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# PROPERTIES OF SLAGS IN THE SYSTEM CaO-MgO-$Al_2O_3$-$SiO_2$, IMPORTANT IN DEOXIDIZATION AND DESULPHURIZATION OF LOW CARBON ALUMINIUM KILLED STEELS

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## ABSTRACT

*Properties of refing slags belonging to the system CaO-MgO-$Al_2O_3$-$SiO_2$ are important in simultaneous or succesive refinig treatment processes in the ladle and other refing metalurgical reactors. The efficiency of treatments depends upon the values of physicochemical properties of treatment slags which become important technological parameters. Surface tension of slags and interfacial tension in teh system slag steel also, viscosity and density are important in managing refining processes which must be correctly evaluated as values and influence exerted by modification of slag composition, mainly by sulphur content.*

KEYWORDS: CaO-MgO-$Al_2O_3$-$SiO_2$ system, surface tension, interfacial tension, viscosity, density, sulphur solubility

## 1. Introduction

In the analysis of the dynamical effects at steel-slag interface during the desulphurization process, usually only the surface tension of steel, the interfacial tension steel-slag effects and the steel side of the interface are taken into account. It is a reality that the influences due to the contribution of solutal effects in slag, seems to be un-approached and sometimes even neglected. Many special characteristics appear from the particularities of the slags used in deoxidization and desulphurization of the low carbon and/or low alloyed steels. Possible contributions of slags to the dynamic effects are due to special nature and properties of refining desulphurizing slags and sometimes to the properties of the steel, which form the interface. For sustaining, besides the criteria classically used to appreciate the possibility that certain dynamic effects as the Marangoni convection occur, it must be supplementary considered the lower solubility of sulphur in slags, taken into account as thermodynamically homogeneous liquid solutions, coupled with the fact that, at industrial scale, the amounts of desulphurizing slags are usually between 8-14kg/tone of steel [1]. While in steel the desulphurization under slags leads to a suphur content decreasing by about 0.01-0.02% mass, in the same time, in the desulphurization slag, the sulphur content increases about one hundred times faster up to contents of 1-2%mass [1]. When desulphurization reaction takes place in a non uniform manner on the whole interface, due to different conditions, higher concentrations of sulphur in slag locally appear, overcoming the limits corresponding to the existence of the thermodynamically and physically homogeneous liquid solutions and the whole panel of conditions are changed. Therefore an extended analysis of such properties as surface and interfacial tension, viscosity and density of slags in the mentioned system could contribute to obtaining an improved image and perception of the conditions leading to performances.

## 2. Influence of the sulphur content on the surface and interfacial tension in CaO-$Al_2O_3$-CaS slags at 1873K

The only available experimental reported data, covering a wider range of compositions, are those reported in the ref.[2][3] for surface tension in the system CaO-$Al_2O_3$-CaS and interface tension between the same slags and a liquid steel of a specified grade. It must be mentioned that the paper [2] is focused on the influence of sulphur in the system CaO-$Al_2O_3$-$CaF_2$, but this research includes points without $CaF_2$. From them, two sets of data have been extracted as selected points from the graphical representation given in ref. [3], mainly taking into consideration their coincidence with the chemical compositions of slags used in practical activities of steel desulphurization and refining. They have been used to generate different statistical dependence relations, finally being selected those having the highest value of the determination coefficient $R^2$.

The regression equations serve to study the comparative behavioral trends of the respective quantities using computed values, not only the impression due to visual aspects, but especially as their values. This procedure will be very useful for the purpose of the present paper. In the legend of figures presented in the present paper, both the regresion relations and determination coefficients are given. As it is shown, in each case $R^2$=1 or it is closed to this value.

According to the initial composition of the slags, in % mass, they will be nominated as slag A (or C/A=1.5) at initial composition of 60% CaO-40%$Al_2O_3$ and slag B (or C/A=1) at initial composition of 50%CaO-50%$Al_2O_3$. They are presented in the form of dependences upon the concentration of sulphur, and the sulphur content is calculated in the sense of the procedure used during the reported experiments, consisting in additions of different percentages of CaS to such slags.

In fig.1 are presented the dependences of the surface tension of both mentioned slags upon the sulphur content (in % mass) at 1873K. In fig.2 are presented the dependences of the interfacial tension between the two mentioned slags and a steel grade H52-3 at a fixed composition of the steel (0.11%C; 0.44%Si; 1.32%Mn; 0.022%P; 0.035%S; 0.0045%O; 0.0115%N) [2].

