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Mineral and chemical characteristics of metallic precipitates in selected types of steel slags, blast furnace slags and waste arising from the production of cast iron

Introduction

The steel industry is a branch of the economy which produces significant amounts of waste, in particular slags from smelting (blast furnace and steel) processes. In 2017, 3,694.4 thousand tons of slag were produced, out of which 2,269.7 thousand tons were still stored at the end of the year, and only 2,041.7 thousand tons have been recovered, which is an upward trend, since in 2016 only 1,928.6 thousand tons of slag have been recovered (GUS 2018). The amount of waste generated during production results from the nature of the steel production

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process itself, as steel production is a material- and energy-intensive process, during which part of the materials and raw resources introduced into the integrated steel production system creates waste (Sitko 2008, 2014, 2016). Due to the fact that it is difficult to reduce the amount of slag created during the steel production process, there is a constant search for innovative ways to utilize it. At present, as a result of pro-ecological activities conducted on a large scale, and in accordance with applicable directives, slag should be used in as high capacity as possible (Xu et al. 2003; Cioroi et al. 2010; Sitko 2016). Such activities are already carried out; steel slags are used, among others, in the production of various types of aggregates used in construction and road engineering, as an additive in cement, for the production of pigments, as well as an additive in the production of ceramic products (Konstanciak and Sabela 1999; Sobierajski 2002; Rzeszowski et al. 2004; Tajchman i Tora 2004; Fidancevska et al. 2009; Iacobescu et al. 2011; Quaranta et al. 2014). Blast furnace slags are a material used in the production of so-called blast furnace cement, which is a mixture of blast furnace slags, clinker, Portland cement, and gypsum. After hardening, this cement is resistant to high temperatures and water (Tajchman et al. 2001). Blast furnace slags are also used for the production of slag wool and slag bricks (Nowak et al. 2013).

One more proposed way to use metallurgical slag is the secondary recovery of metals (Shen et al. 2004). The conducted research indicates that steel and blast furnace slags contain numerous elements, including heavy metals, among which iron has the largest content (Jonczy 2014a). In the case of iron recovery, however, the form in which this element occurs should be noted (Jonczy 2015). Iron can form small metallic precipitates or its own oxide and silicate phases, as well as substitutions in the internal structure of other phase components. A significant proportion of iron is also dispersed in the glass, which is one of the major components of slags (Jonczy 2011). For example in steel slag from Aristrain's iron in Madrid (Spain) wustite, chromite, magnetite, kirschsteinite were described (Garcia-Guinea et al. 2010). Research conducted by Sofilić et al. (2010) showed similar phase composition in an electric arc furnace (EAF) steel slag and the presence of dicalcium and tricalcium silicates, brownmillerite and mayenite has been also found. Phase composition of steel slag was also described by Yang et al. (2015), the authors paid special attention to metal droplets which were characterized by a various morphologies and sizes.

From the point of view of recovery, the most interesting iron forms are the precipitates of metallic iron (Iwamasa and Fruehan 1996). Attempts to obtain it using magnetic separation were undertaken, among others, for slag from the processing of steel dust in a rolldown furnace. As a result, a technology concept for the use of these slags has been developed. Its key element is the magnetic separation of slags that have been ground to achieve appropriate granulation (Sitko 2016). Iron recovery from metallurgical slags present in the dumping grounds was carried out at the Slag Recycling Sp. z o.o. company, where metallurgical scrap and pig iron or a mixture thereof is obtained in the production processes of metallurgical aggregates in a multi-stage system of magnetic separation (Rzeszowski et al. 2004). The separation of the metallic iron from slag, followed by its use in various fields, would lead to greater savings and the conservation of natural resources. The metallic iron from slag may be used as raw material in steelmaking or in other technological processes (Iluţiu-Varvara et al. 2014).

The aim of the work was a qualitative mineral and chemical identification of metallic precipitates occurring in the composition of slags typical for the production of steel, cast iron, and pig iron. This paper is also the first part of a series of publications aimed at understanding the functional properties of steel and blast furnace slags in the aspect of their destructive impact on the components of devices involved in the process of their processing, which is a significant operational problem.

1. Materials and methods

The tests were carried out for slags resulting from the open-hearth process and slags that are a by-product during EAF furnace operation in electric steelworks. Reference is also made to the results of research on slags resulting from the production of ductile cast iron and blast furnace slags (Fig. 1a–d).

