

ZOFIA KALICKA\*

**EVOLUTION OF THE COMPOSITION OF CaO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> INCLUSIONS DURING ADDITION OF CALCIUM OR CALCIUM-SILICON INTO LIQUID STEEL****EWOLUCJA SKŁADU WTRĄCEŃ CaO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> PODCZAS DODAWANIA WAPNIA LUB WAPNIOKRZEMU DO CIEKŁEJ STALI**

Basing on the data of Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> thermodynamic activities in SiO<sub>2</sub>-containing calcium aluminates of three formulae, CaO·Al<sub>2</sub>O<sub>3</sub>, 12CaO·7Al<sub>2</sub>O<sub>3</sub> and 3CaO·Al<sub>2</sub>O<sub>3</sub> (shortly denoted as C<sub>1</sub>A<sub>1</sub>, C<sub>12</sub>A<sub>7</sub> and C<sub>3</sub>A<sub>1</sub>), at 1873K for the wide range of SiO<sub>2</sub> mole fractions [1], we propose their activities expressed as functions of CaO contents provided there is no change in SiO<sub>2</sub> mole fraction. The proposed relations allow to follow the change of the inclusions and steel composition during calcium treatment when calcium or calcium-silicon are added. An evolution of inclusion and steel compositions during calcium treatment was investigated starting from the partly modified inclusions C<sub>1</sub>A<sub>1</sub>–SiO<sub>2</sub> with  $x'_{\text{SiO}_2} = 0.10$  and 0.03. It was shown that the change of calcium aluminosilicates composition is slightly different for the pure calcium and calcium-silicon additions. With the calcium treatment the mole fraction of SiO<sub>2</sub> in inclusions is decreasing less significant.

Na podstawie danych literaturowych aktywności Al<sub>2</sub>O<sub>3</sub> i SiO<sub>2</sub> w glinianach wapnia CaO·Al<sub>2</sub>O<sub>3</sub>, 12CaO·7Al<sub>2</sub>O<sub>3</sub> oraz 3CaO·Al<sub>2</sub>O<sub>3</sub> (oznaczanych krótko jako C<sub>1</sub>A<sub>1</sub>, C<sub>12</sub>A<sub>7</sub>, C<sub>3</sub>A<sub>1</sub>) zawierających dodatek SiO<sub>2</sub> w 1873K [1] zaproponowano wyrażenie tych aktywności w funkcji % mas. CaO dla wybranych wartości ułamka molowego SiO<sub>2</sub>. Umożliwiło to zbadanie zmiany składu wtrąceń glinokrzemianów wapnia oraz równowagowych stężeń pierwiastków w stali przy dodawaniu wapnia lub wapniokrzemu w procesie modyfikacji wtrąceń. Ewolucję składu wtrąceń rozważono zakładając wtrącenia już częściowo zmodyfikowane C<sub>1</sub>A<sub>1</sub> z dodatkiem SiO<sub>2</sub> w ilości  $x'_{\text{SiO}_2} = 0.1$  i 0.03 (w przeliczeniu na skład CaO–AlO<sub>1,5</sub>–SiO<sub>2</sub>). Wykazano, że skład wtrąceń zmienia się nieco inaczej w przypadku dodawania samego wapnia w porównaniu z dodawaniem wapniokrzemu (przy tej samej ilości wprowadzonego wapnia). Spadek zawartości ułamka molowego SiO<sub>2</sub> jest mniejszy w przypadku wapniokrzemu.

\* WYDZIAŁ METALURGII I INŻYNIERII MATERIAŁOWEJ, AKADEMIA GÓRNICZO-HUTNICZA, 30-059 KRAKÓW, AL. MICKIEWICZA 30

## 1. Introduction

Transformation of alumina inclusions – which are causing nozzle clogging during continuous casting – into liquid inclusions by calcium is called the calcium modification. Calcium treatment is performed by calcium or calcium-silicon addition into a deep aluminium-deoxidized steel. Calcium aluminates inclusions are very differentiated in their composition. The double oxide of  $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$  formula with 48.5 mass % of CaO, has the lowest melting temperature of 1688K. The other liquid calcium aluminates in steel at 1873 K are:  $\text{CaO} \cdot \text{Al}_2\text{O}_3$  (35.4% CaO) and  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$  (62.2% CaO). The above aluminates are shortly called  $\text{C}_{12}\text{A}_7$ ,  $\text{C}_1\text{A}$  and  $\text{C}_3\text{A}_1$ . In a steel deoxidised first by silicon, then by aluminium, there are likely to exist mixed inclusions  $\text{Al}_2\text{O}_3\text{-SiO}_2$ . Then, calcium aluminosilicates  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$  inclusions may be formed as a result of calcium treatment.

