

The Analysis of the Chloride and Fluoride Influences on the Reducer Refinement Processes (Carbo-N-Ox) Aluminum Alloys

A.W. Bydalek^{a*}, P. Schlafka^b, S. Biernat^c

^a AGH University of Science and Technology, Mickiewicza 30, 30-059 Krakow, Poland

^b Department of Mechanical Engineering, University of Zielona Góra, Prof. Z. Szafrana 4, 65-516 Zielona Góra, Poland

^c Jan Amos Komenski State School of Higher Vocational Education, Mickiewicza 5, 64-100 Leszno, Poland

*Corresponding author. E-mail address: adam_bk@poczta.onet.pl

Received 27.03.2013; accepted in revised form 27.05.2013

Abstract

Slag refining slag with west materials was analysed used the DTA methods. In the paper a method of determining the reduction capability, with the Carbo-N-Ox method, of slag solutions was used. Some relations between the stimulators in the environment - slag - metal system allow to initiate mass exchange reactions in the process of slag refining. The presented in work course of behaviour permits on choice of basic composition of slaglite, the of necessary components stimulating quantities, as well as on accomplishment of opinion of ability refinement. The worked out programme Slag-Prop, after introduction of data with experiment, it allows on next corrections in composition of proposed mixtures also, should be put on properly elaborated factors of multistage reaction with essential usage of suitable stimulators.

Keywords: Refinement, Data base, Copper alloys

1. Introduction

Quality of the alloy depends on the composition of slag properties (viscosity, surface tension, liquid, wetting angle). Optimization of the alloy is varied accordingly to the complex requirements of the properties that must be reached. Refiners are the core impact of related to the non-metallic impurities of refined copper alloys. Number of concepts was carried out the metallurgical process. The introduction of stimulating compounds of fluorine into the slag requires the knowledge of chemical and thermodynamic. The mixtures are used in various stages of the reduced process Carbo-N-Ox, metallurgical: fluxes, modifiers, solvents and stimulators [1, 7]. The slag mixtures present in the form of dilute concentrations [4, 5]. In the scientific works [1, 2, 3] there were analyzed the properties of the stimulating compounds in the system M - Z - St - WN - A: substances that

stimulate are considered to be more stable than the oxides, which favors the possibility of improving the viscosity of slag η_s , lowering its melting temperature T_T , and providing high speed response in the gas phase. The schemes of composition the properties of material built and established for silicon slags is presented on Fig. 2 [2]. The authors of [3] reported the chemical diffusivity of the individual compounds. They found that self diffusion is a measure of the random motion of atoms in the melt, and the chemical diffusion affects the chemical the gradient across the boundary layer of slag.

The stability of the compounds NaF and CaF₂ is different in the vapor area. In [6] there is presented an analysis of mass transfer on the basis of SiO₂ slag containing metal oxides with promoters at comparable temperatures. The use of NaF, CaF₂ in industry has been limited due to the detrimental effect on human health and environment. Because of the law of EU it is necessary to use the single fluorides participating in the refining process.

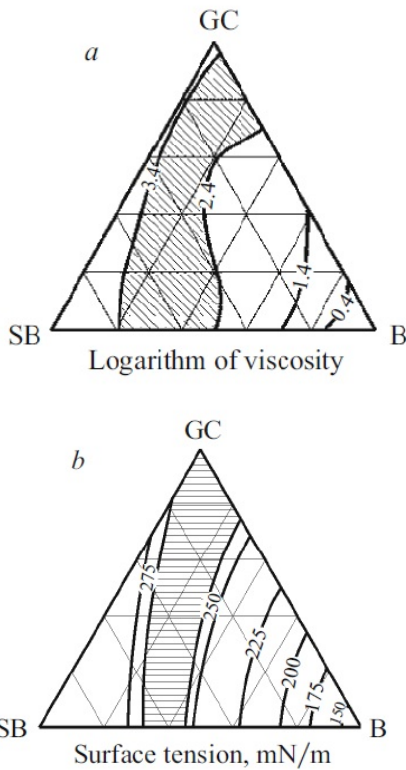
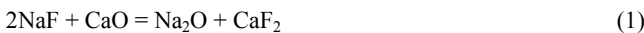


