

## STUDY OF THE METALLURGICAL SLAGS PROPERTIES FROM THE VIEWPOINT OF PHASE TRANSFORMATION

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## STUDIUM VLASTNOSTÍ METALURGICKÝCH STRUSEK Z HLEDISKA FÁZOVÝCH TRANSFORMACÍ

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### Abstrakt

V předložené práci je věnována pozornost některým fyzikálně-chemickým vlastnostem metalurgických strusek. Výzkumu byl podroben reálný struskový systém, který slouží jako základ rafinačních strusek určených pro zpracování na pánvových pecích. Dominantními složkami tohoto systému jsou  $CaO$ ,  $MgO$  a  $Al_2O_3$ , kromě nich obsahuje řadu doprovodných chemických příměsí, jako například  $Fe_2O_3$ ,  $TiO_2$ ,  $K_2O$ ,  $SiO_2$  a další. Jako hodnotící kritérium tohoto systému bylo zvoleno povrchové napětí v závislosti na teplotě a chemickém složení, které se měnilo postupným přidáváním  $CaO$  při zachování poměru ostatních složek. Z důvodu posouzení vlivu minoritních složek na povrchové napětí byla analogickým způsobem vytvořena řada syntetických vzorků, obsahujících pouze odpovídající poměry majoritních složek. U takto připravených vzorků reálných i syntetických struskových systémů se měřilo povrchové napětí v závislosti na teplotě metodou ležící kapky. Jako doplňující informace byla u těchto systémů sledována teplotní závislost hustoty. Získané výsledky jsou interpretovány i na základě provedených rtg-fázových analýz vybraných vzorků.

### Abstract

The focus of the presented thesis is the study of some of the physical - chemical properties of metallurgical slags. A real slag system was investigated, which serves as a basis of the raffinate slags used for processing on the ladle furnaces. Dominant components of this system are  $CaO$ ,  $MgO$ , and  $Al_2O_3$ , except from these it contains a range of additional chemical admixtures, e.g.  $Fe_2O_3$ ,  $TiO_2$ ,  $K_2O$ ,  $SiO_2$  and other. As rating criterion of this system it was chosen the surface tension in dependence on the temperature and chemical composition which changed during gradual increasing of  $CaO$  preserving the proportion of the other compounds. Because of the assessment of the minority compounds influence on the surface tension, by analogical way there were produced series of other synthetic samples which contained appropriate proportions of majority compounds only. At these samples of the real and also synthetic slag systems which were prepared in this way, there was measured by the method of a lying drop the surface tension in dependence on the temperature. As completion data there was observed the density temperature dependence at these systems. The obtained results are interpreted on the basis of realized rtg - phase analyses of chosen samples.

**Key words:** metallurgical slags, surface tension, phase analysis, temperature dependence

## 1. Introduction

The optimal slag mode, on which depends the effectivity of series of metallurgical reactions, closely depends on physical – chemical properties of chosen slag systems. These are determined mainly by their chemical structure and by the temperature in the course of the process. Despite the fact there were worked out many models for calculation of their properties, their character is mostly perfunctory and with limited application area. Because of this reason the presented thesis is focused on experimental study of chosen properties (surface tension and phase transformation) of the chosen slag systém [1 – 5].

## 2. Measuring method

From the viewpoint of metallurgical slags character it was chosen the method of a lying drop as an optimal method for the surface tension measurement of the slag systems. Its principle and merits have been described in the studies [6 –7].

During the measurement of the surface tension temperature dependences there were found out many behaviour anomalies in the slag systems. Because of this fact some of the measurements were completed with high temperature diffraction analysis which may be used to interpret eventual phenomena.

The measurement was realized using the automatic rtg – diffraction meter D 500 Siemens completed by high temperature PAAR cell and by directive ELPHYSE detector. The area of the diffraction spectrum from  $20^\circ 2\theta$  to  $80^\circ 2\theta$  in the stepping mode labeled by the firm „FAST - SCAN“ was scanned by radiation CoK and stored into the external memory of the connected self – testing computer. Except from this the starting samples and the final products were investigated in classical (Bragg – Bretan) setting with crystallic monochromator by scintillation detector. To gain the information about the phase structure, the measured intensity functions were confronted to the database system PDF 1. The high temperature records were plotted in axonometric projection and the major diffractions (displaced in the temperature) were assigned to the phases according to the identification of the starting and the final states at the room temperature.

