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A R C H I V E S O F M E T A L L U R G Y A N D M A T E R I A L S
Volume 59 2014 Issue 2
DOI: 10.2478/amm-2014-0079

I. JONCZY*

DIVERSIFICATION OF PHASE COMPOSITION OF METALLURGICAL WASTES AFTER THE PRODUCTION OF CAST IRON AND CAST STEEL

ZRÓŻNICOWANIE SKŁADU FAZOWEGO ODPADÓW HUTNICZYCH PO PRODUKCJI ŻELIWA I STALIWA

Basing on mineralogical studies, the characteristic of phase composition was carried out with respect to slags after the production of cast iron and wastes from casting moulds after the production of cast steel. Their composition is dominated by glaze, metallic precipitations and oxide phases, e.g. wustite, and they contain a considerably smaller amount of silicate phases represented by olivines, fayalite or fosterite. These wastes are characterized by different phase composition or chemical composition which depends on the technological process and charge material.
Keywords: metallurgical wastes, cast iron, cast steel, phase composition

W oparciu o badania mineralogiczne dokonano charakterystyki składu fazowego żużli po produkcji żeliwa oraz odpadów z form odlewniczych po produkcji staliwa. W ich składzie dominuje szkliwo, wytrącenia metaliczne oraz fazy tlenkowe np. wüstyt, w znacznie mniejszych ilościach występują w nich fazy krzemianowe reprezentowane przez oliwiny: fajalit lub forsteryt. Odpady te charakteryzują się odmiennym składem fazowym i chemicznym, który jest zależny od procesu technologicznego oraz rodzaju materiału wsadowego.

1. Introduction

The wastes generated at steelworks include blast furnace slags, steel slags, scale, scrap metal as well as dusts and slurry. Considering all wastes, slags make up one of the most numerous and diversified groups. Their chemical and phase compositions depend on the applied technology and the type of metallurgical charge [6, 7].

In the mineral composition of metallurgical slags we can single out glaze, metallic clusters and phase components: oxides and silicates. Their share in particular types of slags is variable. A different phase composition is attributed to e.g. steel slags and blast furnace slags. A lot of slag components contain the same silicate phases, e.g. pyroxenes or olivines, but their chemical composition can be variable, dependant on the chemistry of slag alloy from which they crystallized, and they can contain in their structure the substitutions of elements which are not encountered in crystallizing minerals in natural conditions. Due to this variability of chemical and phase composition, we can not apply generalized opinions with respect to metallurgical slags. Each of their types should be treated individually and each of them should be subjected to separate research studies.

Metallurgical slags, being one of more numerous groups of industrial wastes, have been investigated in terms of their reuse, impact on the environment and revitalization of areas which serve presently as waste dumps. The carried out research studies have demonstrated that most of the metallurgical slags, in particular the ones after the production of steel, are characterized by favourable engineering properties which determine their application as raw material for the production of aggregates. There are attempts in progress currently to return the slags to metallurgical processes and to carry out their utilization through the reduction with carbon reducers. Works on the utilization are also carried out for other types of metallurgical wastes, e.g. so called scrap metal [2, 8, 9].

Due to a wide applicability potential of metallurgical wastes, it is necessary to subject them to detailed investigation studies, which would ensure their economic and environmentally safe use. A lot of information on metallurgical wastes can be obtained through the analysis of their phase composition. It involves among others in what forms the metals occur in slags, substitutions of elements in crystalline networks of phases, resistance to the weathering of particular phase components and the possibility to liberate metals from them [3, 4, 5, 10].

In the paper we characterized and compared the phase composition of two types of metallurgical wastes, being the side effect products of technological processes realized at that steelworks. The first one was made up by slags after the production of cast iron, and the second one was made up by the remains – scrap metal from casting moulds after the production of cast steel, which could potentially be returned to the metallurgical process.

