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Rule of the Fluoride Stymulators in to the Carbo-N-Ox Method During Aluminium Bronze Melting Process

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Abstract

During the slag refining process, in the real systems, the complex processes of mass exchange appear. Some relations between the stimulators in the environment - slag - metal system allow to initiate mass exchange reactions in the process of slag refining. Due to this kind of influences there is a possibility of direction and control of melting copper and it's alloys.

Keywords: Refining, Stimulators, Slag, Thermal analysis, Copper alloys

1. Introduction

The influence of particular ingredients of refinement slags on both the mass exchange and the natural environment is one of the important and not yet fully explained issues [1-5]. These ingredients include, so called, reaction stimulators [2]. One of their aims is to commence or accelerate the refining process. However, in the search of the appropriate composition of the slag mixture for metal refining one must consider the impact of individual stimulating ingredients on the technological process. The safety regulations imposed on foundries lead to the strive towards limiting the amounts of chlorides, phosphates and fluorides used in slags. Hence the need for conducting analyses and trials to limit the amount of these compounds to minimum.

The analysis of the actual fusion conditions (Fig. 1) occurring in slag refining of copper alloys in to the Carbo-N-Ox [2] method has not been completed.

Stimulating compounds introduced into the slag react not only with it but also with the atmosphere and the liquid metal. In their presence the capability of forming the atmosphere rises, which allows to influence the ability to refine copper and its alloys. The theoretical considerations show a possibility to utilize CCI compounds in the process of extra-furnace refining to form the atmosphere. Another compound possessing stimulating properties, which allows to form the atmosphere, is fluorine.

Numerous works of A.W. Bydałek and A. Bydałek suggest that dissolution of oxides (Na_2O, B_2O_3, Al_2O_3) in fluorides in the presence of halides may cause changes in the atmosphere, enriching it with F_2 and Cl_2, which should facilitate reduction of the oxides and much faster reactions in the gas phase.

a) b)

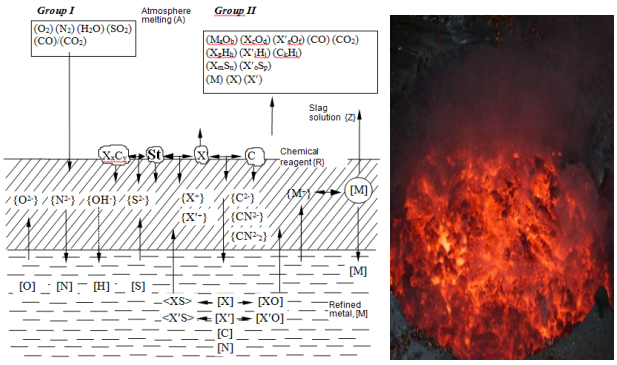


Fig. 1. The melting process: a) Diagram [2] of the refining process for the actual fusion atmosphere system- carbo-nitro-oxygen slag- liquid metal, where: { }- substance dissolved in liquid slag, ( )- gas substance, [ ]- substance dissolved in liquid alloy, <>- solid substance, X, X'- metallic ingredients of the chemical slag reagent, St- reaction stimulator in slag, M refined alloy b) The melting processing real conditions

Further literature analyses suggest that fluoride compounds are more stable than chlorides, which facilitates the emission of Cl_2, and absorption of F_2 from the fusion atmosphere. As a result, there is a possibility of an exchange reaction with possible influence over the slag properties, e.g. cohesiveness (η_z). The introduction of fluorine compounds into chloride slags, as additional reaction stimulators, may also influence the atmosphere composition, enriching it with active chlorine. The anions of fluorides and chlorides, which react with Ca, cause weakening of the bonds with C, which also allows to form the atmosphere in a reducing way. This results in occurrence of compounds of very high stability. Additional dissolution of carbides in the slag causes the increase in the intensity of the reagent reactions [3]. The reagents, linking with nitrogen, create compounds of lower T_T. The atmosphere with a higher amount of nitrogen may be an additional stimulator of surface reactions [4, 5]. The reaction of nitrogen with slag alone may also cause decrease in oxygen dissolubility in such an oxide system.

2. Stimulating substance reaction

The development of industry as well as more and more intense tendencies connected with environment protection force metallurgists to face new challenges. The use of refining blends utilized until now in metallurgy of copper and its alloys is often not advised. 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.

In papers [2, 6, 7, 8, 9] a range of chloride and fluoride use has been presented. The results of the described studies suggest that there is a possibility of using halides as a stimulating substance in aluminosilicate slags [Tab. 1].

Table 1.
The composition of the slag

	Ż		WN	R	St
component	borate glass	Soda	Al_2O_3	CaC_2	NaCl
part	70	30	20*	15*	10*

*Participation % by weight based on the total weight of the slag

The analyses reveal the possibility of introducing stimulating compounds, such as fluorides, into the slag. They cause the increase of simple anion participation against weakening of bonds in complex anions, which should facilitate the exchange reactions. The authors have pointed out the possibility of exchange reactions (Fig. 2, 3).

