

BEHAVIOUR OF IRON DURING REDUCTION OF SLAG OBTAINED FROM COPPER FLASH SMELTING

Received – Prispjelo: 2014-01-30
Accepted – Prihvaćeno: 2014-06-20
Preliminary Note – Prethodno priopćenje

In a technological process of copper production in the flash smelting furnace, slags with high metal contents, such as copper, lead and iron, are generated. These slags differ in their chemical compositions from slags obtained in processes of copper concentrate flash smelting or bath smelting. With the technology used at KGHM, the slag discussed in the article is processed during smelting reduction that is carried out in the electric furnace. As a result, a Cu-Pb-Fe alloy is obtained and subjected to the converting process along with waste slag which contains ca. 0,5 % mass Cu. The article presents an analysis of results of the research on behaviour of iron in the course of slag reduction where diverse fine-grained carbon-bearing materials function as reducers.

Keywords: Cu-Pb-Fe alloy, flash smelting, reduction, iron, slag decopperisation

INTRODUCTION

In many pyrometallurgical processes aimed at metal production, slags of highly diverse chemical compositions are generated. As a result, some of them cannot be directly managed and require further processing. Recently, slags with higher metal contents have been a subject of increasing interest with respect to their reuse as additional, metalliferous components of charge material due to depletion of primary raw materials including metal ores and energy resources [1-3]. The reuse of metallurgical slags as metal carriers in a technological process mainly refers to extraction of non-ferrous metals – basically copper, zinc and lead. For instance, slags generated during copper production are not only processed for recovery of this particular metal but also for lead, iron etc. [4-8]. During a technological process of copper production in the flash smelting furnace at “KGHM” Polska Miedź, slags with very high contents of copper, lead and iron are generated. These slags markedly differ in their chemical composition from slags obtained in processes of copper concentrate flash smelting or bath smelting, mainly due to various chemical compositions of Polish ores. The discussed slag is processed during smelting reduction which is performed in the electric furnace. As a result, a Cu-Pb-Fe alloy is obtained and subjected to the converting process along with waste slag which contains ca. 0,5 % mass Cu. In the paper, an analysis of results of the research on behaviour of iron in the course of slag reduction where various fine-grained materials function as carbon-bearing materials is presented.

RESEARCH MATERIALS AND METHODS

For the reduction process, industrial slag obtained during copper blister flash smelting at KGHM “Polska Miedź” was used. Its chemical composition is presented in Table 1.

The slag was analysed for its microstructure and phase composition. The first analysis was performed with the use of a HITACHI - 3 400 N scanning electron microscope (SEM). The phase composition analysis was carried out by means of the x-ray diffraction (XRD) method using a JEOL JDX-7S diffractometer.

Table 1 **Chemical composition of the investigated slag**

Component	Content / %mass
Cu	11,6
Pb	3,25
Fe	10,63
Zn	1,31
S	0,03
CaO	13,28
SiO ₂	31,84
MgO	5,08
Al ₂ O ₃	8,95

Sample images of the initial (industrial) slag microstructure are presented in Figure 1. The analysis of slag microstructures revealed their complex and diverse morphologies – especially slag particle sizes that ranged from several hundred nanometres to several micrometres. Particle sizes in the investigated slags varied for all the samples. Moreover, morphology of the slag particles changed from markedly flat surfaces to rounded and spherical shapes.

In Figure 2, an x-ray diffractogram of the initial slag sample is presented. As it shows a lot of diffraction

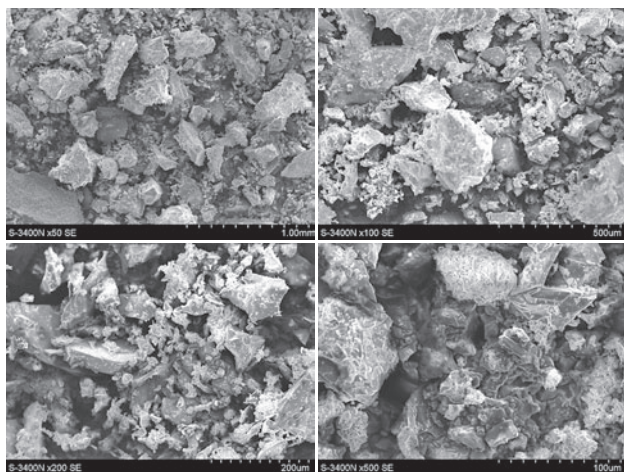


Figure 1 Images of the initial slag microstructure

lines, a definite identification was difficult. The phases that were identified in the analysed sample included: $\text{Ca}(\text{Mg},\text{Al})(\text{Si},\text{Al})_2\text{O}_6$, Cu_2O , Fe_3O_4 , Fe_2O_3 ,