* SILESIAN UNIVERSITY OF TECHNOLOGY, FACULTY OF MINING AND GEOLOGY INSTITUTE OF APPLIED GEOLOGY, AKADEMICKA 2A STR., 44-100 GLIWICE, POLAND

2. Research methods

Chemical composition of slags was shown on base mass spectroscopy. Researches were made in Activation Laboratories Ltd. – ACTLABS in Canada.

The following methods were used for determination of mineral composition of wastes: microscopy analysis in reflected light, X-ray analysis and Scanning Microscopy.

Microscopy analysis in reflected light was carried out at the Institute of Applied Geology of the Faculty of Mining and Geology of the Silesian University of Technology using the microscope AXIOPLAN 2 of the firm ZEISS for the research in transmitted light and reflected light. In the same Institute the X-ray analysis was made using the X-ray diffractometer with HZG-4 goniometer, high-voltage generator – IRIS-3 and X-ray tube with copper anode.

The research with the application of scanning microscopy was carried out at the Scanning Microscopy Laboratory of Biological and Geological Sciences of the Department of Biology and Earth Sciences of the Jagiellonian University (Laboratory at the Institute of Geological Sciences). For the research we applied a scanning electron microscope with field emission HITACHI S-4700, furnished with the EDS analysis system (energy dispersion spectrometry) NORAN Vantage.

3. Results

The slag after the production of cast iron is fine-grained and is characterized by black color, it is porous and it crumbles easily. The waste after the production of cast steel is semi-crystalline (Fig. 1).

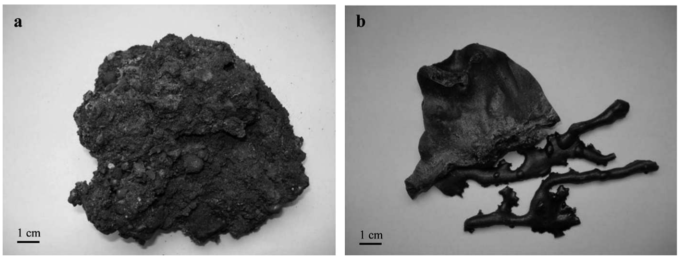


Fig. 1. Metallurgical wastes after the production of: a) cast iron, b) cast steel

In the investigated metallurgical wastes some amounts of metals were noticed (Table 1).

As demonstrated by the research on phase composition of the wastes after the production of cast iron and cast steel, their basic component is glaze, and then there are also metallic precipitations, oxide phases and small amount of silicate phases. Wastes come from the current production of the steelworks and they have not been subjected to dumping, and hence to the impact of external factors, their phase components are well preserved and they do not show any symptoms of weathering.

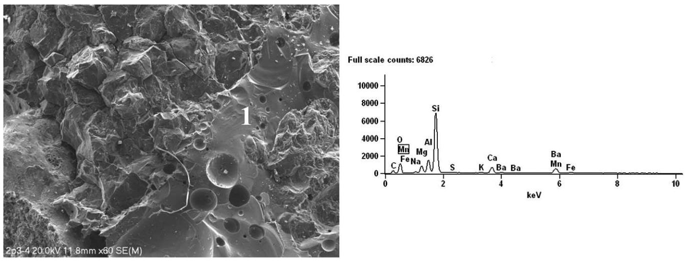
The microscope tests have demonstrated that the glaze has smooth, uncracked surface. In both investigated types of wastes we can observe in the glaze the presence of metallic precipitations and fine nucleating agents of silicate or oxide phases.

TABLE 1

Concentration of metals in metallurgical wastes

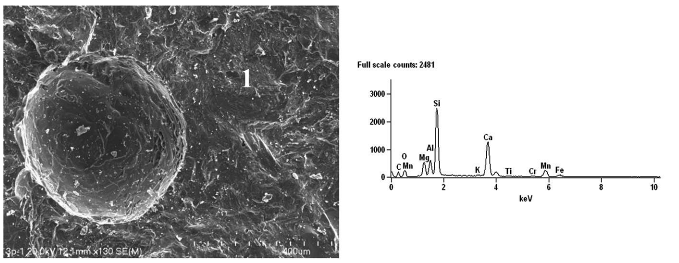
Element		Wastes after the production of	
		cast iron	cast steel
Fe	[Mass%]	16,40	1,59
Mn	[Mass%]	>1,0	>1,0
Ti	[Mass%]	0,128	0,126
As	[ppm]	3,5	1,9
Cd	[ppm]	0,2	0,8
Cr	[ppm]	1260	1770
Co	[ppm]	9,6	1,7
Cu	[ppm]	110,0	67,7
Ni	[ppm]	57,3	43,5
Pb	[ppm]	7,2	35,5
V	[ppm]	10	142
Zn	[ppm]	29,9	57,5

