

MODELLING OF INCLUSION MODIFICATION IN CALCIUM TREATED STEELS

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Synopsis: Proposed model has been developed to determine the optimal conditions for the use of calcium, taking into account the influence of chemical composition and activities in molten bath, temperature, ... Those data are the basis for the mathematical modelling of the reactions of calcium to assure the proper calcium addition resulting in high steel cleanliness (regarding the content, form and shape of nonmetallic inclusions) as well as to understand the mechanism of inclusion formation.

Actually, the uncontrolled formation and precipitation of CaS in calcium treated and aluminium killed steels, can represent one of the major causes for poor castability of such steels (resulting in nozzle clogging during continuous casting). This is why the thermodynamic conditions for precipitation of liquid calcium aluminate inclusions without solid calcium sulphide formation at the same time were calculated.

Key words: Steel, Modelling, Thermodynamics, Calcium, Slag, Inclusions, Modification,

1. Introduction

Reactions analysis of calcium used in quality steel production was carried out in order to improve the knowledge and control of processes taking place in melts and to enable the proper decisions about quantity of added calcium as CaSi cored wire. Fundamentals of the analysis were based on the thermodynamical principles controlling direction and rate of reactions caused by calcium addition.

Today, the application of calcium in quality steelmaking is no longer a speciality, but a "general recipe" for correct amount of calcium addition (in our case as CaSi-cored wire) has not been commonly accepted yet. It is known, though, that the motive for calcium addition is based on modification of pure alumina inclusions with a high melting point to complex calcium-aluminate inclusions with low melting point.

Previous researches /1/, /2/, /3/, /4/, /5/, /6/ have already established the fundamental and common thermodynamical relations of possible calcium reactions in the molten steel and slag particles (where non-metallic inclusions can be taken as a part of slag). The phase and chemical analyses of inclusions have proven /7/ that the correctness of calcium addition can be confirmed and that the analysis of those phenomena can give answers to effects of previous calcium treatment of aluminium killed steel.

Steel, containing too high amount of calcium could have CaS inclusions with a high melting point, while too low content of calcium causes unsatisfactory modification of solid alumina inclusions to complex liquid calcium-aluminate inclusions.

During the steelmaking process the steel and a share of slag can only be checked on chemical composition, temperature and oxygen activities in melt. Hence, the reaction model determined by corresponding thermodynamic reactions and relations as a whole has to be considered.

Our latest research has covered mainly the influence of sulphur activities on the reactions model and the creation of the mathematical model for calculation of optimum calcium additions.

General bases for determination of optimum calcium concentration area for each individual case could be set by known temperature, chemical analysis of steel and slag as well as activity coefficients of individual elements in the molten melt.

Such optimum frame determination can bring our wish, for reliable prediction of necessary optimum calcium addition in steel at a required moment, close to realisation.

2. Model conception

The construction of the basic calculation model to determine the optimal calcium addition to assure the modification of solid alumina inclusions and to prevent the CaS formation was our basic purpose. Such model needs a lot of suppositions, but we already have enough data to be able to predict the model based on favourable modification of solid alumina to liquid calcium aluminate inclusions.

Model tends to obtain control of aluminium and calcium deoxidation by a system capable of comparing the molten steel analysis to corresponding equilibrium of inclusion composition applying temperature measurements and oxygen activity particulars. By corresponding thermodynamical assumptions a preliminary control of aluminium deoxidation and later calcium treatment could be introduced.

3. Thermodynamic data base

To study the behaviour of calcium and its effects on reactions taking place in liquid steel the relationship between calcium, oxygen or aluminium and sulphur and between individual phases within the binary system CaO-Al₂O₃ has to be known. Considering that only dissolved calcium in steel plays a decisive part in such reactions, the following equations have to be implemented:



and

$$\lg K_{CaO} = \lg(a_O \cdot a_{Ca} / a_{CaO}) = -25655/T + 7.65 \quad \text{Ref./5/} \quad (2)$$



and

$$\lg K_{CaS} = \lg(a_S \cdot a_{Ca} / a_{CaS}) = -28300/T + 10.11 \quad \text{Ref./5/} \quad (4)$$