Any theoretical analysis of the existence of such inclusions in steel needs the information about the chemical activities of CaO,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  in  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$  system. In paper [1] there are presented the plots of CaO,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  activities in molten calcium aluminates  $\text{C}_1\text{A}_1$ ,  $\text{C}_{12}\text{A}_7$  and  $\text{C}_3\text{A}_1$  with  $\text{SiO}_2$  additions at 1873 K and in paper [2] the equilibrium relations between concentrations of O, Al and Si in steel for such inclusions were studied. For  $\text{C}_1\text{A}_1$ ,  $\text{C}_{12}\text{A}_7$  and  $\text{C}_3\text{A}_1$  calcium aluminates with some amounts of  $\text{SiO}_2$  dissolved, the abbreviated notation of type:  $\text{C}_1\text{A}_1\text{-SiO}_2$ ,  $\text{C}_{12}\text{A}_7\text{-SiO}_2$  and  $\text{C}_3\text{A}_1\text{-SiO}_2$  will be used. Calcium aluminosilicates of any oxide composition will be denoted as  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ .

The calcium added into steel reacts with oxygen (the soluble and the bonded one, as well) and CaO formed is being incorporated into alumina or alumina-silica inclusions. Solubility of calcium in steel is extremely low. The whole amount of the added calcium produces an increase, step by step, CaO contents in inclusions. The change of inclusions composition causes the change of oxide activities in inclusions so some new equilibrium concentrations of the elements dissolved in steel are to occur. The knowledge of change of the oxide activities with the growth of CaO contents facilitates studying the evolution of inclusion composition during the calcium treatment.

## 2. Activities of $\text{Al}_2\text{O}_3$ and $\text{SiO}_2$ in $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ systems

Basing on the data of  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  thermodynamic activities in the  $\text{SiO}_2$ -containing calcium aluminates of three formulas,  $\text{CaO} \cdot \text{Al}_2\text{O}_3$ ,  $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$  and  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$  (shortly denoted as  $\text{C}_1\text{A}_1$ ,  $\text{C}_{12}\text{A}_7$  and  $\text{C}_3\text{A}_1$ ), at 1873 K for the wide range of  $\text{SiO}_2$  mole fraction [1], we propose their activities be expressed as functions of CaO contents, provided there is no change in  $\text{SiO}_2$  mole fraction.

In Figures 1 and 2, there are presented the approximated functions of  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  activities in  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$  system related to the mass % of CaO in  $\text{CaO-Al}_2\text{O}_3$  “subsystem”, in the range from  $\text{C}_1\text{A}_1$  (35.4% CaO) to  $\text{C}_3\text{A}_1$  (62.2% CaO), fitted for the