The dominant component of chemical composition of glaze is silica. But the concentration of silica in the slag after the production of cast iron is much higher (62,04% of SiO_2) then the concentration in the waste after the production of cast steel – 47,07% of SiO_2 (Fig. 2, 3).



Oxide [Mass%] – point 1											
SiO_2	TiO_2	Al_2O_3	Cr_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	SO_3	BaO
62,04	-	11,03	-	1,79	10,38	6,32	5,37	1,22	0,36	0,65	0,85

Fig. 2. Glaze of slag after the production of cast iron (SEM, EDS spectrum with chemical analysis)



Oxide [Mass%] – point 1											
SiO_2	TiO_2	Al_2O_3	Cr_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	SO_3	BaO
47,07	0,29	8,97	0,58	1,34	9,23	9,48	22,75	-	0,28	-	-

Fig. 3. Glaze of waste material after the production of cast steel (SEM, EDS spectrum with chemical analysis)

Apart from silica, the glaze from the wastes after the production of cast iron contains 11,03% of Al_2O_3, 10,38% of MnO, 6,32% of MgO, 5,37% of CaO with the admixture of iron, sodium, potassium, barium and sulfur oxides. The glaze from the wastes after the production of cast steel as compared to the glaze from the slag after the production of cast iron contains higher amount of CaO (22,75%). The oxides of Al, Fe, Mn, Mg, K occur in comparable amount, and the oxides of Na, Ba or sulfur compounds were not found. Yet this glaze contains small admixtures of chromium and titanium oxides.

The glaze contains metallic precipitations in the form of round, single droplets or microcrystalline aggregates. They also form aureoles around the pores brought about during the cooling of slag alloy. They are characterized by high reflexivity (above 60%), and it was found that they are almost pure droplets of iron (Fig. 4, 5).

Around some metallic aggregates we can observe places coloured in yellow, which can bespeak of the accumulation of pyrite.

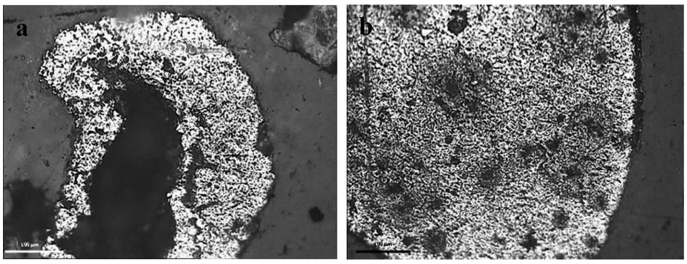


Fig. 4. Slag after the production of cast iron: a) pore surrounded by metallic aggregates, b) metallic aggregate; reflected light, magnification 100x, one nicol

