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Prediction of SiO_2-Al_2O_3-CrO_x complex inclusions in steel containing 16 per cent Cr-Si-Al-Mn

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In order to predict the composition of inclusions and to ascertain a method to prevent inclusions from forming in liquid Fe-16 mass Cr alloy, a thermodynamic database was developed through a quantitative determination of thermodynamic relationships of Cr-Al-Si-Mn systems in the liquid Fe alloys. Applications of the databases to the prediction of Mn/Si complex deoxidation with Al in Fe-16 mass Cr alloy were demonstrated in succession.

The electromagnetic levitation technique using a cold crucible was employed to separate inclusions from liquid metallic alloys completely and to prevent any contamination from surroundings. Various interaction parameters in the liquid Fe-16 mass per cent Cr alloy system were determined; these are: $e^{Cr}_{Al(Fe)} = 0.19/T$, $r^{O,Cr}_{Al(Fe)} = -0.01$, $r^{O,Cr}_{Al(Fe)} = -0.00013$, $e^{Cr}_{S1(Fe)} = -0.38/T$, $r^{O,Cr}_{Si(Fe)} = 0.007$, $r^{Si,Cr}_{O(Fe)} = 0.0044$, $r^{Si,Cr}_{A1(Fe)} = -0.0075$, $r^{A1,Cr}_{Si(Fe)} = -0.0078$, $r^{Mn,Cr}_{Si(Fe)} = 0.005$, and $r^{Si,Cr}_{Mn(Fe)} = 0.01$.

An improved database, utilizing interaction parameters for molten metal determined in this study, and the FactSage slag database of the MnO-SiO_2-Al_2O_3-CrO_x-MgO system were used for thermodynamic calculations. These were carried out under various thermodynamic conditions, and results were compared with experimental data of Si/Al, Mn/Si, and Mn/Si/Al deoxidation equilibria.

With the abovementioned results, together with experimentally obtained data, thermodynamic conditions were determined, in particular Mn and Si contents, under which liquid inclusions form in liquid Fe-16 mass per cent Cr alloy. The critical Al content in liquid Fe-16 per cent Cr alloy, above which solid inclusion of corundum phase ($(Al,Cr)_2O_3$) formed, was as low as 10 ppm. This indicates that extreme care must be taken in controlling the Al content in the metal to avoid formation of solid corundum phase ($(Al,Cr)_2O_3$) inclusion.

The compositional change prediction of inclusions, which originate from slag entrapment and by Ca addition, was demonstrated by use of the alloy database optimized through this study, and the FactSage oxide database. For Si-deoxidized Fe-16 per cent Cr alloy, high Si and low basicity of slag are effective to obtain liquid inclusions. For Al-deoxidized Fe-16 per cent Cr alloy, it is important to keep the Si content lower than 0.1 per cent and it is required to add Ca.

Keywords: inclusion, thermodynamic simulation, deoxidation, Fe-16 per cent Cr alloy, stainless steel, interaction parameter, cold crucible

Introduction

Fe-16 per cent Cr alloy, the representative ferritic stainless steel, is used as a material for heat resistant instruments, burners, top plates of sinks, bolts, nut CD bars, mesh and other corrosion resistant and high temperature materials, because of its low thermal expansion and predominant plasticity and oxidation resistance[1,2]. It gained higher demand recently due to its low cost and high mechanical performance.

The surface quality for this steel is very important as the frequency of defect generation on its surface is still high. Inclusions generated during the deoxidation process are closely related to the surface quality. In particular, Al_2O_3 and SiO_2 inclusions in the alloy are harmful to surface quality. It is known that these inclusions form even with Mn/Si deoxidation due to extremely small amounts of Al present in the alloy used in the process. In order to reduce the amount of harmful inclusions such as Al_2O_3 and SiO_2 by controlling the composition of Al, Si and Mn in high Cr alloys, that is, in order to control inclusion formation during the deoxidation process, the thermodynamic relationship between deoxidizing elements and inclusions in these alloys should be defined.

