REM-O-S COMPOUND INCLUSIONS GROWTH MODEL

[1]Sergii GERASIN, [1]Dorota KALISZ

[1]*AGH University of Science and Technology, Kraków, Poland, EU, dak@agh.edu.pl*

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Abstract

The program Bi-Growth were used for simulating the formation of non-metallic inclusions (REM-O-S), and their growth. In the process of refining, the non-metallic inclusions are heterogeneous and create a mixture of different oxides or oxides and sulfides. These compounds are a consequence of the introduction of metals and ferroalloys in the form of complex deoxidants. The current work proposes a solution to the bi-growth of oxide and sulfide precipitates by focusing on the formation of precipitates after introducing REM to steel. Because high mixing energies are used during refining, the role of reactant diffusion into the reaction zone was neglected, and the system was treated as perfectly homogeneous in terms of chemical composition. Each precipitate was assumed to grow only on its surface, e.g REMxOy. In this case, the particle growth rate was found to depend solely on the concentration of all three components (REM,O,S).

Keywords: Yttrium, non-metallic inclusions, REM, steel

1. INTRODUCTION

Non-metallic inclusions in steel affect the microstructure and properties of steel [1]. They are usually considered a detrimental part of the refining process. However, the final properties of steel products can be enhanced and shaped by their controlled growth, quality, quantity, chemical composition. Rare earth metals have a high chemical affinity for sulfur, oxygen and nitrogen and are therefore used as modifiers of non-metallic inclusions [2]. Their modifying effect is possible over a wider range of non-metallic inclusions in liquid steel because it can also include the nitride group. The rare earth group includes Sc and Y and lanthanides. These elements have been classified into two groups of light REM: La, Ce, PM, Nd, Sm, Er) and heavy: Y, Gd, Tb, Dy, Ho, Tm, Yb, Lu).

REMs are used to reduce the sulfur and oxygen content in steel to the level of 10^{-6}. REM elements are used to improve the metallurgical purity, and the formation of certain REM-based inclusions increases the strength and hardness of steel. Oxides can be used as centers for heterogeneous nucleation of sulfides, nitrides, and carbides, thus playing an indirect role in regulating the sulfur, carbon, and nitrogen content in steel [3].

The formation of oxide and sulfide non-metallic inclusions with REM content can be described in general by the following equations [4]:

$2[REM] + 3\,[O] \rightarrow (REM_2O_3)$

$2[REM] + 3[S] \rightarrow (REM_2S_3)$

$2[REM] + 2\,[O] + 3\,[S] \rightarrow (REM_2O_2S_3)$

$(REM_2O_2S) + [O] \rightarrow (REM_2O_3) + [S]$

$(REM_2S_3) + [O] \rightarrow (REM_2O_2S) + 2[S]$

The compounds possible to form between rare earth metals and oxygen and sulfur can be identified as: RES, RE_2S_3, RE_5S_7, RE_5S_7, RE_3S_4, RE_2S_4, RE_2O_2S. The current work proposes a solution to bi-growth of oxide and sulfide precipitates by focusing on the formation of inclusions after introduction yttrium to the liquid steel.

2. MATERIALS AND METHODS

Bi – component nucleus growth model (Bi-growth)

The current work proposes a solution to the bi-growth of oxide and sulfide precipitates by focusing on the formation of precipitates after introducing REM (yttrium) to steel. Each precipitate was assumed to growth only on its surface, e.g. yttrium oxide grows only on the surface Y_2O_3, yttrium sulfide on the surface of Y_2S_3. In this case, the particle growth rate was found to depend solely on the concentration of all three components (Y, S, O). It was assumed that the nucleus consists of n_1 moles of sulfide 1 and n_2 moles of oxide 2. Coefficient *Aij* is a quantity dependent on the supersaturation defined by the difference between the current and equilibrium yttrium concentration in steel and the reaction rate constant *kij*. An assumption was made that *Aij*>0, which means that a deficiency in any of the components terminates the growth process of a given precipitate, but neither terminates the growth process of the entire precipitate, nor the dissolution of the particles [5]:

$$A_{ij} = k_{ij} \cdot S_i^{\alpha_i} = k_{ij}\left(c_{[Y]}(t) - c_{[Y]}^{(i)}\right)^{\alpha_i}, \quad (1)$$

where:

- A_{ij} – coefficient,
- S_i – supersaturation,
- *B* – mass penetration parameter,
- α – order of reactions in the calculation (assumed = 1),
- k_{ij} – rate constant, depends on the yttrium„*i*" and surface „*j*".