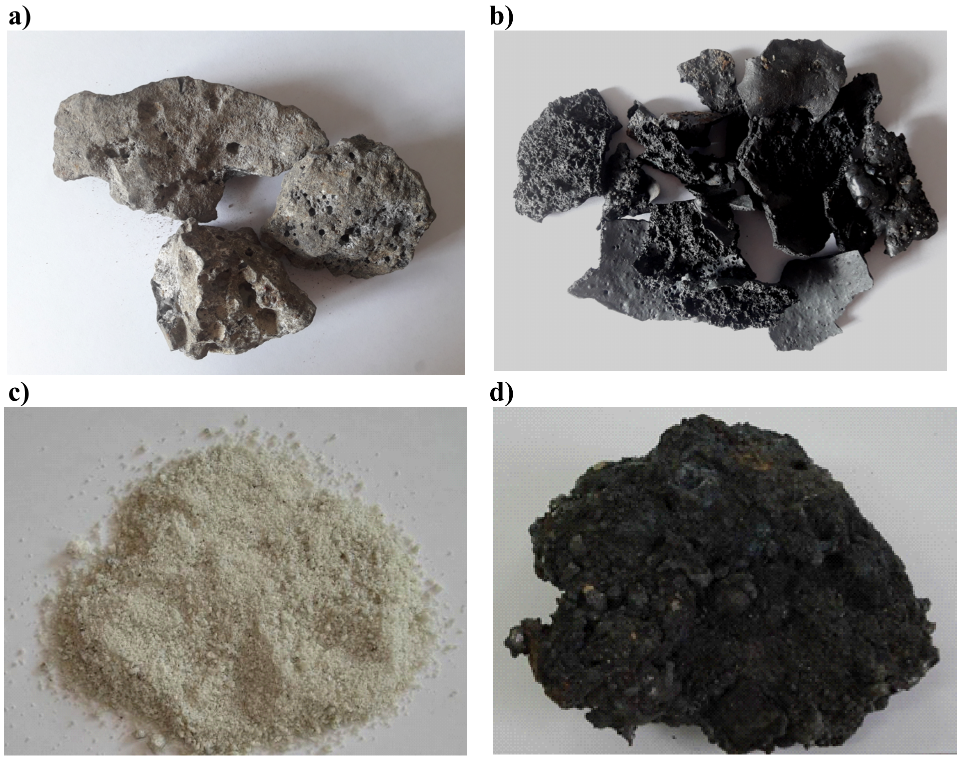


Fig. 1. Samples: a – open-hearth furnace slag; b – slag from an electric arc furnace; c – blast furnace slag; d – waste arising from the production of ductile cast iron

Rys. 1. Próbki: a – żużel z procesu martenowskiego; b – żużel z łukowego pieca elektrycznego; c – żużel wielkopiecowy; d – odpad po produkcji żeliwa sferoidalnego

Open-hearth furnace slag is formed as a by-product during the smelting of steel from pig iron and steel scrap in open-hearth furnaces. In the open-hearth process, hot gases obtained from burning coal gas are used to heat up the air blown into the furnace, which allows a high melting temperature to be achieved (Tarabrina et al. 2000). Slag from the open-hearth process is characterized by a gray color, medium-grained structure, and a dense, sometimes porous texture. This waste is concise and it is not subject to crushing. Samples for testing were obtained from a dump area from Łabędy Steelworks (Gliwice) where the slag was stored for several dozen years. Therefore, a white coating of secondary crystallizing minerals (rapid reaction to cold with HCl indicates $CaCO_3$ calcite) can sometimes be observed on the slag surface and in the pores.

Slag from an electric arc furnace is formed as a result of the production process in electric steelworks. The steelworks use electric arc energy for smelting steel and the whole process is based on the use of steel scrap, which is subject to technical treatment in the EAF electric arc furnace (Techzel 2019). The slag resulting from the operation of the electric arc furnace from Ferrostal Steelworks (Gliwice) is characterized by a black color, fine-grained structure, porous texture, and crumbles easily.

Blast furnace slag is formed in the blast furnace process, which consists of a series of chemical reactions and physical processes taking place in the blast furnace, where, at high temperatures achieved during the combustion of coke, the iron compounds contained in the ore are reduced. The reducers include carbon, carbon monoxide, and hydrogen generated as a result of the presence of water in the feed. The by-products of this process are slag and blast furnace gas. The analyzed blast furnace slag is characterized by a white-gray color, a fine- or medium-grained structure, and loose texture. The samples were taken from ArcelorMittal Steelworks in Dąbrowa Górnicza.

