PHYSICAL - CHEMICAL PROPERTIES OF THE METALLURGICAL SLAGS

Dudek R., Dobrovský Ľ., Dobrovská J.
VŠB – Technical University of Ostrava, 17.listopadu 15, 708 33 Ostrava – Poruba, CZ

FYZIKÁLNĚ - CHEMICKÉ VLASTNOSTI METALURGICKÝCH STRUSEK

Dudek R., Dobrovský Ľ., Dobrovská J.
VŠB –Technická univerzita Ostrava , 17.listopadu 15, 708 33 Ostrava – Poruba, ČR

Abstrakt

V práci se věnuje pozornost problematice fyzikálně chemických vlastností roztavených metalurgických strusek, především z hlediska povrchových jevů. Provádí se experimentální metoda měření povrchového napětí tavenin metodou ležící kapky, inovovaná začleněním CCD – kamery a následným přenosem dat do PC. Na vybraných anorganických systémech jsou prezentovány kontinuální změny fyzikálně – chemických vlastností v závislosti na teplotě a chemickém složení. Současně s výzkumem vlivu obsahu vybraných komponent na povrchové vlastnosti tavenin se porovnávaly průběhy jejich teplotních závislostí s hodnotami laboratorně připravených struskových soustav na stejné bázi. Změnami hmotnostních procent CaO ve vzorcích se prokázaly odlišnosti v trendech průběhů teplotních závislostí povrchového napětí. Dále byly zaznamenány značné odchylky v absolutních hodnotách a v celkovém chování zkoumaných veličin u laboratorních a reálných systémů. Měření jsou doplněna teplotními závislostmi hustot zkoumaných systémů.

Abstract

The aim of the presented study is to solve the problems of physical – chemical properties of the melted metallurgical slags, especially from the surface phenomena point of view. The experimental method for the surface tension measurement of melts has been practised, using the method of the lying drop, inovated by including the CCD – camera and consequent data transfer into PC. There are presented continual changes of physical – chemical properties using the examples of chosen systems , with dependance on the temperature and chemical structure. Concurrently with the influence research of the content of chosen components on the surface properties of melts, there were compared the courses of their temperature dependances to the values of laboratorary prepared slag systems on the same basis. The changes of percentages by weight of CaO in the samples proved the differences in the course trends of the surface tension temperature dependences. Consequently, considering the laboratorary and real systems, there were also proved considerable divergences in absolute values and in total reactions of the analysed quantities. The measurements are completed with the temperature density dependences of the examined systems.

Key words: surface tension, slag, temperature of smelting, density, calcium oxide

1. Introduction

The melted slags represent a very important part in forming the basic physical and techological parametres of the final product; not only during the production of the steel, but also

in another wide spectrum of metallurgical applications. The choice of the optimum slag régime during the steel production process determines, except from the correct course of metallurgical reactions, also the basic technical – economical indices values of the whole steel process.

From the physical – chemical point of view, the slags represent a multicomponent system, which consists mainly of the oxides of some compounds of the metal charge, oxidative or slag formers and another products which come into being during the reaction between the molten metal and the heat resistent material. The chemical composition and the temperature strongly influence their structure, on which depend a number of physical and physical – chemical properties. The formation of a slag melt is a result of a very complicated process, which consists mainly of the thawing and dissolving of the starting compounds of the heterogeneous mixture conducted by a series of chemical reactions. Because of the complicated course of this process and polycomponent character of the industrial slags, it is not possible to compile either any exact description or a model of the processes which run during the slag system heating.

The knowledge of the raffinate slags surface tension brings the information about the structure and the conditions of the interphase reactions on the boundary slag – metal, which is very narrowly connected i. e. with the problem of leaving non - metallic inclusions.

The presented study concerns the experimental studium and analysis of the metallurgical slags surface properties with an effort to put near the reciprocal connections among the used parametres and the chemical and structural changes of the analysed systems [1,2].

