The Innovative Analysis of the Refinement Ability Extractive Slag

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Abstract—This article contains information concerning the analysis of the possibility of defining refinery qualities of slag, based on thermo physical and thermo dynamical data. The paper presents a model of slag refining processes and a method of determining the reduction capability of slag solutions. Slag was analyzed by means of DTA methods. The study of computer programme contains all necessary thermo dynamical and experimental data, taken from the literature and our own investigations, which enables establishing optimal proprieties of slag in an easy way. It is possible thanks to the method of modeling of the refinement by means of DTA method, which is recommended by Adam W. Bydałek, or directly in industrial conditions. The main subject of the research was oxide based slags. The base system was the ternary system of Al2O3 – CaO – SiO2. This system was enriched with an additional fourth component in the form of such compounds as MgO, Na2O, NaCl, KF or B2O3. 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.

Index Terms—slag, extraction coating, refining, influence, database, program.

I. INTRODUCTION

The work concentrates particularly on the slag extraction process which is commonly used in the casting processes of copper alloys. The effectiveness of diffusive influences depends on physical and chemical interactions which are changing continuously during the melting process. The influence of the atmosphere on the processes in slag and its surroundings causes continuous disruptions of the thermodynamic equilibrium of the system of melting atmosphere - slag - refined metal. Surface phenomena, including interfacial tension, are of great significance in slag. At the same time, another properties such as: viscosity, conductivity and chemical kinetics affect the exchange of mass, what makes a clear description of the phenomenon complicated.

Therefore, it was necessary to create a program which enabled relating all the interactions mentioned above. By means of such a program, it is possible to specify the refining capacity and refining properties of slag.

II. ANALYSIS OF THE PROBLEM

A. Stages of refining

According to Nernst’s distribution law, in such a configuration as metallurgical slag, the balance in the solution of metal and slag with non-metallic inclusions is established very quickly.

In the process of melting slag several functions of slag can be distinguished:
- disposal of harmful admixtures and pollutions from the refined alloy
- protection of the mirror of liquid metal from the influence of the atmosphere,
- Limitation of negative interactions with the facing of stove.

The effectiveness of diffusive influences depends on physical and chemical proprieties which change during the next phases of melting. The phase of melting can be divided into two stages:
1) During the first stage, accompanied by the reactions from the outer atmosphere, the gradual heating of metal takes place,
2) During the second stage, when the metal is in a liquid state, the composition of the atmosphere is influenced by some factors from the surface of slag and metal.

Many complex reactions between the elements involved take place during these phases. Those reactions depend on the construction of furnaces and other individual characteristics of the indicated, given foundry.

B. Stages of refining the influence of slag

Slag is a very important element, which is responsible for the effects resulting from the rules which determine the conditions of equilibrium of the atmosphere-slag-metal [1,2]. In addition, slag is the cause of the corrosion of the furnace linings, as well.

In literature, one can find publications referring to individual properties of slag [3,4] and descriptions of chemical reactions [5-7]. It turns out that there are big differences in opinions concerning the structure and the basic characteristics of slag and its interaction with metal and with the atmosphere.

In the technological processes of melting, it is difficult to control the technological parameters. [8]. It is necessary to take into account fluxing agents and viscosity. The
parameters and properties of slag are changing in the time of duration of the process. [1,2, 8-10,14-20]. Moreover, the atmosphere causes continuous interferences between slag and metal [14-16,20]. Besides that, slags are not exactly colloidal systems that the superficial analysis is fully justified for. Table 1 shows the results of investigations in different measuring conditions. It is the reason of additional difficulties in comparing the results of researches on surface properties.

Table 1. Demonstrative on variety of laboratory conditions near determination the property of superficial slag compositions.

<table>
<thead>
<tr>
<th>Property</th>
<th>Measuring conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Literature</td>
<td>Viscosity</td>
</tr>
<tr>
<td>R*</td>
<td>MA*</td>
</tr>
<tr>
<td>14</td>
<td>X</td>
</tr>
<tr>
<td>15</td>
<td>X</td>
</tr>
<tr>
<td>16</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>X</td>
</tr>
<tr>
<td>18</td>
<td>X</td>
</tr>
<tr>
<td>6</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td></td>
</tr>
</tbody>
</table>

Explanation: The R* - the measurements of viscosity by the rotameter, it MA* - the settlement the stickiness from utilization the right Archimedes, the LK - the method of lying drop

The double layer theory constitutes a base for the description of interactions between metal and slag. This conception, for example, makes the explanation of the mechanism of deoxidation possible. Lippman's function [1,6] enables to analyze thermodynamic functions and surface phenomena simultaneously. However, it does not take time into account.

