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To cite this article: I Jonczy 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **261** 012017

IOP Conf. Series: Earth and Environmental Science **261** (2019) 012017 doi:10.1088/1755-1315/261/1/012017

Forms of occurrence of selected alloying elements in slag from an electric arc furnace

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Abstract. The chemical composition of steel slag is dependent on the type of the charge and thus the alloying elements used in the process. The conducted tests of slag from an electric arc furnace have indicated that their chemical composition contains elements classified as so-called alloying elements – with the highest content of manganese and chromium. Besides these, smaller amounts of cobalt Co, molybdenum Mo, titanium Ti and tungsten W were identified. Due to the significant concentration of Mn and Cr, it was assumed that these elements were added to the alloy on purpose to achieve certain steel properties. The presence of Co, Mo, Ti and W may be related to the type of scrap introduced into the process. To determine what components of the slags are the analysed metals related with, phase composition tests of slag were conducted based on electron scanning microscopy and X-ray diffraction method. It was established that chromium occurs in the form of impurity in the solid solution of FeO-MnO-MgO, called the "RO phase" and forming characteristic dendritic forms. Wolfram, on the other hand, creates its own cryptocrystalline phases classified as tungstates: hübnerite and ferberite. The remaining metals, that is Co, Mo, and Ti occur in a dispersed state in the amorphous substance.

1. Introduction

Steel slags are characterized by a relatively variable chemical composition, which is related to the type of the technological process of its formation. To be more precise – it is related to the type of the charge materials and the additives introduced in the process.

Part of the elements constituting alloying elements may pass into the slag, creating substitutions in the internal structure of oxide phases (e.g. iron phases) or silicate phases (especially in calcium silicates). The elements may also occur in a dispersed state in the amorphous substance and rarely create their own crystalline phases [1, 2].

In steel slags, also metallic precipitates are present that were not separated from the alloy during the metallurgic process. In their chemical composition, the metallic iron is considerably dominant – its content may reach 80-90%. Besides iron, the precipitates may also contain impurities of other metals, i.e. the ones that are used as additives improving the properties of the produced steel. The presence of the metallic precipitates in the waste material raises special interest, as many ideas regarding the reuse of the wastes often include projects aimed at the recovery of metals from slags. Such attempts were made i.e. by researches from Korea, who studied silicomanganese slag. In such slag, 10 to 14% of mass may be constituted by Mn; at such a concentration of manganese it is well substantiated to find a method for the recovery of this element [3].

Based on the phase composition of slag from an electric arc furnace, this article exhibits which of the alloying elements may pass to the waste material and in what forms the elements occur in the slag.

2. Alloying elements – literature research

Most metal alloys contain alloying elements added to modify their properties what allow to used them for specific applications.

Additives called "alloying elements" are elements introduced to the alloy in small amounts to modify and improve its properties. Among others, these elements include: chromium Cr, manganese Mn, molybdenum Mo, titanium Ti and tungsten W.

Chromium is the 13th most abundant element in the Earth's crust, with an average concentration (clarke) of the order of 400 ppm. Chromium increases the hardenability of steel, heat and high-temperature creep resistance; moreover it improves the resistance of steel to corrosion. All these properties cause the addition of chromium to be used in tool, structural and special steel (stainless and heat resistant). The content of chromium in the alloy also positively impacts the resistance of steel to oxidizing acids such as sulphuric acid. Due to its strength and its resistance to corrosion, chromium is used in plating and metal finishing [4, 5, 6, 7, 8].

Cobalt is 30th in order of abundance in the Earth's crust, its clarke achieves 20 ppm. Cobalt improves the fine-grained structure of steel and highly improves its hardness; it is the only element that decreases the hardenability of steel [8, 9].

Manganese is the 12th most abundant element in the Earth's crust, with an average concentration (clarke) of the order of 1,100 ppm. Manganese increases the mechanical strength, hardness and hardenability of steel; moreover, manganese steel is characterized by a higher elasticity threshold and higher resistance to abrasion. An addition of manganese prevents cracking in hot working. Manganese is important to steel making because of following properties: its ability to combine with sulphur and its deoxidation capacity. Mn is added into steel in order to eliminate noxious sulfur by forming MnS inclusions. Mn in steel stabilizes austenite and it has a higher solubility in austenite than in ferrite [8, 9, 10, 11, 12]. For example, TWIP steels are a family of high-Mn austenitic steels having both high strength and high ductility used as automotive-body steels [13].