On the basis of calcium treatment in aluminium killed steel the oxygen content before treatment by calcium was determined by the following relation:



and by the following equilibrium constant /5/:

$$\lg K (Al_2O_3) = 61304/T - 20.37 \quad (6)$$

The Fe-Ca-O-Al-S system dependence on temperature, CaO- and Al₂O₃- activities were determined by combination of equations (1) to (6):

Calcium activity (in Fe-Al-Ca system) =

$$= a_{CaO} \cdot 10^{(-25655/T)+7.65} \cdot \%Al^{2/3} \cdot 10^{(20434/T)-6.79} / a_{Al_2O_3}^{1/3} \quad (7)$$

and

Calcium activity (in Fe-Ca-S system) =

$$= a_{CaS} \cdot 10^{(-28300/T)+10.11} \cdot \%S^{-1} \quad (8)$$

By application of different activities of Al₂O₃ and CaO to different phase equilibria of CaO-Al₂O₃ system a temperature affected Al-O equilibrium determines the liquid phases between CaO/LIQUID phase border and LIQUID/CaO.Al₂O₃ phase border (Fig. 1) - naming this area "liquid pocket" - known also as "liquid window" /3/, /4/, /8/, /9/. We have used the following values for activities of CaO and Al₂O₃ on phase border of 12CaO.7Al₂O₃:

$$\begin{aligned} a_{CaO} &= 0.340 \\ a_{Al_2O_3} &= 0.064 \end{aligned}$$

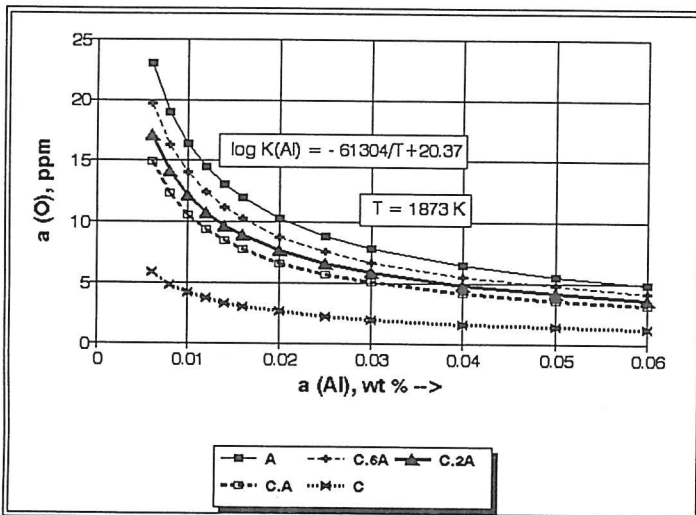


Fig.1: Influence of Al- and O-activities at different phase borders in CaO-Al₂O₃ system