Instead of investigating superficial effects, the interactions between slag, the atmosphere and metal can be accessed on the base of the method of differentiation of the phenomena of heat and mass [9,10]. It allows to analyze the interactions in function of time.

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C. Modeling a real metal refining process - model conduction

An existing literature suggests that a real metallurgical system should be analyzed along with all the interactions occurring inside it [11-14]. The extraction of metallurgical slag during the process of melting copper alloys can be intensified by addition of carbides [12]. In order to analyse the process the author [4] has made an effort to estimate refining efficiency of complicated sets of reagents in real industrial systems. The widely used simplifications refer mainly to the chemical compositions and temperature which is established at a constant level. Because the simplifications provide a very weak correlation with the reality, the author has made an effort to use thermal \( Q = f(T, \tau) \) and mass changes \( m = f(T, \tau) \) as the temperature increases.

The division explains the necessity of the analysis of the whole system starting from ambient temperature up to alloy melting points [4,15]. Taking into consideration the characteristic of the metallurgical processes the latter stage, in which diffusion processes are considerably accelerated, should be recognised as the most influential. Fig.1 presents a scheme of interactions taking place during liquid metal refining with a slag carbide-cyanamide solution. The established (Fig.1a) conditions of the metallurgical process in the hearth furnace required creating a similar empirical system, which with the use of a thermal-differential method will allow monitoring all the changes taking place. Trials of modelling such a process are presented in Fig.1b. A refining alloy has been replaced by a mixture of oxides occurring in the metal bath as a result of interactions with melting atmosphere and other accidental factors of metallurgical processes. The oxides were introduced in the amounts and mutual proportions corresponding with melting losses of the tested alloy. They are marked with WN. The metal drops marked M are registered during the structural investigations.

In figure 1 group I comprise components of the furnace atmosphere such as: oxygen, nitrogen, and water steam, sulphur dioxide, etc; group II comprises gaseous products of the reaction of agents from group I along with the components of vapour of refining metal. The scheme presents the melting process referring to the real conditions.

The remaining external factors in the crucible (Fig.1.b) were taken into considerations in the model system by analogy to real conditions (Fig.1a). The factors referred mainly to the rising in time temperature and limited influence of external atmospheric factors (the cover on the measurement crucible). Mutual interactions between active reagents and oxides of refined components of alloys occur in the discussed slag model system. The interactions were
analysed through investigating thermal and mass effects in function of temperature rising linearly. It corresponded with assumption of the advisability of evaluation of the interactions changing in time during the complete technological cycle.

D. Elaboration of a method of estimation slag refining factors

Two melting stages have been specified in the analysis of metallurgical changes for real conditions of slag refining of copper alloys [1,2,8]: - heating the metallic charge of a solid state, - meltdown and overheating of liquid metal alloy. The main idea of thermal-differential investigations relies on the assumption that the total sum of all the mass and thermal effects occurring while keeping the sample in the temperature conditions can be estimated. Thus, the main effort to interpret the results of the research should be focused on selecting the changes that are interesting as far as the reaction with the WN equivalents in the refined alloy is concerned. This was expected to achieve through algebraic summation of the characteristic effects in specially elaborated measurement cycles.

Mass decrements in the reaction space may be connected with occurring only volatile products. The author proposed assuming coefficient \( \tau \) (according to formula 1, 2) recognised as an indicator of the rate of coal consumption in reduction processes in the investigated system. It has been decided to consider the registered on TG-curves mass changes from an initial reduction phase vividly marked on DTA curves.

\[
\Delta m = \frac{\Delta m - y \cdot \Delta m_1}{a_t} \cdot 100\% \quad (1)
\]

Where:
- \( \Delta m \) - mass decrement of slag with oxide calculated from the beginning of the reduction processes,
- \( y \) - Slag participation in the slag-oxide system,
- \( \Delta m_1 \) - Mass decrement of slag without oxide,
- \( a_t \) - total initial amount of oxygen, resulting from stoichiometrical calculations, referring to the sample mass.

\[
\Delta m = \frac{\Delta m - y \cdot \Delta m_1 - x \cdot \Delta m_2}{a_t} \cdot 100\% \quad (2)
\]

Where:
- \( \Delta m_2 \) - Mass decrement of the analysed oxide (WN),
- \( x \) - WN participation in the total mass of the tested sample.