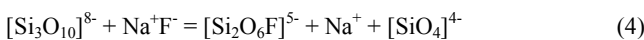
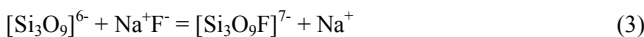
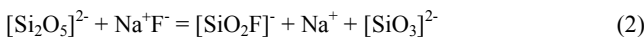
Fig. 1. Isolines of the melting slag in relation to the properties [2]

In slag systems containing CaC_2 introduced fluoride stimulators affect the Ca resulting in weakening of links with the C. As a result of such an effect there is a possibility on the formation the atmosphere of a reducing agent. Compounds are formed with high stability Fig. 1.

The analyzes also showed the possibility to compound slag with substances such as fluorides (e.g. NaF , CaF_2) [1, 3, 4] which increase the participation of simple anions at the expense of the weakening of bonds of complex anions, which should favor the exchange reaction. In a study by Gusev and Gullykin [7] reported that in accordance to the reaction:



Dissociated fluorine can react with oxygen O° and create type reactions:



NaF reacts with CaO the slag component forming Na_2O , and CaF_2 . The resulting products modify the SiO_2 changing the crystal structure (2). In the result of this, the viscosity is reduced. Analysis of the molten NaF is only possible in an ion. With more silica content of NaF reaction according to the model 3 and 4. In

the scientific work [10] there was found that a greater effect on modifying the structure of the slag is NaF than CaF_2 . The introduction of fluorine compounds to chloride slag as an additional stimulator reaction can also modify the atmosphere enriching it in the active chlorine [1, 3].

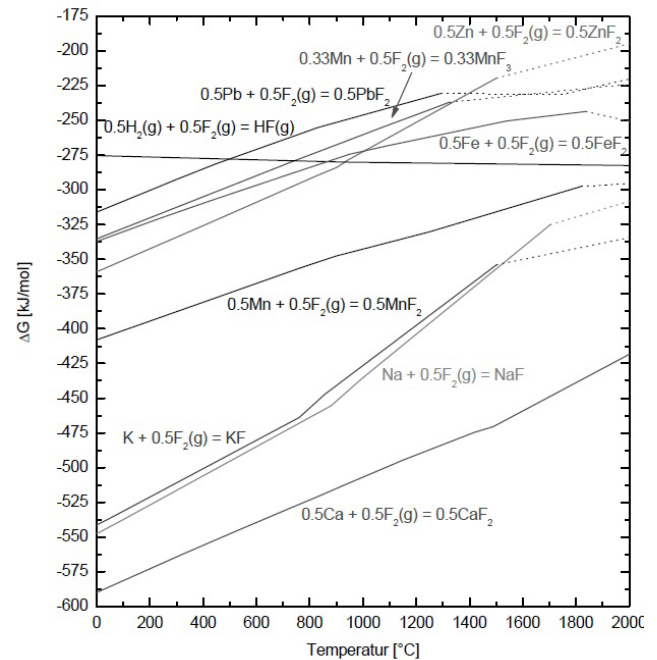
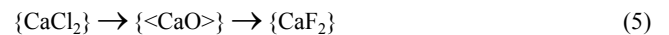


Fig. 2. The reactions of the enthalpy of single fluorides in the function of the temperature [3]

It is worth to pay attention also to the sustainability fluorides as they are more stable than the oxides of K, Na, Mg, Ca, Mn, Ti, Zn, Cu, P, B, Fe [3]. This gives us the possibility to use reaction (5) of the slag type:



2. Stimulating substance reaction

There is a need to find an optimal composition of slag mixture for metal refining, which will allow to consider the influence of individual ingredients, i.e. the refiner, the fluxing material and the stimulating substance. The study described in [1] shows the possibility of utilizing halides as catalysts of chemical reactions. A strong influence of alkali metal chlorides over the structure has been presented as well, with a suggestion that KCl is beneficial for SiO_2 slags and chloride SrCl_2 for Al_2O_3 slags. Papers [1, 10] present a strong influence of alkali element compounds, such as CaO , B_2O_3 , $\text{Na}_2\text{B}_4\text{O}_7$, Na_2CO_3 , over the structure of silicate slags (Fig. 2).