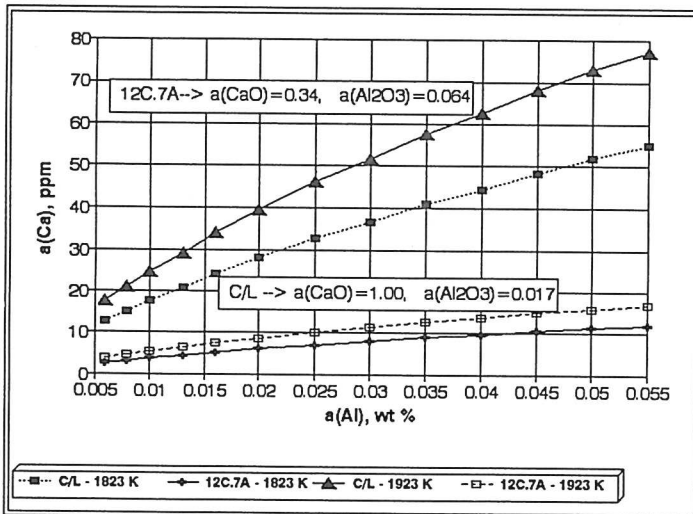


Fig. 2: Influence of temperature on Al-O-Ca equilibrium at C/L and 12C.7A phases

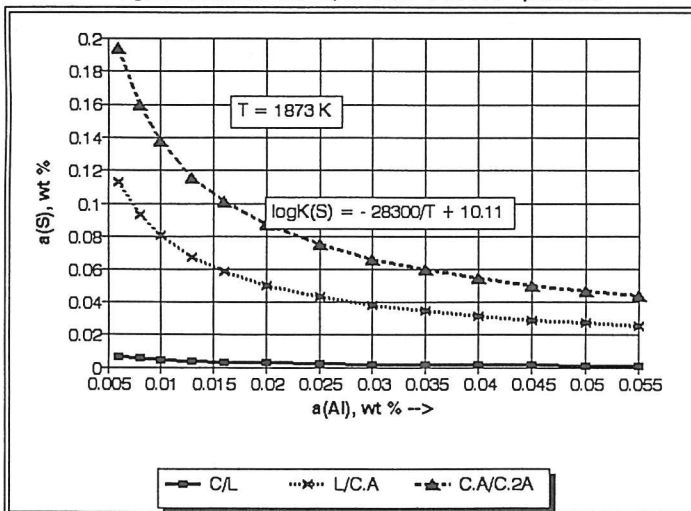


Fig.3: Influence of Al- and S-activity on equilibrium

It is understandable that the successful process of the mentioned modification needs only certain calcium quantity - but solid CaO or mixtures of CaO (s) + CaS (s) could be formed by too high calcium additions, while too low content of calcium causes unsatisfactory modification of solid alumina inclusions to low melting point complex inclusions.

The relation between aluminium and calcium activity in steel is shown in Fig. 2 for the equilibrium of 12CaO . 7Al₂O₃ liquid inclusion on the CaO / LIQUID border. The modification of alumina inclusions to 12CaO.7Al₂O₃ asks for relatively small quantities of calcium, higher temperatures require higher calcium contents but even larger calcium contents remains in the "liquid pocket".

The steels treated by calcium contain also larger or smaller contents of sulphur. The reaction between calcium and sulphur is very intensive, so the application of the latter to Ca-Al-O-Fe must be taken into consideration.

The relation between aluminium and sulphur was determined by consideration of different activities of CaO and Al₂O₃ as well as by supposition the activity CaS = 1. Fig. 3 shows a minimum and maximum contents of sulphur within the area of liquid complex inclusions-between the CaO/LIQUID and LIQUID/CaO.Al₂O₃ phase border, by constant temperature (1873 K) and the detailed oxygen contents.

It is evident, that in melts with relatively high sulphur contents the precipitation of calcium sulphide can be avoided if the soluble aluminium content is low enough and calcium addition is just sufficient to form liquid aluminate inclusions.

The mentioned equations and consideration of specific conditions on individual phase borders could be used to determine the conditions for simultaneous formation of aluminates and solid calcium sulphide.

The uncontrolled formation and precipitation of CaS in calcium treated aluminium killed steels is assumed to be one of the major reasons for diminished castability of such steels (which causes nozzle clogging during continuous casting) /3/, /4/, /6/, /10/, /11/, /12/.

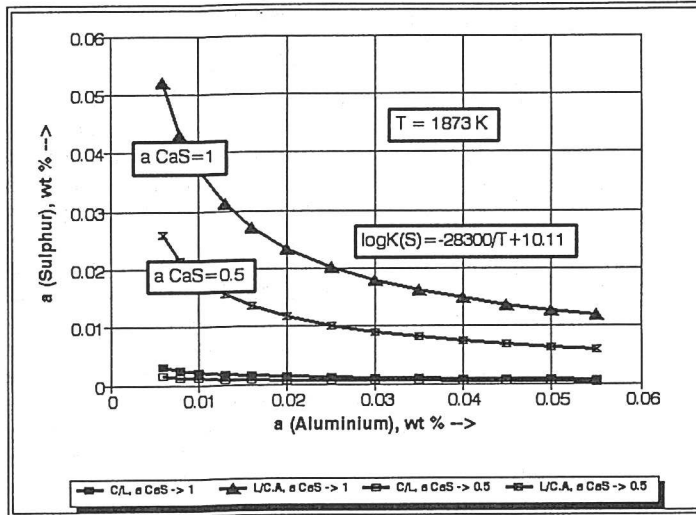


Fig. 4: Influence of S- and Al- activities on formation of CaS by different CaS activity

