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THERMODYNAMIC MODELING OF DEOXIDATION PRODUCTS AND INCLUSION CHEMISTRY IN MN / SI KILLED TIRE-CORD STEEL

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Abstract

The present work deals with thermodynamic modeling of oxide systems, in the context of slags and inclusions in steelmaking. The work has emphasis on oxides encountered during the production of tire – cord steel. Control of inclusion chemistry and variation in eutectic temperature and eutectic composition of MnO-$Al2O_3$-SiO_2 slag system have been studied, using Thermo-CalcR software. Relatively low liquidus temperatures are obtained for ratio of MnO / SiO_2 = 0.5 - 1.5 and $Al2O_3$ content from 10 - 20 mass%. It has been observed that the addition of Alumina leads to further increase in the liquidus temperature. The stability of inclusions is analyzed in terms of free energy values of related slag systems; and an appropriate minimum of Gibbs free energy value of slag phase observed at around 50 ppm of Oxygen. The observations could not be verified using thermodynamic experiments, but have been compared with findings in the open literature.

Keywords: Thermodynamic modeling, Tire – cord steel, Inclusion engineering, Deoxidation, Thermo-CalcR, Oxide slags

1. Introduction

Mn / Si complex deoxidation has to be understood properly, for production of high-value steels such as tire-cord steel and high Ni- steel, given the harmful effects of solid Al_2O_3 inclusions formed during Al deoxidation. Al_2O_3 inclusions usually cause wire breakage during tire-cord production, where inclusions should be deformable

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during wire drawing process. Therefore, Mn/Si deoxidation, which results in MnO-Al_2O_3-SiO_2 inclusions of low melting temperature, are usually preferred. Inclusion engineering, modification of inclusion compositions in such a way so as to make them less harmful during manufacturing, in steel making is key tool for 'ultra clean steel' production in the last decades. Thermodynamics, particularly high temperature chemical thermodynamics provides an important tool to identify and control the variables that are essential for optimizing production process and product quality of steel. The phases observed in the MnO-Al_2O_3-SiO_2 system are Cristobalite and Tridymite (SiO_2); Mullite ($3Al_2O_3.2SiO_2$); Corundum (Al_2O_3); Rhodonite ($MnO.SiO_2$); Tephorite ($2MnO.SiO_2$); Galaxite ($MnO.Al_2O_3$); Spessartite ($3MnO.Al_2O_3.3SiO_2$) [1]. The phase diagram of MnO – SiO_2 – Al_2O_3 system is shown in figure (1). Out of all the phases listed above, the inclusions lies in spessartite phase region are soft, deformable, low viscosity, low wettability and having low liquidus temperature [2]. But, as shown in ternary of MnO-Al_2O_3-SiO_2, the inclusions in spessartite phase exists only over a restricted range of composition [3] and [4]. The objective of the present work is to predict appropriate composition of inclusion chemistry for inclusions have low liquidus temperature and maintain those inclusions in the desired spessartite phase region shown in figure 1. Also, have to check at what content of oxygen the desired products of inclusions are stable, by checking thorough Gibbs free energy. This required thermodynamic analysis of the Mn – Al – Si complex

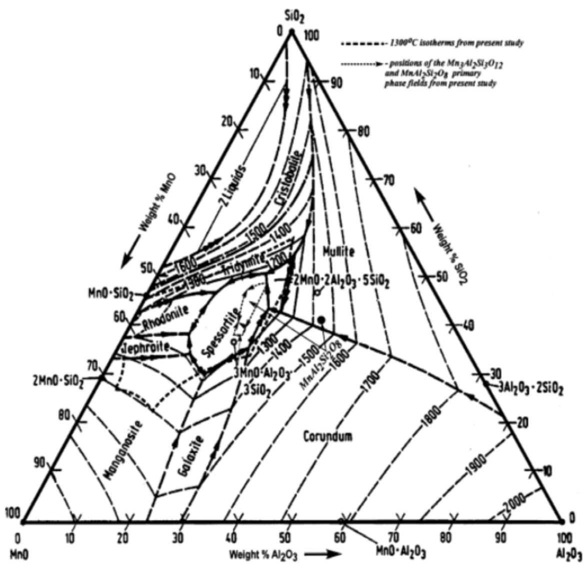

Figure 1. Phase diagram of MnO – SiO_2 – Al_2O_3 system [1]

deoxidation process. In the present work, we used Thermo-Calc^R software with relevant databases (TCFE 3 and SLAG 2) and the results obtained for different process conditions have been presented. The variation in liquidus temperature of the MnO-Al_2O_3-SiO_2 slags at various compositions of MnO, SiO_2 and Al_2O_3 are presented and analysed here.