Hence the quantitative increase of oxide 1 and oxide 2 in the bi-component nucleus is:

$$\mathrm{d}n_i/\mathrm{d}t = (A_{i1} \cdot n_1 + A_{i2} \cdot n_2)/r^{\beta}, \quad (2)$$

where:

$i = 1{,}2$,
β = 1,

hence:

$$\frac{\mathrm{d}n_1}{\mathrm{d}t} = \frac{A_{11}n_1 + A_{12}n_2}{r}, \quad (3)$$

$$\frac{\mathrm{d}n_2}{\mathrm{d}t} = \frac{A_{21} \cdot n_1 + A_{22} \cdot n_2}{r}, \quad (4)$$

- β = 1,
- n_1 – moles of sulfide1,
- n_2 – moles of oxide 2,
- A_{i1} – coefficient dependent on yttrium concentration (for sulfide 1),
- A_{i2} - coefficient dependent on yttrium concentration (for oxide 2).

Where the radius of a growing nucleus:

$$r = \sqrt[3]{\frac{\frac{3}{4} \cdot \frac{1}{\pi} \cdot (v_1 \cdot n_1 + v_2 \cdot n_2)}{z}} \quad (5)$$

- v_1 - molar volume of sulfide 1 ($cm^3 \cdot mole^{-1}$),
- v_2 - molar volume of oxide 2 ($cm^3 \cdot mole^{-1}$).

The molar volumes of examples of non-metallic inclusions are shown in (**Table 1**)

Table 1 Calculated molar volumes of selected non-metallic inclusions

Chemical compound	Molar volume *v* of precipitate ($cm^3 \cdot mole^{-1}$),
Y_2O_3	45.07
Y_2S_3	70.80
Y_2O_2S	49.39

The block diagram of the computer program is shown in **Figure 1** [1]

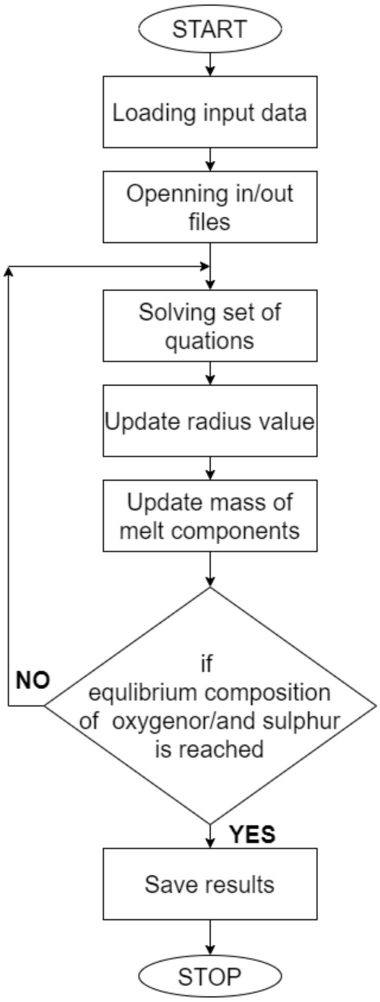

Figure 1 Block diagram of a program to calculate the Bi-growth of non-metallic inclusions during ladle refining of steel [1]

3. SIMULATION RESULTS

Calculations were performed, and the following data were used for the calculations: number of nuclei in 1 cm^3 of steel equals to 10^6, concentration: S = 0.008%, Y = 0.09%, O = 0.01%, equilibrium concentration for Y = 0.005%, molar volume v_1 of sulfide 20 ($cm^3 \cdot mol^{-1}$), molar volume v_2 of oxide 20 ($cm^3 \cdot mol^{-1}$) [1].

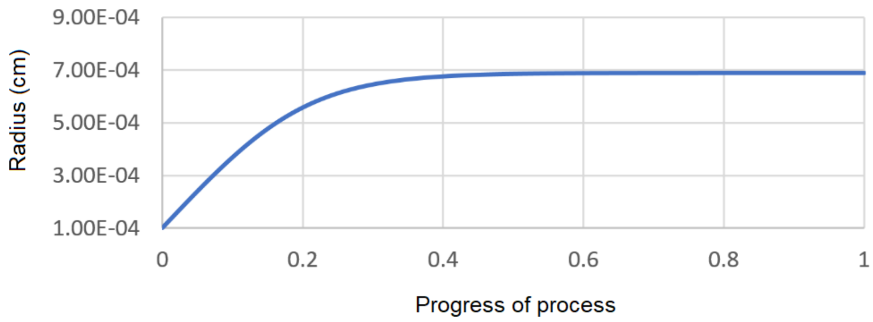

Figure 2 Growth of the radius of nucleus (with an initial radius r_0 = 1 μm) in steel