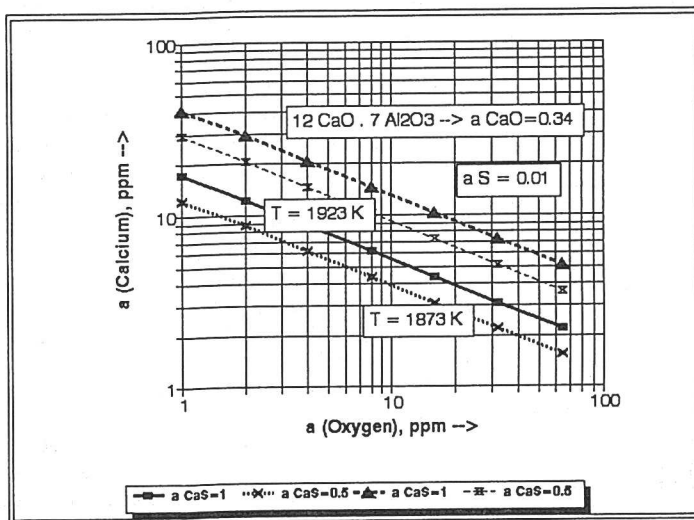


Fig. 5: Influence of CaS activity and temperature in Ca-O-S equilibrium

4. Calculation model for optimal calcium additions

Our wish has been the construction of the basic calculation model to determine the optimal calcium addition to assure the modification of solid alumina inclusions and to prevent the CaS formation.

The comparison of some basic equations for deoxidation by equilibrium between aluminium and oxygen as well as modified inclusions of the binary system CaO - Al₂O₃ on both phase borders of the "liquid window" was the basis for our first estimation and confirmation if the chosen model enables also the application of industrial data.

Slags of the optimum composition CaO-Al₂O₃ have by CaO saturation low melting points and high sulphide capacity and that the reason for their use for removal of sulphur from molten metals. The product between aluminium and sulphur activity is practically constant for certain slag composition in the system CaO-Al₂O₃ saturated with CaS /13/, /14/. And on the basis of this fact the CaO- and Al₂O₃ activities can be calculated without taking care of the CaO- and Al₂O₃ portion of the slag. It has been also stated /15/, /16/ that the activity of CaO in the system CaO-Al₂O₃ depends by low CaS contents (below wt. 5 %) only from Al₂O₃ portion respectively from formation of intermediate phases CaO.6Al₂O₃, CaO.2Al₂O₃, CaO.Al₂O₃ and 12CaO.7Al₂O₃.

The influence of different CaS activity and aluminium on the CaS formation in the system Ca-O-Al-S is shown in Fig. 4 (at 1873 K). The difference between the equilibrium of forming CaS by activities of CaS is 1 and 0.5 for phase equilibrium L/CaO.Al₂O₃ and CaO/L (borders of "liquid window") is shown on presented figure.

Influence of CaS activity and temperature on equilibrium with modified liquid inclusion 7CaO.7Al₂O₃ is shown on the next Fig. 5.

All the mentioned equations allow by taking into account the specific conditions on separate phase borders to calculate the conditions for simultaneous precipitation of solid alumina and CaS.

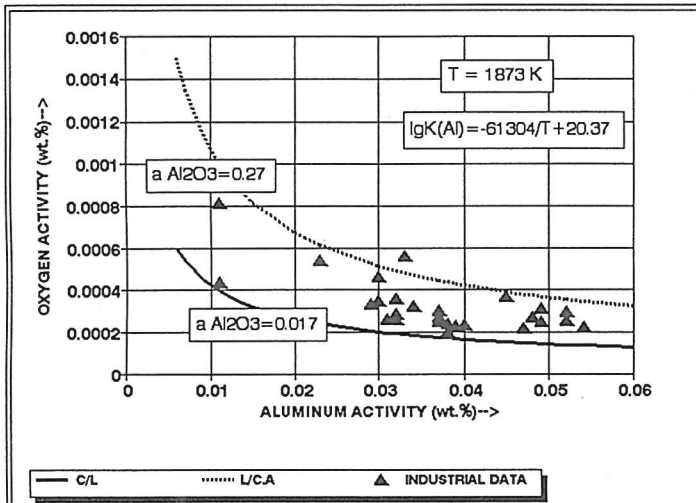


Fig. 6 : Comparison of test measurements and model calculation on Al-O equilibrium

