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Neutron activation analysis of minor elements in deoxidized steel samples

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Abstract The capabilities of the nuclear method Neutron Activation Analysis (NAA) for the determination of minor and trace constituents of deoxidized steels have been investigated. The steel samples involved in the deoxidation stage of the steelmaking process in LD converter and steel standards were obtained from the Iron and Steel Works of Galati. Application of NAA technique followed by gamma spectrometry, has led to the identification of the following minor and trace elements in the iron matrix of the steel samples: Mn, Al, V, Cu, As, W, Cr, Ni, Mo, Co, Zr, Sb, Na, K, La, Ce, Sc, Sm, Zn, Ta, Te, Au, Hf, Se, Ga, Ba, Ir, Yb and Tb. A qualitative discussion is made regarding the transfer of some elements from raw materials to final steels.

Keywords: neutron activation, minor elements, environmental samples, metallurgical samples.

1. Introduction

Knowledge of the chemical composition of iron and steel materials involved in steelmaking process is important for the ferrous metallurgy and accurate methods of analysis must be used for this purpose. Trace and minor elements existing in the raw and intermediate materials can remain in steels as residual elements (some of them being beneficial and others not) and influence their properties, a well known fact [1]. Among the methods used for such analyses, neutron activation analysis (NAA) was applied for the determination of minor elements in iron and steel materials [2-4]. In previous papers we have applied thermal neutron activation analysis for the determination of the compositional scheme of different metallurgical materials [5-8] and environmental samples [9-13].

The purpose of this work was to determine the composition of minor elements of some final steel samples involved in the deoxidation stage of the steelmaking process in LD (Linz-Donowitz) converter. The first stage of this process is refining of the steel bath that is accomplished by the injection of oxygen which results in the oxidation of various elements present in the metallic bath. The main raw materials for the basic oxygen process are hot metal (cast iron) from the blast furnace and scrap. Deoxidation - the second stage of the steelmaking process - is applied in order to prevent the forming of the non-metallic inclusions as a result of the oxygen content increasing at the end of the refining. The traditional method of deoxidation is to add elements with a higher affinity for oxygen than that of iron to the liquid steel [1]. The most commonly used deoxidants are aluminium, coke, Si-Ca (and the ternary alloys Si-Ca-Ba, Si-Ca-Zr, Si-Ca-Ce etc) and the ferroalloys: Fe-Si, Fe-Mn, Fe-Cr, Fe-Ni, Fe-V, Fe-Ti, Fe-Co, Fe-W, Fe-Zr, Fe-Mo, Fe-Ta, Fe-Nb, Fe-Ce, Fe-Te etc. Some of the component elements of these ferroalloys are used in steel industry for alloying and micro alloying in order to improve the mechanical, chemical and physical properties of steels.

2. Experimental

NAA was applied to a set of deoxidized steel samples (DS1, DS2, DS3) involved in the steelmaking process in the Iron and Steel Works at Galati (Romania). The samples were taken from the LD converter charges. For a quantitative determination of elements the samples were simultaneously irradiated together with appropriate multi elemental standards such as British Chemical Standard No. 320, CRM No. 085-1, EOP [14], Al_2O_3 and metallic gold. The samples and standards were carefully weighed into small polyethylene vials

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which, in turn, were enclosed in another polyethylene vial for irradiation. They were irradiated in the rabbit system of the Nuclear Reactor of the Institute of Physics and Nuclear Engineering in Bucharest, at a neutron flux of 10^{12} $n.cm^{-2}$ s^{-1} for a period of 15 s for short-lived nuclides and 30 m or 2 h for long - lived nuclides. The cooling times of the short - lived nuclides were 2-8 m for Al and V and 2 h for Mn. For the long - lived nuclides counting were carried out at different decay times, ranging from 1 to 4 days, in order to best detect radio nuclides of various half lives. The counting system for the measurement of the induced radioactivity in the samples and standards consisted of a 130 cm^3 Ge(Li) ORTEC detector with an electronic amplification system and a 4096 multichannel analyzer CANBERRA coupled to a PC. The energy resolution of the system was 2.3 keV at 1.33 MeV of ^{60}Co. We used four source-detector distances (1 cm, 5 cm, 6 cm and 12 cm) for which the photo peak efficiencies of the detector were determined.