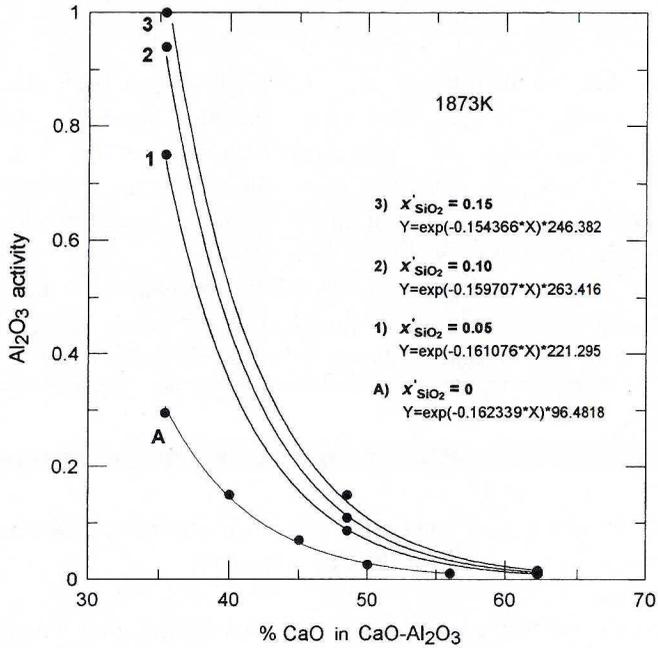


Fig. 1. The chemical activities of Al<sub>2</sub>O<sub>3</sub> in CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system as the functions of % CaO in CaO-Al<sub>2</sub>O<sub>3</sub> subsystem at 1873 K for different values of SiO<sub>2</sub> mole fraction based on the activities of Al<sub>2</sub>O<sub>3</sub> in C<sub>1</sub>A<sub>1</sub>, C<sub>12</sub>A<sub>7</sub>, C<sub>3</sub>A<sub>1</sub> with SiO<sub>2</sub> addition [1]. The curve A is for CaO-Al<sub>2</sub>O<sub>3</sub> without SiO<sub>2</sub> [3]

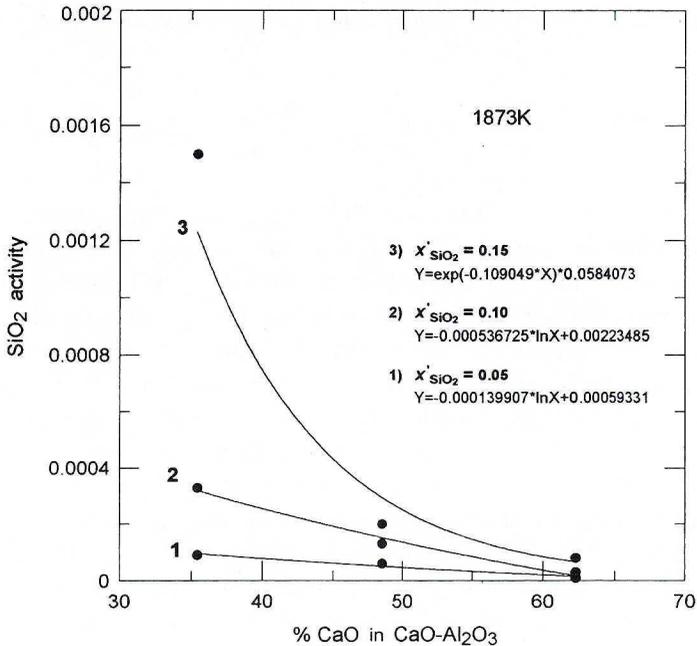


Fig. 2. The chemical activities of SiO<sub>2</sub> in CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system as the functions of % CaO in CaO-Al<sub>2</sub>O<sub>3</sub> subsystem at 1873 K for different values of SiO<sub>2</sub> mole fraction based on the activities of Al<sub>2</sub>O<sub>3</sub> in C<sub>1</sub>A<sub>1</sub>, C<sub>12</sub>A<sub>7</sub>, C<sub>3</sub>A<sub>1</sub> with SiO<sub>2</sub> addition [1]

selected values of  $\text{SiO}_2$  mole fraction,  $x'_{\text{SiO}_2} = 0.05, 0.10$  and  $0.15$ . The mole fraction of  $\text{SiO}_2$ , denoted by  $x'_{\text{SiO}_2}$ , is calculated by converting  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$  oxide composition to  $\text{CaO-AlO}_{1.5}\text{-SiO}_2$  one. The circles on the curves 1, 2, 3 denote the activities in  $\text{C}_1\text{A}_1\text{-SiO}_2$ ,  $\text{C}_{12}\text{A}_7\text{-SiO}_2$  and  $\text{C}_3\text{A}_1\text{-SiO}_2$  systems [1]. In Fig.1 the circles on the curve A apply to pure calcium aluminates and are based on the  $\text{Al}_2\text{O}_3$  activity data in pure  $\text{C}_1\text{A}_1$ ,  $\text{C}_{12}\text{A}_7$  and  $\text{C}_3\text{A}_1$  [3].

The suggested relations are necessary to follow the change of both the inclusions and steel composition during calcium treatment. For the values of  $x'_{\text{SiO}_2}$  different from the ones presented in Fig. 1 and 2, but not higher than 0.15, the  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  activities will be calculated by the interpolation procedure using the data for the two nearest  $x_{\text{SiO}_2}$  values.

