existing research infrastructure at "Dunarea de Jos" University of Galati, Romania, consisting of a scanning electron microscope of Quanta 200 FEI type, with EDX integrated system [2-4], having 5 detectors of secondary and backscattered electrons, 1 detector for transmitted electrons and software for: processing of data, quantification of chemical composition using correction algorithm of ZAF

(Z–atomic number, A–absorption, F–fluorescence) type, multi-point chemical analysis with matrix effects corrections and analysis of concentration profile along a defined line.

3. Results and discussion

By using wavelength-dispersive XRF analyzers in iron and steel industry laboratories (**Fig. 1**), a fast analysis is possible for major oxides (FeO, SiO_2, CaO, MgO, Al_2O_3, MnO) in metallurgical materials involved in ironmaking and steelmaking [1], which allows the regularization of the quantities of fluxing materials, the concentrations of different elements in metallic bath and the slag basicity index [5].

Besides the major oxides, by using energy-dispersive XRF, several microelements could also be determined in metallurgical samples at part-per-million (ppm) level.

Figure 1: *Preparation of homogenized samples and WD-XRF automatic analyzers used in iron and steel industry laboratories*

X-ray spectra obtained for some steel plate samples by the application of ED-XRF using radioisotope excitation reveal the existence of some minor elements in the steel matrix, such as K, Ca, Cr, Mn, Fe, Ni, Zn, Ga, As (**Fig.2**). The identification of chemical elements in the samples is based on the energies corresponding to the X-ray peaks in the spectra, using Moseley's law [1]. The energies (in keV) corresponding to the X-ray peaks in the spectra are presented in **Table 1**. Pb could be determined by ED-XRF using the interference-free line L_β, because the principal L_α line interferes with As-K_α.

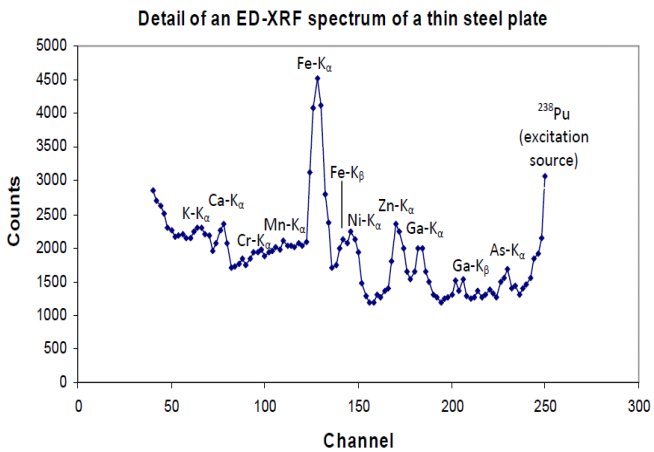

Figure 2: *ED-XRF spectrum of a steel sample irradiated with a ^{238}Pu radioactive source*

Table 1: *X-ray energies for the main peaks in the spectrum illustrated in Fig. 2, in keV*

Element	Z	K_α	K_β	L_α	L_β	L_γ
K	19	3.691	4.012			
Ca	20	4.510	4.030			
Cr	24	5.405	5.946			
Mn	25	5.898	6.490			
Fe	26	6.403	7.057			
Ni	28	7.477	8.264			
Zn	30	8.630	9.57			
Ga	31	9.251	10.263			
As	33	10.540	11.725			
Pb	82			10.549	12.611	14.76
U*	92			13.613	17.210	20.16

*U X-rays resulting from ^{238}Pu

Application of SEM-EDX for the investigation of micro-composition of steels and metallurgical slag allows the extension of the list of determined chemical elements in industrial samples (B, C, O, La, Ga, Mo, Pr, Rh, Na, K, Mg, Al, Ti, Si, V, P, Nd, Ca, Cr, Ni, Cu, Sm, Mn, Fe, Co, Zn), as could be seen from **Fig. 3**. This technique has also been extensively applied lately for the investigation of environmental and biological micro-objects in order to correlate the trace element compositional scheme with the distribution pattern of constituent particles and their shape in relation with different physical-chemical properties [2-4,6]. However, a greater number of trace elements could be analyzed in complex samples by coupling XRF with other nuclear analytical techniques such as neutron activation analysis (NAA) [1,2].

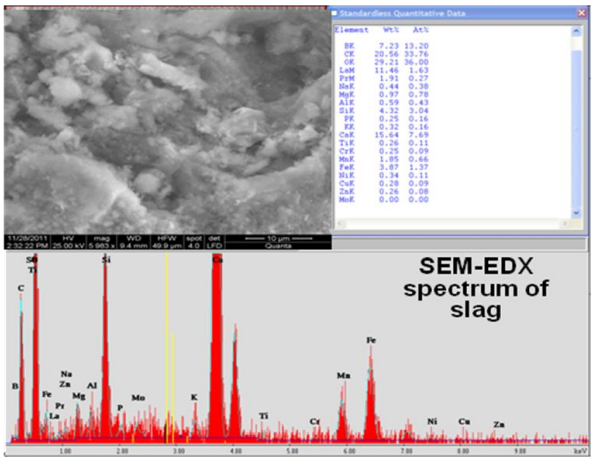

Figure 3: *Detail of the SEM-EDX spectrum of a slag sample*

XRD technique [7,8] can be employed for the evaluation of size and shape of amorphous and crystalline phases, dimensions of mosaic blocks, lattice parameters, texture, internal tensions, and density dislocations in different materials and by using advanced software for processing the XRD spectra, the automatic determination of phases and chemical compounds existing in inclusions is possible. A typical XRD diffractogram obtained with a DRON-3.0 diffractometer (Cu-K_α radiation) for a slag sample is presented in **Fig. 4**.