Fig. 6. shows the comparison between theoretically calculated data (both lines on the figure) with measured industrial data and a good agreement has been achieved with theoretical supposition. That means that our basic concept for the calculation model was based on the acceptable and enough reliable basis.

The basic data for developed calculation model are activities of aluminium, oxygen, sulphur and calcium as well as influences of temperature and activities of CaO , Al_2O_3 and CaS .

Fig. 7 shows the basic model structure and the calculation succession.

The following technological conditions has to be fulfilled for the successful use of the model:

- FeO and MnO contents in the cover slag below 1.5 wt.%,
- Proper basicity and quantity of ladle slag,
- Fully Al - killed heats with Al contents between 0.015 and 0.035 % of total Al,
- Sulphur contents in steel before Ca - treatment below 0.020 wt.%,
- Sufficient argon bubbling before Ca - treatment,

The mentioned parameters assure such operating conditions in our technology that the average calcium yield of 18 % can be adopted in presented calculation model to determine the quantity of $CaSi$ in cored wire of diameter 13 mm.

The model has already been installed into the industrial technological practice and a lot of experiments have been done to verify the obtained results. We may conclude that this model have already been successfully accepted as a part of technology by production of some steel grades in Slovenian steelworks.

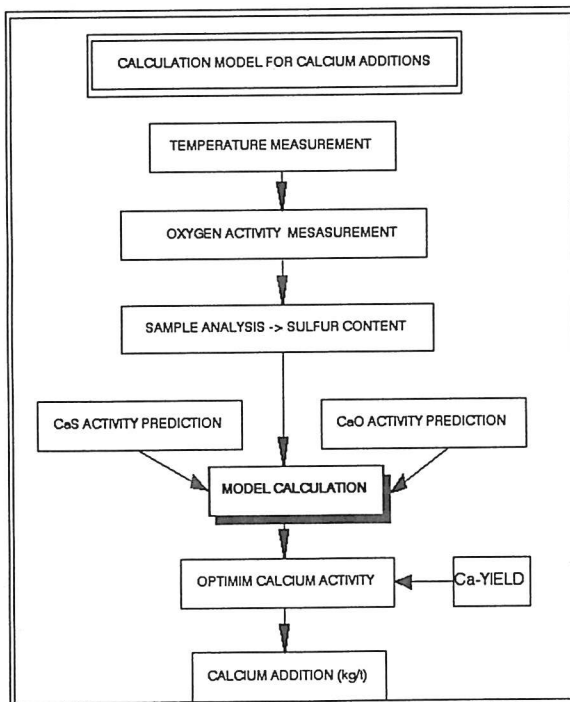


Fig. 7 : Calculation model structure

5. Conclusions

The construction of the basic calculation model to determine the optimal calcium addition to assure the modification of solid alumina inclusions and to prevent the CaS formation was the main purpose of the research.

The comparison of equations for deoxidation and desulphurisation by equilibrium between oxygen, aluminium and sulphur as well as modified inclusions of the system CaO - Al₂O₃ on both phase borders of the "liquid window" was the basis for our first estimation and confirmation if the chosen model enables also the application of industrial data.

The basic data for the model applied by known and standard conditions are activities of aluminium, oxygen, sulphur and calcium as well as influences of temperature and activities of CaO, Al₂O₃ and CaS.

The model has already been installed into the industrial technological practice and a lot of experiments have been done to verify the obtained results.

We may conclude that this model have been successfully tested and accepted as a part of standard technology by production of some steel grades in two Slovenian steel-works.

6. References

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