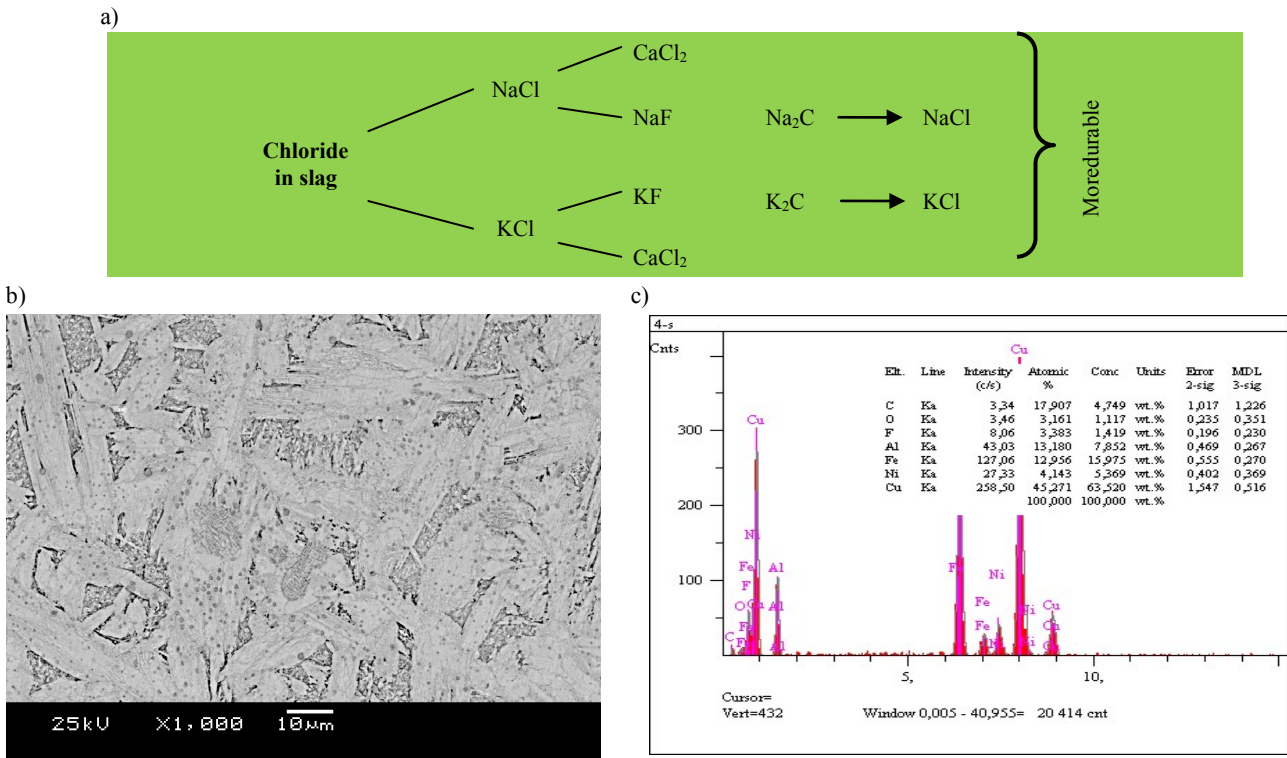


Fig. 3. Chloride in slag: a) diagram of possible influence of chlorides in slag mixtures of Al-bronze, b) microstructure, c) the results of the qualitative and quantitative analysis of EDS

As a result of mutual reaction with carbide chemical reagent, it may be expected that the following complexes will occur, as on the diagram of possible reactions of chlorides and fluorides in slag mixtures in the presence of a chemical reagent – Fig. 3-6.

