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ASSESSING THE REFINING ABILITIES OF SLAGS BY MODELLING A REAL PROCESS OF METAL MELTING

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Abstract

The paper presents a model of slag refining processes and a method of determining the reduction capability of slag solutions. Slag was analysed with the use of the DTA methods. The analysis of slag containing oxides allowed to establish the possible combinations of two indicators: *EW* and *r* values together with the proposed explanation.

Keywords: DTA, metallurgical slags

Introduction

The existing literature suggests that a real metallurgical system should be analysed along with all the interactions occurring inside it [1–3]. The extraction of metallurgical slag during the process of melting of copper alloys can be intensified by addition of carbides [2]. To analyse the process the author has made an effort to estimate refining efficiency of complicated sets of reagents in real industrial systems [4]. The widely used simplifications refer mainly to the chemical compositions and temperature which is established at a constant level. Because the simplifications provide 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.

Measurement system

Two melting stages have been specified in the analysis of metallurgical changes for real conditions of slag refining of copper alloys [2, 4]:

1. Heating the metallic charge of a solid state
2. Meltdown and overheating of liquid metal alloy.

The division explains the necessity of the analysis of the whole system starting from ambient temperature up to alloy melting points [5]. Taking into consideration the characteristic of the metallurgic processes the latter stage, in which diffusion processes are considerably accelerated, should be recognised as the most influential. Fig-

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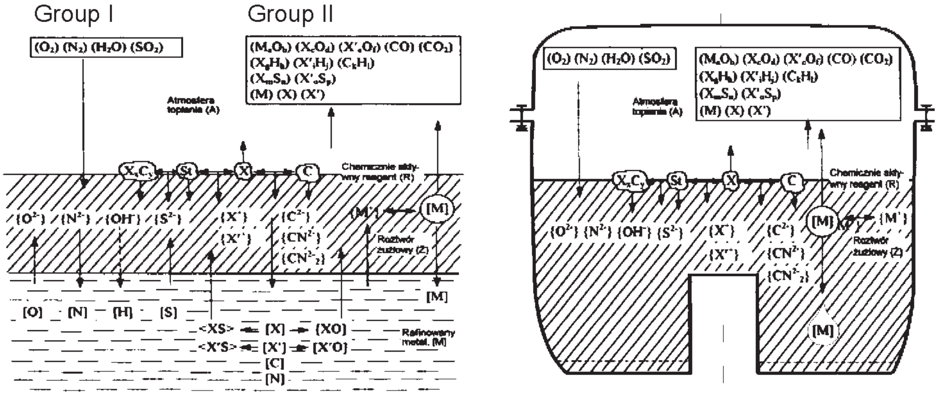
ure 1 presents a scheme of interactions taking place during liquid metal refining with a slag carbide-cyanamide solution.

The established (Fig. 1a) conditions of the metallurgic process in the hearth furnace required creating a similar empirical system, which, together with the use of a thermal-differential method, will allow monitoring all the changes taking place. Attempts 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 metallurgic processes. The oxides were introduced in the amounts and mutual proportions corresponding to melting losses of the tested alloy. They are marked with WN. The metal drops marked M are registered during the structural investigations.



a **b**

Fig. 1 A proposed scheme of refining process of a liquid metal with a carbide-cyanamide slag solution [6] where A – the melting atmosphere, Ż – slag, ( ) – gas, M – melting metal, X – reagent, St – reaction stimulator, { } – ions in the slag, [ ] elements in the melting metal, a – real conditions under the cover, b – model conditions

In Fig. 1 group I comprises components of the furnace atmosphere such as: oxygen, nitrogen, steam, sulphur oxide, 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. 1b) 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 as a function of temperature rising linearly. It was in agreement with the assumption of the advisability of evaluation of the interactions changing in time during the complete technological cycle.