During the above investigations the essential differences between the DTA curves for various compositions of slag-creating mixtures were observed. It encouraged search for wider and more common application of the measurement method through the analysis of the registered differences of the thermal effects.

On the basis of the presented elaboration, the following routine (Fig. 2) for determining the refining abilities of the tested sets has been proposed:

1. Determination of the thermal effect and the mass decrement derived from TG measurement for S+R+WN with reference to S+R (1 on Fig. 2).
2. Determination of the thermal characteristic of slag (S) and reducer (R) through DTA measurement of the mixture S+R relative to \( \text{Al}_2\text{O}_3 \) (2 on Fig. 2).
3. Determination of the thermal characteristic WN measuring DTA with reference to - Al₂O₃ (3 on Fig. 2).
4. Estimation of thermal effects resulting from the lack of interaction between WN and S + R. The estimation was carried out with the use of a graphical sum of 2 and 3 (4 on Fig. 2).
5. The effect of interaction between WN and S+R producing a graphical difference of 1 and 4 (5 on Fig. 2).
6. Calculation of the energetic indicator EW on the basis of the estimated surface areas of the endothermal effects occurring in the melting temperature range of the analysed alloy (Fig. 2).
7. Calculation of the reduction indicator r on the basis of estimated mass decrement values S+R+WN (equations 1 and 2). The values are achieved from the TG curve.

Fig 2. Specification of the DTA curves and graphical analysis presenting the routine while estimating the indicator of refining abilities on the basis of endothermal measurement of the reduction effect (S-slag, R-reagent, WN- oxides, EW - energy reduction indicator)

It is expensive and time-consuming to carry out the analysis according to 1-7 (for determining the refining differences in Fig.2.1-2.5) for each case. ΔH is calculated for the registered change using the values of the determined fields (Fig. 2.5) with the use of the Kissinger’s method. The value EW is regarded as an indicator of entropy ΔH.

In order to calculate precisely the value EW it was necessary to carry out all the measurements according to curves in Fig.2.1 Thus, it was decided to determine a relationship between the value ΔH estimated from the measurements (derived from Fig. 2.1) and the value EW derived from the presented above routine which resulted in Fig 2.5. The calculated values EW (for over 100 Z-R-WN systems) allowed to establish the correlation coefficient "  eₖ ". On the basis of the carried out analysis the value of the correlation coefficient was estimated at 2.8-4.0 for endothermal effects. For exothermal effects the correlation was 1.5-3.5. Exothermal effects were decided not to be analysed while interpreting the slag reductive interaction on WN. On the basis of statistic calculations at a confidence level at 0.90, the value of "  eₖ " correlation coefficient was estimated between ΔH and EW at 3.1.

The analysis of slag containing WN [16] allowed to establish the possible combinations of EW and r values (Table 2) together with a proposed explanation. On the basis of calculations it was also found that due to the differences in vaporisation or reaction with the atmosphere of compositions the simultaneous consideration of two values (r and EW) is necessary.

Table 2. The explanation of results on the basis of indicators EW and r

<table>
<thead>
<tr>
<th>Lp.</th>
<th>Value of EW</th>
<th>Size of r</th>
<th>Explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>EW &lt;&lt; 0</td>
<td>r &lt;&lt; -10</td>
<td>strong reductive interaction</td>
</tr>
<tr>
<td>2</td>
<td>EW &lt;&lt; 0</td>
<td>r (-5, -1)</td>
<td>weak reductive interaction</td>
</tr>
<tr>
<td>3</td>
<td>EW ≤ 0</td>
<td>r (-1, 0)</td>
<td>no reductive interaction</td>
</tr>
<tr>
<td>4</td>
<td>EW &gt; 0</td>
<td>any r</td>
<td>oxidizing reaction</td>
</tr>
</tbody>
</table>