2. Measuring method

With respect to the character of the measured systems for our measurement there has been evaluated as optimal the method of the lying drop. Its principle lies in the assessment of geometrical parametres of a melt drop on a non – dipping base. Basically it also enables to assess the density of the measured samples and of their dipping angles. The calculation of the surface tension values is possible to realize i. e. by using the Dorsey relation:

$$\sigma = \rho.g.x^2 \left(\frac{0,052}{f} - 0,12268 + \frac{0,0481}{f} \right) \tag{1}$$

The symbols are: σ - surface tension [N.m^{-1}]
               g   - gravitational constant [m.s^{-2}]
               f, x - geometrical parametres of the sample [m^{-1}], [m]
               ρ - density [kg.m^{-3}]

The classical method of photographic record was in our workplace gradually replaced by using the CCD – camera, which enables continual record of the changes of a sample during the heating. This system also enables the transmission of the picture into PC, where it is compiled on the software level, using the Vizir programme, which was especially developed for these purposes, with a possibility of consequent archivation [3,4].

This arrangement of the measuring systems offers a wide range of advantages and it also very effectively eliminates most imperfection of the method of maximum pressure in the bubble. It is possible to measure the arbitrary viscose materials, using the small size of a sample, which guarantees sufficient chemical and thermal homogenity.

Credibility and reproducibility of the results were proved on the sample MgF_2. Comparison of the measured results to the literary values proved good agreement [5].

3. Choice of the samples

With respect to a wide range of examined raffinate slags, there are presented the results gained for slags A and B. Using these characteristic systems (the chemical structure shows tab.1), there was measured the surface tension and density in dependance on the temperature. For the sample 1 it was searched the influence of CaO contents on the change of the course of the surface tension temperature dependence. Results of some of the measurements of synthetic operational slags were also compared to laboratory prepared ternary systems, which contain also equivalent amount of $CaO – Al_2O_3 – MgO$. Basic materials for their preparation disposed of purity p. a. and before the measurement the samples were divested of possible air moisture by annealing.

Table 1 Chemical structure of the examined slag systems

component	sample A wt.%	sample B wt.%
CaO	11.3	34.4
MgO	10.5	6.4
SiO_2	0.077	0.2
Al_2O_3	77.7	58.2
Fe_2O_3	0.63	0.33
TiO_2	0.110	0.127
MnO	0.068	0.094
K_2O	0.015	< 0.3
Na_2O	< 1	< 1
SO_3	< 0.01	< 0.05
Cl	0.004	0.072
Annealing lose	-0.87	-1.09

4. Experimental results

Sample A did not show during the temperature load up to 1650°C any marks of smelting and therefore the statements about the surface tension of this sample are missing in the original state. In this sample there was also searched the influence of graded content of CaO in the amount of 30, 40, 50 and 60 wt.% (Fig.1 – the temperature dependences are interlarded polynoms of the 3rd degree).

In the system of 30 wt.% CaO there were observed the first signs of smelting at 1490°C and the sample was completely smelted and sintered into ball – shaped form at 1520°C. At the temperature interval of 1528 – 1580°C the surface tension rises, at 1580°C it comes to maximum and then it is followed by a fluent regress to the temperature of 1610°C, which approximately represents upper limit for technical possibilities of the measuring equipment.

Different temperature dependence shows a sample of 40 wt.% CaO; in coparison to the other samples it is featureless, mainly at the temperature area of 1373 – 1514°C. The temperature interval of smelting represents a narrow temperature interval of 1335 – 1345°C.

The sample of 50 wt.% CaO smelts at similar temperature interval 1330 – 1350°C, but it shows very strong temperature dependence in which the maximum is moved down to the lower temperatures 1390°C, and the minimum at 1490°C.

Similar character of the course shows the sample of 60 wt.% CaO content, moved into the area of higher temperatures. The temperature interval of smelting is 1400 – 1420°C.
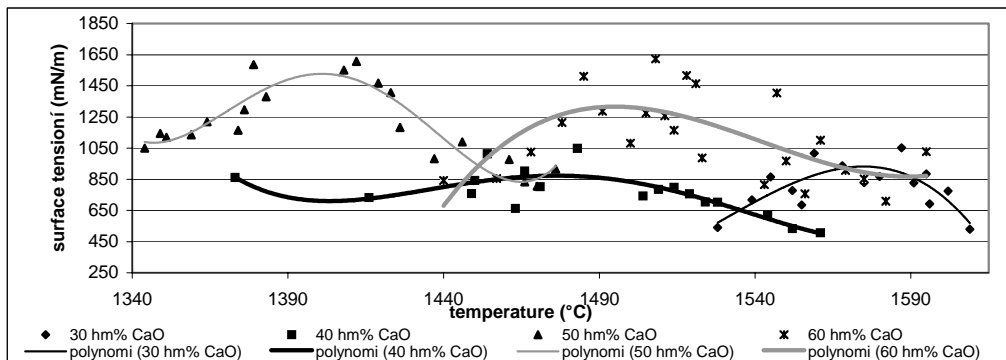
Fig.1 Comparison of the surface tension temperature dependance of the sample A to various contents of CaO

Consequently there was studied the influence of the less supplied accessory admixtures in real slag system A.