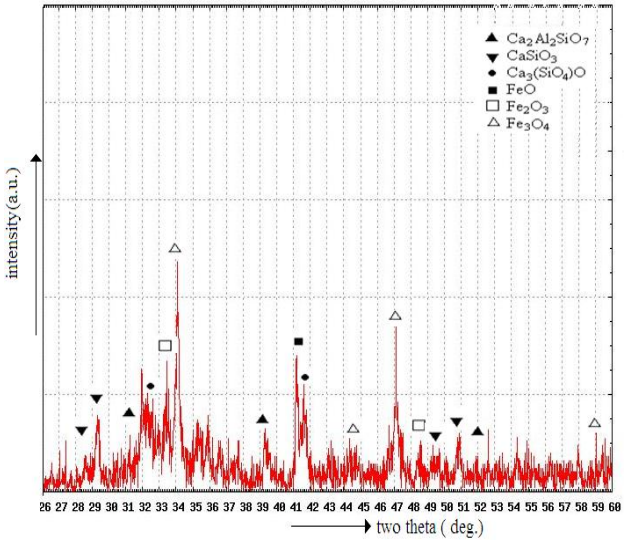

Figure 4: *Detail of the XRD diffractogram of a slag sample*

XRF and SEM-EDX could be applied for the characterization of high purity advanced materials such as lithium nitride [2,9] and cubic boron nitride [10] in combination with their structure characterization using imaging techniques (SEM,

XRD). Extended work will be carried out in the future for the investigation of micro-composition and microstructure of these advanced materials with special properties, used for hydrogen storage and various engineering purposes.

4. Conclusions

The complementarity of ED-XRF and SEM-EDX with instrumental neutron activation analysis (INAA) nuclear technique is discussed based on the performed analyses at "Dunarea de Jos" University of Galati (UDJG), Romania, and Frank Laboratory of Neutron Physics (FLNP) of Joint Institute of Nuclear Research (JINR) at Dubna, Russia, on metallurgical materials (slags) and environmental samples (soils).

The perspectives of applying XRF for the characterization of high purity advanced materials such as lithium nitride and cubic boron nitride in combination with their structure characterization using imaging techniques (SEM, XRD) are described.

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References

[1] Ene, A., *Tehnici radiometrice de analiză și control (Radiometric techniques of analysis and control; in Romanian)*, Editura Fundației Universitare Dunărea de Jos din Galați, Galați, 2006.

[2] Ene, A., Pantelica, A., Frontasyeva, M. and Cantaragiu, A., Nuclear and imaging techniques used in material sciences, 20th International Seminar on Interaction of Neutrons with Nuclei, "Fundamental Interactions & Neutrons, Nuclear Structure, Ultracold Neutrons, Related Topics" ISINN-20, Alushta, Ukraine, May 21-26, 2012, p. 100.

[3] Ene, A., Bosneaga, A., Georgescu, L., Cantaragiu, A. and Gogoncea, V., SEM-XRF analysis of soils from Lower Prut Meadow, 1st International Symposium on Applied Physics – Materials Science, Environment and Health, November 28-29, 2009, Dunarea de Jos University of Galati, Romania, Symposium Program, p. 18, 2009.

[4] Ene, A., *Scientific report - Project no. 72172/2008*, National Plan of Research PNCDI-2 (2008-2011), High precision and sensibility methods applied in the bio-monitoring networks of the environmental pollution with polluted factors in South, South-East and Central regions of Romania, 2010.

[5] Ivanescu, A., Ene, A., Ivanescu, L., Catana, C. and Doniga, A., Mathematical modelling of the refractory lining of the LD converter, 15th International Metallurgical & Materials Conference METAL 2006, May 23 – 25, Hradec nad Moravicí, Czech Republic, Proceedings on CD-ROM (150.pdf), 2006, pp. 1-6.

[6] Frontasyeva, M.V., Pavlov, S.S., Zinicovscaia, I.I., Kirkesali, E.I., Kalabegishvili, T.L., Murusidze, I.G, and Faanhof, A., Application of some microorganisms for synthesis of gold and silver nanoparticles. JINR Communications, E14-2012-4, Dubna, 2012, pp. 5.

[7] Gheorghies, C., *Analiza structurii fine a materialelor*, Ed. Cermi, Iasi, 2008.

[8] Gheorghies, C., Cantaragiu, A.M., *Fizica radiatiilor X. Aplicatii*. Ed. Cermi, Iasi, 2008.

[9] Ignatenko, O.V., Komar, V.A., Leonchik, S.V., Shempel, N.A., Ene, A., Cantaragiu, A., Frontasyeva, M.V., Shvetsov, V.N., Changes of nitrides characteristics in Li-N system synthesized at different pressures, JINR Preprint, D18-2012-102, Dubna, 2012, pp. 12 (in English and in Russian).

[10] Shipilo, V.B., Ignatenko, O.V., Shempel, N.A., Azarko, I.I. and Lebedev, S.A., Crystallization of cubic boron nitride in the system Li_3N–BN (4–10 wt % Li_3N), Inorg. Mater. 44(3), 2008, pp. 310-314.