It is evident a similar influence exerted by sulphur content up to 2.5%mass, on surface tension dependences (fig.1) and the ratio K(fig.3) in the case of both slags, A and B.

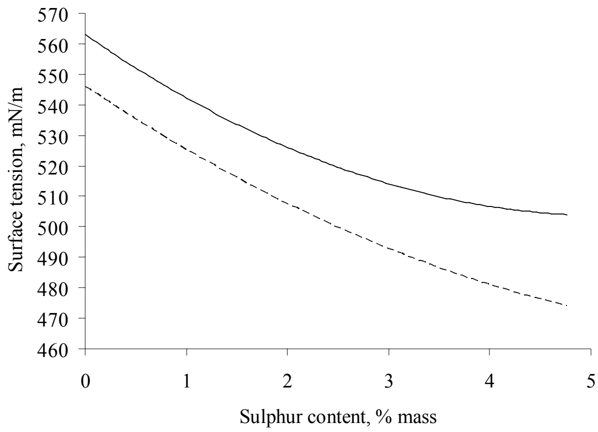


***Fig. 1.*** *Dependence of the surface tension upon the sulphur content in CaO-$Al_2O_3$- CaS slags at 1873K.*
*—— C/A=1.5 $\sigma_A$=2.1217(%S)$^2$-22.922(%S)+563 ($R^2$=1);*
*– – – C/A=1 $\sigma_B$=1.4781(%S)$^2$-22.159(%S)+546 ($R^2$=1)*

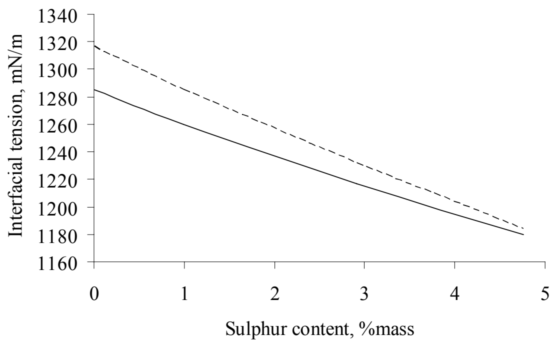


***Fig. 2****. Influence of the sulphur content in slag on the interfacial tension between CaO-$Al_2O_3$-CaS slags and a low carbon steel (H52-3 grade) at temperature of 1873K;*
*—— C/A=1.5, ($\sigma_{interf.A}$=0.7353(%S)$^2$-25.504(%S)+1284.8);*
*– – – C/A=1, ($\sigma_{interf.B}$ =0.7928(%S)$^2$-31.548(%S)+1316.5)*

In fig.4 are represented dependences of the surface tension variations of the slags A and B obtained based on the partial molar surface tension of each slag upon the mole fraction of sulphur in slags, compared to the predictions made using the general statistic relation deduced and presented in ref. [4] based on the relation given in ref. [5]. In the fig.4, besides the similarity of the trends, consisting in a parabolic type dependence and therefore in the existence of a minimal value at a specific sulphur concentration, on each curve, it is obvious the difference between the predicted values in the cases of the slags A and B, belonging to CaO-$Al_2O_3$-CaS, and the predicted values using the general statistic relation.

This means that all effects connected to this quantity are less intensively influenced in the particular cases of slags A and B than those obtained with the general statistical averaged relation. It can be noticed also that the dependences of the products $X_S\partial\sigma/\partial X_S$ for slags A and B are practically superposed in the range of sulphur concentration

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lower than $X_S \leq 0{,}015$.The value of the interfacial tension at 1873K, between $CaO$-$Al_2O_3$ slag and iron decreases from 1238mN/m for a ratio C/A=1 decreases to 1200mN/m at C/A=1.5[6]. A slight increasing to the value 1250mN/m results from the ref. [7] at C/A=1.5 and iron containing 0.1%C. At 1843K from the ref. [8] it results, at 0.1%mass carbon content in iron, an interfacial tension about 1300mN/m, between this alloy and a slag of 50% CaO-50%$Al_2O_3$.