For a reliable prediction of deoxidation equilibria, thermodynamic data related to deoxidation of Al, Si and Mn in a high Cr alloy are indispensable. For thermodynamic calculation, the existing data have been reviewed and put in a database.

Experiments were carried out with an electromagnetic levitation-melting technique in a cold crucible to avoid contamination of the alloy by the crucible. In levitation melting the oxidation products collect on the surface of the liquid alloy.

Finally, prediction of the composition of inclusions in liquid Fe-16 per cent Cr alloy was attempted and the methods to eliminate inclusions were suggested based on the thermodynamic simulation.

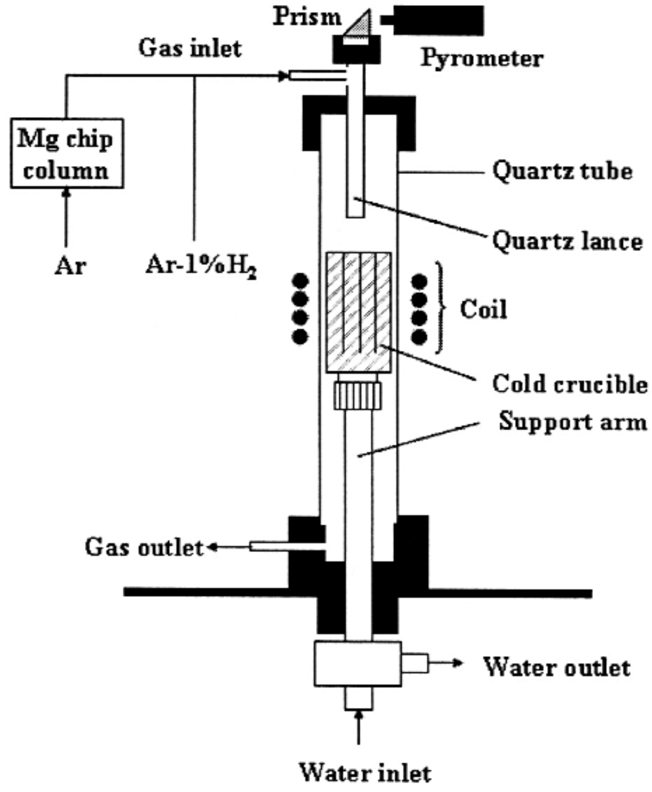

Figure 1. Schematic diagram of experimental apparatus (cold crucible)

Experimental

Levitation melting method

Conventional methods of deoxidation equilibrium experiments using solid oxide crucibles have some problems because of the possibility of contamination of the alloy from the crucible and difficulty with fast cooling of samples due to the low thermal conductivity of oxide. In order to solve these, an electromagnetic levitation-melting technique was employed to study the deoxidation equilibrium in liquid metal. This non-contact levitation melting prevents any contamination or side effects, which could otherwise result from a container such as an alumina crucible. In this study, the contamination problem is critical because only a small quantity of Al can change the composition of inclusions. Furthermore, inclusion particles, which are deoxidation products, are mostly exposed on the surface of the molten metal (reported as over 85 per cent[3]) and accumulate at the bottom of the metal, in the form of a thin film, due to gravity. Therefore, it is reasonable to regard all oxygen and aluminum existing in the metal as solute, not in the form of oxide. Particularly, a relatively large amount of metal can be accommodated and temperature can be kept stable by using a cold crucible compared with other levitation-melting techniques[4,5]. Therefore, the amount of inclusions collected on the surface of a sample is enough for quantitative chemical analysis of the composition.