### 3. Equilibrium between liquid steel and calcium aluminates inclusions containing silicon dioxide dissolved

The calculations of the chemical activities of aluminium, silicon and oxygen dissolved in steel,  $a_{[\text{Al}]}$ ,  $a_{[\text{Si}]}$ ,  $a_{[\text{O}]}$ , which are in equilibrium with  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$  inclusions, are based on the knowledge of the equilibrium constants  $K$  for the formation of  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  in liquid steel

$$2[\text{Al}] + 3[\text{O}] = (\text{Al}_2\text{O}_3), \quad \log K = \log \frac{a_{\text{Al}_2\text{O}_3}}{a_{[\text{Al}]}^2 \cdot a_{[\text{O}]}^3} = 64004/T - 20.5705 \quad (1)$$

$$[\text{Si}] + 2[\text{O}] = (\text{SiO}_2), \quad \log K = \log \frac{a_{\text{SiO}_2}}{a_{[\text{Si}]} \cdot a_{[\text{O}]}^2} = 30080/T - 11.449 \quad (2)$$

and the chemical activities of  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ ,  $a_{\text{Al}_2\text{O}_3}$ ,  $a_{\text{SiO}_2}$  in inclusions. The change of the calcium activity in steel with the variation in  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$  composition will not be taken into considerations because the calcium solubility in steel is extremely low.

As an example of the calculations, the inclusions containing  $\text{SiO}_2$  of three values of mole fraction ( $x'_{\text{SiO}_2} = 0.03, 0.07, \text{ and } 0.13$ ) and the activity of oxygen in steel equal to 0.0005 (5 ppm) at 1873 K are chosen. The results are illustrated by the plots in Fig. 3 and 4. They show that the aluminium activity in steel is slightly increased by the increase in  $\text{SiO}_2$  contents, and, what is more important, decreases strongly with the CaO-enrichment of inclusions (i.e. when transforming from  $\text{C}_1\text{A}_1$  to  $\text{C}_3\text{A}_1$ ) by constant oxygen activity. The silicon activity is going down with the increase of CaO content, but the higher is the CaO content, the lower is the difference between the silicon activities for two different amounts of  $\text{SiO}_2$  in inclusions (see  $\text{C}_3\text{A}_1$  with 62.2% CaO).

Thus, the calcium treatment makes it possible for silicon to form  $\text{SiO}_2$  at the calcium aluminate inclusions. Pure  $\text{SiO}_2$  inclusions cannot exist in equilibrium with very low activity of oxygen in steel because they would need very high activity of silicon dissolved in steel.

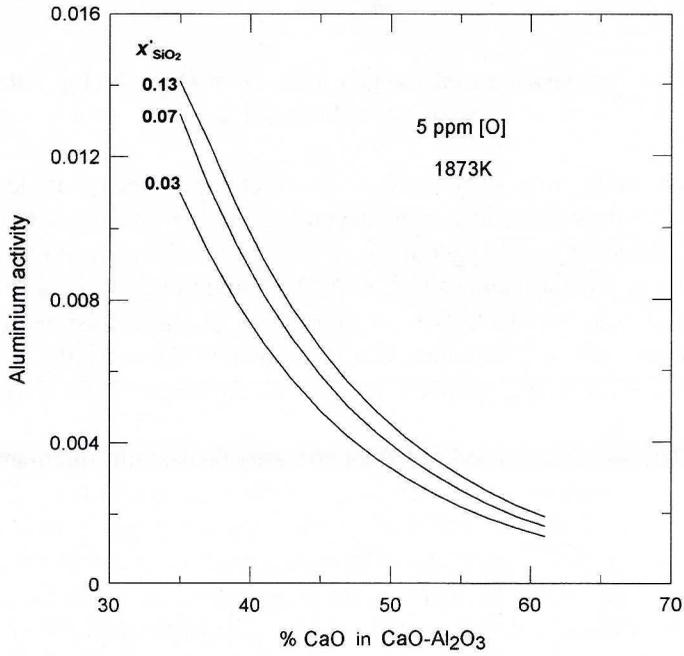


Fig. 3. The aluminium chemical activity in equilibrium with 5 ppm of oxygen dissolved in steel at 1873K and CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> inclusions for selected values of SiO<sub>2</sub> mole fraction