2. Deoxidation of steel with Mn, Al and Si

Steelmaking is carried out under oxidizing conditions. Oxygen is bound to dissolve in iron-melt. The solubility of oxygen in pure iron at 1600^{o}C is 0.23% rises to 0.48% at 1800^{o}C and drops to 0.003% in solid steel melt. If such steel cast, the excess oxygen is evolved in the form of gases leading to adverse effects in casting and subsequent manufacturing processes.

The removal of residual oxygen content of refined steel is known as deoxidation. Al, Si, Mn and C are commonly used as deoxidizers. According to Kobayashi [5], the Mn / Si deoxidized steel-cord contains 0.69-0.74 mass% C, 0.40 – 0.65 mass% Mn and 0.15 – 0.35 mass% Si and oxide inclusions are controlled so as be lie in spessartite phase ($Mn_3Al_2Si_3O_{12}$) and containing 20 mass% of Al_2O_3 [3]. The ideal metal compositions for low liquidus inclusions is found to be in the range of Mn / Si = 2 - 5 for the constraint of Mn + Si=1 mass% at 1823K (1550°C) [4].

3. Thermodynamic modeling and prediction of inclusion chemistry

Over the years, significant development has taken place in the area of slag modeling [2]. Various models, eg., regular solution model [6], Kapoor-Frohberg model [7] have been reported and discussed. Modeling of molten oxide solution is particularly difficult, because of its short range ordering behaviour at a certain composition and immiscible characteristic at acid component rich composition such as SiO_2 [4]. In addition to above mentioned types of modeling, compound energy formalism [8] is also used for modeling of oxide solution. However, the preceeding approaches have been carried out using only activity data of oxide [2, 4] in the system at a given temperature. This approach would give acceptable result for prediction of inclusion composition at the given temperature, but fails to give at other temperatures accurately [2, 3]. In the present work, we tabulated the measured eutectic temperatures and eutectic composition at various compositions of Al_2O_3, MnO and SiO_2, restricted to acceptable constraints using Thermo-Calc^R software. In Mn/Si deoxidized steel, inclusions formed in tire-cord steel are the compounds of MnO-Al_2O_3-SiO_2 system [9]. Our main interest is then to predict for what steel chemistry the inclusions formed should lie in low liquidus region i.e. in spessartite phase region. In the subsequent sections, it will be shown how thermodynamic calculations can be applicable to predict the above mentioned inclusion behaviour in liquid / solid steel.

Calculations based on accurate thermodynamic databases can give useful information, such as variation of inclusion chemistry with Mn / Si ratio in Mn / Si killed steel and the variation in liquidus temperature of slag with variation on inclusion composition. It is seen from the figure 1, that the spessartite primary phase region gives the liquidus temperature as low as of 1100°C – 1200°C. If the inclusion chemistry can be brought into this region, it will be possible to control them to become a glassy phase in the solid steel. The ratio of MnO / SiO_2 in this region varies from 0.5 to 2 [4]. But, the work presented here has demonstrated that low liquidus temperatures are obtained in the ratio of MnO / SiO_2 is of 0.5 -1.5 and most probable Al_2O_3 content is 10 - 20 mass %. A question then arises on how to control the inclusion chemistry, so that inclusions lie in this desired region of spessartite phase. The inclusions composition can be estimated from the thermodynamic calculation as a function of steel composition between steel and inclusion is established. Furthermore, the control of inclusion chemistry is possible through the control of steel chemistry only. Figure 2 [4] shows variation of inclusions composition at different steel chemistries in