The experimental apparatus is shown in Figure 1. The cold crucible* is a gold-coated copper crucible constructed in segments, each of which is water-cooled. A high frequency current with 20kW and 170kHz was applied to

Table I
Experimental results on deoxidation equilibria of Al, Si, Al/Si at 1650°C and Mn/Si at 1510°C

No.	[%Al]	[%O]	No.	[%Al]	[%O]	
1	0.0012	0.038	10	0.0366	0.0020	
2	0.0022	0.019	11	0.0474	0.0017	
3	0.0028	0.017	12	0.0551	0.0021	
4	0.0027	0.012	13	0.0616	0.0025	
5	0.0027	0.011	14	0.1332	0.0021	
6	0.0037	0.012	15	0.2016	0.0014	
7	0.0068	0.0052	16	0.3666	0.0016	
8	0.0098	0.0045	17	0.6243	0.0037	
9	0.0124	0.0050				
No.	**[%Si]**	**[%O]**	**No.**	**[%Si]**	**[%O]**	
18	0.46	0.041	22	1.40	0.021	
19	0.65	0.032	23	2.10	0.014	
20	1.10	0.026	24	2.30	0.011	
21	1.40	0.020	25	2.40	0.007	
No.	**[%Al]**	**[%Si]**	**[%O]**	**$(\%Al_2O_3)$**	**$(\%Cr_2O_3)$**	
26	0.0020	0.46	0.010	90.10	9.90	
27	0.0022	0.19	0.019	97.10	2.94	
28	0.0023	0.46	0.015	91.10	8.85	
29	0.0027	0.20	0.011	97.40	2.59	
30	0.0028	0.19	0.012	92.10	7.86	
31	0.0029	0.18	0.017	90.50	9.50	
No.	**[%Si]**	**[%Mn]**	**[%O]**	**(%MnO)**	**$(\%SiO_2)$**	**$(\%CrO_x)$**
32	0.094	0.920	0.017	46.10	3.90	50.0
33	0.14	0.820	0.014	36.30	23.20	40.5
34	0.18	0.810	0.013	27.30	53.20	19.5
35	0.19	0.160	0.019	26.50	45.70	27.8
36	0.20	0.260	0.016	35.40	43.40	21.2
37	0.25	0.330	0.015	42.70	8.90	48.4
38	0.53	0.093	0.011	0.00	100.00	0.0
39	0.61	0.310	0.011	14.10	74.40	11.4
40	0.69	0.570	0.0080	28.00	60.60	7.5
41	0.78	0.012	0.0075	0.00	100.00	0.0
42	0.94	0.240	0.0075	0.00	100.00	0.0

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* The cold crucible is made by Crystalox Ltd, UK

Table II
Interaction parameters used in this paper

Elements		Interaction parameters	References	Interaction parameters	References
i	J	e_i^j		$r_i^{j,Cr}$	
Al	Al	80.5/T	6	-	
	Cr	0.19/T (1550º-1650º)	Present study	-	
	Mn	0.035 (1600º)	22	-	
	O	-1.98 (1600º)	23	-0.001 (1650º)	Present study
	Si	0.056	6	-0.0075 (1650º)	Present study
Mn	Al	0.027 (1600º)	22	-	
	Cr	0.0039 (1600º)	6	-	
	Mn	0	6	-	
	O	-0.083 (1600º)	6	-	
	Si	-0.0327 (1600º)	6	0.01 (1773K)	Present study
O	Al	-1.17 (1600º)	23	-0.0001 (1923K)	Present study
	Cr	-0.045 (1550º-1650º)	7	-	
	Mn	-0.021 (1600º)	6	-	
	O	-1750/T+0.76	6	-	
	Si	-0.066 (1600º)	6	0.0044 (1650º)	Present study
Si	Al	0.058 (1600º)	6	-0.0078 (1500º)	Present study
	Cr	-0.38/T (1510º-1650º)	Present study	-	
	Mn	-0.0146 (1570º)	6	0.005 (1500º)	Present study
	O	-0.119 (1600º)	6	0.007 (1650º)	Present study
	Si	0.103 (1600º)	6	-	

the coil surrounding the crucible. In order to levitate metal uniformly, the shape and location of the coil is optimized. A two-colour optical pyrometer, calibrated preliminarily against a thermocouple (Pt-30 per cent Rh/Pt-6 per cent Rh), was used to measure the melt temperature. There is a 5°C temperature difference between the top and the bottom of the metal. The inlet gas flow was designed to flow from top to bottom to prevent pyrometer error readings due to the fumes formed from the liquid metal.