Molybdenum is in 38th position in the Earth's crust with an average concentration of 15 ppm. Molybdenum increases hardenability and strength of steel, increases creep resistance and improves resistance to high temperatures. It also positively impacts the weldability and increases the resistance to hydrogen and hydrogen sulphide. The high melting point of molybdenum makes this element very important for giving strength to steel and other metallic alloys at high temperatures. Molybdenum is also added to metallic alloys because of its resistance to corrosion [8, 9].

Titanium is the 9th most abundant element in the Earth's crust, with an average concentration of the order of 6,000 ppm. Titanium is an element exhibiting propensity to form carbides. A slight addition of that element to the steel alloy decreases the amount of carbon dissolved in austenite. Due to these properties, titanium serves as an addition in stainless, acid-resistant and heat-resistant steel, where it prevents intercrystalline corrosion [8, 9, 12, 14].

In the earth's crust, clarke of tungsten achieves concentration of 1.25 ppm. Tungsten impacts the fine-grained structure of steel, increases its strength and resistance to abrasion. Steel with an increased tungsten content is resistant to the tempering activity of heat, thus maintaining high hardness up to the temperature of 600°C. In steel, tungsten forms carbides that are extremely hard and resistant to abrasion and thus the element is the basic addition to high-speed steel and certain tool steel types [6, 8, 9, 15].

3. Research methods

The scope of the study encompassed steel slag from a current production using an electric arc furnace. Tests were conducted for 4 samples acquired in subsequent production cycles.

The tests of the chemical composition were conducted in Activation Laboratories Ltd. – ACTLABS in Canada using the ICP/MS method.

Tests using electron scanning microscopy were conducted in the Scanning Microscopy Laboratory of the Institute of Biological and Geological Sciences, Faculty of Biology and Earth Sciences at the Jagiellonian University (Laboratory at the Institute of Geological Sciences). A HITACHI S-4700 Field Emission Scanning Electron Microscope equipped with NORAN Vantage EDS (Energy Dispersive Spectroscopy) analysis system was used in the tests. An accelerating voltage of 20 kV was used, while the counting time of each analysis was 100 s. YAG BSE backscattered electron images were taken for thin samples and secondary electron SEM images were taken for bulk preparations. Prior to the test, the preparations were dusted with carbon.

The identification of phases using X-ray diffraction was conducted in the Silesian Centre for Education and Interdisciplinary Research in Chorzów using an Empyrian diffractometer manufactured by Panalytical, equipped with a cobalt lamp. The voltage was 40 kV while the current intensity was 30 mA.

4. Results

The tests of the chemical composition have exhibited that the percentages of each of the components in the analyzed slag samples are similar. In a vast majority of samples, iron (mean of 31.35%) and calcium (mean of 15.48%) were dominant. The remaining components according to average content were as follows: silicon (5.22%), magnesium (2.29%), aluminum (2.04%) as well as barium (0.118%), phosphorus (0.173%) and sulphur (0.08%) and the others; in total, the presence of 60 elements was determined in the slags [16]. These were also accompanied by metals included in the so-called group of alloying elements, the content of which has been presented in table 1.

Table 1. Concentration of selected alloying elements in slag from an electric arc furnace [16].

Alloying element	No. of sample / content [ppm]				Average content [ppm]
	1	2	3	4	
Cr	>5.000	>5.000	>5.000	>5.000	5.000
Co	4	3	4	5	4
Mn	>10.000	>10.000	>10.000	>10.000	10.000
Mo	42	45	49	43	45
Ti	2.070	2.120	1.670	1.610	1.868
W	148	138	185	181	163

The content of metals in slag is variable; the highest amounts were exhibited by manganese, the content of which exceeded 10,000 ppm in all samples, as well as chromium, which exceeded 5,000 ppm. Besides, titanium and tungsten were found; molybdenum and cobalt have been exhibited in smaller contents.

To determine the forms of occurrence of the elements referred to above, an analysis of the chemical composition of each of the components constituting the slag was conducted using electron scanning microscopy – figure 1 and 2, table 2 and 3.