Some of the slags fluxed already by  $1100^\circ\text{C}$  and by  $1300^\circ\text{C}$  were so liquid, that when the heating element was sloped (to keep the Breg – Bretan semi – focuses conditions) they poured to the cooler endings of the heating element, so it was not possible to keep the demanded temperature conditions. In these cases the chosen temperature interval was  $1100^\circ\text{C}$  to  $1400^\circ\text{C}$  with respect to the fact, that at higher temperatures the sample was usually amorphous.

## 3. The sample choice

During the implementation of new metallurgical slags into the technological practice in our workplace there was measured a wide range of anorganic oxidic systems which served as a basis of the raffinate slags intended for processing on the ladle furnaces. Because of the economical reasons these systems represented waste materials from other technological processes. Except from the dominant components which are mainly  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  it contained also many additional admixtures among which there are  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{MnO}$ ,  $\text{K}_2\text{O}$ ,  $\text{Na}_2\text{O}$  and other.

For the surface tension investigation itself in connection with the structure dependences analyses which are presented in this thesis it was chosen one characteristic slag system with low contents of  $\text{SiO}_2$  (sample A). Its chemical composition is shown in the Table 1.

Table 1 Chemical composition of the real slag system (sample A)

Compound	wt. %
CaO	34.4
Al <sub>2</sub> O <sub>3</sub>	58.2
MgO	6.4
SiO <sub>2</sub>	0.2
Fe <sub>2</sub> O <sub>3</sub>	0.33
TiO <sub>2</sub>	0.127
K <sub>2</sub> O	0.03
Na <sub>2</sub> O	0.9

Consequently, using similar principle as in some earlier studies [8] it was investigated the influence of the chemical composition on the surface tension temperature dependences and phase structural changes.

In the real slag system (sample A) which was analysed, the content of *CaO* was increased of three percent in the range of 34.4 – 46.4 wt. % of *CaO*.

In the second phase of the measurement it was observed the influence of the accompanying additives on the surface tension of the investigated system. Using the pure materials (*CaO*, *MgO*, *Al<sub>2</sub>O<sub>3</sub>*) there were set together analogical systems with increasing proportion of *CaO* and they were experimentally investigated under the same conditions as the real samples.

In all samples which were produced in this way it was observed the surface tension temperature dependence up to 1600°C and the phase changes to 1500°C. Both temperatures represent the limit of technological possibilities of the used measuring equipment.

## 4. Experimental Results

### 4.1 System A

The temperature melting interval of the sample A relates to the temperature range of 1300°C (first optically visible shape changes of the sample during the heating) up to 1360°C, when the sample is already formed into the shape of a drop.

The figure 1 shows the surface tension increase up to the temperature of 1480°C, which relates to global maximum of the surface tension in the whole investigated temperature interval, and consequently it is followed by a slow decrease. From 1630°C in the melt it starts to develop the gas phase. It comes to swelling and breaking of the drop form of the slag melt, which disables the relevant surface tension calculation. This is the reason why the surface tension values of the sample during the cooling are missing.

Completely different trend in the change of the surface tension with temperature shows the synthetic system which was set together from the pure components only: *CaO* – *Al<sub>2</sub>O<sub>3</sub>* – *MgO* in the analogical proportions as in the real sample. The temperature interval of melting is advanced to the values of 1480 – 1550°C. During the heating it comes to a slight surface tension decrease at first which is afterwards followed by a rapid increase until the measurement is finished. Similar trend is apparent also during the cooling from the viewpoint of the surface tension absolute values the curve is moved a bit higher. Particularly in the area of the lower temperatures the difference of the surface tension values is during the heating and cooling more prominent. The surface tension values difference in the course of the highest measured temperature between the curves of the heating and of the cooling is possible to explain by inertia

of the Tamman's furnace. Before the start of the cooling it always comes the the „stamina“ at the particular temperature, optionally to its slight exceeding. This phenomenon is more or less possible to observe also in the other following graphs.