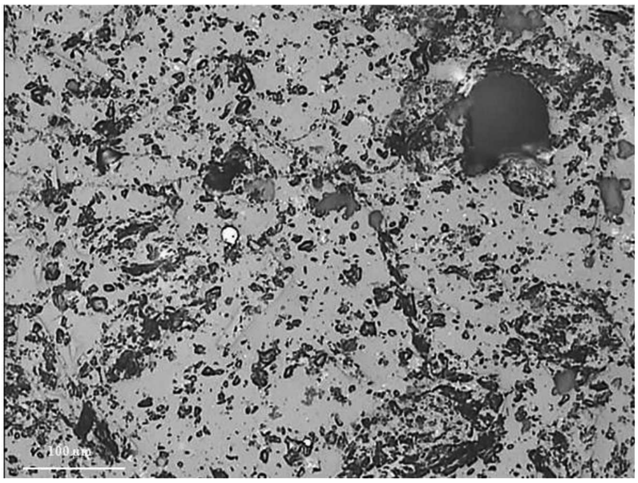
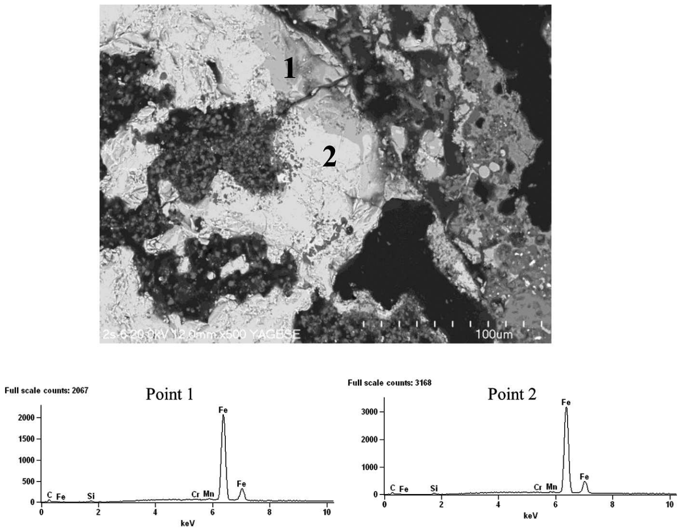
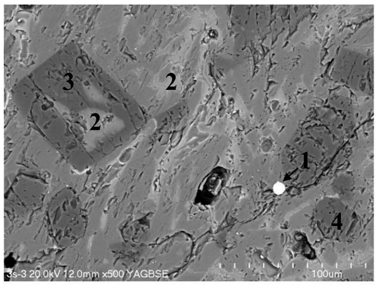


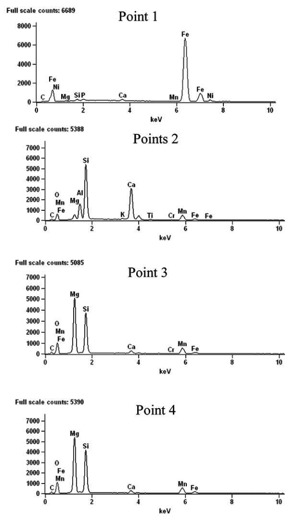
Fig. 5. Waste after the production of cast steel; metallic precipitations (with high reflexivity) and fine crystallites in glaze; reflected light, magnification 100x, one nicol



Element [Mass%]	Point 1	Point 2
Si	0,37	0,41
Cr	0,39	0,19
Fe	97,95	98,92
Mn	1,29	0,48

Fig. 6. Microphotography of slag after the production of cast iron (BSE, EDS spectrums, with chemical analyzes); points: 1, 2 – metallic precipitations





Element [Mass%]	Point 1
Si	0,63
Fe	94,14
Mn	0,34
Mg	0,44
Ca	0,42
Ni	3,39
P	0,64

Oxide [Mass%]	Points 2	Point 3	Point 4
SiO_2	46,83	40,86	41,93
TiO_2	0,38	-	-
Al_2O_3	11,88	-	-
Cr_2O_3	0,32	0,22	-
FeO	1,12	1,50	1,48
MnO	9,09	10,52	9,99
MgO	4,13	44,84	44,83
CaO	25,97	2,06	1,77
K_2O	0,28	-	-

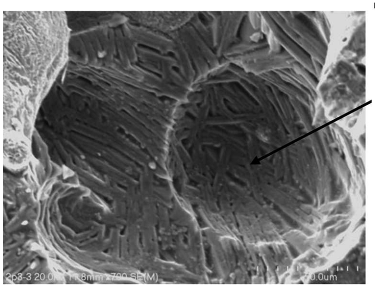
Fig. 7. Microphotography of waste after the production of cast steel (BSE, EDS spectrums, with chemical analyzes); points: 1 – metallic precipitation, 2 – glaze, 3,4 – olivine (forsterite)

