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Assessment of the Possibility of Utilising Waste Materials from the Aluminium Production in the Copper Alloys Refining Processes

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Abstract

The analysis of possibilities of utilising waste materials as equivalents of substances stimulating in copper alloys refining processes was presented. The results of thermogravimetric investigations determining the refining ability of the slag with the selected waste materials from the aluminium production were discussed. The possibility of optimisation of the refining slag composition on the basis of the Slag-Prop software was indicated.

Keywords: Reaction stimulators, Slag, DTA

1. Introduction

Interdependence between a melting atmosphere, liquid slag, liquid metal and non-metallic inclusions is essential in metallurgical processes [1]. The determination of the influence of individual components of the system satisfying the above requirements is important due to technological and ecological reasons, since the slags should be meeting not only technological requirements but also should be environmentally friendly. Due to a very high environment load with waste materials a determination of the application possibility of such materials in technological processes, including refining processes, is an important problem.

2. Assessment of slags properties

2.1. Comprehensive methodology of optimisation refining properties of the refining slags

There are several methods allowing to determine the selected slag properties. The methodology proposed in this paper, with an application of a new software, allows – as the first one – the analysis of the influence of extraction coatings physical and chemical properties on their refining ability. The proposed way of analysing [2-4] refining properties of the metallurgical slag based on the author's computer program – material database 'Slag-prop' – utilises the laboratory method of determining refining properties on the bases of DTA analyses [5,6]. This method combines a comprehensive analysis of thermal effects occurring in the refining coating, during physical and chemical influences, with its main thermodynamic, physical, chemical and technological properties. The performed analyses of available data, together with own laboratory and technological investigations, indicated the possibility of utilizing the database contained in the SLAG – PROP software for a fast analysis of assessing refining properties of the metallurgical slags with regard to ecology also. Within attempts to achieve the most environment friendly technologies [7], this software can become not only the database but also the tool for estimating the environment parameters.

The author's software SLAG – PROP built to determine the influence of physical and chemical properties of extraction coatings on their refining ability, allows – among others – for analysing the refining ability of copper alloys by the chemically active refining slag, for the selected zone of the ternary system: Al_2O_3 – CaO– SiO_2, with a possibility of being supplemented with successive components from a group of oxides (MgO, B_2O_3, Na_2O), chlorides (KCl, NaCl) or fluorides (KF, KF_2, NF_2), which in such way constitute the five-component slag coating.

The methodology proposed in this work (after appropriate changes of zones and data supplementing), can be utilized for practically all pseudophase oxide systems and in relation to slag refining of every alloys.

2.2. Determination of slag refining abilities by the thermo-differential method

The method [5,6] of tracing effects of joint influencing between slag and oxide equivalents of contaminations of the analysed alloy, provides the possibility of determining the refining ability of the selected slag mixture, including its elements.

Taking into consideration the necessity of a complex analysis of the whole metallurgical system A – Z – WN – ST – R (where: A- melting atmosphere, Z- slag/refiner, WN- amount of oxides, corresponding to dross, ST- reaction stimulator, R– chemical reagent, M-refined metal/alloy) it was decided to analyse the influence of the selected waste materials on the refining ability in relation to copper melting conditions.

Two indicators are the refining ability meters [6]: EW – energy-related, [kJ/mol], r – mass-related, [%]. They are obtainable directly from the thermo-differential investigations (DTA/TG) at taking into account the differentiating methodology of the tested and reference samples. In the case of the described below analyses the slag with equivalent of non-metallic inclusions from copper melting (Cu_2O) was the tested sample, while the slag without any addition was the reference one. In such case refining ability indicators are related to the total effect of the slag influence with oxide Cu_2O.

2.3. Chemical influences

Analyses [9-11] indicated the possibility of introducing into the slag such substances as fluorides (e.g. NaF, CaF_2), causing increased fractions of simple anions at the expense of complex anions, which should support exchange reactions. Gusiew and Gulyukin [12] found in their investigations, that the following reactions are possible:

$$2NaF + CaO = Na_2O + CaF_2 \quad (1)$$

$$[Si_2O_5]^{2-} + Na^+F^- = [SiO_2F]^- + Na^+ + [SiO_3]^{2-} \quad (2)$$

$$[Si_3O_9]^{6-} + Na^+F^- = [Si_3O_9F]^{7-} + Na^+ \quad (3)$$

$$[Si_3O_{10}]^{8-} + Na^+F^- = [Si_2O_6F]^{5-} + Na^+ + [SiO_4]^{4-} \quad (4)$$