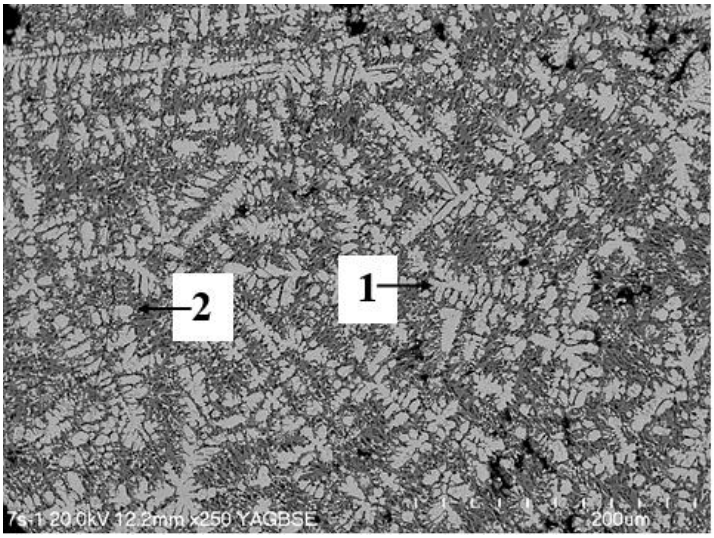

Figure 1. Microphotography of slag – example 1.

Table 2. Chemical composition of slag components; according to figure 1.

Oxide	No. of analysis point / content [%]	
	1[a]	2[b]
SiO_2	0.40	17.81
Al_2O_3	1.16	24.48
CaO	1.26	39.85
MgO	8.88	0.68
FeO	79.03	12.43
MnO	6.99	1.33
TiO_2	0.00	1.76
Cr_2O_3	2.28	0.00
MoO_3	0.00	1.12
BaO	0.00	0.54

[a] FeO-MnO-MgO solid solution
[b] amorphous substance

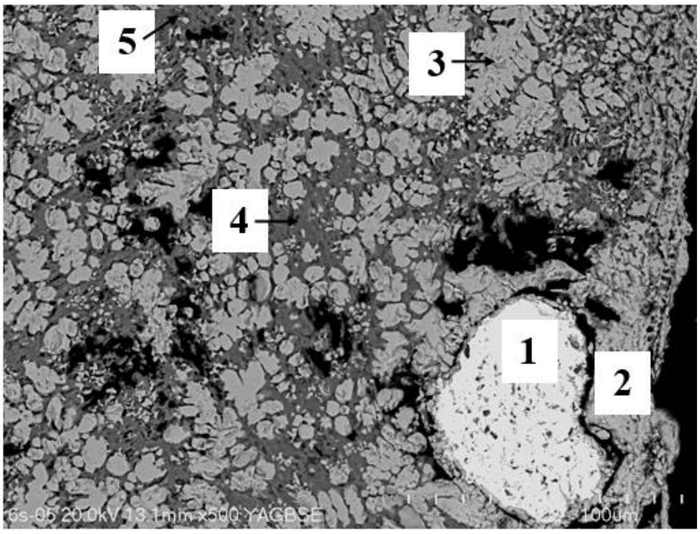

Figure 2. Microphotography of slag – example 2.

Table 3. Chemical composition of slag components; according to figure 2.

Oxide	No. of analysis point / content [%]			
	2[a]	3[b]	4[c]	5[d]
SiO_2	0.18	0.25	22.73	17.84
Al_2O_3	0.34	2.58	15.91	22.66
CaO	0.30	0.73	10.72	38.34
MgO	1.20	8.31	1.59	0.00
FeO	96.97	78.10	13.58	14.34
MnO	0.66	6.24	1.68	1.48
TiO_2	0.00	0.00	1.42	1.65
Cr_2O_3	0.00	3.80	0.00	0.00
CoO	0.00	0.00	0.19	0.00
MoO_3	0.00	0.00	0.00	0.12
BaO	0.00	0.00	0.00	0.00
P_2O_5	0.00	0.00	0.71	0.31
SO_3	0.34	0.00	1.48	3.25

[a, b] FeO-MnO-MgO solid solution
[c, d] amorphous substance
Point No. 1 according to figure 2 – drop of iron (Fe 99.85%)

Observations using electron scanning microscopy have exhibited that in the structure of the analyzed slags, the oxide phase in the form of dendrites is dominant. Besides the oxide phase, accumulations of metallic iron occur in the form of globular precipitations with variable dimensions; amorphous substance occurs between these components.

The study of the chemical composition of the dendrites has shown that they are represented by a solid solution of three oxides: FeO, MnO and MgO. In all the conducted analyses, it was found that FeO is dominant in the solution (80–90%), while the remaining oxides (MnO and MgO) occur in smaller amounts. The content of each of the oxides was usually around up to 10%. The chemical composition of dendrites also contained impurities of other elements, i.e. calcium and aluminum. Moreover, the presence of chromium was found (figure 1, table 2, point 1; figure 2, table 3, point 3).