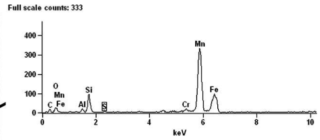
In the chemical composition of metallic precipitations, the share of iron was determined as dominant, above 90% of Fe (Fig. 6 points 1, 2; Fig. 7 point 1). In the wastes after the production of cast iron, metallic phases were enriched with Mn (0,48-1,29%) and also with Si and Cr. And in the wastes after the production of cast steel, the admixture in metallic precipitations was made up by Ni (3,39%) and P, Si, Mg, Ca, Mn (without oxygen).

The investigated wastes, apart from glaze and metallic precipitations, contain also considerably smaller amounts of oxide and silicate phases.

In the slags after the production of cast iron we also found solid solution of FeO-MnO with the admixture of SiO_2 and the other oxides (Fig. 8). The solid solution frequently contains also the admixture of MgO, and then it is referred to by Bielankin et al. [1] as "phase RO". The quantitative ratio of particular oxides of the solution can be variable due to the unlimited possibility of reciprocal substitution of Fe, Mn and Mg, which are characterized by roughly the same ionic radius. In the investigated slags, the share of manganese oxide is dominant.

The phase RO was also found in steel slags, where this phase was assuming the characteristic skeletal shape interlaid with dicalcium silicate [5]. In the investigated slags this phase forms radially arranged structures made from fine slats. They frequently fill up the pores made during the cooling process of slag alloy.

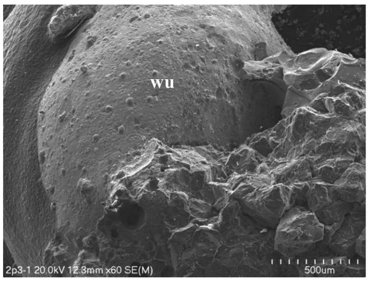


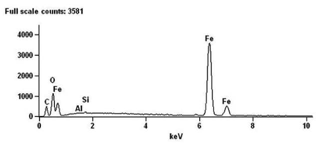


Oxide [Mass%]	
SiO_2	10,90
Al_2O_3	1,44
Cr_2O_3	0,85
FeO	15,75
MnO	70,45
SO_3	0,61

Fig. 8. Solid solution of FeO-MnO crystallized in pore of slag after the production of cast iron (SEM, EDS spectrum with chemical analysis)

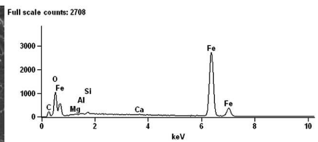
Both investigated wastes contained wustite of the characteristic globulin forms (Fig. 9, 10). Globules are formed when wustite is created in effect of metallic iron oxidation (it assumes then the form of reduced component). They are also characteristic for the alloy which is heavily enriched in iron in which also the liquid silicate phase is present [11].





Oxide [Mass.%]	
SiO_2	0,75
Al_2O_3	0,55
FeO	98,11
MnO	0,58

Fig. 9. Globule of wustite (wu) in slag after the production of cast iron (SEM, EDS spectrum with chemical analysis)



Oxide [% mas.]	
SiO_2	1,23
Al_2O_3	0,47
FeO	97,66
MgO	0,43
CaO	0,22

Fig. 10. Spherical forms of wustite in waste after the production of cast steel (SEM, EDS spectrum with chemical analysis) [5]

Silicate phases in the investigated wastes are represented by olivines. In slags after the production of cast iron, occasionally the presence of fayalite $Fe_2[SiO_4]$ was determined. And in the wastes after the production of cast steel, forsterite with admixtures (Mn, Ca, Fe, Cr) crystallized (Fig. 7 points 3, 4); the calculated formulae (based on the chemical analyzes) of forsterite are as follows:

– $[Mg_{1,66}\ Mn_{0,22}\ Ca_{0,05}\ Fe_{0,03}\ Cr_{0,004}][SiO_4]$,
– $[Mg_{1,66}\ Mn_{0,22}\ Ca_{0,05}\ Fe_{0,03}][Si_{1,03}O_4]$.