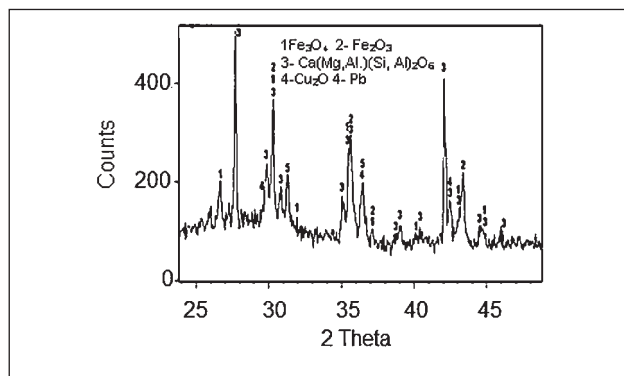
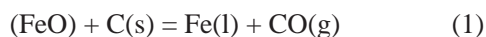


Figure 2 Part of the x-ray diffractogram of the initial slag

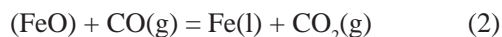
For the investigations of slag smelting, coke breeze, anthracite dust and coke dust were used as reducers. Such a selection resulted from the assumed potential use of cheaper, fine-grained, carbon-bearing fractions as reducers in pyrometallurgical processes. Some of them were successfully applied in iron ore sintering, steel dust treatment and acid-lead accumulator scrap processing [9-12]. All experiments were conducted in the test stand; its main component was an electric resistance furnace. For each test, the amount of reducer additive was 3 % mass of the slag. Moreover, in some tests, the charge was supplemented with CaCO_3 in the amount of 7 % mass of the slag.

STUDY RESULTS AND ANALYSIS

During the reduction process of flash-smelting slag, direct reduction with solid carbon and indirect reduction with CO are observed. While analysing iron transfer to Cu-Pb-Fe during smelting reduction, the process was assumed to occur due to reduction of FeO contained in the liquid slag with solid carbon according to the equation [8]:



It is a resultant of the following equations:



and



In the investigated flash-smelting slag, the iron content was over 10 % mass.

In Table 2, results of the analysis of iron content in the alloy following the reduction process are presented. The results suggest a slight degree of iron oxide reduction during processing. The effects of reduction time on the Fe content in the alloy are presented in Figures 3 and 4.

Table 2 Iron content in Cu-Pb-Fe following the reduction process*

Charge materials for the process	Fe content in Cu-Pb-Fe / %mass			
	1h	2h	3h	5h
Slag + breeze coke	0,28	0,39	2,33	2,79
Slag + anthracite dust	0,10	0,07	2,01	2,23
Slag + coke dust	0,13	0,85	2,27	2,93
Slag + breeze coke + CaCO_3	0,07	0,72	1,92	4,12
Slag + anthracite dust + CaCO_3	0,16	1,13	2,17	3,67
Slag + coke dust + CaCO_3	0,25	0,92	3,88	4,59

* Mean values from two tests

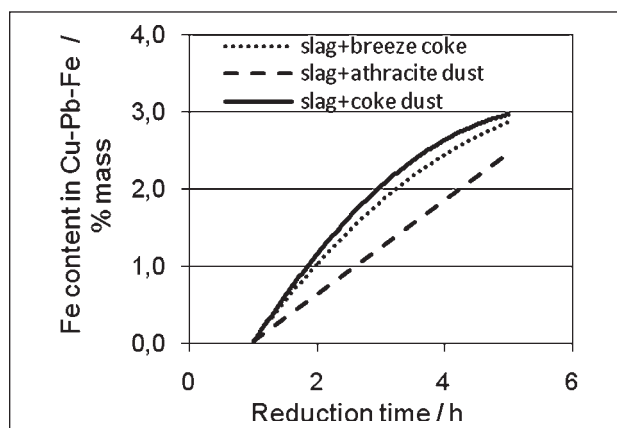


Figure 3 Effects of reduction time on the Fe content in Cu-Pb-Fe (tests without the CaCO_3 additive)

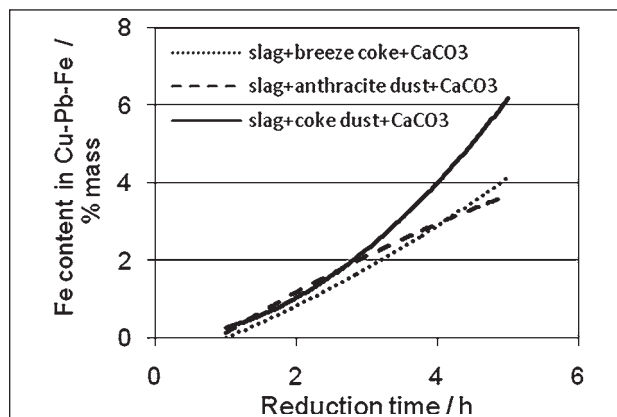


Figure 4 Effects of reduction time on the Fe content in Cu-Pb-Fe (tests with the CaCO_3 additive).