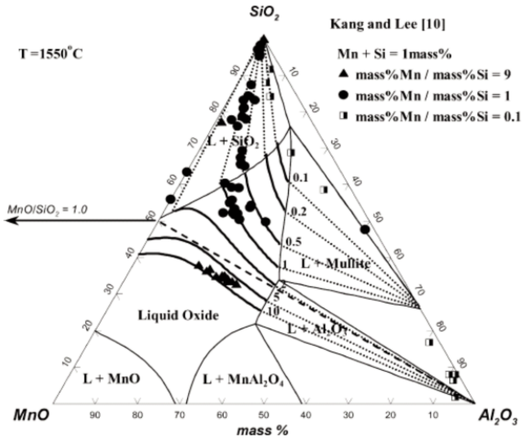

Figure 2. Comparison between experiments and calculations of inclusion compositions in Mn / Si deoxidized steel at 1550°C. Mn / Si in steel is 1 mass %. All lines are calculated from the thermodynamic model [4]

Mn/Si deoxidized steel at 1550^{O} C. By following the approach of Kang *et al* [4], and through the phase diagrams (1&2), and from the constraints provided by Choudhary et al [2], and Kang et al [4], (Mn + Si = 1 and Mn / Si = 2 - 5) one can find the appropriate steel chemistry for getting desired inclusion chemistry such that all the inclusions should lies in desired i.e. Spessartite phase field.

4. Results and discussion

The findings reported here have implications for the steel making and refining practices. This work has been done, for different MnO to SiO_2 ratios. It can be seen from figure 3, that there is a clearly defined eutectic at 1472 K [10]. This is the lowest eutectic observed among all the graphs used in the present study. The diagram generated by fixing the content of silica at 57 mass % and remaining quantity is normalizes among MnO and Al_2O_3 to 100 mass %. The eutectic composition is 16 mass % of alumina and 27 mass % of MnO. From figure 3, we can say that, by the decrease of Al_2O_3 content from eutectic point, the liquidus temperature is raised and inclusions formed are more prone to become SiO_2 phase and melting point touches to 2000 K. Also, by increasing alumina content beyond eutectic point, the similar is observed but the inclusions are fall in the phase of Si_2O_4-Al_6O_9 and liquidus raised to 1900 K. But, both of these should avoid restricting the inclusion into low liquidus region, i.e. Spessartite phase. Hence, the Al_2O_3 content should lie in the neighborhood of 16 mass % for this initial composition. Also, if so, the inclusion form glassy phase during solidification and problem encountered in wire-drawing process may be solved. Similar

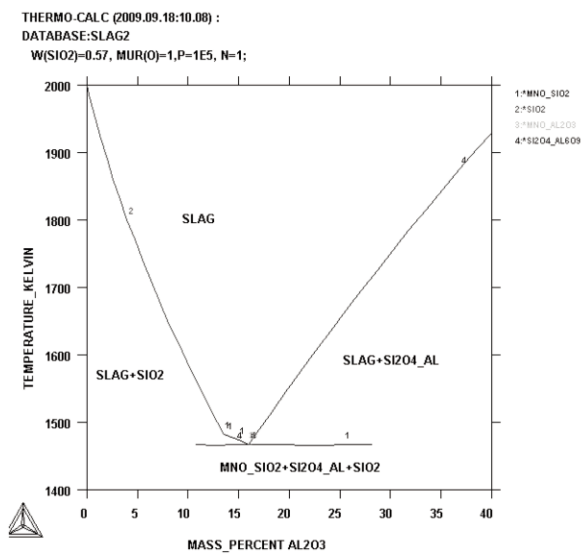

Figure 3. Pseudo – binary phase diagram of MnO – Al_2O_3 – SiO_2 System, with different proportions of Al_2O_3 and MnO along X – axis, with SiO_2 content fixed at 57 mass % [10]

procedure is followed for other inclusion composition and for phase diagrams.