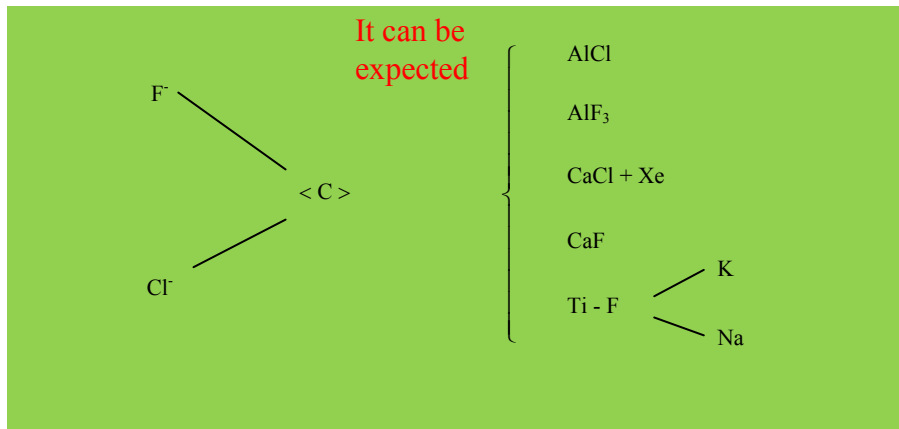


Fig. 4. The impact of stimulants on chemical reagent - diagram of possible reactions of chlorides and fluorides in slag mixtures in the presence of a chemical reagent

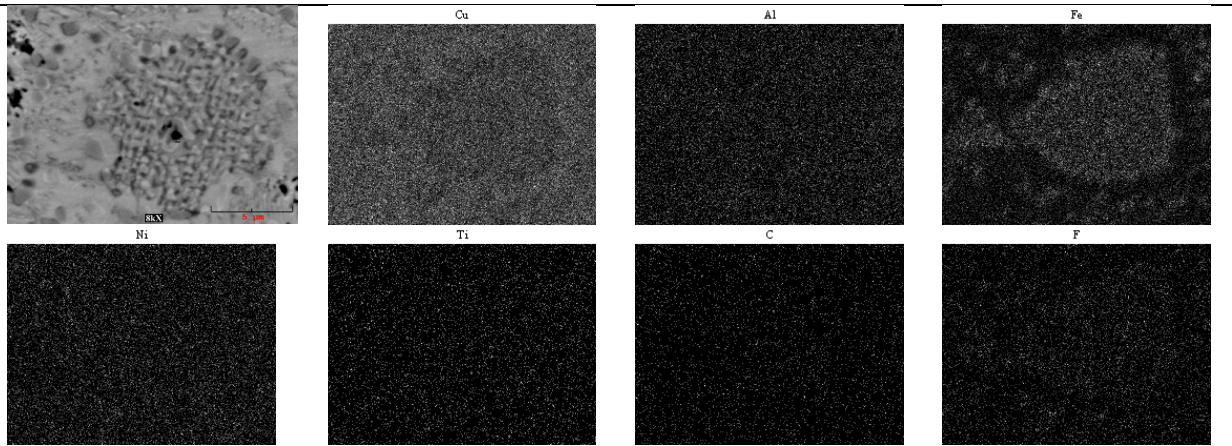


Fig. 5. The impact of stimulants on chemical reagent of Al-bronze - map the distribution chemical elements