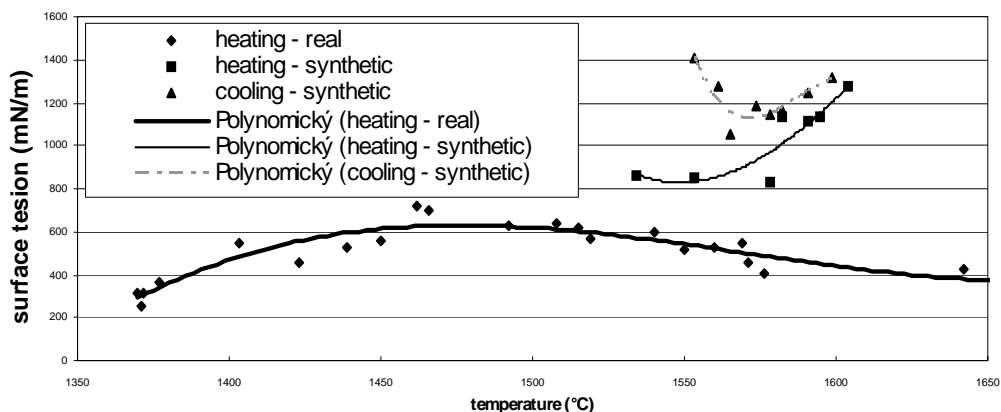


Fig.1 The surface tension temperature dependence of the sample A and the equivalent synthetic systéme

The mineralogical structure of the real system A was analysed using the automatic rtg – diffraction meter. The starting sample spectrum measured at the room temperature is shown in the figure 2. The particular minerals were found out by the confrontation with the database PDF3 (ICDD – JCPDS):4 [9].

In this sample there was found out a major proportion of the following minerals:  $CaAl_2O_4$ ,  $(CaO)_{12}(Al_2O_3)_7$  and  $Ca_{12}Al_{14}O_{33}$ .

Consequently the sample was heated in the temperature interval 1200 – 1500°C with the step of 50°C. The axonometric projection of the particular diffraction records during the heating are presented in the figure 3.

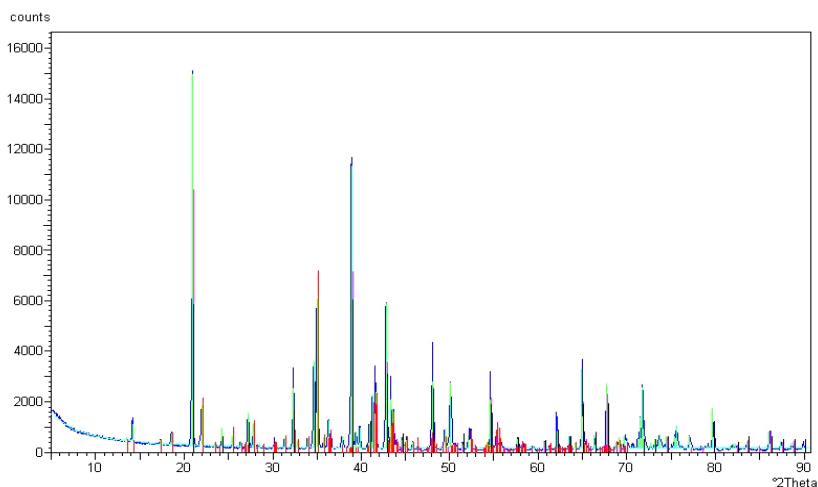


Fig.2 The starting spectrum of the real system A

In the course of the evaluation of the spectrum gained in the high temperature PAAR cell and at the room temperature in confrontation with the database PDF2 it was also found out the calcium aluminium garnet  $Ca_3Al_2(SiO_4)_3$  and the phase  $Ca_5Al_6O_4$ . The phases of the pyroxene and the olivine were disputable.