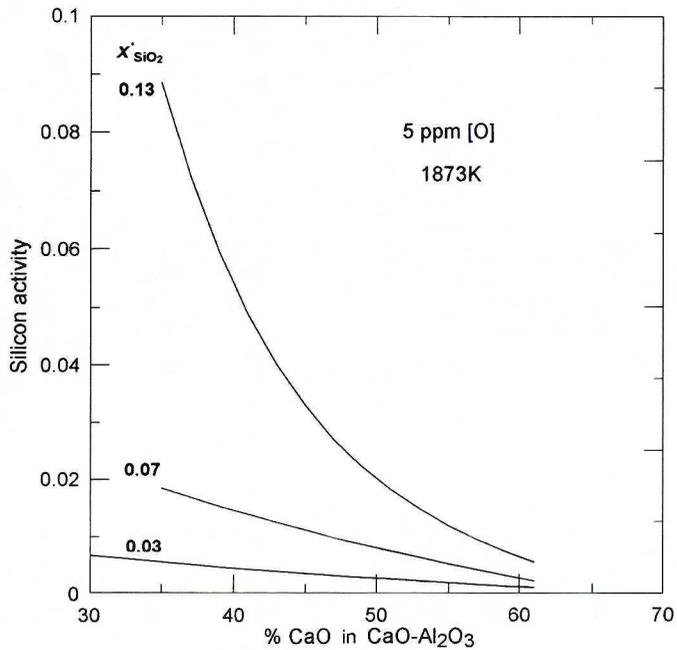


Fig. 4. The silicon chemical activity in equilibrium with 5 ppm of oxygen dissolved in steel at 1873 K and CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> inclusions for selected values of SiO<sub>2</sub> mole fraction

#### 4. The inclusion composition and oxygen activity in steel during calcium addition with or without silicon

The calcium added into steel reacts with either the oxygen soluble in steel or the oxygen bonded in inclusions, in a ratio depending on the quantity and composition of inclusions and the activity of oxygen in steel. As a result, the concentration of oxygen in steel is decreasing and the composition of inclusions is changing, step by step, as the calcium is introduced into steel. The transformation of the inclusions and of the steel composition during calcium treatment can be estimated theoretically by finding a new equilibrium state – according to equations (1) and (2) – every time after an addition of a small dose of calcium.

The calculations were carried out for two cases of calcium treatment: adding pure calcium and calcium-silicon containing 30% Ca, 60% Si and 10% Fe. Evolution of the inclusions composition was investigated starting from the partly modified inclusions  $C_1A_1-SiO_2$  with  $x'_{SiO_2} = 0.10$  and 0.03. The input data for the calculation example were as follows: steel mass –  $10^5$  kg, concentration of oxygen dissolved – 5 ppm, mass of inclusions – 7 kg, mass of calcium addition – 2 kg. The concentrations of aluminium and silicon in steel were the equilibrium ones and resulted from the inclusion composition and oxygen concentration. Calcium was added in 0.1 kg portions. Silicon mass equal 0.2 kg was introduced into steel with every calcium portion when using calcium-silicon. The total calcium added was converted into CaO form. After each 0.1 kg Ca addition,

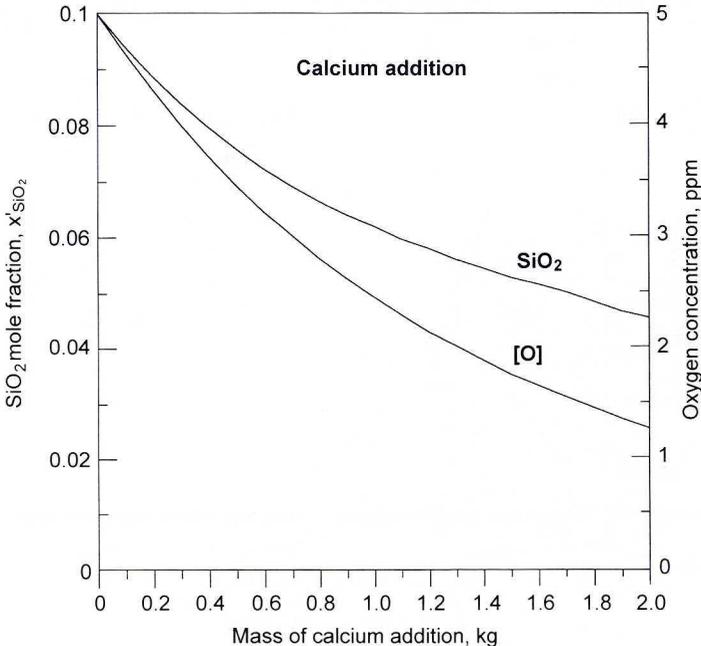


Fig. 5. Effect of calcium addition on the  $SiO_2$  content in the calcium aluminosilicate inclusions and the concentration of oxygen in steel when the starting  $SiO_2$  mole fraction was equal 0.1