As the result of reaction 2 and 3 a viscosity decrease is possible. At a higher content of silica, NaF reacts according to equation 3 and 4. The confirmation that NaF has a higher influence on the slag structure modification than CaF_2, can be found in the cited papers. An introduction of fluorine compounds - as additional reaction stimulators - into the chlorine slag can modify the atmosphere by enriching it with active chlorine. An attention should be also drawn into a higher stability of fluorides as compared with oxides of K, Na, Mg, Ca, Mn, Ti, Zn, Cu, P, B, Fe. This – when calcium compounds are present - provides the possibility of utilising equation (5):

$$\{CaCl_2\} \rightarrow \{<CaO>\} \rightarrow \{CaF_2\} \quad (5)$$

As the result of introducing fluorides or chlorides into the refining system there is a possibility of shaping the atmosphere with fractions of these compounds as well as influencing with alloying compounds and chemical reagents [1]. The above reasons constituted the bases of taking into consideration waste materials from the aluminium production, since their chemical analyses (Table 1) indicated, that they contained such compounds as: KCl, NaCl, KF, NaF, $Na_3(AlF_6)$ and $NaClO_2$.

3. Investigation results

3.1. Selection of basic components of the slag mixture

On the bases of the author's computer software – database 'Slag-Prop' [2-4] – the method of analysing the slag selection and determination of refining properties of the metallurgical slag was proposed. Utilising simultaneously the laboratory method of determining the refining ability on the bases of the DTA analyses [6], the original procedure combining the comprehensive analysis - of thermal effects occurring during physical and chemical influences in the refining coating with its main thermodynamic, physical, chemical and technological properties - was presented.

The analytical zone in the software 'Slag-Prop' was defined and verified for the basic system: Al_2O_3 – CaO – SiO_2 in respect to melting conditions of copper and its alloys, creating the material database open for the user. The determination of the slag refining properties was realised via the specially prepared material database allowing simultaneous use of the available data of the system as well as the results of own investigations. In the developed methodology the fraction of additional slag components, such as: reaction stimulators (e.g. NaCl, NaF), correcting reagents (e.g. Na_2O, MgO, B_2O_3, Na_2PO_4, $Na_2B_4O_7$), other components as equivalents of melting losses (Cu_2O, ZnO, SnO, PbO, P_2O_5), melting atmosphere (neutral, oxidising, reducing) as well as measuring and technological conditions in laboratories and in industry (e.g. measuring temperatures, kind of applied measuring tools, kind of furnace) were taken into account. The proposed procedure (Fig. 1) is possible for the application in practically all systems of pseudophase oxides and in relation to slag refining conditions of every alloys. The example of the composition determination is shown in Figure 2.