In the course of the heating up to 1300°C the crystallinity gradually decreased, keeping similar phase structure. Above the temperature of 1350°C in the sample there is only one phase 0.461 nm there, which has not been successfully identified yet. This phase expires in the temperature interval 1400 – 1450°C and then the sample is amorphous only. Distinct diffractions apparent at higher temperatures belong to the platinum heating element.

The mineralogical structure of the synthetic system was assessed using the phase ternary diagram. The figurative point of the system is located in the area of the spinel. Another phase which will be exuded during the cooling is  $CaO.Al_2O_3$  and consequently  $12CaO.7Al_2O_3$ .

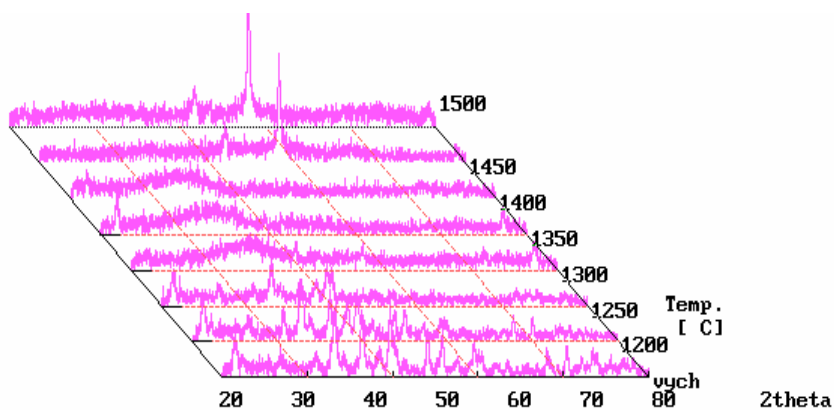


Fig. 3 The axonometric projection of the sample A diffraction spectra in the course of heating.

#### 4.2 The concentration series set out of the CaO additives

The surface tension temperature changes of the real and synthetic slag system in the course of heating with changeable contents of CaO shows the figure 4.

The CaO content increase of 3 wt.% towards the original content leads to distinct increase of the surface tension values in the whole investigated temperature interval. Although the basic trend of the regression curve course was kept, the temperature dependence is much less distinct. Another increase of the CaO content leads to re – producing characteristic maximum during the first phase of the heating with consequent decrease to the temperature area of 1540°C. Here the system of 9% CaO addition forms minimum and the surface tension increases again. The regression curves of the other systems keep the decreasing trend up to the upper limit of the measured interval. The surface tension decrease which is close to the temperatures of 1600°C is usually not too slope and so it is possible to suppose, with another temperature increase, a local minimum formation.

The analogical comparison of the reaction of the real concentration series with increasing CaO content, which is shown in the figure 4, is presented for the synthetic system in the figure 5.

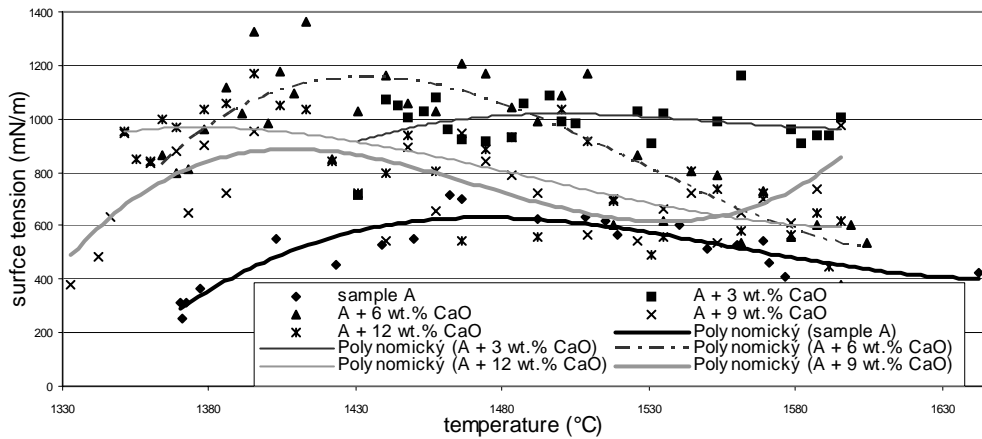


Fig.4 The comparison of the surface tension temperature dependences courses of the real slag system A with the gradual increase of the  $CaO$  content.