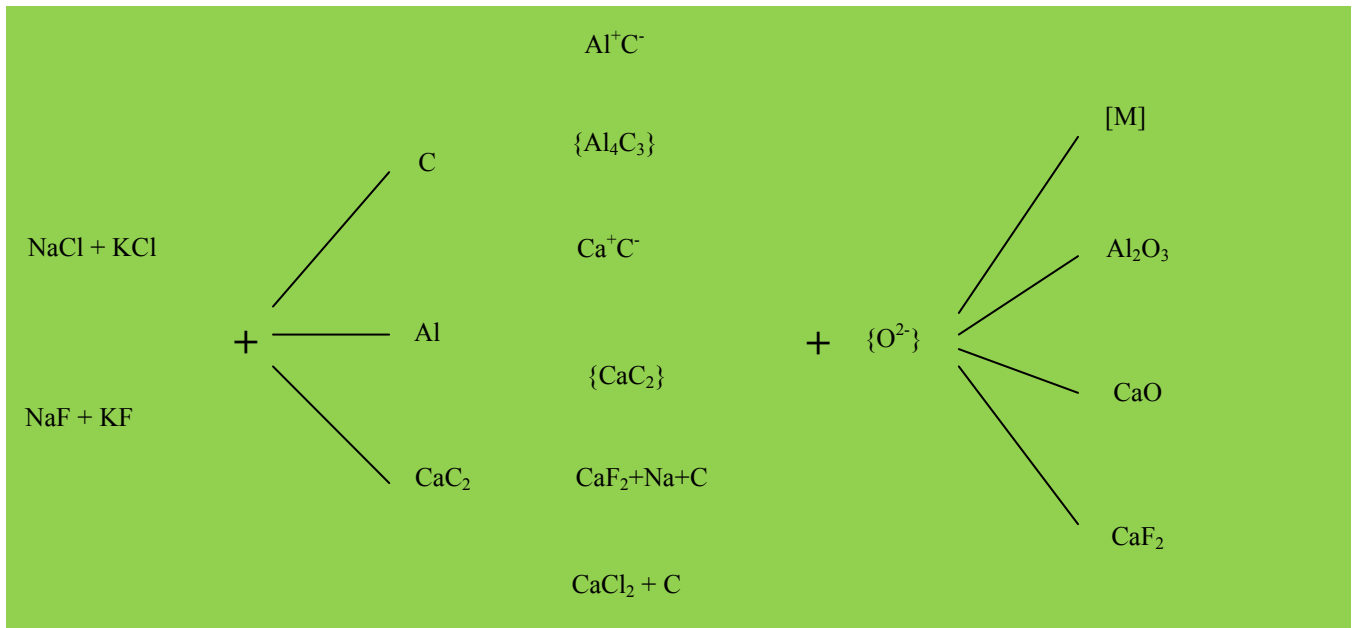


Fig. 6. Reactions of stimulating substances occurring in the process of mass exchange