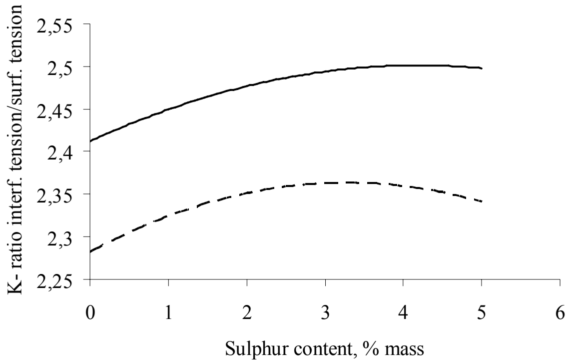


***Fig. 3.*** *Ratio(K) between the interfacial tension and the surface tension in the system CaO-$Al_2O_3$- CaS at 1873K, upon the sulphur content in slags;*
*—— C/A=1.5($K_{1.5}$= -0.0051(%S)$^2$+ +0.0425(%S)+2.412);*
*– – – C/A=1($K_1$= -0.0076(%S)$^2$+ +0.0489(%S)+2.282)*

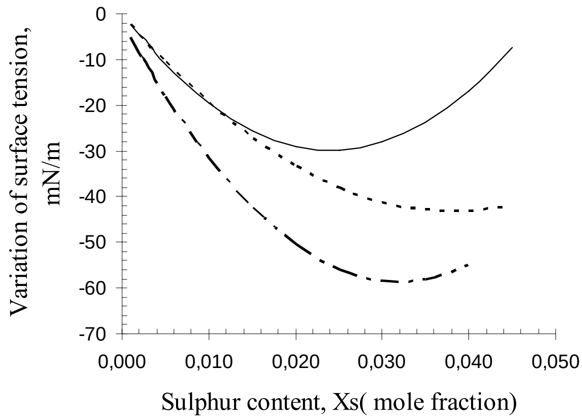


***Fig.4**. Dependence of the surface tension decreasing ( $X_s\partial\sigma/\partial X_S$) upon the sulphur content ($X_S$) in CaO-$Al_2O_3$- CaS at temperature of 1873K.*
*—— C/A=1.5($X_S\partial\sigma/\partial X_S$= 55778$X_S^2$- -2498$X_S$+0.2919);*
*······ C/A=1($X_S\partial\sigma/\partial X_S$ =28894$X_S^2$- -2226.3$X_S$+0.3045);*
*— · — · according to ref. [3]*

Many difficulties are due to the atypical behaviour of the system $CaO$-$Al_2O_3$, which is proven to be in a way "out of rules" in many respects, making difficult the including of the system in a general model of establishing the quantities contributing to viscosity, density, and even to the surface tension.

## 3. Viscosities in $CaO$-$Al_2O_3$-$CaS$ slags, at 1873K

Despite the presumed simplicity due to the number of components, the viscosity values in the system $CaO$-$Al_2O_3$ are not accurate enough as the experimental or predicted values using models. Some trials to establish the general trend of the viscosities in the $CaO$-$Al_2O_3$ system, have led to finding a decreasing one and another one, of increasing value with the increasing of the CaO content.

In ref.[9], in a systematic experimental research, at a slag composition of 50% CaO-50%$Al_2O_3$ it was obtained the value 0.23Pa.s.

From the relations established in the [10], it results the value η=0.1956Pa.s at a close composition of 51.5%CaO+ 48.5%$Al_2O_3$ and the value η=0.199Pa.s at a composition of 49.5% CaO +50.5% $Al_2O_3$. Using Urbain model, a value 0.4396Pa.s is obtained.

In slag 60%CaO-40%$Al_2O_3$ a value η=0.1184Pa.s is obtained by extrapolating at 1873K a statistic relation ($\lg\eta = 23.10^{-7}T^2 - 0.010556T + 10.776$, $R^2=1$), established in the present study, based on data obtained in ref.[1], on the interval 1973-2073K. From ref.[10], at a relatively close composition (55.5% CaO-43.5%$Al_2O_3$-1% $SiO_2$) a value η=0.162Pa.s is obtained. Using Urbain model, a value η=0.2735 Pa.s is obtained. The values obtained using the Riboud model are much lower than the lower experimental value, in case of both compositions of slags.

There are not data concerning the influence of the sulphur content on the viscosity in slags based on the simple $CaO$-$Al_2O_3$ system. Some trends of influence result from data in other systems. In the system $CaO$-$CaS$-$SiO_2$, at 1873K and ratios of mole fractions representing ($X_{CaO}$+ $X_{CaS}$)/ $X_{SiO2}$=1.5-2, at contents of $X_{CaS}$=0.02-0.1, there are not sensible influences of the sulphur content [11][12]. At 1773K, in a complex system $CaO$-$SiO_2$-$Al_2O_3$-$MgO$-$MnO$-$CaS$, at basicity index b=%mass$CaO$/%mass$SiO_2$=1.3, the replacing of about 3%CaO by CaS leads to increasing of the viscosity by about 10% (from 0.3 to 0.33Pa.s) and at b=1.43, the replacing of about 6%CaO by CaS leads to decreasing of the viscosity with about 16% (from 0.38 to 0.32Pa.s)[13]. The presented data lead, by a certain similitude, to the acceptance of a low influence of the sulphur content on the viscosity, in the system $CaO\text{-}Al_2O_3\text{-}CaS$ at 1873K, up to 6% CaS.