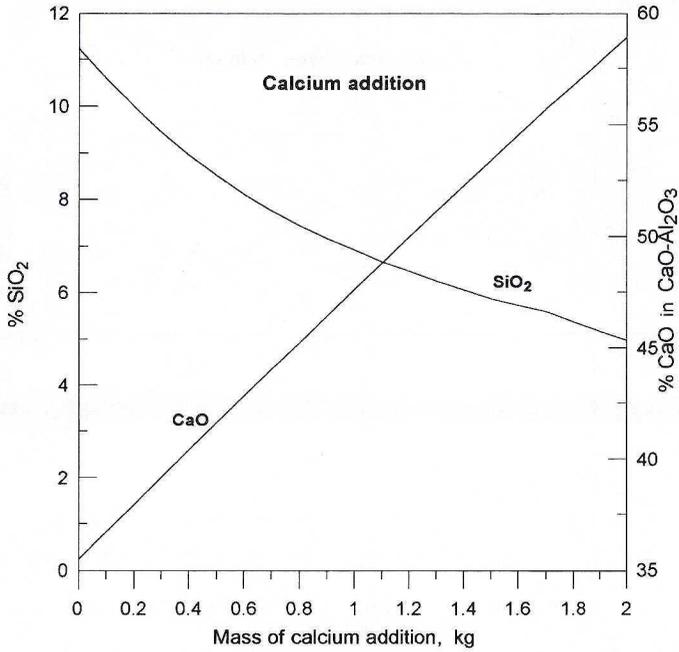


Fig. 6. Effect of calcium addition on the SiO<sub>2</sub> and CaO contents in the calcium aluminosilicate inclusions when the starting SiO<sub>2</sub> mole fraction was equal 0.1

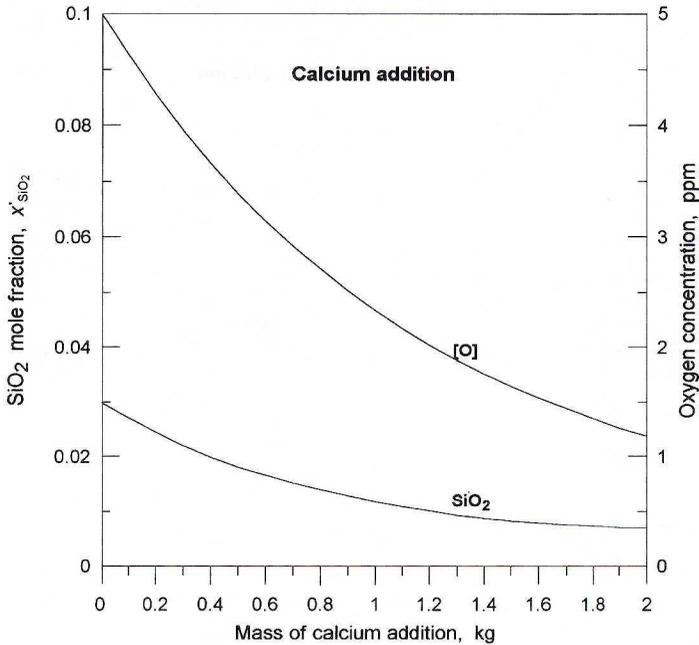


Fig. 7. Effect of calcium addition on the SiO<sub>2</sub> content in the calcium aluminosilicate inclusions and the concentration of oxygen in steel when the starting SiO<sub>2</sub> mole fraction was equal 0.03