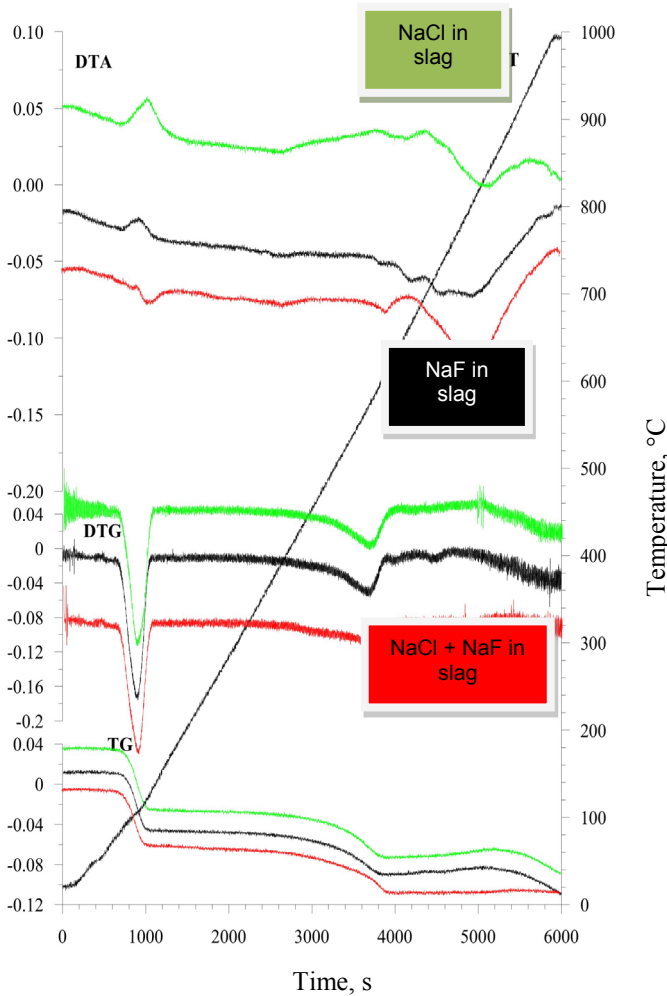


Fig. 7. Derivatogram slag mixtures containing stimulants:
a) NaCl, b) NaF, c) NaCl + NaF

3. Investigation the Slag-Prof database

It is possible thanks to the method of modeling of the refinement by means of DTA method, which is recommended by Adam W. Bydalek, or directly in industrial conditions. The main subject of the research were oxide based slags. The base system was the ternary system of $Al_2O_3 - CaO - SiO_2$. This system was enriched with an additional fourth component in the form of such compounds as MgO , Na_2O , $NaCl$, KF_2 , or B_2O_3 . A computer program, which was created on the base of SQL language and graphical interpretation of the system, determines the best combination of refining mixtures (according to DTA analysis) and checks their refining ability (according to DTA). The program was designed for fast and easy searching and checking of specific data concerning particular types of slag and its properties (7-9).

Change kind of the alloys

Alloys	Symbol	Kind of the oxides - for the DTA analysis
Copper	Cu	Cu_2O
Brass	MO59	$Cu_2O + ZnO + Pb_2O_3$
Silicon bronce	BK331	$Cu_2O + SiO_2 + MnO + Fe_2O_3$
Aluminium bronce	BA93	$Cu_2O + Al_2O_3 + Fe_2O_3$

Select the composition of refiner

Base: $Al_2O_3 - SiO_2 - CaO$ 2% MgO 1% B_2O_3

3% NaO 0% KCl

Enter the desired values $Al_2O_3 - SiO_2 - CaO$

Temperature minimum 1500 K
Temperature maximum 1800 K

Select the type of atmosphere

Oxidizing atmosphere
Reducing atmosphere
Neutral atmosphere

Minimal temperature K	Maximal temperature K	Minimal value Al_2O_3 %	Maximal value Al_2O_3 %	Minimal value CaO %	Maximal value CaO %	Minimal value SiO_2 %	Maximal value SiO_2 %	Surface tension limits N/m
1500	1700	0	5	20	25	70	75	305
1500	1700	15	20	0	5	65	80	390
1500	1549	20	25	45	50	25	30	305
1500	1596	25	30	40	45	25	30	304
1500	1596	25	30	5	10	65	70	100
1500	1700	25	30	5	10	65	70	184
1530	1680	20	25	10	15	60	65	250

Fig. 8. a) Principle of procurance of information the regard of indicated area: user clique opens on passed area, then mouse representative window his propriety physics chemical.
b) Presentation the programmscrean and the results of filtration the database the regard limits of the value chosen physic-chemical proprieties

Al_2O_3	SiO_2	CaO
33.3 [10 ⁻⁶ m ³ /mole]	8.2 [10 ⁻⁶ m ³ /mole]	21.1 [10 ⁻⁶ m ³ /mole]
MgO	B_2O_3	Na_2O
22.9 [10 ⁻⁶ m ³ /mole]	[10 ⁻⁶ m ³ /mole]	33.5 [10 ⁻⁶ m ³ /mole]
KCl	$NaCl$	KF
[10 ⁻⁶ m ³ /mole]	[10 ⁻⁶ m ³ /mole]	[10 ⁻⁶ m ³ /mole]
KF_2	NF_2	
[10 ⁻⁶ m ³ /mole]	[10 ⁻⁶ m ³ /mole]	

calculator

Enter the temperature for which you want to determine the viscosity

[K] designate

Fig. 9. This form is used to provide volume and temperature for the calculated molar relationships