Waste arising from the production of ductile cast iron from Zabrze Steelworks is a by-product in the process of cast iron spheroidizing, which consists in introducing magnesium additives along with other elements in the form of master alloys or wire to the ladle with gray iron. As a result of this treatment, the form of the graphite changes into a spherical one, which occurs in the vicinity of a ferrite-perlitic or perlitic matrix. Ductile cast iron is characterized by a high strength, making it a good structural material for applications in strenuous components of machines and devices (Perzyk et al. 2017; Huta Zabrze SA 2019). It should also be noted that ductile cast iron is also used as a starting material for the production of ADI cast iron with properties comparable to alloy steel and forged steel (Wieczorek 2014a, b). The waste arising from the production of ductile cast iron has a dark gray color, medium-grained or coarse structure, and a dense texture.

In order to determine the presence of metal precipitates in slags as well as to determine their chemical composition, tests were carried out using X-ray spectral microanalysis and scanning electron microscopy.

The X-ray spectral microanalysis was conducted in the Institute of Non Ferrous Metals (Department of Material Engineering and Powder Metallurgy) in Gliwice, using an X-ray JXA 8230 microanalyzer manufactured by JEOL. The analyses were conducted using metallographic specimens dusted with a thin layer of carbon to transfer the electric charge. X-ray mapping of elements was conducted using Energy Dispersive Spectroscopy. Local quantitative analyses of selected grains were conducted.

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.

2. Results

Based on the observations made using scanning electron microscopy and X-ray spectral microanalysis, it was established that metallic precipitates are present in all types of tested slags.

In ***open furnace slag*** the metallic precipitates are one of the main components, along with glass and crystalline phases (Jonczy 2011; Jonczy et al. 2012). During the tests it was found that metallic precipitates are characterized by a varied size and shape (Fig. 2a–d). Among them, we can distinguish:

- accumulations of fine drops of metal surrounded by glass (diameters < 5 µm),
- single precipitates with a characteristic round or oval shape and of various sizes, co-occurring with the crystalline phases (diameters > 200 µm),
- metallic aggregates with irregular, varied shapes, often filling the free spaces between crystalline components (size 100–200 µm).

In the chemical composition of all the analyzed metallic precipitates, metallic iron is the dominant component, regardless of their shape. Its content is over 90%, and in some cases reaches 99%. In the precipitates, impurities of Mg, Si, and Ca were found. Example analyses are shown in Fig. 3a, b.

The content of metallic precipitates in the ***slag from an electric arc furnace*** is much lower as compared to the open-hearth slag. The form of occurrence of the precipitates is also different. In this slag, the presence of regular, spherical metallic precipitates occurring individually surrounded by glass and with a diameter of 5 to 50 µm was mainly observed. Their chemical composition is quite diverse; apart from iron there are impurities of other elements, including heavy metals, like Cr, Zn, Pb (Fig. 4).

In ***blast furnace slag*** there are regular, spherical metallic precipitates with a diameter of several to 20 µm in which the metallic iron content usually exceeds 99% and, in many cases, reaches 100%. The precipitates occur surrounded by glass containing small crystallites of