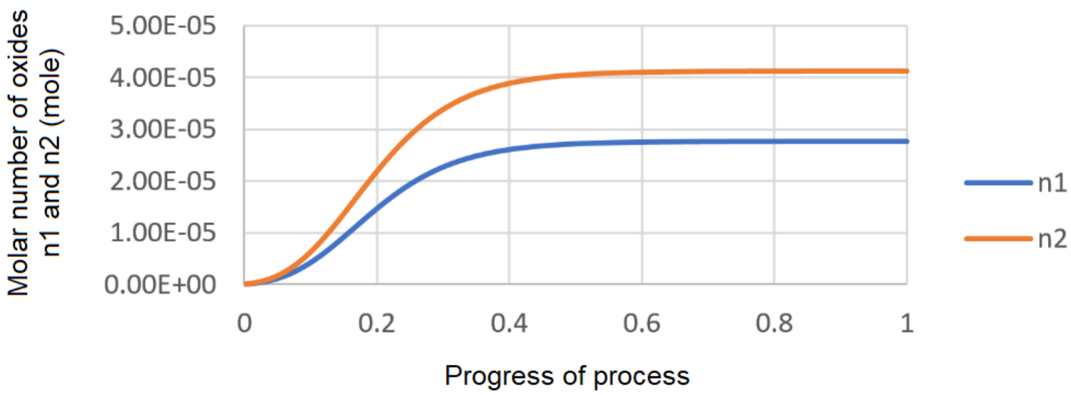

Figure 3 Growth of bi-component nuclei of sulfide n_1 (Y_2S_3) and oxide n_2 (Y_2O_3) in steel (for r_0 = 1 μm)

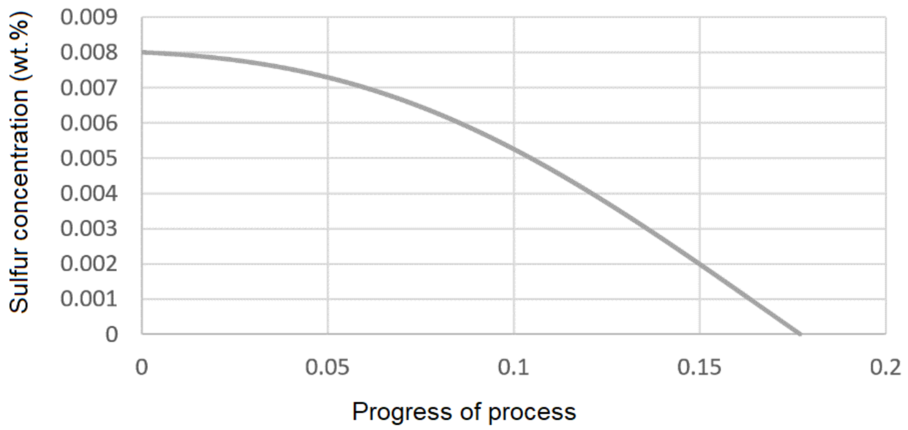

Figure 4 Change of component concentration during the growth of a bi-component nucleus (Y_2O_3–Y_2S_3) in steel (for r_0 = 1 μm)

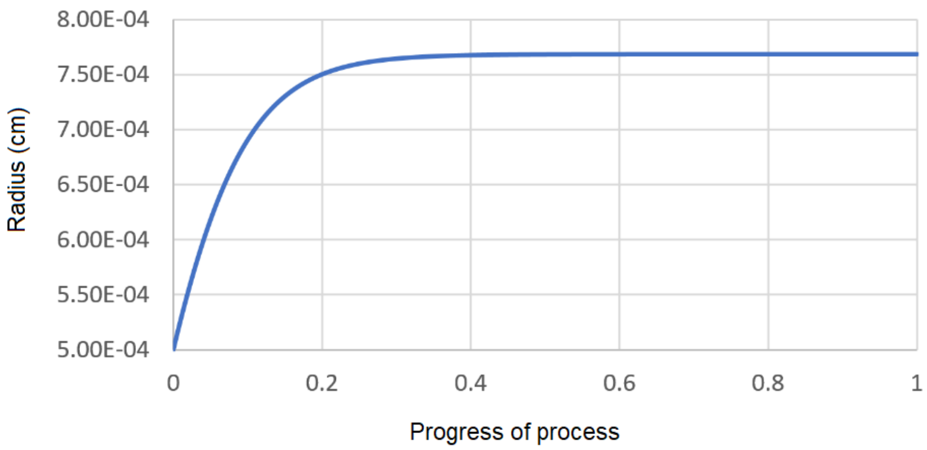

Figure 5 Growth of the radius of nucleus (with an initial radius r_0 = 5 μm) in steel