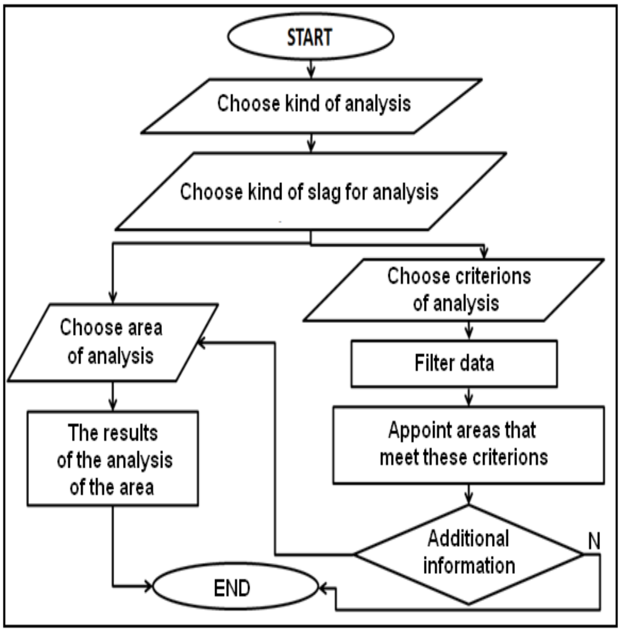
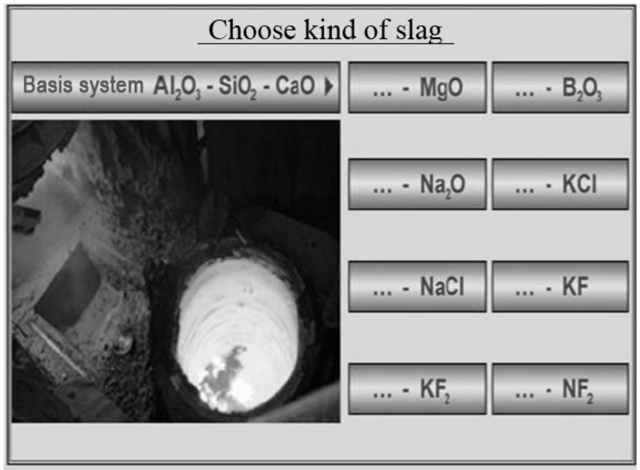
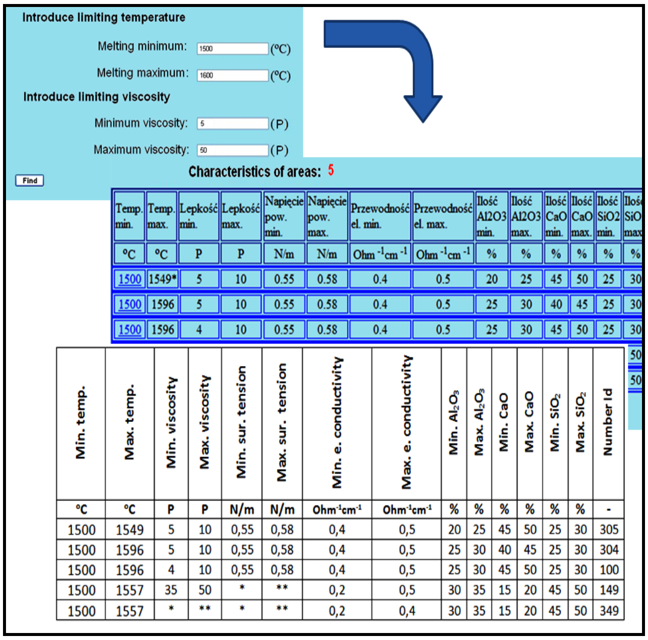


Fig. 1. Operation algorithm of the proposed optimisation program

The basic composition of the refiner for the copper melting conditions (Table 1) were determined on the bases of the analyses performed with the application of the Slag-Prop software and with taking into account the data from the analyses of the introduced waste materials chemical composition. In each case, 20 % CaC_2 was introduced into the refiners composition.



a)



b)

Fig. 2. Examples of windows showing the way of selecting a) and the result indicating the optimal selection of the refining coating components b)

3.2. DTA analyses

The compositions for thermo-differential analyses were singled out according to the Slag-Prop software, according to the melting temperature criterion and in relation to the copper melting conditions. The DTA analyses of mixtures prepared according to compositions given in Table 1 are presented in Figures 3-5. Six various waste materials were analysed and the composition of refining mixtures were supplemented with substances stimulating reactions, such as NaCl or NaF – depending on the Slag-Prop software suggestions.

Table 1.
Composition of the analysed materials

Fig. number	Basic system of the slag [%]				Waste materials [%]	Additional ingredients [%]		Indicator refining capacity	
	Al_2O_3	Na_2CO_3	$Na_2B_4O_7$	SiO_2		NaCl	NaF	EW, [kJ/mol]	r, [%]
3.a	20	25	15	40	The frst set of the filters above the galvanizing process - 5%Σ(Al_2O_3, MgO, FeO, KCl, C)	10	-	-1,0	- 5
3.b	20	25	15	40	The second set of the filters above the galvanizing process - 15%Σ(Al_2O_3, MgO, FeO, KCl, NaCl, C)	-	-	+1.0	- 4
4.a	20	30	-	50	The third set of electrode processes - 5%Σ (Al_2O_3, MgO, FeO, Na_2O, CaO, KCl, NaF)	15	10	0,0	+ 3
4.b	20	30	-	50	The fourth set of electrode processes - 15%Σ (Al_2O_3, MgO, FeO, Na_2O, CaO, KCl, NaF, NaCl)	-	-	+ 50,0	- 5
5.a	25	20	-	55	The fifth set of anode material without carbon - 5%Σ ($Na_3(AlF_6)$ + $NaClO_2$ (5:1), Al_2O_3)	-	-	- 15,0	- 8
5.b	25	20	-	55	The sixth set carbon anode material - Σ10 (C, $Na_3(AlF_6)$ + $NaClO_2$ (5:1), Al_2O_3)	-	-	- 60,0	- 11
6	30	15	55	-	The fifth set of anode material without carbon - 5%Σ ($Na_3(AlF_6)$ + $NaClO_2$ (5:1), Al_2O_3)	10	-	- 85	- 9