Elaboration of a method of estimation slag refining features

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 r (according to formula 1) recognised as an indicator of the rate of coal consumption in reduction processes in the investigated system. It has been decided to consider the mass changes registered on TG-curves from an initial reduction phase vividly marked on DTA curves.

$$r_1=\frac{\Delta m-y\Delta m_1}{a_\mathrm{t}}100 \tag{1}$$

where:

Δm – mass decrement of slag with oxide calculated from the beginning of the reduction processes,

y – slag participation in the slag-oxide system,

Δm_1 – mass decrement of slag without oxide,

a_t – total initial amount of oxygen, resulting from stoichiometrical calculations, referring to the sample mass.

$$r_2=\frac{\Delta m-y\Delta m_1-x\Delta m_2}{a_\mathrm{t}}100\% \tag{2}$$

where:

Δm_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 applications 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 derived from the DTA measurement and the mass decrement derived from TG measurement for Ż+R+WN with reference to Ż+R – Fig. 2.1,

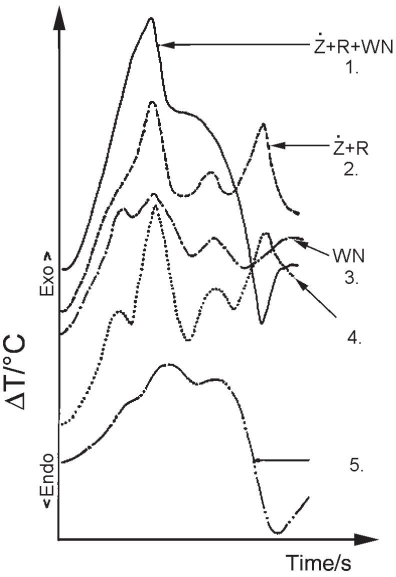


Fig. 2 Specification of DTA curves and graphical analysis [6] presenting the routine while estimating the indicator of refining abilities on the basis of endothermal measurement of the reduction effect (Ż – slag, R – reagent, WN – oxides)

2. Determination of the thermal characteristic of slag (Ż) and reducer (R) through DTA measurement of the mixture Ż+R relative to – Al_2O_3. – Fig. 2.2,

3. Determination of the thermal characteristic WN measuring DTA with reference to – Al_2O_3. – Fig. 2.3,

4. Estimation of thermal effects resulting from the lack of interaction between WN and Ż+R. The estimation was carried out with the use of a graphical sum of Fig. 2.2 and Figs 2.3–Fig. 2.4,

5. Producing a graphical difference of Figs 2.1 and 2.4–2.5. The aim is to get the effect of interaction between WN and Ż+R,

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. 2.5,

7. Calculation of the reduction indicator r on the basis of estimated mass decrement values Ż+R+WN (Eqs (1) and (2)). The values are achieved from the TG curve. Only values from the reduction range are considered in the calculations.

Verification of the measurement method

As shown in Fig. 3a, the curve, which is a graphical difference between c and d, is not a straight line. It resulted from the effect of dissolving WN in slag (Ż). The analysis of over 30 various slag compositions, 6 samples for each composition allowed to determine the graphical range for the differences c and d for slag systems not interacting