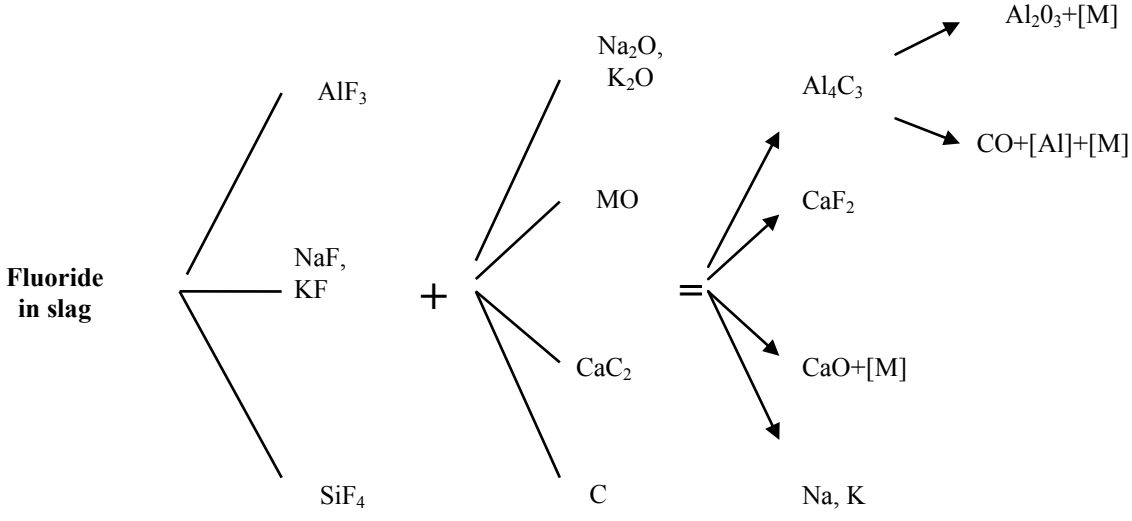


Fig. 2. Fluoride in slag - diagram of possible reactions of fluorides in slag mixtures

a) b)

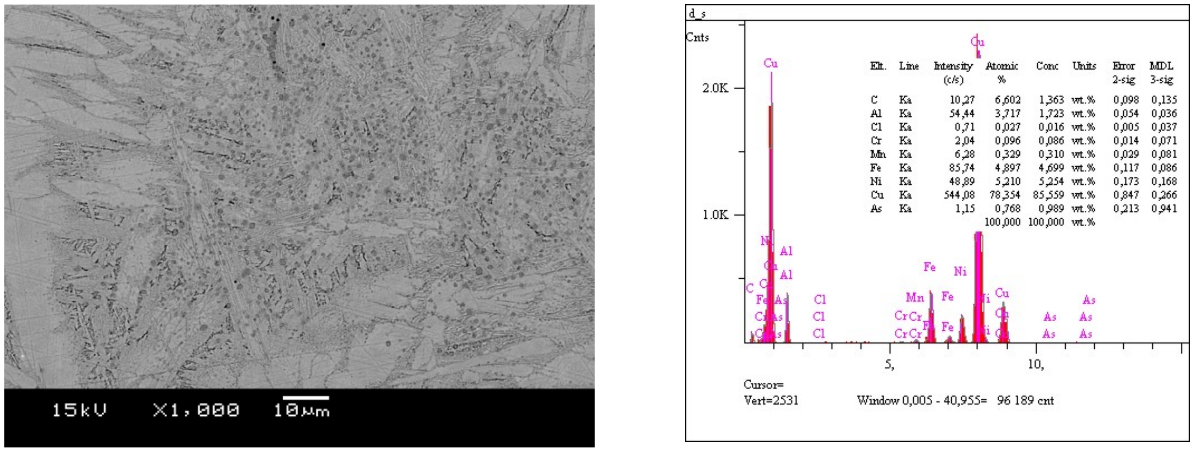
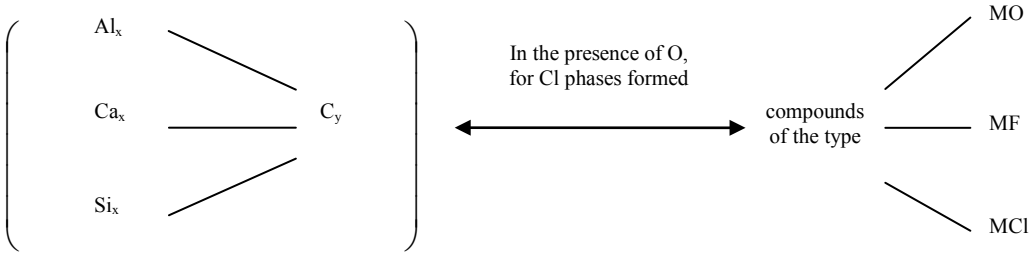


