The effect of yttrium addition on the chemical composition of the non-metallic phase in liquid steel

S Gerasin1, D Kalisz1, P L Żak1, K. Kuglin1 and J Iwanciw2

1 AGH University of Science and Technology, Faculty of Foundry Engineering, 23 Reymonta Street, 30-059 Kraków, Poland

2 retired

E-mail: dak@agh.edu.pl

Abstract. The introduction of yttrium as an alloy additive to steel is connected with the formation of non-metallic inclusions resulting in the losses of this element. The presence of yttrium is expected to minimize the precipitation processes caused by sulphur and oxygen in steel. Therefore the order in which the additives are introduced during refining processes decides about yttrium final content in steel in bounded and dissolved form. For defining the amount of the generated non-metallic phase and kinetics of deoxidation and desulphurization processes authors used a non-commercial computer program based on the worked out calculation models. The process was analyzed in view of the order of introducing additives: Al, Y and Ca to preliminarily deoxidized steel. It was revealed that yttrium dosing is connected with the formation of oxide and sulphide phases. The introduction of yttrium prior to aluminium brings about huge losses, mainly as far as oxides formation is concerned. In the case of higher participation of sulphur, this effect is even stronger. When yttrium is introduced after aluminium and calcium, yttrium is used for the formation of its sulphide, and in this way the manganese sulphide formation is reduced. The simulations showed that yttrium should be introduced at the end of the refining process after adding aluminium and calcium. In this case the yttrium losses for the formation of its sulphide and oxide and least.

1 Introduction

The modification of steel composition with alloy additives can be realized after taking into account potential melting losses of added metal in the form of liquid or solid dross, mainly oxides. In particular cases attention should be also paid to the formation of sulfides and nitrides. Such losses are observed mainly during preliminary deoxidation of steel during flow-off, though they may also take place at any stage of secondary processing, e.g. flow-off, or at any stage of secondary processing of steel, during argon blowing and refining. Processes leading to the formation of dross are in line with the tendency of the system to establish the state of thermodynamic equilibrium in the system where the total free energy reaches minimum at a given temperature, pressure and mass of particular components. As a consequence the four-phase system, consisting of liquid steel, liquid slag, solid or liquid non-metallic precipitates forming a dispersed and gaseous phases should be accounted for. In the near-real conditions observed in the metallurgical processes no such a state of equilibrium is generally established. More realistic and important image of alloy addition processes can be obtained by limiting investigations only to the analysis of equilibrium between liquid steel and non-metallic dispersed phase.
The deoxidant \([R]\) and oxygen \([O]\) are dissolved in liquid steel with oxide. The product of the reaction can \([1-5]\):
- remain in the form of small particles suspended in liquid steel, because small particles flow off very slowly,
- form a particle of liquid oxide solution with other oxides. A solution of some oxides has a definitely lower liquidus temperature,
- form a compact or loose aggregate with other non-metallic particles as a result of operation of capillary forces.

The analysis of deoxidation, refining and introduction of alloy additives to steel requires taking into consideration two basic elements: thermodynamic characteristic of phases appearing in the process, which allows for determining the states of equilibrium, and kinetic description of elementary processes. On this basis particular elementary processes can be qualitatively evaluated at a given moment of process, and the final effect can be determined \([1-3, 6, 7]\).

Yttrium is highly active in steel and shows a considerable chemical affinity, especially to oxygen and sulphur. In reaction with dissolved elements forms solid crystalline precipitates: oxides and also sulfides, oxysulfides, nitrides and carbonitrides \([8]\). For this reason attention should be paid to the loss of elements reacting with oxygen and sulphur dissolved in metal bath.

Hence the aim of this paper is mainly to work out a method simulating the evolution of non-metallic precipitates content in the deoxidation process and during introduction of an additive, e.g. yttrium to steel. In this way the yttrium dross as an alloy component of steel can be predicted.

2 Description of the computer simulation program for deoxidation reactions

The WYK_STAL computer simulation program worked out by J. Iwanciw and others \([9-11]\) was used for real-time simulating and aiding secondary metallurgical processes. This program calculates the successive stages of a system consisting of liquid steel, non-metallurgical precipitates, liquid slag and gas.

The starting point for the simulations is liquid steel of definite weight, chemical composition and temperature. When deoxidizing steel the whole mass of iron alloys of a given composition can be added directly during flow-off, or in portions; in the boundary case the dosing can be represented as continuous. The processes taking place among introduced steel components at that time are very dynamic as the system is subject to strong mixing energy of the streaming liquid steel. Chemical reactions take place, and in a relatively simple model they can be reduced to the oxidation of steel components, mainly the non-metallic ones. Slag and non-metallic precipitates have a similar chemical character, i.e. they are oxides solutions. Mass proportions of slag and precipitates can be assessed on the basis of oxygen concentration in steel during the flow-off. The total mass of slag is a sum of slag-generating additives (lime), furnace slag which entered the ladle during the flow-off and precipitates which few out from steel to slag.