Figure 2 shows the comparison of temperature dependences of the surface tension course of real and laboratory prepared slag system consisting of pure ingredients CaO – Al_2O_3 – MgO, which represent the basic components in the analysed slags in equivalent rates.There were compared only systems with 40 and 50 wt.% content of CaO, in which was during the previous measurements proved operationaly acceptable melting temperature. With respect to the pure systems, the graph was completed with temperature dependences of surface tension during the cooling process.

Fig.3 shows temperature dependence of analogical systems density in Fig.2.
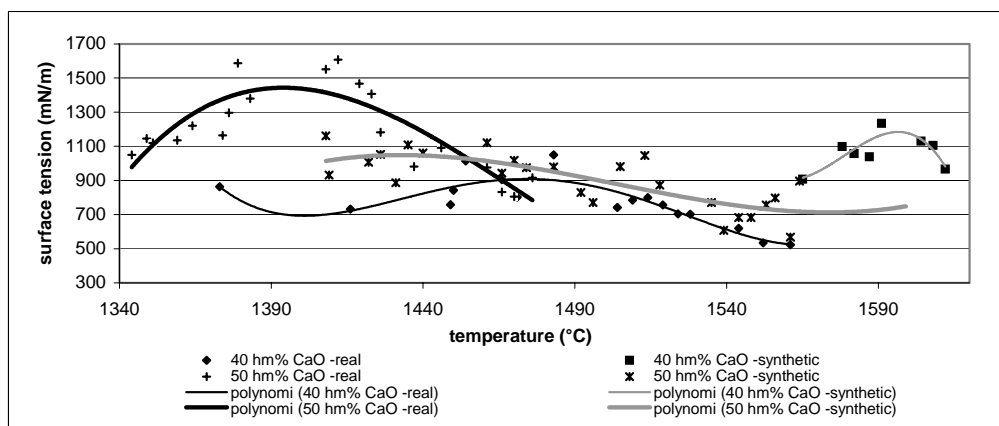

Fig.2 Comparison of the surface tension temperature dependence of real and synthetic slag system, sample A

Sample B melts at temperature interval of 1330 – 1360°C. Figure 4 shows its surface tension temperature dependence and consequently its comparison to laboratory prepared pure ternary system CaO – Al_2O_3 - MgO. Because of absence of the accessory admixtures, it comes to total melting and homogenization of this system just at 1570°C, and therefore the data at lower temperatures are missing.
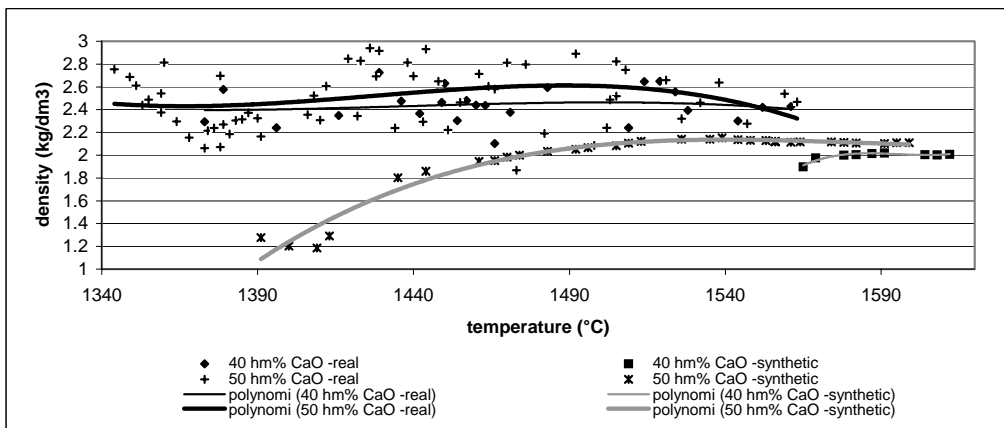
Fig.3 Comparison of temperature dependence of the real and synthetic slag system, sample A

Figure 4 shows in the real system noticeable rise of the surface tension up to 1470°C and consequent regress to the measurable bound of 1650°C. Completely different character of temperature dependence shows the pure system during heating and also during cooling; it is moved up to higher values of the surface tension. The difference of the surface tension absolute values at 1580°C is approximately 360 mN/m, and with temperature rise it consequently rises.