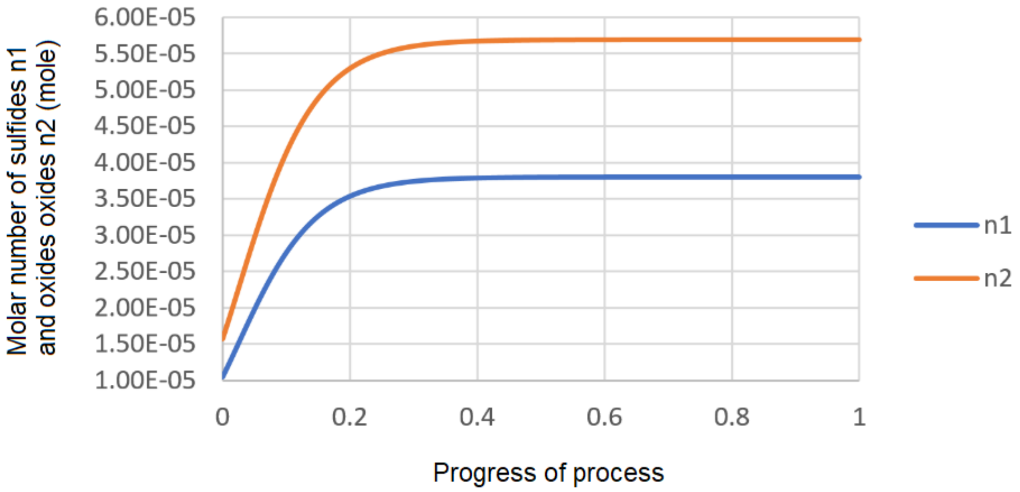

Figure 6 Growth of bi-component nuclei of sulfide n_1 (Y_2S_3) and oxide n_2 (Y_2O_3) in steel (for r_0 = 5 μm)

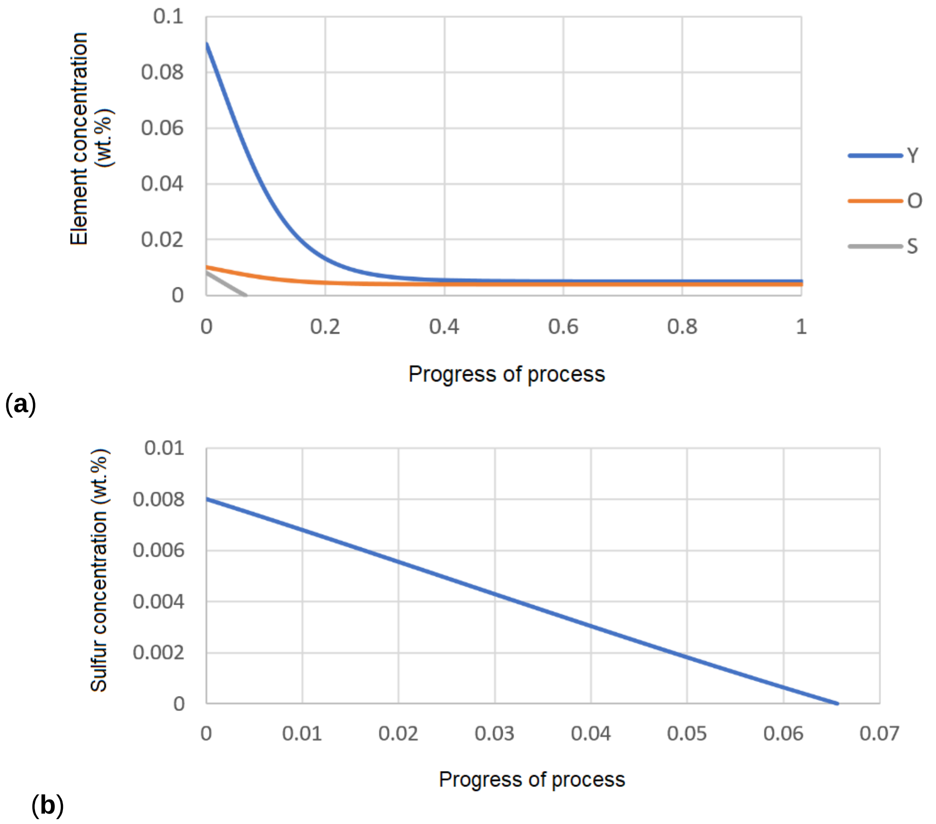

Figure 7 (**a**,**b**) Change of component concentration during the growth of a bi-component nucleus (Y_2O_3–Y_2S_3) in steel 3 (for r_0 = 5 μm)