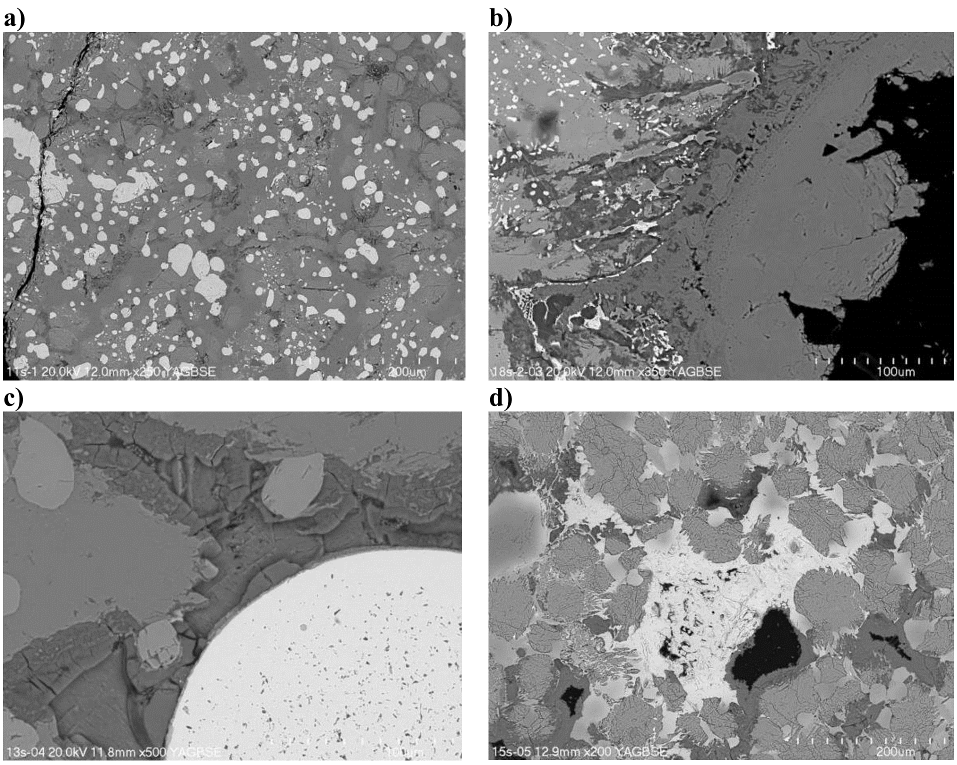


Fig. 2. Forms of metallic precipitates in the open-hearth furnace slag (white areas):
a, b – fine precipitates surrounding by the glass; c – a single drop of metal; d – an irregularly shaped aggregate

Rys. 2. Formy występowania wytrąceń metalicznych w żużlu martenowskim (białe pola):
a, b – drobne wytrącenia w otoczeniu szkliwa; c – pojedyncza kropla metalu;
d – agregat o nieregularnym kształcie

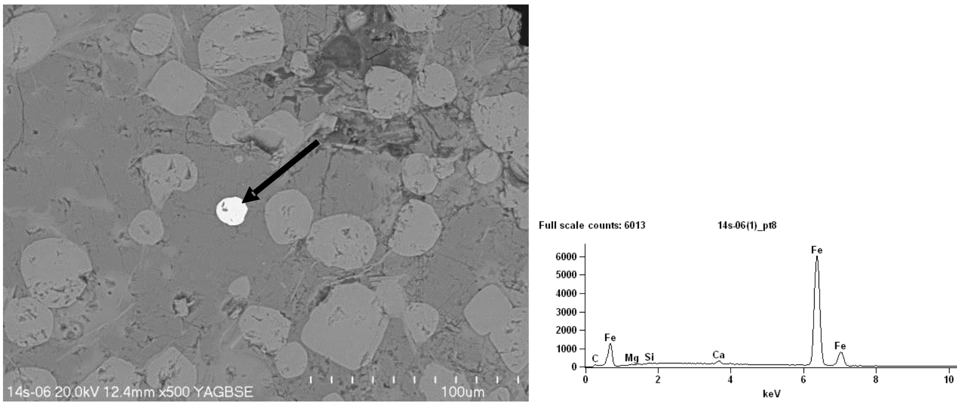
phase components, the identification of which is difficult due to the cryptocrystalline form (Fig. 5).

Metallic alloys in the form of spherical precipitates are rare in ***waste resulting from the production of ductile cast iron***. They usually form irregular aggregates, with the content of Fe in the range of 97–99%; Si and Cr were found in the form of impurities (Fig. 6a, b).