In Figure 5 the surface tension measurement of the sample B is also completed with temperature dependences of density of the equivalent systems.
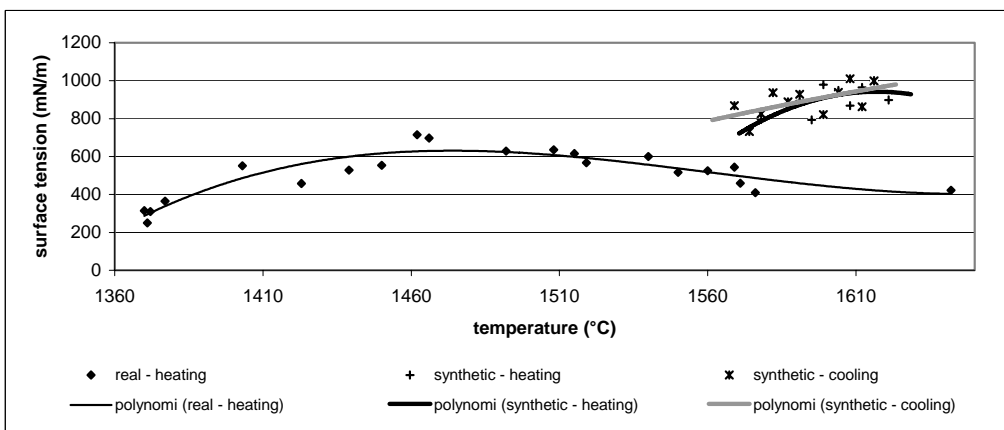

Fig.4 Comparison of the surface tension temperature dependence of real and synthetic slag system, sample B

5. The results discussion
The influence of CaO contents

Considering the influence of CaO content on the values of surface tension (Fig.1), there is a noticeable moving of maximum temperature dependences into the area of lower values. This trend is kept up to 50 wt.% CaO content when it comes to regression and the maximum is again moved to higher temperatures. Also at this concentration interval it comes to

gradual rise of absolute values of the surface tension. The only exception represents the sample with 40 wt.% CaO content, which surface tension temperature dependence is quite featureless. The presented courses correspond with the temperature intervals of melting, which show analogical movings in dependence on CaO contents according to the phase diagrams.
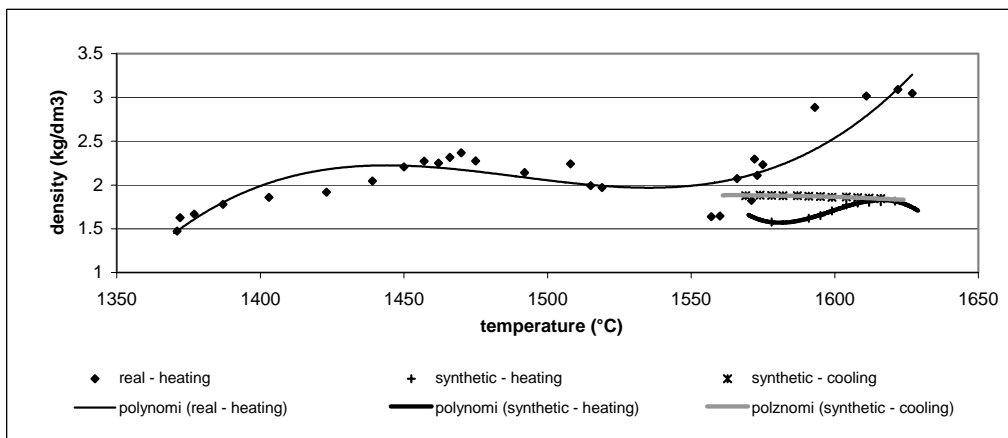

Fig.5 Comparison of the density temperature dependence of real and synthetic slag system, sample B

Cation Ca^{2+} has got quite large radius and low ionic potential and as a modifier of the structure it arises the surface tension of melt. CaO as an O^{2-} donor causes the shortening of polyanionic chains. This fact probably causes the total arise of absolute values of the surface tension up to certain CaO contents. The consequent surface tension regress might be caused by phase transformation, which demand more detailed research. The causes of the anomalies with 40 wt.% CaO contents can be explained by the influence of accessory admixtures [6,7].