3. Results and discussions

The NAA spectrum of a deoxidized steel sample (DS2) is presented in **figure 1** and the gamma lines corresponding to the numbered peaks in the spectrum is given in **Table 1**. The minor and trace elements determined in the iron matrix of the steel samples were the following: Mn, Al, V, As, Cu, W, Ni, Mo, Cr, Sb, Co, Na, K, Ce, La, Sm, Sc, Zr, Zn, Au, Ga, Hf, Ta, Te, Se, Ba, Rb, Yb, Tb and Ir. The concentrations of the elements are given in **Table 2** and they are indicated in parts per million (ppm). The statistical error of counting does not exceeded 10 %. It was considered the possibility that other nuclides could contribute to the analysed peak. Corrections for interferences could easily be done as the relative intensities of lines emitted by the isotopes and the efficiency function of the detector were known. Only a qualitative analysis was made for Se, Ba, Rb, Yb, Tb and Ir. From Table 2 it can be seen that in the deoxidized steels remain some minor elements with beneficial influence upon steels properties: W, Mo, Cr, Mn, V, Al, Zr, rare earths (Ce, La, Sm), Ni, Co, Sb, Zn, Ta and Te.

Arsenic and copper are undesirable elements in steels [1, 5] and they remain in the final product – the deoxidized steel. The arsenic content of the analyzed steels exceeds the admissible value of 100 ppm. The alkali (Na, K) content of steels is small (with the exception of Na in sample DS3) because these elements generally pass in slag [5].

Also some trace elements were identified in steels, which came from the converter charge and cannot be removed from steels; they represent rare elements or noble metals existing in ores – Sc, Rb, Hf, Tb, Yb, Ir – or in ferroalloys – Au. Hafnium always exists in ores which contain zirconium and these two elements cannot be separated during the ferroalloys production because of their similar chemical properties. The role of the rare and noble elements upon steel properties was not sufficiently studied in literature but some of the identified elements (Ga, Au, Hf), besides Mo, Co, Zr and Zn, have beneficial effects upon the pitting corrosion resistance [1]. In the steel samples we couldn't identify the beneficial elements Ti and Nb because of the short half-lives of the radio nuclides resulted from thermal neutron activation; we mention that Nb and Ta have similar chemical properties and it is very probably that the steel samples contain Nb. Knowing the concentrations of the residual elements in the final steel, the steelmaking process in LD converter can be conducted so that the recuperation of the elements with favorable influence upon steel characteristics (Mn, Al, V, Cr, Ni, Mo, W, Ta, Te, Zr, Co, La, Ce, Sm) should be realized. As regards the undesirable elements for steel (As, Cu), they are transferred from the iron ores [5] to the deoxidized steel. Taking into account this fact it is very important to choose the appropriate proportions of iron ores which contain these elements in high concentrations.

4. Conclusions

The presented technique is known for its sensitivity, accuracy, precision, simplicity of target preparation and the ability to perform non-destructive multi-elemental analysis of a large number of samples, sometimes quickly, requiring small amounts of material.

From this work it results that by applying NAA technique, a very good overall picture of the elemental composition of a complex sample may be obtained.