The first and the second addition of the  $CaO$  content which is always of 3 wt.% leads to the melting temperatures decrease to the values of 1340 – 1420°C, which is closer to the real system.

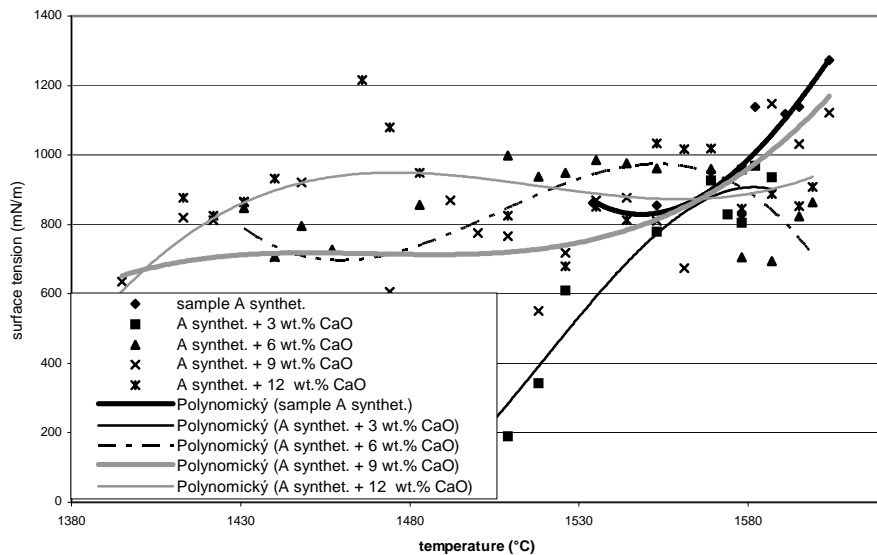


Fig.5 The comparison of the surface tension temperature dependences courses and of the synthetic slag system density with gradual increase of  $CaO$  content.

In the system with the additive of 3 wt.%  $CaO$  also comes to the considerable increase of the surface properties values when the temperature is increased in the first phase, but at 1580°C it is not so distinct and another increase of the temperature even leads to the surface tension decrease. In the samples with 9 and 12 wt.%  $CaO$  additive content the regression curve

forms into the surface tension temperature dependence which is characteristic for the real system.

From the viewpoint of the phase changes the slag system with additive of 6 and 12 wt.%  $CaO$  was investigated in comparison to the original content.

The real system with addition of 6 wt.%  $CaO$  was measured at the room temperature in the PAAR cell only and there were found these phases: andradite ( $Ca_3Fe_2(SiO_4)_3$ ), optionally calcium aluminium garnet, the phase of montycellite ( $CaMgSiO_4$ ) was disputable, there were also  $MgO$ ,  $CaO$  and  $Al_2O_3$ . In the course of the smelting the investigated sample had already at  $1300^\circ C$  an amorphous character, which it kept until the measurement was finished. After the melting and cooling there were found  $CaAl_2O_4$ ,  $Ca_3MgAl_4O_{10}$  and  $Ca_2Al_{26}Mg_3Si_3O_{68}$ .

The axonometric projection of the sample with 12 wt.% of  $CaO$  additive is shown in the figure 6. The starting spectrum was measured in the HTK cell using the PSD detector and it was compared to the PDF1 database. The phases which were found out are:  $AlFeO_3$ ,  $MnSiO_3$  and  $Ca_3Al_2O_6$ .