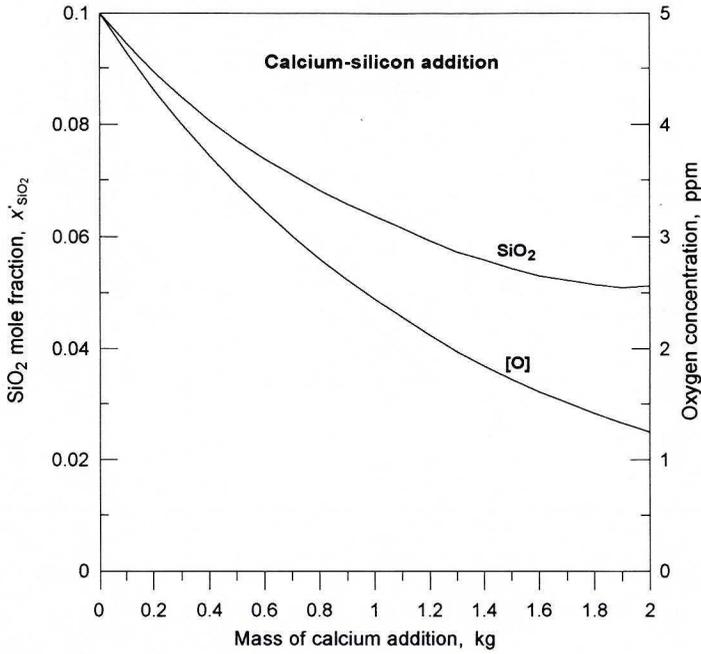


Fig. 8. Effect of calcium-silicon addition on the SiO<sub>2</sub> content in the calcium aluminosilicate inclusions and the concentration of oxygen in steel when the starting SiO<sub>2</sub> mole fraction was equal 0.1

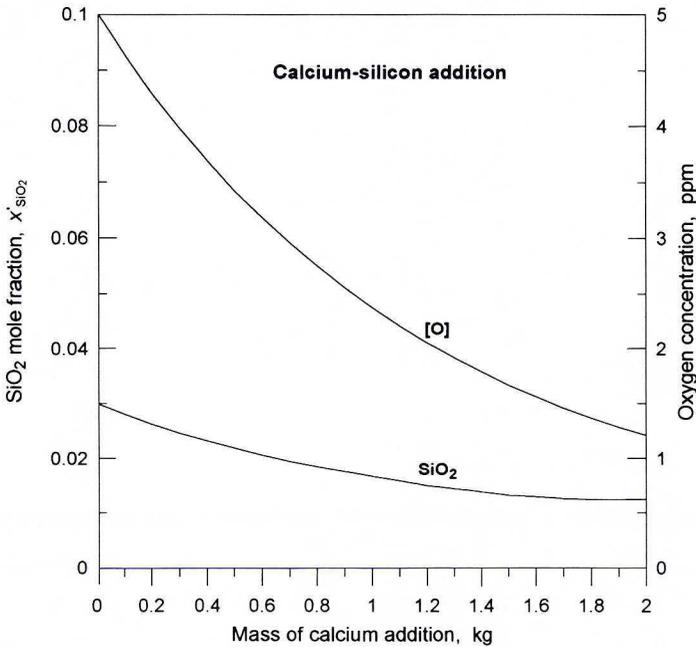


Fig. 9. Effect of calcium-silicon addition on the SiO<sub>2</sub> content in the calcium aluminosilicate inclusions and the concentration of oxygen in steel when the starting SiO<sub>2</sub> mole fraction was equal 0.03

new concentrations of oxygen, aluminium and silicon, and inclusions composition and mass were calculated. For simplicity, an identity of the mass percent of the elements dissolved in steel with their activities is assumed.

The changes of  $\text{SiO}_2$  mole fraction in inclusions and the chemical activity (concentration) of oxygen in steel during calcium treatment are presented in Fig. 5 and 7 for the pure calcium addition, and in Fig. 8 and 9 for the calcium-silicon. Fig. 6 shows %  $\text{SiO}_2$  and % CaO (recalculated for  $\text{CaO-Al}_2\text{O}_3$  system) variations for the one calculation example.

As one can see the inclusions' compositions for pure calcium are slightly different from the ones for calcium-silicon addition but the levels of the oxygen concentration achieved are the same. Silicon dioxide mole fraction is decreasing more slowly when the calcium-silicon instead of the pure calcium is added and the less is  $x'_{\text{SiO}_2}$  the more pronounced effect is noticed.

## 5. Final remarks

It is possible to follow the variation of inclusions' compositions during calcium modification when the relationships between the chemical activities of oxide components and the increase of CaO contents in inclusions are known.

The change of the composition of calcium aluminosilicates inclusions is a little different for the pure calcium and calcium-silicon additions.

When CaO content in inclusions is high, silicon dioxide  $\text{SiO}_2$  is allowed to be present in the inclusions even for very low concentration of oxygen in steel.

The mole fraction of  $\text{SiO}_2$  in inclusions is decreasing during calcium modification process being lower for calcium-silicon than for pure calcium addition.

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