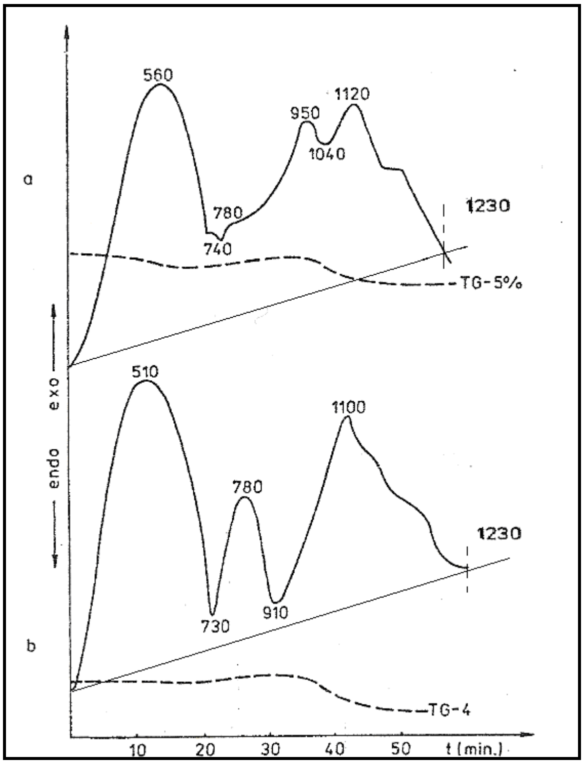


Fig. 3. Results of the DTA analysis of samples 3a and 3b, acc. to Table 1

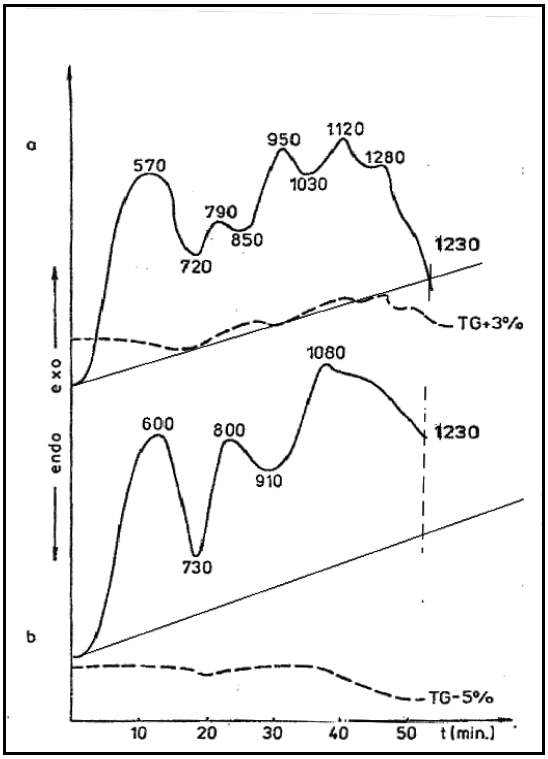


Fig. 4. Results of the DTA analysis of samples 4a and 4b, acc. to Table 1

In accordance with the procedure allowing the assessment of the slag mixture refining ability the tested sample was of the composition according to Table 1 supplemented with 20 % Cu_2O (as an equivalent of oxide dross of non-metallic inclusions), while the reference sample was of the same composition but without copper oxide. The results of EW and r (refining ability) indicators listed in Table 1 indicate, that out of the selected compositions only mixtures containing anodic materials (5a) and carbon (5b) allow to achieve the high refining ability. In respect to the copper melting conditions, apart from the mentioned above, kinetic conditions do not allow to obtain the energy minimum within the interval to app. 1250 K.