Procedure

For the preparation of the alloys, electrolytic grade iron and high purity chrome, aluminium, silicon and manganese were used. An Fe-16 mass per cent Cr master alloy was made using an arc melter to prevent contamination from the oxide crucible. Master alloys of Fe-16 mass per cent Cr-1 mass per cent Al, Fe-16 mass per cent Cr-5 mass per cent Si and Fe-16 mass per cent Cr-5 mass per cent Mn were made by using a cold crucible. Pieces of pure Fe_2O_3 are used to supply oxygen. For each experimental run, 35 g–40 g of the alloys and appropriate amounts of each alloy containing Al, Si, and Mn respectively were placed in the cold crucible and then purged under a purified Ar-1 vol per cent H_2 gas mixture for 15 minutes (flow rate: 21 (STP)/min, oxygen partial pressure: 10^{-15}Pa). Oxygen partial pressure in the gas phase inside the quartz tube was determined by using a commercially available oxygen sensor, DS700*. After the sample was heated to the desired temperature, the atmosphere was changed to argon gas (oxygen partial pressure: 10^{-10}Pa), which was purified by being passed through an Mg chip column at 500°C. Argon is an inert and insoluble gas used to prevent from contact with air[6].

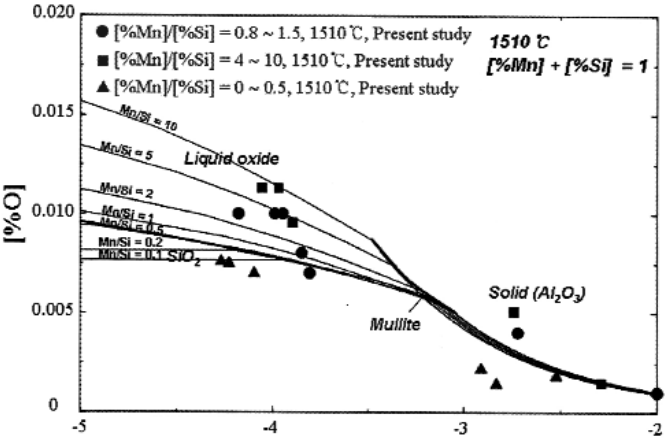

Figure 2. Variation of oxygen content with respect to Al content in Fe-16 per cent Cr ([per cent Mn]+[per cent Si]=1, 1510ºC)

It was confirmed that the system reached equilibrium in approximately 10 minutes at 1550°C by experiments. In order to ensure complete equilibration, samples were kept levitated for 15 minutes and then quenched by turning off the power. The melt fell on the water-cooled cold crucible and was rapidly quenched in a purified He gas stream (flow rate: 21 (STP)/min). In this condition the sample cooling rate is about 20ºC sec^{-1} from 1500º to 1000ºC. After quenching it was confirmed that inclusions collected on the surface around the bottom of the metal sample. The inclusions were separated from the metal using a 10 per cent Br-methanol solution, and dissolved by acids for the ICP-AES analysis. The metal sample was cut into cube-shaped pieces and the concentration of oxygen, aluminium, silicon and manganese in sample was analysed.