Enter the correction factors in the Ida method

Al ₂ O ₃	SiO ₂	CaO
0.1	1.48	1.53
MgO	B ₂ O ₃	Na ₂ O
1.51	1.12	1.94
KF ₂	NF ₂	

Calculate

Modified coefficient value is

$\alpha = 47.2254$

Alkalinity indicator is

0.0159

Fig. 10. This form is used to enter the weightings. Below is an example of the calculated value of the modified α -factor and alkalinity (B) slag under consideration

4. Summary and conclusions

Visible effect on the mix of stimulant effects a slag. Effect of the substance stimulates the microstructure visible in Fig. 2b, 3b. This may indicate that there is an exchange reaction with possible influence on physicochemical characteristics of slags. Introducing fluorine compounds into chloride slags as additional reaction stimulators allows to further modify the atmosphere, enriching it with active chlorine. Such influence over carbide slag allows to form the atmosphere, making it reductive, and may lead to increase in reduction, Carbo-N-Ox conduction effectiveness.

In proposed programme Slag-Prof will be possible introduction to basic arrangement fourth component, for example the admixture or stimulus of reaction. The language SQL is the structural language the servants to building, creating, of modifying and the management the database. Every gathered during literature analyses' and investigations information in basis this will be kept. Constructing it is possible suitable questions from database to get different information, which can be sorted,

grouped and filtered in any prepare. The investigations were planned for processes the refining the copper chosen alloy. The interface of programme be becomes leaning on fenestrate graphic coat, not only with aesthetical visual regards, but also the simplicity of service of programme. The database will be open and will make possible initiation own data got with or observation industrial investigations.

References

- [1] Bydalek, A.W. (1998). *Carbo-oxygen slag systems in the process of melting copper and its alloys*. Zielona Góra: Technical University of Zielona Góra, Publ. Zielona Góra.
- [2] Bydalek, A.W. (1994). Surface effects of nitrogen in the slag refining of copper. In: *Surface phenomena in foundry*. Poznań – Kołobrzeg.
- [3] Antrekowitsch, J.D. & Offenthaler, D. (2010). Die Halogenproblematik in der Aufarbeitung zinkhaltiger Reststoffe. *BHM* 155(1), 31-39. DOI: 10.1007/s00501-009-0527-1.
- [4] Kharitonov, D.N., Golubeva, E.N., Pergushov, V.I., Kokorin, A.I. & Smirnov, V.V. (2001). Immobilized Complexes of Copper (II) Chloride with Triethylene-tetramine as Catalysts for the Reaction of C-Cl Bond Metathesis. *Kinetics and Catalysis*. 42(5). 673-678. Translated from *Kinetika I Kataliz*, 42(5). 741-746. DOI: 10.1023/A:1012375731860.
- [5] Jafarian, M., Mahjani, M.G., Gopal, F. & Danaee, I. (2006). Electrodeposition of aluminum from molten AlCl₃-NaCl-KCl mixture. *Journal of Applied Electrochemistry*. 36(10), 1169-1173. DOI: 10.1007/s10800-006-9192-1.
- [6] Kochkarov, Zh.A. & Kunashev, R.A. (2007). Five-component reciprocal systems Na,K/Cl,CO₃,MoO₄,WO₄ and Na, K/F, CO₃, MoO₄, WO₄. *Russian Journal of Inorganic Chemistry*. 52(12), 1974-1977. DOI: 10.1134/S0036023607120261.
- [7] Schlafka, P. (2002). *Assessment of the impact of stimulants in refining ladle of selected copper alloys – testing their own. Refining silicon brasses*. Diploma thesis. Technical University of Zielona Góra.