Microphotographs 3 and 4 exhibit the characteristic dendritic forms. Also the direction of the growth of crystals along the pores in the slag may be observed.

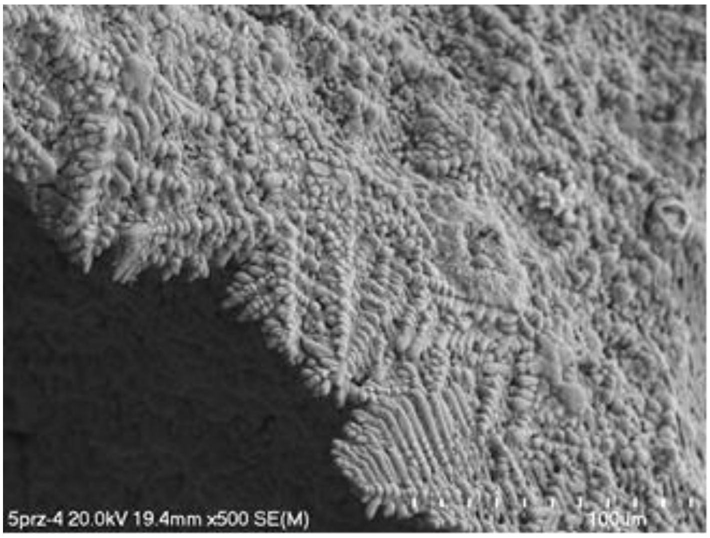

Figure 3. Dendritic forms of Fe-MnO-MgO solid solution; SEM image, electron scanning microscopy.

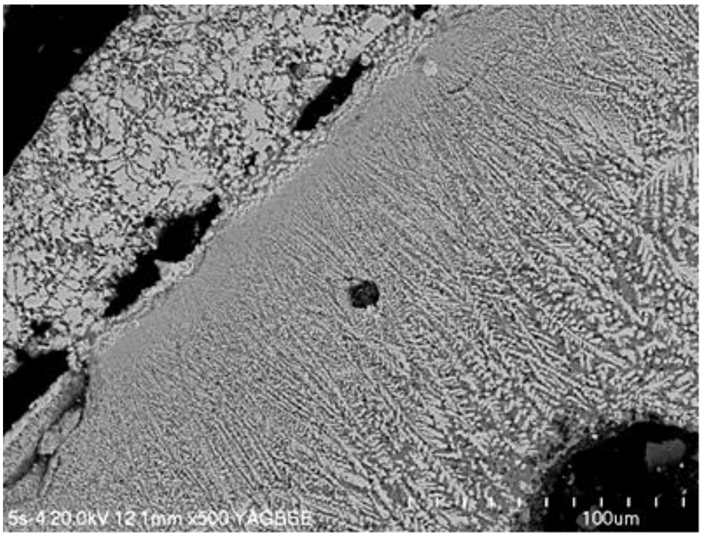

Figure 4. Dendrites growing around the pores; BSE image, electron scanning microscopy.

A solution with the formula (Fe,Mn,Mg)O was described in 1957 by Russian scientists [17]. It was named “the RO phase” and was determined to be one of the dominating components of slag from steel production, especially slag from electric arc furnaces and O.H. furnace slag. Besides the three oxides: FeO, MnO, MgO dominating in the chemical composition of the solution, also the possibility of occurrence of impurities was indicated, mostly CaO. Moreover, the dendritic or skeletal formations that are characteristic to that solution were noted.

Among crystalline phases, besides the RO phase containing Mn and Cr, the presence of cryptocrystalline forms related to tungsten phases was confirmed. Their identification in microscopic observations was largely hindered. Only the tests using X-ray diffraction have exhibited the presence of manganese tungstate (hübnerite $MnWO_4$) and iron tungstate (ferberite $FeWO_4$) – figure 5; as also wustite FeO and polymorphic forms of calcium silicate of the formula $Ca_2[SiO_4]$ – larnite and