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*DS700 is a trademark of Australian Oxytrol System Pty Ltd, Victoria, Australia

Table III
Experimental results on Al/Si/Mn complex deoxidation in liquid Fe-16 per cent Cr alloy(1510ºC)

[ppm Al]	[%Si]	[%Mn]	[%O]	(%Al_2O_3)	(%MnO)	(%SiO_2)	(%CrO)	(%Cr_2O_3)
0.8	0.16	1.00	0.0113	9.2	48.9	4.3	14.6	23.0
1.1	0.09	0.92	0.0113	8.8	42.1	3.5	12.4	33.1
1.3	0.14	0.82	0.0096	21.5	28.5	18.2	7.3	24.5
18.1	0.18	0.81	0.0050	12.6	23.9	46.5	16.7	0.4
51.5	0.03	0.78	0.0015	51.0	10.7	2.2	1.2	34.9
0.7	0.19	0.16	0.0100	0.4	26.4	45.5	26.3	1.4
1.0	0.20	0.26	0.0100	1.3	34.9	42.8	20.0	1.0
1.1	0.25	0.33	0.0100	0.4	42.5	8.9	15.0	33.3
1.4	0.66	0.77	0.0080	9.3	31.0	50.5	9.0	0.2
1.5	0.35	1.01	0.0070	9.9	37.7	39.8	12.2	0.4
19.0	0.54	0.78	0.0040	6.2	39.2	45.9	8.4	0.2
110.4	0.61	0.49	0.0010	40.9	13.9	2.1	1.9	41.2
0.5	0.53	0.09	0.0076	0.9	3.8	77.8	16.6	0.8
0.6	0.78	0.01	0.0075	4.8	0.7	88.0	6.3	0.2
0.8	0.61	0.31	0.0070	4.0	13.6	71.5	10.7	0.3
12.3	0.59	0.33	0.0022	65.5	5.4	7.7	2.3	19.1
15.0	1.32	0.00	0.0015	50.0	3.5	5.3	2.2	39.1
30.0	1.22	0.46	0.0018	38.4	6.4	8.4	3.5	43.2

Thermodynamic calculation

The inclusion composition change with respect to deoxidizing elements is predicted by thermodynamic simulation in this study. In this regard, the accuracy of the simulation depends on that of the thermodynamic database. The comparison and evaluation of the data reported in literature were done for the calculation. From the discordance among thermodynamic data for high-Cr alloys, experimental studies were done to determine interaction parameters for the relationship among Cr, Al, Si and Mn in the alloys. The thermodynamic calculations using interaction parameters determined in this study were verified with experimental data. The FactSage liquid slag database was used to calculate the activity of each oxide in the molten oxide. FactSage is a commercial thermodynamic calculation program made by CRCT at École Polytechnique in Canada.

Detailed descriptions of thermodynamic calculations such as thermodynamic models are elsewhere[7,8].

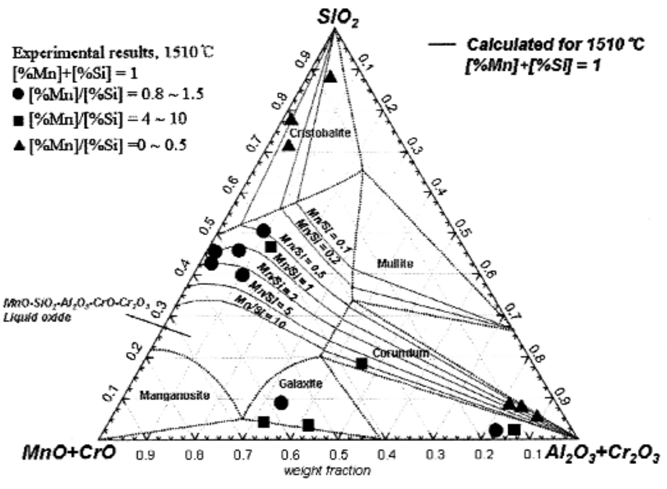


Figure 3. Variation of inclusion composition equilibrated with liquid Fe-16 per cent Cr alloy according to [per cent Mn]/[per cent Si] (1510ºC)

Results and discussion

In order to determine interaction parameters, many experiments were carried out on Al, Si, Mn, Mn/Si, Si/Al deoxidation equilibria. These were achieved by the iterative method using experimental results as listed in Table I.