3. Discussion

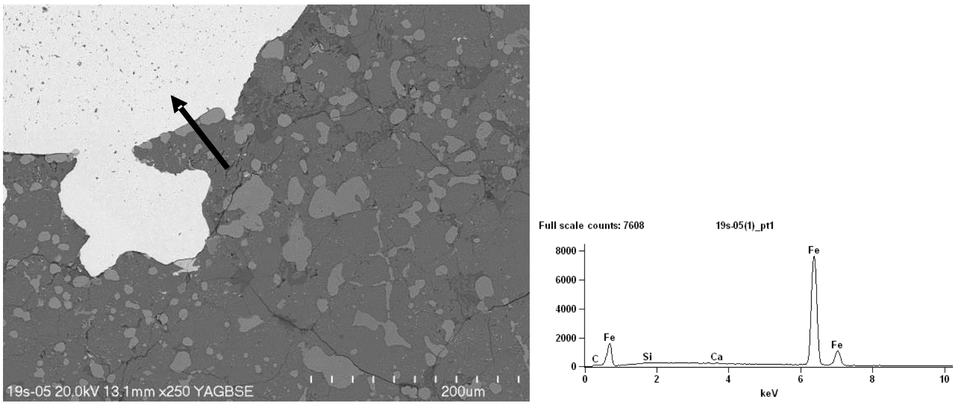
Iron is one of the basic elements of the chemical composition of steel and blast furnace slags. Previous research has shown that its content in the analyzed slags is quite diverse and amounts to an average of: 8.84% – open-hearth slag, 31.35% – slag from an electric arc furnace, 18.7% – blast furnace slag and 16.40% – waste resulting from the production of ductile

a)



Fe 98.66 wt%; Mg 0.43 wt%; Si 0.51 wt%; Ca 0.40 wt%

b)



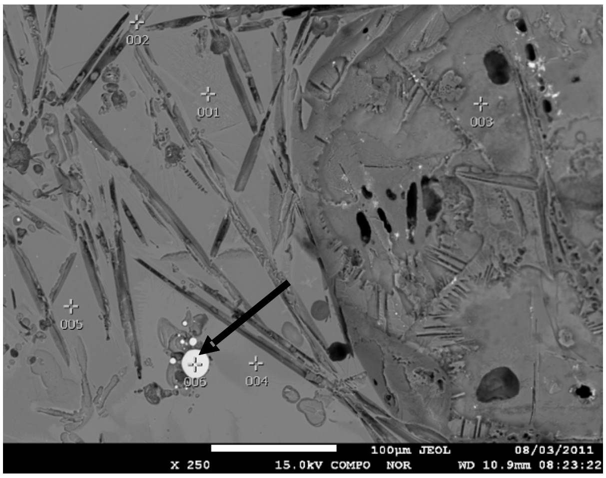
Fe 99.34 wt%; Si 0.57 wt%; Ca 0.09 wt%

Fig. 3.a, b. BSE microphotography of the open-hearth furnace slag with EDS spectrums and analysis of the chemical composition of metallic precipitates

Rys. 3.a, b. Mikrofotografie BSE żużla martenowskiego wraz z widmami EDS i analizą składu chemicznego wytrąceń metalicznych

cast iron (Jonczy 2014a, b). The form in which the iron appears in the slags is equally diverse (Jonczy 2015). There are iron silicates, e.g. fayalite $Fe_2[SiO_4]$, in addition to the oxide phases represented mainly by magnetite Fe_3O_4, hematite Fe_2O_3 and wustite FeO, while iron is also often present in the steel slag as a component of the solid solution of three FeO-MnO-MgO oxides. This phase is called the "RO phase", it crystallizes in the form of dendrites and is one of the characteristic components of slags (Bielankin 1957; Jonczy 2019).

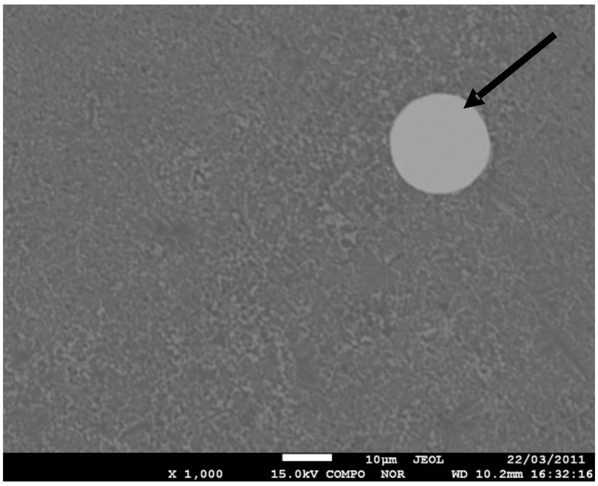
In addition to iron bound in the form of oxide or silicate phases, metal iron precipitates appear in the slags. The conducted analyses showed that in the open-hearth slags, metallic



Fe 97.21 wt%; Mg 0.18 wt%; Ca 0.59 wt%; Mn 0.92 wt%; V0.02 wt%; Ni 0.06 wt%; Cr 0.66 wt%; Zn 0.10 wt%; Pb 0.26 wt%