## *Densities in $CaO\text{-}Al_2O_3$ system, at 1873K*

In slags 50% CaO-50%$Al_2O_3$, values 2710kg.m$^{-3}$[14], 2750kg.m$^{-3}$ [15][16] and 2870kg.m$^{-3}$ [17] have been found as points in diagrams[12]; in ref.[18], a value of 2710kg.m$^{-3}$ is given also. For slag 60% CaO-40%$Al_2O_3$, a value 2685kg.m$^{-3}$ is given [11][19].

## *Sulphur solubility in slags and its influence*

From data presented before it results that the major effect, during the desulphurizatin of the steels using slags based on the oxydic system $CaO\text{-}Al_2O_3$, is the decreasing of the surface tension of the slag and of the interfacial tension between the slag and the mentioned low carbon steel, due to the increasing of the sulphur content of the slag. In the industrial practice only rarely the final sulpur content is higher than 2%mass. At each temperature in the range of interest, a certain value of the sulphur capacity $C_S$' corresponds to each chemical composition of the slag, at equilibrium with metallic bath and therefore, there is a limit of solubility of sulphur; up to this limit the sulphur forms with the other components of slag fully liquid slags. The content of sulphur overcoming the solubility limit will precipitate in slag as CaS, which will float in the slag as cristals, as it was observed experimentally [20].

The limits of CaS solubility in $CaO\text{-}Al_2O_3$ slags are given by the relation in fig.5 and can be transformed in the corresponding limits of sulphur solubility. For the considered $CaO\text{-}Al_2O_3$ slags, the limit of sulphur solubility is 2.092 % mass at C/A=1.5 and 1.46% mass at C/A=1.

It follows that all effects taking into consideration the chemical composition of the slag must be analyzed under the consideration of the effects due to CaS precipitation as crystals in the slag. In ref.[20] it is mentioned that the CaS precipitation inhibits the generation of interfacial convection.

Using the effects of the chemical composition shown in fig.3 and fig.5 this could be explained by the strong lowering of the sulphur content in the liquid surrounding the CaS precipitated crystals and the corresponding lowering of the product $X_S\partial\sigma/\partial X_S$ which gives a measure of the maximal surface tension decreasing which could contribute to the interfacial convection evaluated as Marangoni effect.

This can be seen also in fig 4. where at lower sulphur contents the decrease of the surface tension is more important than at higher sulphur contents.

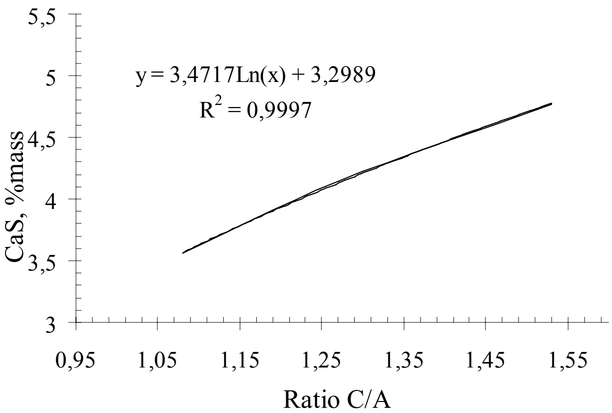


***Fig. 5.** Solubility limit of CaS in slags CaO- $Al_2O_3$ at 1873K, as function of the ratio C/A =(%mass CaO)/(%mass $Al_2O_3$), according to experimental values of sulphur solubility from ref.[2]. The equivalent relation of the solubility of sulphur in slag is (%S)=1.5428Ln(C/A)+1.466*

## 4. Conclusions

The present values of physico-chemical properties of slags in the system $CaO\text{-}MgO\text{-}Al_2O_3\text{-}SiO_2$ are important by their values and influence exerted by sulphur content in refining processes of deoxidization and desulphurization which occur simultaneously and subsequantly during steel treatment in ladle reactors and other refining reactors. Based on several values of important quantities and parameters influenced by these properties, the processing route and parameters of treatment could be better established to obtain an optimized maximal efficiency in steel refing processes at industrial scale. All these are possible only based on correct evaluations of the properties presented. Because of some important differences of values found in the literature, it is necessary to improve and to establish a standard procedure for measurements of slag properties and not only.

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