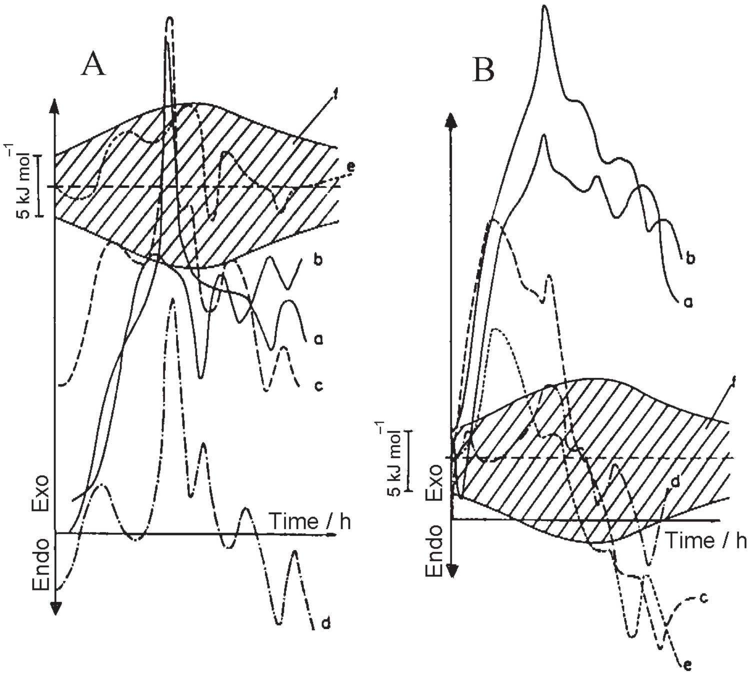


Fig. 3 Specification of the results of the thermal-differential analysis (DTA) for two slags: A – presents the result showing the lack of reducing interaction of a mixture of the slag and R referred to WN, B – shows the opposite

with WN. A rule was assumed that the arithmetic average $\Delta\overline{H}$ of particular endothermal or exothermal effects is close to the real value. An apparent error of particular measurements $p_i=\Delta\overline{H}-\Delta H_i i$ was considered and an arithmetic average of measurements

$$\sigma_s=\frac{1}{n}\sqrt{\sum_1^n p_i^2}$$

was calculated.

The respective DTA curves in Fig. 3 refer to:

a) slag+40% CaC_2 as reducer (reference sample – Al_2O_3)
b) Cu_2O (reference sample – Al_2O_3),
c) slag+40%CaC_2+15%Cu_2O (reference sample – slag+40% CaC_2),
d) graphical sum of diagrams b and a,
e) graphical difference of diagrams c and d,
f) graphical representation of standard dispersion for the difference between the diagrams c and d determined on the basis of DTA analysis, in which there was no interaction between the chemical reagent R and slag Ż and WN.

The fact that the curves c and d do not fall into the graphical range of the assessed standard deviation proves that the interaction between the A–Ż–R system and WN takes place. Based on the shapes of the DTA curves and the simultaneously registered TG curves, it is visible that the maximum of the mass decrements of the tested systems was connected with the maximum of the endothermal effects. In order to confirm it, the following cycle of tests was carried out:

1. Slag of a composition according to Table 1 containing 40% of technical calcium carbide and 20% of Cu_2O was held at a temperature of T=1000, 1050, …, to 1300 and 1400 and 1500 K for 15 min in argon atmosphere.
2. The received material was weighed and subjected to analysis on mass spectrometer PW-1480.

Table 1 The content of examinated slag

The main slag content					Additive	
Al_2O_3	B_2O_3	CaO	Na_2O	SiO_2	NaCl	NaF
20	7	14	13	46	18	13

For comparison a DTA/TG analysis was carried out for the tested mixture prepared according to the presented method. The results prove that within the range 1150–1200 K the most intense reduction in Cu_2O takes place in carbide slag. It is consistent with the maximum of the endothermal effect established for the analysed system. It was recognised as a confirmation of the possibility of taking the value of the endothermal effect of A–Ż–WN/A–Ż–R system as an energetic indicator of refining abilities of the slag. The indicator was marked with EW symbol.

The following symbols were accepted:

EW – as an indicator showing the direction and intensity of reaction in progress.

r – as a measure of reduction of WN by carbide reducer.

Summary and conclusions

It is expensive and time-consuming to carry out the analysis according to 1–7 (for determining the refining differences in Figs 2.1–2.5) for each case. $\Delta\overline{H}$ 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 enthropy $\Delta\overline{H}$. In order to calculate value *EW* precisely, 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 $\Delta\overline{H}$ estimated from the measurements (derived from Fig. 2.1) and *EW* derived from the presented above routine which resulted in Fig. 2.5. The calculated values *EW* (for over 100 Ż–R–WN systems) allowed to establish the correlation coefficient 'e_k'. 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 'e_k' correlation coefficient was estimated between $\Delta\overline{H}$ and *EW* at 3.1.

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

Lp.	Value of *EW*	Size of *r*	Explanation
1	$EW<<0$	$r<<-10$	strong reductive interaction
2	$EW<<0$	$r\in(-5, -1)$	weak reductive interaction
3	$EW\leq 0$	$r\in(-1, 0)$	no reductive interaction
4	$EW>0$	any *r*	oxidizing reaction

The analysis of slag containing WN [6] 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.

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