EW - as an energy reduction indicator showing the direction and intensity of reaction in progress. r - as a measure of reduction of WN by carbide reducer

III. CONCEPTION OF BUILDING OF THE PROGRAMME

The study of a computer programme, including the satisfactory number of data, both thermo dynamical as well as experimental, gathered with literature and own investigation, would make simpler qualification of optimum proprieties of slag possible. Settled by programme of areas the verification it is possible to the end to conduct in the support about proposed by A. W. Bydalka [17] the method of the modeling processes of refinement from it utilization the derivatograph or directly in conditions industrial. A program user [18-20] should have the possibility to select which kind of information he would like to get. Should have the possibility to indicate composition of his interest and be given all accessible information on chosen subject. He from second side should have the possibility of introduction border data the arrangement also, which would like to receive. The principle of working of programme was introduced on Fig. 3.

Accepting the jump near division of system what 5%, for simple system Gibbsa it gets oneself 400 different areas. Areas these were one should describe in support about data with literature and experiences. In proposed programme will be possible introduction to basic arrangement fourth component, for example the admixture or stimulus of reaction. In this way programme will make possible the individual modifications of composition.
in composition of studied material substance. Every point in arrangement answers the not only different quantitative composition of substance, but it is characterizes different proprieties physics chemical also.

**Fig 3. Ideological scheme kelter of the programme**

Near remembered frequency of sampling arrangement the quantity of information will grow up to 1600 elements then and gives the spatial figure. So the peck of information and necessity of management the datum feature the SQL shows on choice of language. 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 it is possible suitable questions from database to get different information, which can be sorted, grouped and filtered in any prepare. At random chosen compositions will become verified in real conditions obviously. The investigations were planned for processes the refining the copper chosen alloy. Gathered data could also find for different alloys use. 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 utilization in this aim will become the HTML as well as language PHP enabling the implementation of query structural language. The database will be open and will make possible initiation own data got with or observation industrial investigations. It was it been possible was already now however to move following:

- there are possible and purposeful the construction optimization programme engaging all of the physics chemical influence the slag in processes of melting metals alloys,
- the proposed results, ranges of areas on graphs of phase equilibrium’s, demonstrative on the optimum values, will be verified in laboratory conditions and industrial,
- The initiation of the new data the gathered base will be built in system of open base enabling.

**IV. LABORATORY STUDIES**

A. The estimation of quality refining slag for the extractive slag refining

After actuation programme and introduced three-phase user Gibbs arrangement becomes the recess the suitable kind of the slag material, for example oxides diagrams. It is then equilateral triangle which tops answer the concrete entering

**Fig 4. Principle of procurance of information the regard of indicated area: user clique opens on passed area, then mouse representative window his propriety physics chemical.**

Arrangement was partite on 400 areas, which answers changes composition of material, what 5 % on every component. Restricting area and division him what 5 % makes possible the comparatively precise qualification of propriety studied material regard of his molar composition. User it after recess any area, clicking on him, gets information about the most important proprieties him characterizing. Additionally following drawing represents the principle of procurance of information the regard of passed area and kind of the alloys (Fig. 4, 5).

After correct realization [7] question user gets in tabular figure information about possible occurrence about set proprieties areas. The results of question was it been possible additionally to broaden about information about remaining proprieties physic-chemical of the slags – in this work for CuSn5Zn5Pb5 and CuSn10P alloys. It the kind of the database was presented the permissive on calculation for arrangement of oxides Al₂O₃-SiO₂-CaO with the B₂O₃ , Na₂O and MgO (Table 4. ) optimal co-ordinates areas in reference to conditions of this alloys.

The recently elaborated method of observing effects of co-reaction between slag and oxide inclusions and the programme made possible to estimate the reduction capacity of the slag composition (Table 3), with addition reagent as another metal, carbon and carbide and reactions slag stimulators (Table 4), in comparison to the CuSn10P and CuSn5Zn5Pb5 alloys melting conditions. Carbon, carbide (CaC₂ or Al₂C₃) and metal are used to created condition lake as reducing [8, 17].