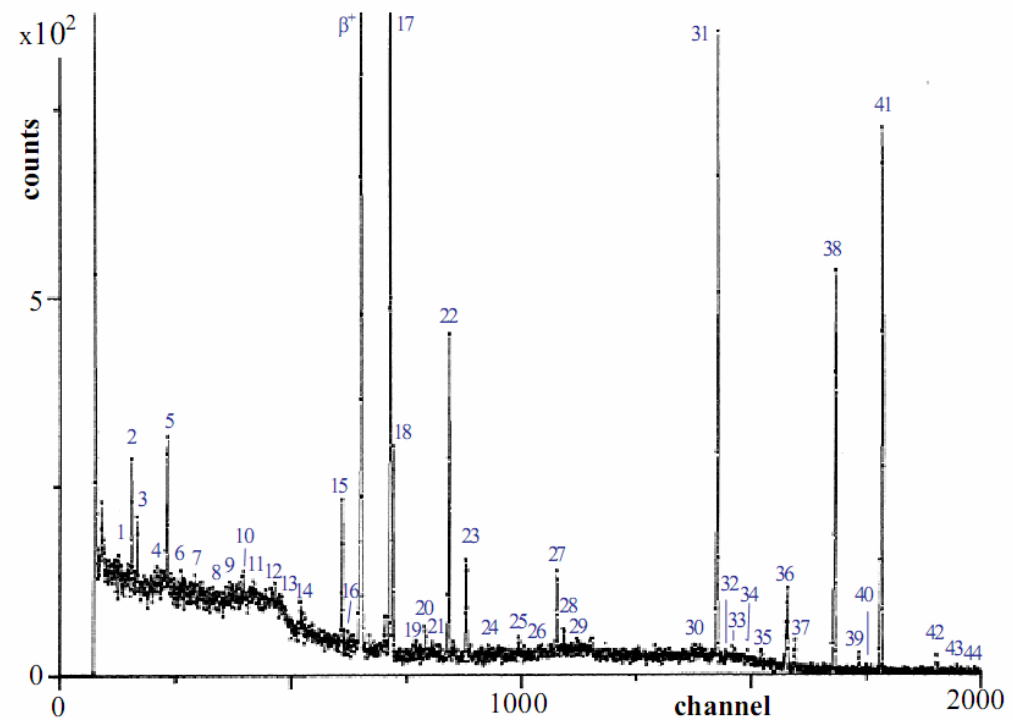

Fig.1. NAA spectrum of a deoxidized steel sample irradiated for 30 min.

Table 1. Gamma lines in the NAA spectrum of steel sample presented in Fig. 1

Peak no.	E_γ (keV)	Radioisotope	Peak no.	E_γ (keV)	Radioisotope	Peak no.	E_γ (keV)	Radioisotope
1	103	^{153}Sm	16	482	^{181}Hf	31	1099	^{59}Fe
2	134	^{187}W	17	559	^{76}As	32	1115	^{65}Zn
3	142	^{59}Fe	18	564	^{122}Sb	33	1120	^{46}Sc + ^{182}Ta
	145	^{141}Ce	19	603	^{122}Sb	34	1141	^{122}Sb
4	169	^{177}Yb	20	619	^{187}W	35	1172	^{60}Co
5	192	^{59}Fe	21	630	^{72}Ga	36	1216	^{76}As
6	210	^{192}Ir	22	657	^{76}As	37	1220	^{182}Ta
7	220	^{131}Ba	23	686	^{187}W	38	1292	^{59}Fe
8	264	^{75}Se	24	724	^{95}Zr	39	1332	^{60}Co
9	299	^{160}Tb	25	740	^{99}Mo	40	1345	^{64}Cu
10	320	^{51}Cr	26	811	^{58}Ni(n,p)^{58}Co	41	1368	^{24}Na
11	329	^{140}La	27	834	^{72}Ga	42	1460	^{40}K (background)
12	346	^{181}Hf		835	^{54}Fe(n,p)^{54}Mn	43	1528	^{42}K
13	364	^{131}Te(n,p)^{131}I	28	847	^{56}Mn	44	1596	^{140}La
14	412	^{198}Au	29	889	^{46}Sc			
15	479	^{187}W	30	1077	^{85}Rb			

Table 2. The concentrations of minor and trace elements in the steel samples, in ppm

El.	ppm element in deoxidized steel sample (mg)			El.	ppm element in deoxidized steel sample (mg)		
	DS1 (10.36)	DS2 (14.25)	DS3 (7.44)		DS1 (10.36)	DS2 (14.25)	DS3 (7.44)
Mn	14860±148	987±29	12125±121	**Na**	5±0.9	7±1	1894±18
Al	34±4	690±14	828±16	**K**	25±5	25±5	40±6
V	48±5	33±4	28±3	**La**	4±0.1	2.5±0.1	8±0.2
As	213±2	230±2	250±3	**Ce**	34±4	26±3	30±3
Cu	458±36	504±40	580±46	**Sm**	2.4±0.04	0.9±0,08	1.6±0.08
W	28±2	7±0.4	87±4	**Sc**	2.7±0.4	2.4±0.2	1.9±0.2
Ni	-	313±31	-	**Zn**	210±21	170±17	340±27
Mo	4400±130	1812±54	1169±35	**Au**	1.9±0.1	1.2±0.06	0.9±0.04
Cr	696±70	402±40	199±20	**Ga**	21±5	18±4.5	-
Sb	143±7	159±8	55±4	**Hf**	18±5	26±5	36±7
Zr	-	1800±60	2110±65	**Ta**	309±19	245±15	101±7
Co	146±4	136±3	58±2	**Te**	340±34	473±47	405±40

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