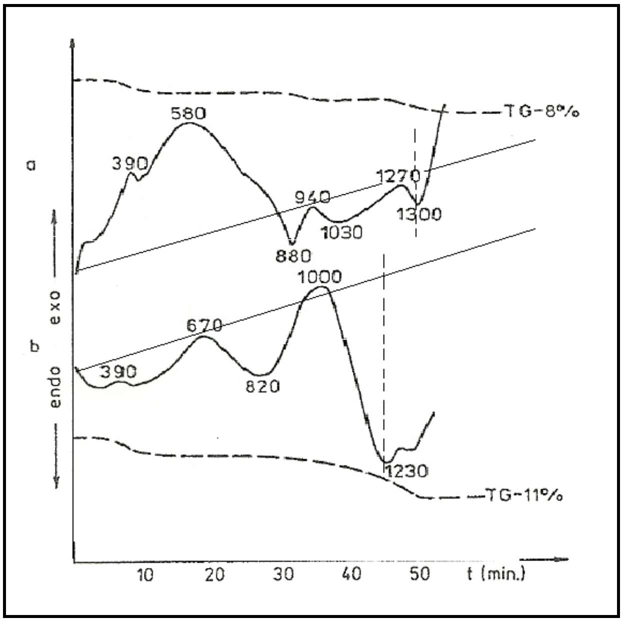


Fig. 5. Results of the DTA analysis of samples 5, acc. to Table 1.

The carbon presence in waste materials (set 6) influenced the energy minimum shifting by several dozen degrees, from 1300 to 1230 K. Results obtained for the mixture supplemented with waste materials from filters (set 1 and 2) seems also promising. Thus, the obtained results indicate the neutral conditions (of the energy indicator) with a tendency to reducing conditions of these compositions influence in relation to Cu_2O oxide. In this case using a strong chemical reagent of a reducing influence should widen the possible applications of this composition. In case of the remaining mixtures (3 and 4) combinations of refining indicators EW and r do not provide perspectives to applying them, under copper melting conditions. The high fraction of oxides Na_2O, CaO and the carbon absence in these compositions, does not favour reducing melting conditions. It is possible to introduce stimulating additions to these compositions, but such procedure was not the purpose of the hereby work.

Figure 6 illustrates the effect of the summary influence of the mixture of the given refining ability (the highest - out of existing - in the programme database) singled out by the Slag-Prop software. As the listing of data in Table 1 indicates the programme suggested the change of the basic composition, introducing $Na_2B_4O_7$ instead of SiO_2 and additionally NaCl. This composition was determined on the bases of searching for the highest refining ability, within a similar zone, with the results: EW = - 85 kJ/mol and r = - 9%.

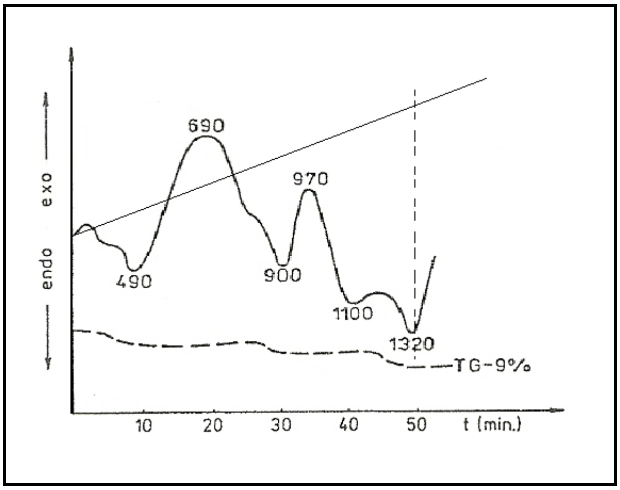


Fig. 6. Results of the DTA analysis of samples 6, acc. to Table 1.

4. Conclusions

The application of waste materials in refining processes can be considered with regard to products formed during high temperature melting processes as well as with regard to the expected technological effects. The analyses indicate that the presence of chlorine and fluoride compounds in waste materials must not be explicit with the stimulating influence of such materials. A strong influence of cryolite and chlorite in mixtures 5 and 6 could be caused by the presence of ions: F^{-2}, Cl^- and ClO_2^-. That time reactions 2-5 can be initiated leading to the melting temperature and viscosity decrease of individual components of the refining mixture.

The train of procedures presented in the paper allows for the selection of the slag mixture basic composition, amounts of necessary stimulating components, and for the assessment of the refining ability of the total refiner composition. The developed program, after introducing experimental data allows also for successive corrections in the proposed mixtures composition. The database of the Slag-Prop software being currently supplemented with data concerning toxicity of the applied chemical compounds will also allow to select the waste materials from the point of view of their influence on the environment.

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