The WYK_STAL program allows to calculate pure elements or multi component additives which are to be admixed to the liquid metal bath, process simulation, accounting for the calculated additives and checking out the composition after the simulation. This program is equipped with additional modules and such options as deoxidation, desulphurization, formation of nitrides or verification of simulation results.

Hence this program can be used for simulating, secondary refining technologies and establishing the composition of steels which have never been produced in the steel mills before. This program makes use only of own databases and user process data in the form of text files. A specific process can be defined on the basis of the following files, which have to be worked out and used:
- (a) process parameters,
- (b) required composition of metal,
- (c) initial composition of metal,
- (d) initial composition of slag,
- (e) additives files,
- (f) configuration files.

The program calculates the successive states of a system made of liquid steel, liquid slag, non-metallic inclusions and alloy additives.
For simulating the behaviour of alloy additives when introducing them to steel, authors developed the files for computer program to make it work for the yttrium oxides, sulphides and nitrides formation concurrently with the reactions relating to the basic oxides formation. Apart from this an elementary thermodynamic parameters base was created for the formation of particular compounds, including the changes of standard free energy of formation, and parameters of oxygen and sulphur interaction with the components of the solution. Moreover the database for yttrium oxides and sulphides as well as the parameters of yttrium interaction with steel components was updated. The base of parameters for oxides and nitrides formation base on the literature data [1, 9-13].

3 Calculation results

The process of non-metallic phase formation as a result of introduction of deoxidizing additives was analyzed. Authors analyzed the basic system Fe–O–S–Al–Y, where 30 kg aluminum was added in the fifth minute, and 76 kg Yttrium in the twentieth minute of the process.

The program allows for choosing a model for thermodynamic calculations:
• Model a: activity of the formed compound $a = 1$;
• Model b: computations for partition coefficient $L_S$.

For simulating the deoxidation and desulphurization process, the following data were assumed:
• process duration: 30 minutes;
• weight of metal in ladle: 140 000 kg;
• weight of slag: 100 kg;
• temperature of metal at the beginning of the process: 1670 °C;
• pressure of gaseous phase 1 atm;
• initial maximum oxygen bounded in inclusions: 0.0001%;
• initial total oxygen content in steel: 0.01%;
• initial slag composition: CaO–45%; Al₂O₃–2%; MgO–9%; MnO–5%; SiO₂–12%; FeO–27%;
• change of additives introduced to slag: 100 kg CaO was added in the first minute, 100 kg SiO₂ was added in the second minute.

The steel composition chosen for the calculations is shown in the Table 1.

| Element | C | Mn | Si | P | N | S | Fe |
|---------|---|----|----|---|---|---|----|
| wt. %   | 0.054 | 0.05 | 0.23 | 0.007 | 0.005 | 0.01 | balance |

The results of calculations for model a are presented in figures 1 – 3.

At the initial stage of the refining process the non-metallic inclusions consist of FeO and MnO, the formation of which is hindered by the addition of aluminum and then yttrium. The introduction of yttrium at the final stage results in the formation of oxide and sulfide inclusions, where the participation of oxygen in the system is much lower. This low oxygen content in the system is caused by the preliminary deoxidation with the use of aluminum. The slag composition was observed to change after adding elements. At the final stage of refining small amounts of yttrium sulfide and oxide were present, being a consequence of precipitation and absorption of the outflowing non-metallic inclusions by slag.
Figure 1. Change of element content in liquid steel vs process duration

Figure 2. Change of chemical composition of slag vs process duration

Figure 3. Change of chemical composition of non-metallic inclusions vs process duration
Analogous calculations were performed for model b, accounting for partition coefficient $L_S$. The results of calculations are presented in fig. 4-6.

Figure 4. Change of element content in liquid steel vs process duration

Figure 5. Change of chemical composition of slag vs process duration

Figure 6. Change of chemical composition of non-metallic inclusions vs process duration
A very similar course of plots representing the chemical composition of elements dissolved in liquid steel in model a was observed in this case. FeS was identified in the slag. The presence of parameter $L_S$ in the calculations had an influence on the chemical composition of non-metallic inclusions containing yttrium. The participation of $Y_2S_3/Y_2O_3$ in inclusions was lower as compared to the results of calculations performed for model a. Apart from this, the sulfur content in liquid steel was higher.

4 Conclusion
Yttrium in liquid steel plays the role of a complex deoxidizer and desulphurizer. Its addition also affects the composition of steel, slag and the formed non-metallic inclusions.

Computer calculations of inclusions formation in thermodynamic equilibrium conditions allow for determining the chemical composition of the formed non-metallic phase in a given deoxidation situation. On this basis the amount of oxygen dissolved in metal bath and chemical composition of refined liquid steel can be also established.

The results of calculations showed that the products of chemical reactions taking place during preliminary deoxidation mainly consisted of oxides, though the participation of specific phases depended on the yttrium addition.

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