Fig. 4. Microphotography of the slag from an electric arc furnace and an analysis of the chemical composition of metallic precipitates; X-ray spectral microanalysis

Rys. 4. Mikrofotografia żużla z łukowego pieca elektrycznego wraz z analizą składu chemicznego wytrącenia metalicznego; rentgenowska analiza spektralna w mikroobszarach

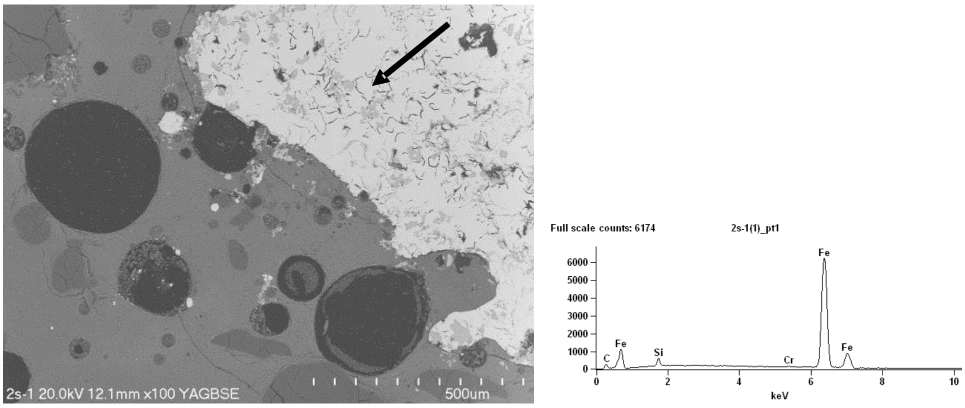


Fe 99.40 wt%; Ca 0.42 wt%; Pb 0.09 wt%; Mn 0.06 wt%; Si 0.03 wt%

Fig. 5. Microphotography of blast furnace slag and an analysis of the chemical composition of metallic precipitates; X-ray spectral microanalysis

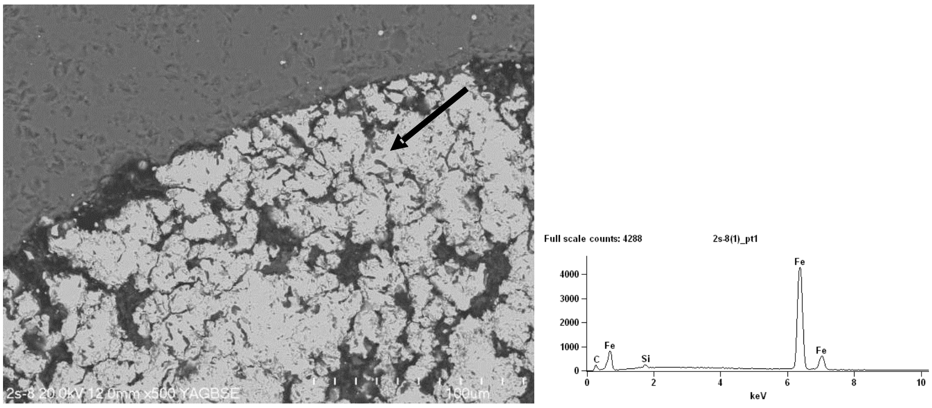
Rys. 5. Mikrofotografia żużla wielkopiecowego wraz z analizą składu chemicznego wytrącenia metalicznego; rentgenowska analiza spektralna w mikroobszarach

a)



Fe 97.62 wt%; Si 2.15 wt%; Cr 0.23 wt%

b)



Fe 98.69 wt%; Si 1.31 wt%

Fig. 6a, b. BSE microphotography of waste arising from the production of ductile cast iron with an EDS spectrum and analysis of the chemical composition of metallic precipitates