In the course of smelting the calcium aluminium garnet, mayenite ( $Ca_{12}Al_4O_{33}$ ),  $FeO$  and other phases which could not be identified were found out during the heating up to the temperature of  $1250^\circ C$ . At  $1300^\circ C$  a thermocouple dropped out and so the particular spectrum is missing. Above  $1350^\circ C$  there is slightly detectable phase of wüstite and at  $1500^\circ C$  the sample is already amorphous.

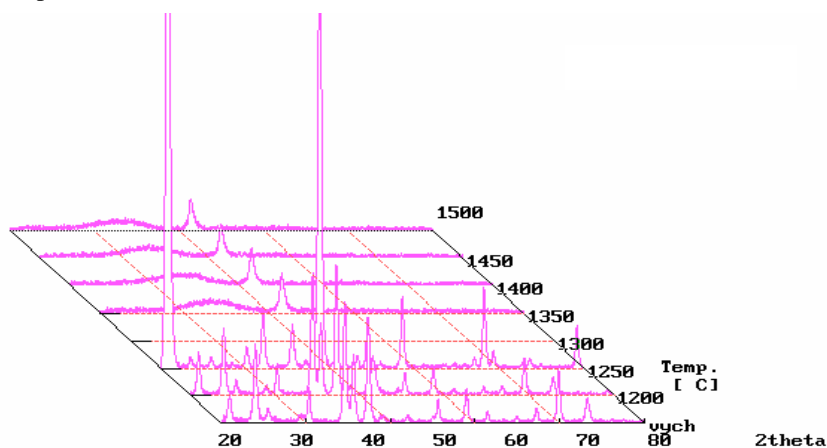


Fig.6 The diffraction spectra axonometric projection of the sample A + 12wt.%  $CaO$  in the course of heating.

The synthetic slag system which responds to the real slag system with 6 wt.% of  $CaO$  additive was confronted with the ternary diagram  $CaO - MgO - Al_2O_3$  (see figure 7). In comparison to the original sample, here during the melt cooling the first phase of the spinel will be missing and the phase  $CaO.Al_2O_3$  will be exuded as the first one; nevertheless after the cooling it will dispose of similar mineralogical structure.

The synthetic system structure with 12 wt.% of  $CaO$  additive moves into different phase triangle in the ternary diagram. As the first one will be exuded the phase  $3CaO.Al_2O_3$ , then periclase and at the point of the peritecticum will be exuded  $12CaO.7Al_2O_3$ .

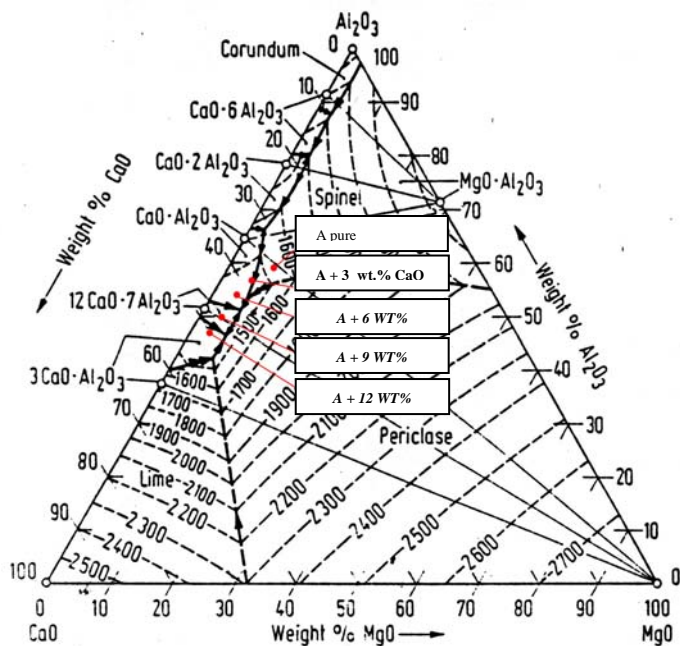


Fig.7 The layout of the of the synthetic system A figurative points in the ternary diagram

## 5. The results discussion

From the viewpoint of the melt structure in the system A it is possible to assume the polyanionic nets creation because of the presence of the  $Al_2O_3$  compound. The proportion of  $O/Al = 2.171$  [10,11] reflects the transition of the  $Al^{3+}$  portion to the tetrahedral coordination and so its part on the new structures networking. This fact is consistent with the theory in which Kazakewitch [12] expresses an opinion that the mixture  $Al_2O_3$  acts as a „network conductor“ providing that the proportion is  $x_{MeO}/x_{Al_2O_3} > 1$  which in this case has the value of 1.126. The initial surface tension increase of this real system together with the temperature increase may be explained exactly by the extinction of these complex structures and by the complete system energy increase.