Figures 2-7 present calculation results the molar growth of a bi-component inclusion composed of n_1 of sulfide (Y_2S_3) and n_2 of oxide (Y_2O_3) for an inclusion with initial radius r_0 = 1 μm and 5 μm. **Figures 2** and **5** show the growth of a bi-component nucleus. For a particle with initial radius r_0 =1 μm, the radius grows mainly in the first phase of the process up to about 0.4 process progression; further increment is small and is due to yttrium reaching equilibrium concentration and sulfur deficiency. In the case of a nucleus with an initial radius of r_0 = 5 μm, growth also takes place at an early stage of growth, with equilibrium establishing earlier, i.e., by about 0.2 process progression. It is observed that the low content of sulfur in the steel causes that it to be consumed for the precipitation of the sulfide phase.

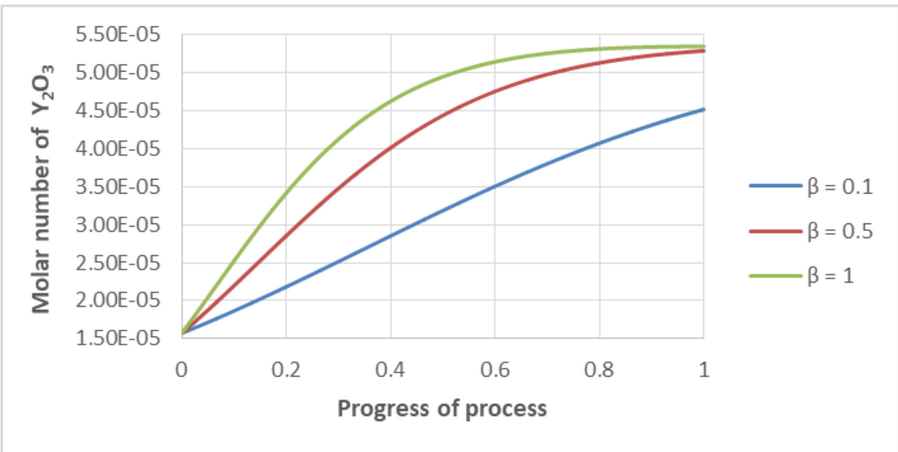

Figure 8 Growth of n1 (Y_2O_3) in steel (for r_0 = 5μm) (parameter β = 0,1; 0,5; 1)

Finally, calculations were performed in view of the magnitude of the parameter β and its effect on the growth process of bi-component oxide-sulfide inclusions. The parameter β has a significant influence on the results of the simulation process. A significant decrease in the value of β clearly slows down the growth process.

4. CONCLUSIONS

The growth of bi-component oxide-sulfide inclusions containing yttrium depends on the sulfur content in steel. A low sulfur concentration results in sulfur deficiency thus inhibiting the growth of sulfide. Further growth of the inclusion takes place through the formation of oxide until yttrium reaches an equilibrium concentration. Since the formation and growth of non-metallic inclusions occurs at every stage of liquid steel processing and also during crystallization, the parameter β must be taken into account when analyzing the growth process. The adoption of low values of the parameter β in the calculations affected the kinetics of this process, though did not change its nature. Still the main factor influencing the chemical composition of complex inclusions is the deficit of the component of the inclusion.

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REFERENCES

[1] KALISZ, D., ŻAK, P. L., SEMIRYAGIN, S., & GERASIN, S. Evolution of Chemical Composition and Modeling of Growth Nonmetallic Inclusions in Steel Containing Yttrium. *Materials*. 2021, vol. 14, p. 7113.

[2] WILSON, W.G., HEASLIP, L. J., SOMMERVILLE, I. D. Rare Earth additions in continuosly cast iron. *Journal of Metals*. 1985, pp. 36-41.

[3] MIKHAILOV, G.G., MAKROVETS, L. A., SMIRNOV, L. A. Thermodynamic simulation of phase equlibria of oxide systems containing rare earth metals. Report 2. Phase Diagrams of Oxide Systems with Y_2O_3. Bulletin of the South Ural State University. *Ser. Metallurgy*. 2014, vol. 14, pp. 5 – 10.

[4] WANDBY P. E. Rare earth additions to steel. *International Metals Reviews*. 1978, vol. 2, no. 74.

[5] MERDER, T., PIEPRZYCA, J., WARZECHA, M., WARZECHA, P., HUTNY, A. Evolution of the numerical model describing the distrbution of non-metallic inclusions in the tundish. *Materials.* 2021, vol. 14, p. 2229.