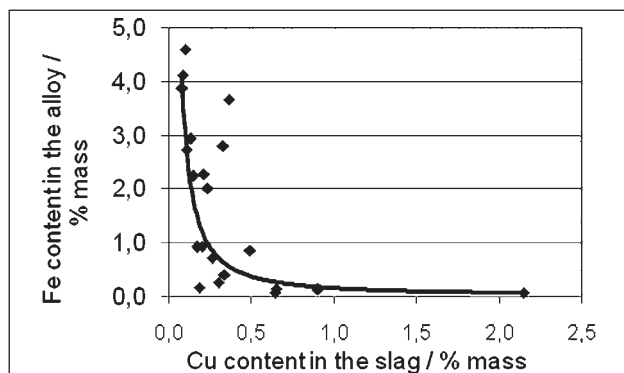


Figure 5 Iron content in the alloy versus the copper content in the slag

As shown in previous studies [14-15], intensification of iron oxide reduction does not take place until the copper content in the slag is decreased to less than 0,6 %mass, which was successfully confirmed by the obtained results. It is illustrated by the data presented in Figure 5.

SUMMARY

The research on reduction of copper flash smelting slag using various carbon reducers showed a small degree of iron transfer to the metal alloy. The maximum transfer for 5-hour tests did not exceed 7 %. Moreover, it was found that intensification of FeO reduction clearly occurred with decreased copper content in the slag below 0,6 %mass. However, no effects of the carbon reducer type on the rate of reduction of iron contained in the flash smelting slag were not demonstrated.

Acknowledgements

The study was conducted under the Research Project No. PST1/A5/21/2012, financed by the National Research and Development Centre – Poland.

REFERENCES

[1] A. Ziębik, W. Stanek, Energy and exergy system analysis of thermal improvements of blast-furnace plants, *International Journal of Energy Research* 30 (2006) 2, 101-114.

[2] J. Szargut, A. Ziębik, W. Stanek, Depletion of the non-renewable natural exergy resources as a measure of the ecological cost, *Energy Conversion and Management* 43 (2002) 9-12, 1149-1163.

[3] K. Lampert, A. Ziębik, W. Stanek., Thermoeconomical analysis of CO₂ removal from the Corex export gas and its integration with the blast-furnace assembly and metallurgical CHP plant, *Energy* 35 (2010) 2, 1188-1195.

[4] M. Sanchez, M. Sudbury, Physicochemical characterization of copper slag and alternatives of friendly environmental management, *Journal of Mining and Metallurgy* 49 (2013) 2B, 161-168.

[5] B. Gorai, R.K. Jana, Characteristics and utilisation of copper slag - a review, resources, *Conservation and Recycling* 39 (2003) 4, 299-313,

[6] L. Li, J. Hu, H. Wang, Study on Smelting Reduction Ironmaking of Copper Slag, *The Chinese Journal of Process Engineering* 11 (2011) 1, 65-71.

[7] K. Li, S. Ping, H. Wang, W. Ni, Recovery of iron from copper slag by deep reduction and magnetic Beneficiation, *International Journal of Minerals, Metallurgy, and Materials* 20 (2013) 11, 1035-1041.

[8] J. Heo, B. Kim, J.H. Park, Effect of CaO Addition on Iron Recovery from Copper Smelting Slags by Solid Carbon, *Metallurgical and Materials Transactions B* 44B (2013) 6, 1352-1363.

[9] M. Niesler, J. Stecko, L. Blacha, B. Oleksiak, Application of fine-grained coke breeze fractions in the process of iron ore sintering, *Metalurgija* 53 (2014) 1, 37-39.

[10] M. Niesler, L. Blacha, J. Łabaj, T. Matuła, A study on the process of fine-grained plumbiferous material agglomeration, *Metalurgija* 52 (2013) 4, 521-524.

[11] J. Lipart, T. Matuła, M. Niesler, L. Blacha, J. Filipczyk, Wastes from the coal-enrichment process as alternative reducers for lead smelting from lead-acid accumulator scrap, *Metalurgija* 52 (2013) 4, 493-498.

[12] J.Łabaj, M. Słowikowski, W. Żymła, J. Lipart, The research on reactivity of alternative carbon reducers, *Metalurgija* 52 (2013) 1, 68-70.

[13] M. Kucharski, Solubility of copper in SiO₂-CaO-Al₂O₃ slags, *Archiwum Hutnictwa* 32 (1987) 1, 27-32.

[14] M. Kucharski, Solubility of copper in outokumpu slags, *Metals Technology* 6 (1979) 9, 354-356.

[15] M. Kucharski: Effect of thermodynamic and physical properties of flash smelting slags on copper losses during slags cleaning in an electric furnace. *Archiwum Hutnictwa* 32 (1987) 2, 307-323.

Note: Nowak P. is responsible for English language, Katowice, Poland