In the experiments the refined alloys are replaced, according with the described methods with follow oxides: - CuSn10P alloy with Cu₂O(60 %), SnO(20 %), P₂O₅(20 %) – compounds 1.1-1.4,
- CuSn5Zn5Pb5 alloy with Cu2O(5 %), SnO(15 %), ZnO(50 %), PbO(30 %) – compounds 2.1-2.4, which oxides respond with the melting losses of its alloys in the real metallurgical condition.

Database analysis showed, that the most profitable effects of the refining from among analysed slag to the CuSn10P alloys should oneself to expect after combination of mixtures stimulating No 1.4. For this composition are EW marked on –168kJ/mol and r on –19,0% and this investigation result point at Na2B4O7 + NaF (3:1) as the best stimulator for analysed slag. From other DTA analysis can be say that best should be the slag 2.2. However it is now from labour and industrial investigation that Na2CO3 after dissociation can give substance about oxidising characteristics. The stimulator composition 2.3 contain only fluoride and chloride there are not indifferent for health the worker at the furnace.

Table 3. Schema of the investigation – kind of the used stimulators and DTA results

<table>
<thead>
<tr>
<th>No</th>
<th>Stimulators [wt. %]</th>
<th>Indicators</th>
<th>EW – kJ/mol</th>
<th>WN</th>
<th>r - % mas</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>---------------------</td>
<td>EW = 0.0 kJ/mol</td>
<td>r = -2.5 %</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.2</td>
<td>Na2CO3 + NaCl (2:1)</td>
<td>EW = -24.0 kJ/mol</td>
<td>r = -8.0 %</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.3</td>
<td>NaCl + NaF + CaF2 (1:1:1)</td>
<td>EW = -70.0 kJ/mol</td>
<td>r = -12.0 %</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.4</td>
<td>Na2B4O7 + NaF (3:1)</td>
<td>EW = -168.0 kJ/mol</td>
<td>r = -19.0 %</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4. The content (wt. %) of basis slag compositions after analysis with the database

<table>
<thead>
<tr>
<th>Al2O3</th>
<th>B2O3</th>
<th>CaO</th>
<th>Na2O</th>
<th>SiO2</th>
<th>MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>1</td>
<td>22</td>
<td>8</td>
<td>56</td>
<td>4</td>
</tr>
</tbody>
</table>

B. The estimation of quality refining slag for the gas-slag refining

The laboratory strange is showing at the picture 1. The alloy marked as MO59 was melted in an induction’s crucible furnace with the capacity 10 kg, then casted in metal moulds.
the value of definite proprieties. The sended suitable form thereon becomes the basis from data to database. After correct realization question user gets in tabular figure information about possible occurrence about set proprieties areas. The result of question was it been possible additionally to broaden about information about remaining proprieties physic-chemical. Besides, in aim the image of location about set properties the area on graph Gibbs (Fig.2), the special navigator was created. After recess area and his click, displayed arrangement 3 becomes user - phase from noted on him at present under examination area. The principle of filtration of database was introduced physics chemical (Figure 3). It the pattern of conduct in the work was presented the permissive on calculation for arrangement of oxides Al₂O₃-SiO₂-CaO B₂O₃ optimal co-ordinates areas in reference to conditions of fusion silicon bronzes. Moved analysis was provided to carry to traditionally appointive in metallurgy of data in basing about measurements of stickiness and melting-point. It was showed on the Figure 4 and they allow on the determining range favorable compositions - appointed with letters polygons.

V. CONCLUSIONS
The paper presents a model of slag refining processes and a method of determining the reduction capability of slag solutions. Slag was analysed by means of the DTA method. The analysis of slag containing oxides allowed to establish the possible combinations of two indicators: EW and r, and their interpretation. The construction of optimization program, containing all of the physical and chemical data concerning the interactions in processes of melting metal alloys, was possible and purposeful. Introducing of new data is implemented in a system of open database. Necessary DTA figures are introduced for verification of the data gathered. The database, in SQL system, is accessible for various users, who have the possibility of creating their own configurations, too. The conception recommended here was used for selecting refineries for CuSn5Zn5Pb5 and CuSn10P alloys. The selected results and ranges of areas on graphs of phase equilibria, presenting optimal values, have been successfully tested in laboratory and industrial conditions.

REFERENCES