Fig. 3. Fluoride in slag: a) microstructure of Al-bronze, b) the results of the qualitative and quantitative analysis of EDS

a)



b)

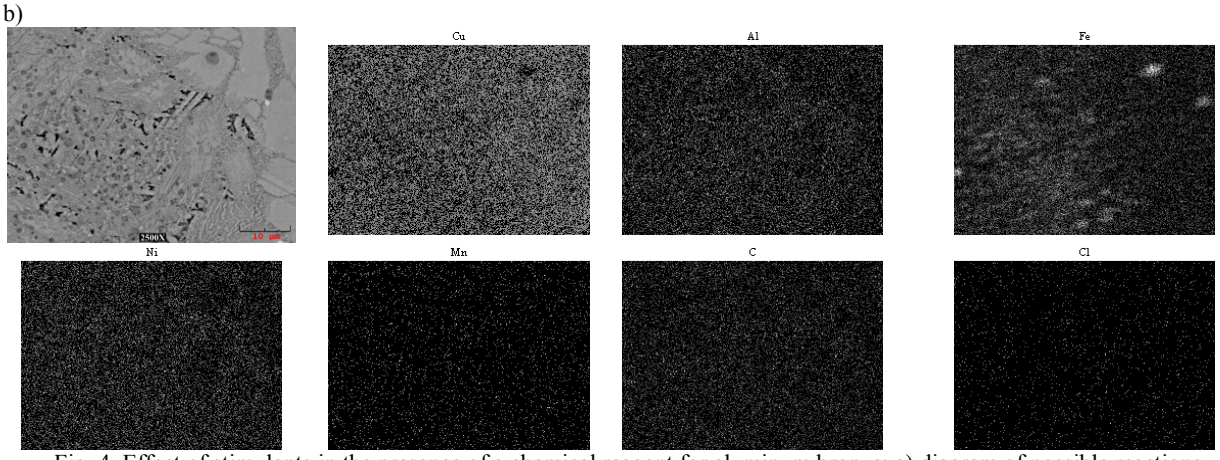


Fig. 4. Effect of stimulants in the presence of a chemical reagent for aluminum bronze: a) diagram of possible reactions of chlorides in slag mixtures, b) map the distribution chemical elements

The liquid complexes which came into being as a result of chloride and fluoride reactions may contribute to occurrence of the following complexes (Fig. 4).

3. Summary and conclusions

The aim of this paper is to show the possibilities of optimizing the slag ingredients, through the use of intentionally introduced stimulating substances and atmosphere of controllable composition in refining processes of given copper alloys.

The literature analysis has shown so far that the mechanisms of processes occurring in slags under the influence of stimulators (Diagram 1) include:

1. Exchange reactions in the system: atmosphere-slag-metal,
2. Reaction leading to occurrence of liquid oxy-carbo-halide solutions.

Introducing fluorine compounds into chloride slags as additional reaction stimulators may further modify the atmosphere, enriching it with active chlorine. Introducing minor amounts of NaCl to the basic compositions of slag with the fluorides leads to increase of the exo effect in derivatographic studies [1].

The presented changes suggest that fluoride compounds are more stable than chlorides, which facilitates emission of Cl_2, and absorption of F_2 from the fusion atmosphere. 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 effectiveness.

References

[1] Bydałek, A. (1977). Neue Hutte. *Studies on Copper and Copper Alloy Refining Using Calcium Carbide*. 12, 663-667.

[2] Bydałek, A.W. (1998). *Slag systems in the process of melting copper and its alloys*. Monograph 86. Zielona Góra: Technical University of Zielona Góra.

[3] Rzadkosz, S., Kranz, M., Nowick, P. & Piękoś M. (2009). Refining processes of selected copper alloys. *Archives of Foundry*. 9(2), 29-34.

[4] Wierzbicka, B & Czyż, M. (1999). Brass melting, *Acta Metalurgica Slovaca*. 5(2), 443-447.

[5] Górny, Z., Kluska Nawarecka, S. & Saja, K. (2013). The Effect of Toughening Combined with Microjet Cooling During Quenching (Solution Heat Treatment) of Calcium Carbide-modified CuAl10Fe4Ni4 Alloy on its Mechanical Properties. *Archives of Foundry Engineering*. 13(1), 29-32.

[6] Antrekowitsch, J.D. & Offenthaler, D. (2010). Die Halogenproblematik in der Aufarbeitung zinkhältiger Reststoffe. *BHM*. 155(1), 31-39. DOI: 10.1007/s00501-009-0527-1.

[7] Kharitonov, D.N., Golubeva, E.N., Pergushov, V.I., Kokorin, A.I. & Smirnov, V.V. (2001). Immobilized Complexes of Copper (II) Chloride with Triethylenetetramine 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.

[8] Jafarian, M., Mahjani, M.G., Gobal, 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.

[9] 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.