Rys. 6a, b. Mikrofotografie BSE odpadu po produkcji żeliwa sferoidalnego wraz z widmami EDS i analizą składu chemicznego wytrąceń metalicznych

precipitates along with glass and crystalline phases are one of the basic components of these slags. During the testing of 20 samples of open-hearth slags, in each of the 100 areas microanalyzed using scanning electron microscopy, the presence of metallic precipitates was observed. The presence of metallic iron in slags is the result of the metallurgical process. During the sintering of ores, iron concentrates, as well as during the melting of steel scrap, a significant part of their components is reduced and melted. These components may also be transferred to the waste material. In a sinter mixture, new phases are formed, depending on the conditions of the process being carried out and the chemical composition of the feed, as the temperature rises. Iron oxides are reduced in the first stage of mineralization.. Due to the combustion of coke, the CO generated already at the temperatures of 400–700°C initiates the process of reduction of hematite to magnetite, while the reduction of hematite in the solid phase in the presence of CaO leads to the formation of calciomagnetite. Subsequently, calcium ferrites are formed, and the synthesis of dicalcium silicates begins. The second stage of mineralisation occurs with the increase of temperature and is associated with the increase in the content of liquid phase in which SiO_2 and CaO are increasingly influential. The result is the formation of silicate connections corresponding to the composition of olivines, pyroxenes and calcium silicates. In the presence of Al_2O_3 and MgO, melilites may also be formed. In the third stage, silicate mineralization and crystallization take place. As the reduction conditions and temperature continue to increase, metallic iron grains appear alongside the previously formed components (Wyderko-Delekta and Bolewski 1995).

The morphology of iron precipitates is another interesting aspect. It is determined by the conditions of formation and solidification of respective metal droplets in the slags. Tests carried out by Yang et al. (2015) show that metal droplets in the blast furnace slag can be classified into three groups according to the morphology: spherical/oval, spherical/irregular and irregular. Larger inclusions of iron, reaching the size of up to 1 mm, or as microscopic inclusions of round, oval or xenomorphic shape of size up to 20 μm were also described by Sofilić et al. (2010) in the slag from an electric arc furnace.

During the microscopic observations of slags, attention was also paid to the form of iron precipitates, which, like other slag components, may show a slightly different form from their natural counterparts (Jonczy 2012; Jonczy et al. 2012). In contrast to native iron found in nature in the form of granular, clumpy clusters and less often six- or eight-sided crystals, metallic iron usually takes the form of spherical precipitates surrounded by glass in steel and blast furnace slags. The occurrence of precipitates in the form of irregularly shaped aggregates, which can fill the free spaces between the crystallizing phase components, was also found in the open-hearth slags and slags resulting from the production of ductile cast iron.

Iron dominates in the chemical composition of all tested metallic droplets; its content changes between 90–99%. Only in blast furnace slags precipitates containing almost 100% metallic iron were found; such iron droplets may also contain a small FeO admixtures which have been described by Yang et al. (2015). Pure iron droplets were also found in EAF steel slags collected from Southern Steel Berhad, a steel manufacturing company in Malaysia (Wei et al. 2018).

In addition to iron, other elements may also be present in the metal droplets. Apart from iron, metallic precipitates from the tested slags usually contain Mg, Si and Ca. Only precipitates from an electric arc furnace slag were characterized by the richer chemical composition and the presence of: Mn, V, Ni, Cr, Zn and Pb was also described. Admixtures of other metals in iron droplets were also found by Loncnar et al. (2017). Their research showed that droplets with diameters of more than 5 μm have a composition which is comparable to that of the austenitic stainless steel, mainly containing iron, chromium and a small amount of nickel. The majority of the small droplets (<5 µm) contained more than 90 wt.% of iron, the rest being chromium. In the chemical composition of iron droplets from an titania bearing slag, apart from iron, other elements were also found: Si, Mn, V, Ti, S and P (Wang et al. 2008). Electron probe microanalysis showed that the droplets may also contain small amounts of carbon, which the percentage is between 0.01 and 0.07% (Gustavsson et al. 2006).

Conclusions

On the basis of the conducted research it was observed that:

- Iron is the dominant element in the chemical composition of steel and blast furnace slags. The form of its occurrence is diverse, as apart from its own oxide and silicate phases, iron occurs in the form of substitutions in the internal structure of other phase components, while also forming metallic precipitates.
- Metallic iron precipitates are present in all the analyzed types of slags; the largest amounts of metallic iron precipitates were found in slags formed as a by-product during the open-hearth process.
- Metallic iron precipitates occur in the form of fine drops of metal surrounded by glass, they also take single forms with characteristic regular, spherical shapes, and aggregates of irregular shape filling free spaces between other phase components.
- The conducted chemical composition tests showed that the content of Fe in the metallic precipitates generally exceeds 90%, with the highest iron content observed in the precipitates occurring in blast furnace slags; in these slags precipitates containing almost 100% metallic iron were found.
- Research shows that in terms of quality, steel and blast furnace slag can be a potential source of iron recovery. However, further quantitative analyses are required regarding the percentage of precipitates in the composition of slags in order to determine the viability of iron recovery.