The variation in liquidus temperature with variation in ratio of MnO to SiO_2 is represented in figure 4. The graph reveals that, by increasing alumina content, the liquidus is going down initially irrespective of ratio of MnO to SiO_2, but the difference is only in the amount depression of liquidus temperature. The lowest point is obtained at ratio of 0.5 (MnO / SiO_2) and at alumina content of 15 mass %. Also, it is observed that, for the ratios 0.1, 1.5 and 2 the liquidus temperatures are not much as low as they required. Hence, it is better to avoid the inclusions which follow the above mentioned ratios and are showed in table. Now, the variation in liquidus temperature with ratio of MnO to SiO_2 at constant Al_2O_3 content is shown in figure 5. One can observe that the variation in liquidus with ratio is small at alumina content of 25 mass % and 30 mass %. Also, it reported that the temperatures are quiet high for present case of application. But, at 10 mass % and 15 mass %, low liquidus points are observed and variation is clearly lying in a definite range of ratio (ratio of MnO to SiO_2), i.e. from 0.5 to 1.5. Now, as far as stability of phases is concerned, one has to monitor Gibbs free energy. Figure 6 shows the graphical representation of Oxygen content versus Gibbs free energy of slag for the composition of Tire-Cord steel, i.e. Fe – C(0.7) – Mn(0.7) – Si (0.3) – Al (1.2 ppm) – O (50 ppm) and at conditions of Temperature 1823K, Pressure 0.1MPa. The graph depicts that, the Gibbs free energy decreases with increase of oxygen content and attains a minimum value of at oxygen content in the range of 45ppm to 60 ppm. From this, we can say that, the inclusions formed in the ternary of MnO-Al_2O_3-SiO_2 are stable, at oxygen content around 50 ppm. And again, increase in Gibbs free energy is observed by increasing oxygen content further. Also, from figure 7, it is observed that the slag amount is maximum, at oxygen content of 50

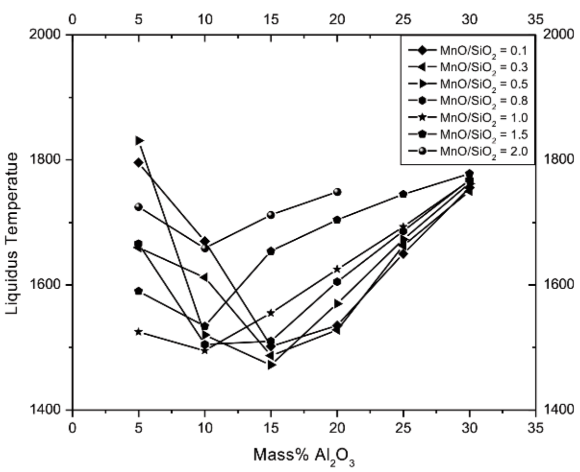

Figure 4. Variation in liquidus temperature (K) with alumina concentration, at different ratios of MnO to SiO_2

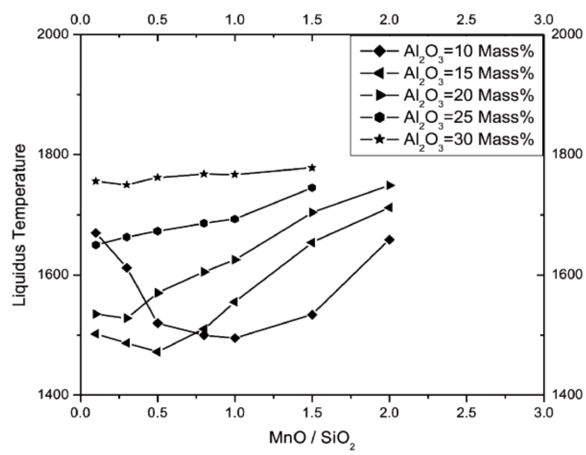

Figure 5. Variation in liquidus temperature (K) with MnO / SiO2, for different initial alumina contents

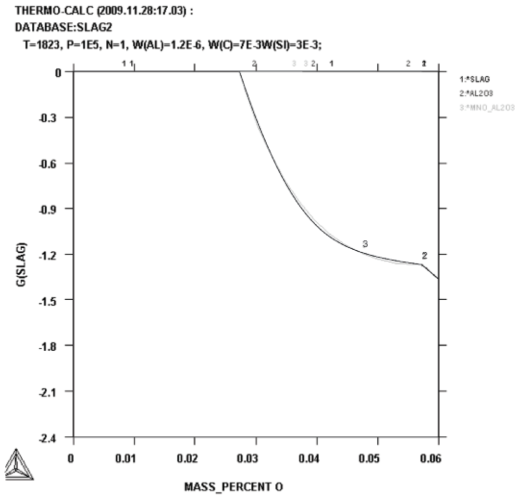

Figure 6. Gibbs free energy of slag phase Vs Oxygen content (ppm)