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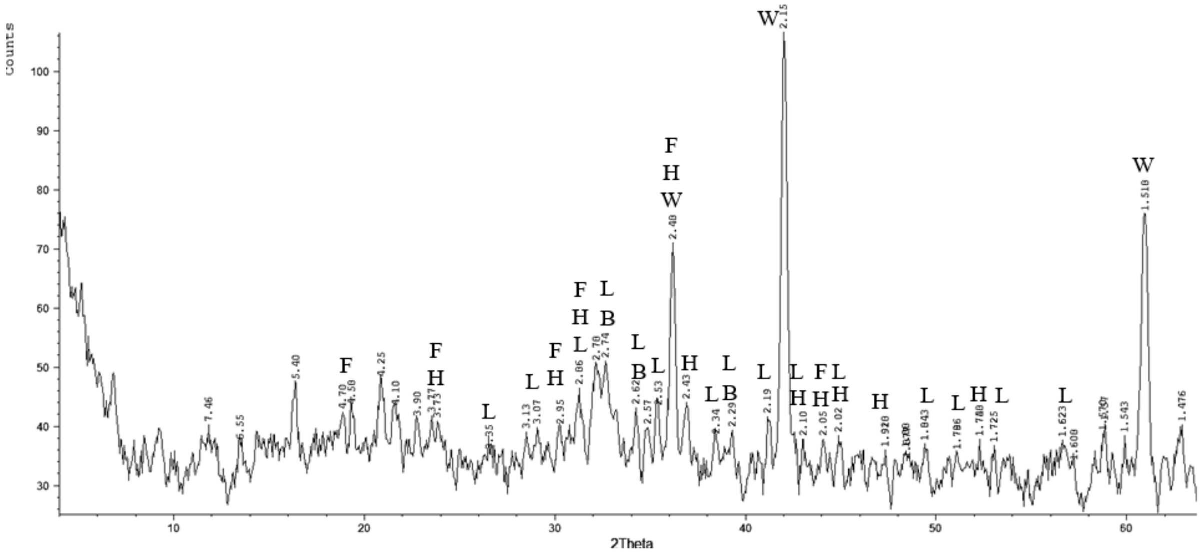
bredigite. These silicate phases were not identified during microscopic observations due to their cryptocrystalline form.

The remaining analyzed elements, that is Co, Mo and Ti are highly dispersed in the amorphous substance (figure 1, table 2, point 2; figure 2, table 3, points 4, 5).



Explanations: F – ferberite, H – hübnerite, B – bredigite, L – larnite, W – wustite

Figure 5. X-ray diffraction pattern of analyzed slag.

Among the slag components in concern, in a single analysis, the presence of metallic precipitation was found in which the content of Fe reached 99.85% (figure 2, point 1).

5. Discussion

The chemical composition of the studied slag from an electric arc furnace reflects the technological processes in the production plant. The presence of metals is related to the type and thus the composition of the charge, the basis of which is remelted scrap.

It has been noted that the slag contains elements classified as the so-called alloying elements, that is, elements introduced in the process to give certain qualities to the produced steel. The elements that were identified include: Cr and Mn as well as Co, Mo, Ti and W. The content of Cr and Mn in all samples reached a value over 5,000 ppm and 10,000 ppm, respectively. Most likely, these elements were introduced to the alloy on purpose as alloying elements. The remaining metals occur in smaller amounts and it may be presumed that their presence in the waste material is related to the scrap added to the charge.

The form of the phase components was found to be interesting in the slag in concern. The components mostly occur in the form of dendrites constituting an aggregate of fine crystallites with a fractal structure. The presence of dendritic forms in slag testifies of an interrupted growth process – most likely due to the rapid cooling of the slag. In conditions of slow cooling, the dendrites grow until the moment of their mutual contact, which inhibits their further growth. Subsequently, the space between dendrites is filled with the solidifying metal. At the final stage, the dendrites assume the form of grains which grow in all directions until the liquid is completely depleted [5].

The shape of the growing crystals depends on the rate of cooling – figure 6 presents the diagram of growth of dendritic forms including a microphotograph of dendrites crystallized in the slag in concern.

The rapid growth of a crystal from point 1 to 2 due to the intensive release of the latent heat of solidification, is inhibited at a certain point. As a result, the temperature rises and the supercooling locally fades right before the crystallization front. The crystal starts to grow in another direction in a location of sufficient supercooling, e.g. from point 3 to 4. If the heat was dissipated and supercooling occurred again in point 2, the growth of the crystal may continue from point 2 to 5 [5]. Such a classic growth of dendrites was noted in the analysed slag; moreover, it was observed that the individual branches of dendrites may grow in 4 directions from a common center – figure 6, 7.