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MINERAL AND CHEMICAL CHARACTERISTICS OF METALLIC PRECIPITATES IN SELECTED TYPES OF STEEL SLAGS, BLAST FURNACE SLAGS AND WASTE ARISING FROM THE PRODUCTION OF CAST IRON

Keywords

slag, metallic precipitates, iron

Abstract

Among the elements that compose steel slags and blast furnace slags, metallic precipitates occur alongside the dominant glass and crystalline phases. Their main component is metallic iron, the content of which varies from about 90% to 99% in steel slags, while in blast furnace slags the presence of precipitates was identified with the proportion of metallic iron amounting to 100%. During observations using scanning electron microscopy and X-ray spectral microanalysis it has been found that the form of occurrence of metallic precipitates is varied. There were fine drops of metal among them, surrounded by glass, larger, single precipitates in a regular, spherical shape, and metallic aggregates filling the open spaces between the crystalline phases. Tests carried out for: slags resulting from the open-hearth process, slags that are a by-product of smelting in electric arc furnaces, blast furnace slags and waste resulting from the production of ductile cast iron showed that depending on the type of slag, the proportion and form of metallic precipitates is variable and the amount of Fe in the precipitates is also varied. Research shows that in terms of quality, steel and blast furnace slag can be a potential source of iron recovery. However, further quantitative analyses are required regarding the percentage of precipitates in the composition of slags in order to determine the viability of iron recovery. This paper is the first part of a series of publications aimed at understanding the functional properties of steel and blast furnace slags in the aspect of their destructive impact on the components of devices involved in the process of their processing, which is a significant operational problem.

CHARAKTERYSTYKA MINERALOGICZNO-CHEMICZNA WYTRĄCEŃ METALICZNYCH W WYBRANYCH RODZAJACH ŻUŻLI STALOWNICZYCH, ŻUŻLACH WIELKOPIECOWYCH ORAZ W ODPADACH PO PRODUKCJI ŻELIWA

Słowa kluczowe

żużel, wytrącenia metaliczne, żelazo

Streszczenie

Wśród składników budujących żużle stalownicze i wielkopiecowe, obok dominującego szkliwa oraz faz krystalicznych, występują wytrącenia metaliczne. Ich głównym składnikiem jest żelazo metaliczne, którego zawartość w wytrąceniach w żużlach stalowniczych waha się w granicach od około 90 do 99%, natomiast w żużlach wielkopiecowych stwierdzono obecność wytrąceń, w których udział żelaza metalicznego wynosił 100%. Podczas obserwacji mikroskopowych przy wykorzystaniu mikroskopii elektronowej skaningowej oraz rentgenowskiej analizy spektralnej w mikroobszarach stwierdzono, że forma występowania wytrąceń metalicznych jest zróżnicowana. Wyróżniono wśród nich drobne krople metalu występujące w otoczeniu szkliwa, większe, pojedyncze wytrącenia o regularnym, kulistym kształcie oraz agregaty metaliczne wypełniające wolne przestrzenie pomiędzy fazami krystalicznymi. Badania przeprowadzone dla: żużli z procesu martenowskiego, żużli stanowiących produkt uboczny przy wytopie z łukowego pieca elektrycznego, żużli wielkopiecowych oraz odpadów po produkcji żeliwa sferoidalnego wykazały, że zależnie od rodzaju żużla udział i forma wytrąceń metalicznych jest zmienna, zróżnicowana jest również zawartość pierwiastka Fe w samych wtrąceniach. Badania dowodzą, że pod względem jakościowym żużle stalownicze i wielkopiecowe mogą stanowić potencjalne źródło odzysku żelaza. Niezbędne są jednak analizy ilościowe odnośnie do procentowego udziału wytrąceń w składzie żużli w celu określenia opłacalności odzysku żelaza. Artykuł stanowi pierwszą część cyklu publikacji ukierunkowanych na poznanie właściwości użytkowych żużli stalowniczych i wielkopiecowych w aspekcie ich niszczącego oddziaływania na elementy urządzeń biorących udział w procesie ich przetwarzania, co stanowi istotny problem eksploatacyjny.