The oxides CaO and MnO are very popular isomorphic admixtures occurring in olivines. In the investigated wastes, olivine crystals are often interlaid with glaze rich among others in silicon, calcium, aluminum, manganese and magnesium oxides (Fig. 7 points 2). Glaze fragments had been probably enclosed around olivines during their crystallization.

The presence of forsterite was also confirmed by X-ray studies, yet a certain shift of reflexes could be observed on diffractograms, which also indicates to the presence of crystals rich in admixtures.

4. Conclusions

Metallurgical wastes are characterized by a very diversified chemical and phase composition. In spite of the fact that they contain the same groups of phase components such as: glaze, metallic precipitations, oxide and silicate phases, yet their mutual quantitative ratios are considerably diversified. The situation is the same when we consider chemical composition of particular phases, the presence of their mixed crystals and the substitution possibility of elements in their internal structures which is not taking place in the conditions of natural crystallization of minerals. Therefore, each waste material should be investigated individually.

The composition of the investigated metallurgical wastes – slags after the production of cast iron and wastes after the production of cast steel is dominated by glaze, yet its chemical composition is diversified depending on the type of wastes. Apart from glaze, the presence of metallic phases represented by fine droplets of metal and polymetallic aggregates was determined, as well as the presence of nonmetallic phases – oxides and silicates. Oxide phases in both investigated wastes are connected with the presence of FeO, which occurs in the form of wustite, or it forms a solid solution with MnO. Silicate phases represent olivines. In the slags after the production of cast iron it is fayalite, and in the wastes after the production of cast steel – forsterite.

The studies on phase composition of metallurgical wastes, bonds of metals occurring in them, supported by chemical analyses are very important, since basing on the above we can draw conclusions involving e.g. the recovery of metals from the wastes or their return to the metallurgical process as well possible migration of metals from waste dumps in effect of the impact of atmospheric factors. Maybe in the future, the investigated waste materials could be used as a secondary material; slags after the production of cast iron to production of aggregates and wastes after the production of cast steel could be returned to the metallurgical process.

REFERENCES

[1] D.S. Bielankin, B.W. Iwanow, W.W. Łapin, Petrografia kamieni sztucznych, Warszawa 1957.
[2] E. Fidancevska, V. Vassilev, T. Hristova-Vasileva, M. Milosevski, Journal of the University of Chemical Technology and Metallurgy **44**, 2 (2009).

[3] I. J o n c z y, Gospodarka Surowcami Mineralnymi **25**, 1 (2009).
[4] I. J o n c z y, Hutnik-Wiadomości Hutnicze, **12** (2011).
[5] I. J o n c z y, J. N o w a k, A. P o r s z k e, E. S t r z a ł k o w s k a, Składniki fazowe wybranych mineralnych surowców odpadowych w obrazach mikroskopowych. Phase components of selected mineral waste materials in microscope images, Gliwice 2012.
[6] M. K a r b o w n i c z e k, Karbo **1** (2006).
[7] A. K o n s t a n c i n i a k, W. S a b e l a, Hutnik-Wiadomości Hutnicze **12** (1999).
[8] J. P o g o r z a ł e k, P. R ó ż a ń s k i, Prace Instytutu Metalurgii Żelaza im. St. Staszica **1** (2010).
[9] A. R a i, J. P r a b a k a r, C.B. R a j u, R.K. M o r c h a l l e, Construction and Building Materials **16** (2002).
[10] T. S o f i l i ć, D. B a r i š i ć, U. S o f i l i ć, Archives of Metallurgy and Materials **56**, 3 (2011).
[11] M. W y d e r k o - D e l e k t a, A. B o l e w s k i, Mineralogia spieków i grudek rudnych, Kraków 1995.

Received: 10 January 2014.