Comparison of real and synthetic slag systems

Because of strong deaeration of a sample it was possible to observe the surface tension values for synthetic system of 40 wt.%. CaO during the heating process from 1565 ^{0}C. This phenomenon can be explained by reducing reactions between the sample and the graphite base.

Generally, the fig.1 and 2 show lower surface tension of the real systems in the area of higher temperatures because of the accessory component presence. This fact is especially apparent in sample B (Fig.4). After Kozakevitch [8], if the ratio is $x(MeO)/x(Al_2O_3) > 1$, all the aluminium corpuscles are coordinated tetraedrically. In this form they can take part on construction of the polyanionic in coincidence with the other accessory ions which are able to make chains (Si^{4+}, Ti^{4+}, etc.). This requirement is in case of both measured systems fully realized, which can lead to the mentioned regress of the surface tension concerning the real systems.

The influence of CaO contents on the course of temperature dependences synthetic systems was less evident according to insufficiently developed net structure which was caused by absence of accessory complements.

During the density of melts research, there were found out relatively featureless temperature dependences. Considering the synthetic systems, there it comes to a very slight arise

during the heating, which relates to the volume dilatation. During the cooling process, there is no regress to the primary values, which can be explained by the beginning of higher meltable compounds in the surface layers of the melt in the furnace atmosphere. Also especially in the real systems, during the whole melting process it came to a slight deaeration, which could lead to creation of the bubbles and consequently to distortion of resultant values [9].

6. Conclusion

The intent of the presented study is the research of heterogeneous anorganic melts surface properties with a view to the analysis of physical – chemical properties of metallurgical slags. Special attention is given to the influence of contents of the components on surface tension of the studied systems, and consequently there are compared the properties of operational and laboratorary prepared systems. Except from the influence of total proportion of CaO in ternary systems on their properties, there were also proved considerable divergences in reactions of real and synthetic metallurgical slags, which was caused by the accessory admixtures coexistence. This study represents a partial contribution to introduction of slag systems without silicium into technological practice.

Acknowledgement

Literature

[1] Turgdogan, E.T.: Physicochemical properties of molten slags and glasses. The Metals Society, London, 1983, ISBN 0 904357 54

[2] Voskobojnikov, V. G., Dunaev, N. E, Michalevič, A. G.: Svojstva židkych domennych šlakov. Metallurgija, Moskva, 1975

[3] Linzer, E., Dudek, R.: Použití CCD - kamery SONY DKC - 5000 při studiu povrchových vlastností metalurgických strusek metodou ležící kapky. in. Metal 2000 - sborník přednášek, Tanger s.r.o. Ostrava, 2000

[4] Linzer, E., Dudek, R.: Možnost stanovení teplotních parametrů licích prášků metodou ležící kapky.in. Metal 99 – sborník přednášek, Tanger s.r.o. Ostrava, 1999

[5] Bochňák, R.: Kandidátská disertační práce. Československá akademie věd –Ústav teorie hutních procesů, Ostrava, 1988

[6] Popel, C. I., Esin, O. A.: Poverchnostnoe natjažene rasplavlennych silikatov. Žurnal neorganičeskoj chimii, 1957, v.11, No.3, s. 632

[7] Sharan, A., Cramb, A. W.: Interfacial Tension of Liquid Fe - Ni Alloys and Stainless Steel in. Contact with $CaO –SiO_2 –Al_2O_3 –$ Based Slags at 1550°C. Metallurgical and Materials Transactions, vol. 26B, No.1, 1995

[8] Kozakevitch P.: in Physical chemistry of Process Metallurgy, Interscience Publ., New York, 1961

[9] Thong, V. V.: Výzkum vztahů mezi viskozitou povrchovým napětím a čeřením křemičitých sklovin. Kandidátská disertační práce, VŠCHT, Praha, 1974