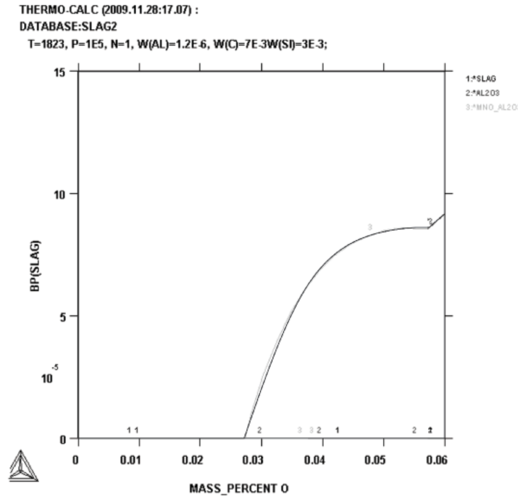

Figure 7. The amount of Slag phase Vs Oxygen content (ppm)

to 60 ppm. It means that the slag formation is high enough, if the oxygen content is around 50 ppm.

Figure 8 shows the variation in eutectic composition (Alumina content) with initial alumina content used. The calculations are made at different ratios of MnO to SiO_2. It is observed that, expect at ratio of 0.1, at all ratios, there is a decrease in eutectic composition (Alumina content), conversely the eutectic content, in terms of MnO, is raised. Also, it shown that, the final eutectic of alumina is getting reduced much at higher ratios, say at 1.5, 2.0 rather than at 0.3, 0.5 etc. Therefore, at higher ratios of MnO to SiO_2, alumina content is getting decreased; but it is also observed that the liquidus temperatures are quite high at these ratios. Hence, depending upon the situation and demand, we have to sacrifice either inclusion of having low alumina content or of having low liquidus temperature.

By using this model, for calculation of liquidus temperature and eutectic composition, we can estimate the different combinations of initial inclusion compositions for different conditions, which will enable us to avoid wire-breakage problem in drawing of tire-cord steel; and hence, decrease the cost of process as well as increase the quality of component. The outcome of the present discussion is that, the

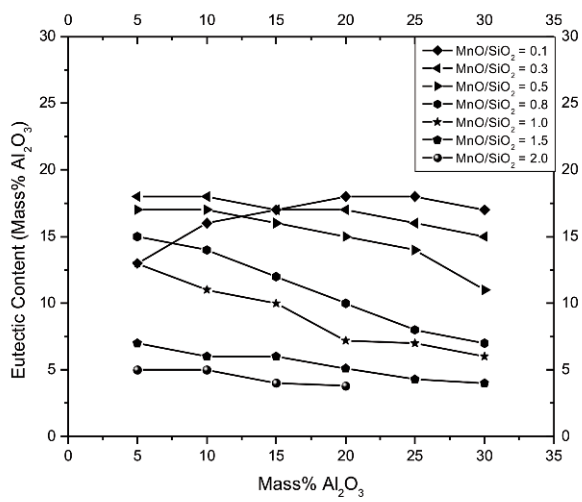

Figure 8. Initial alumina content (mass %) Vs eutectic alumina content (mass %)

spessartite phase (obtained at 15 mass % of Al_2O_3, 28 mass % of MnO, 57 mass % of SiO_2) having low liquidus temperature and the inclusions are stable and soft enough in wire-drawing processes.

5. Conclusions

The suitable inclusion chemistry for production of Tire-Cord steel such that, the inclusions having low liquidus temperature and lying in spessartite phase field, are predicted and analysed by considering various initial inclusion composition on ternary of MnO-Al_2O_3-SiO_2.

In the present study, the lowest liquidus is obtained at composition of Al_2O_3 – 15, MnO – 28, SiO_2 – 57 (mass %) and temperature of 1472K; also, these inclusions are in Spessartite phase field and is confirmed by Slag Atlas.

The range of inclusion acceptable for present considered application is as follows: Al_2O_3 content is from 10 – 20 mass% and ratio of MnO to SiO_2 is in between 0.5 – 1.5.

The inclusions for the composition of Tire-Cord steel mentioned earlier are having a minimum Gibbs free energy at Oxygen content in the range of 50 – 60 ppm.

Also, for the same composition of steel, the amount of slag formed is maximum at around 50 ppm of oxygen.

The above work has reinforced the value of modeling in thermodynamics of metals processing. Thermodynamic calculations, thermodynamic modeling, prediction of phases and the like are becoming increasingly important in wide range of metals and materials [11 – 14]. Utility of thermodynamic tools is possibly underutilized, as on date.

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