This effect may be also a result of the particular phases extinction in the course of the smelting, which were found out by the rtg – phase analysis. Also the presence of the phase 0,461 nm may be considered as worthy of remark; it extinguishes when the temperature is about 1450°C. It is possible to assume that the location of the local maximum corresponds with the temperature area of melting in this phase. The subsequent surface tension decrease may be generally interpreted by increasing the kinetic energy of the molecules and ions which are present in the melt. Due to the proportion values  $O/Al = 2.182$  and  $x_{MeO}/x_{Al_2O_3} = 1.366$  it is possible to assume the structure networking also in the synthetic system.

The figure 1 shows the influence of the underrepresented mixtures on the complete acting of the investigated system. The absence of the mixtures  $SiO_2$ ,  $Fe_2O_3$ ,  $TiO_2$ ,  $MnO$ ,  $K_2O$  and  $Na_2O$ , even though they are represented in tenths and hundredths % only, they cause the emperature interval of melting increase even of 1200°C. Also the trends of the particular surface tension temperature dependences are quite different.



The proportion values of  $O/Al = 2.182$  and  $x_{MeO}/x_{Al_2O_3} = 1.366$  with increasing content of CaO in all samples of the concentration series produced by the additives of CaO slightly increase and in all the systems they are suitable for the polyanionic nets creation.

Despite of the fact that the calcium oxide belongs due to the ionic potential to the group of the „modifier“ mixtures, here it still due to the minimum  $SiO_2$  content facilitates the creation of the complicated complex mixtures of  $Al_2O_3$ . This is the reason why it is possible to assume, from the viewpoint of the polyanionic nets creation, similar structure in all samples of this concentration series. This assumption corresponds with similar basic trend of the regression curves course for various CaO contents, only it comes to the difference of the maximum and minimum on the curves into different areas.

The temperature interval of melting in compliance with the ternary diagram  $CaO - Al_2O_3 - MgO$  moves with increasing CaO content to the area of lower values. Due to the influence of the accompanying additives it is in the real system for the particular chemical structure always dislocated lower towards the pure system of  $CaO - Al_2O_3 - MgO$ .

From the viewpoint of the phase changes it is not possible to determine uniquely the influence of the CaO content increase on the surface tension. Whereas the calcium oxide is generally understood to be a polyanionic nets modifier or its content increase in the particular systems should lead also to the surface tension values increase, the realized phase analyses of the molten samples proved, that with increasing CaO content it comes to the complex mixtures creation. This fact is especially prominent when the samples A+6wt.% of CaO and A + 12 wt.% of CaO are compared. This particular phenomenon is caused exactly due to representation of the minority accompanying elements in the real system.

The changes of acting of the synthetic system samples may also be seen from the figurative points positions in the ternary diagram (figure 7). Nearly each CaO additive dislocated the figurative point of the particular system to another phase area, which was proved also in the surface tension temperature dependences.

## 6. Conclusion

This study presents the investigation of the real slag system surface tension and of the equivalent, synthetically prepared system. The given problem area was assessed from the viewpoint of the phase changes which were experimentally investigated by the rtg – phase analysis.

Comparing the real and the synthetic system acting it was unambiguously proved the influence of the minority represented components on the surface tension temperature dependences of the real and the synthetic system. Due to the subsequent changes of the CaO content there were observed the patterns of the chemical structure influence on the surface tension in connection with the mineralogical structure changes. This measurement proved the influence of the phase transformation on the slag systems acting in the course of the temperature loading.

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