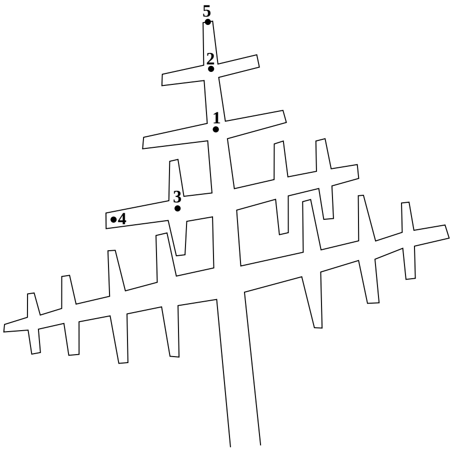


Figure 6. Schema of the growth of dendritic crystals – own sketch according to Głowacka 1996 [5].

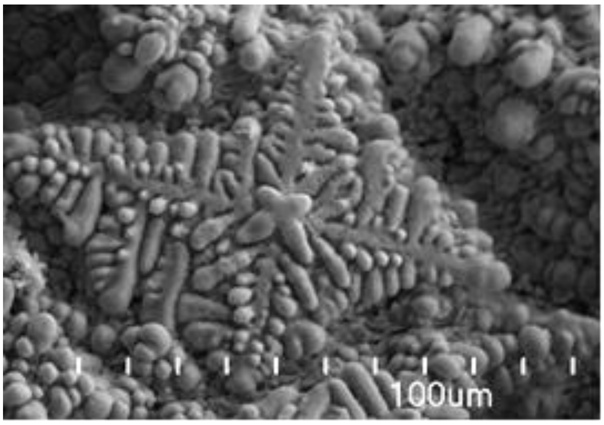


Figure 7. SEM image of dendritic crystals of FeO-MnO-MgO solid solution in analyzed slag.

Dendrites occurring in the studied slags represent the FeO-MnO-MgO solid solution containing also impurities, e.g. CaO and Cr_2O_3. This solution is a common component of slag from electric furnaces and is called the "RO phase". It usually occurs in dendritic or skeletal forms [17]. Dendritic forms are often found in various kinds of alloys. Experiments conducted by Dündar [18] for copper nickel alloy have shown that the growth of dendrites and the level of dendritic segregation of components of an alloy is mostly influenced by the temperature of alloy solidification.

The identification of phases using X-ray diffraction exhibited that tungsten creates its own crystalline phases. Due to their cryptocrystalline form, these were not identified during microscopic observations. The presence of hübnerite $MnWO_4$ and ferberite $FeWO_4$, which constitute an entire series of solid solutions constituting the main mineral of tungsten – wolframite (Fe,Mn)[WO_4], was exhibited. The structure of the solid solution consists of distorted tetrahedral (WO_4) groups and octahedral groups – (Fe,Mn)O_6. The percentage of WO_3 is 76.3 in ferberite and 76.6 in hübnerite. In natural conditions, secondary tungsten minerals constitute a group without mutual crystallographic relations, mostly at the cost of the primary tungsten minerals, e.g. the scheelite. The minerals constitute fine-grained agglomerations and – as in the studied slag – are difficult to characterize in mineralogical terms [19, 20].

6. Conclusions

The following conclusions were made based on the conducted research:

- The highest contents in the slag from an electric arc furnace in concern was exhibited by Fe (mean of 31.35%) and Ca (mean of 15.48%). The remaining elements included: Si, Mg, Al, Ba, P and S as well as metals classified as alloying elements: Cr, Co, Mn, Mo, Ti and W.
- Among the alloying elements, Mn (>10,000 ppm) and Cr (>5,000 ppm) occurred in the highest concentrations. The remaining metals occurred in significantly lower concentrations. It may be assumed that Mn and Cr were added to the alloy on purpose to achieve certain

qualities of steel, while the presence of Co, Mo, Ti and W is related to the charge material, namely the type of scrap that was introduced in the steel production process.

- Tests using electron scanning microscopy have exhibited that the phase composition of slags includes an oxide phase with characteristic dendritic forms represented by the FeO-MnO-MgO solid solution with impurities of Cr_2O_3.
- The identification of phases using the X-ray diffraction method has proven that tungsten creates own cryptocrystalline phases classified as manganese tungstate (hübnerite $MnWO_4$) and iron tungstate (ferberite $FeWO_4$). These phases form a solid solution under the general name of wolframite (Fe, Mn)WO_4.
- The metals Co, Mo and Ti do not form their own crystalline phases or impurities in the structure of other phase components of slags. These elements are only dispersed in the amorphous substance.

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