Al/Si/Mn complex deoxidation equilibrium in liquid Fe-16 per cent Cr alloy

Mn/Si complex deoxidation is applied for the production of high chromium steel such as Fe-16 per cent Cr alloy in order to avoid the harmful effect of solid Al_2O_3 inclusions formed by Al deoxidation. However, Mn/Si deoxidation usually produces MnO-SiO_2-Al_2O_3 inclusions due to an extremely small amount of Al present in the alloy in practice.

In this study, the effects of [per cent Mn]/[per cent Si] and [per cent Al] in Fe-16 per cent Cr alloy on the composition of inclusions were investigated in the area of the MnO-SiO_2-Al_2O_3 system with interaction parameters. All the interaction parameters used in this study are listed in Table II. The experimental results on Al/Si/Mn complex deoxidation of Fe-16 per cent Cr alloy at 1510ºC are shown in Table III. SiO_2 phase, liquid oxide phase of MnO-SiO_2-Al_2O_3-CrO_x system, Al_2MnO_4 galaxite phase and $(Al,Cr)_2O_3$ corundum phase are able to be formed as the stable reaction products of Al/Si/Mn complex deoxidation with respect to the experimental condition.

It is known that chromium is present as Cr^{2+}, Cr^{3+}, or Cr^{6+} in slags depending on the prevailing oxygen partial pressure and it is reported that the activity coefficient of CrO increases with increasing basicity[13]. The distribution ratios of Cr^{2+} and Cr^{3+} in inclusions were determined from thermodynamic calculations using total Cr content in inclusions after experiments.

Figure 2 shows the relationship between Al and O in Fe-16 per cent Cr alloy calculated in various Mn/Si ratios with experimental results at 1510°C. In the condition of [per cent Mn]+[per cent Si]=1, [per cent Mn]/[per cent Si] was changed from 0.1 to 10. If Al content is above 10 ppm, the composition of inclusions is fixed to $(A_l,Cr)_2O_3$ corundum phase. Therefore, the effect of complex deoxidation can be expected in the condition below 10 ppm of Al content, where oxygen content in the alloy decreases with the decrease of [per cent Mn]/[per cent Si].

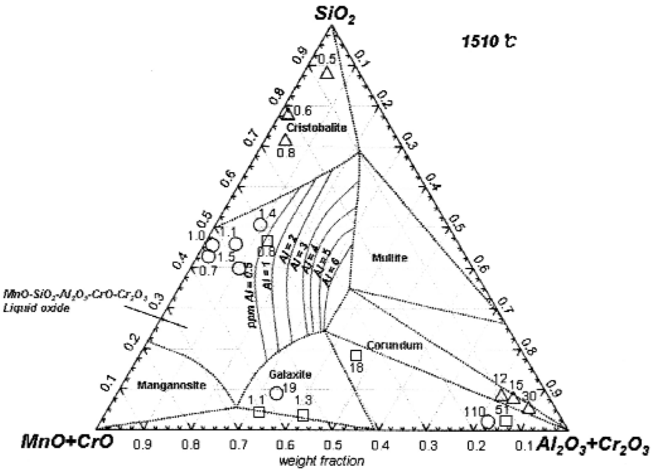


Figure 4. Variation of inclusion composition equilibrated with liquid Fe-16 per cent Cr alloy according to [per cent Al] (1510ºC)

Figures 3–5 represent the variation of inclusion compositions in liquid Fe-16 per cent Cr alloy according to [per cent Mn]/[per cent Si] at 1510°C, where the calculation was carried under [per cent Mn]+[per cent Si]=1. The phases of inclusions which can be produced are SiO_2 (cristobalite), liquid oxide of MnO-SiO_2-Al_2O_3-CrO_x system, $(Al,Cr)_2O_3$ (corundum), $Al_6Si_2O_{13}$ (mullite) and Al_2MnO_4 (galaxite). With an increase of Al content, the composition of inclusions is changed from liquid oxide to mullite or corundum phase according to [per cent Mn]/[per cent Si]. Experimental results on Al/Si/Mn complex deoxidation at 1510°C were co-displayed in Figures 2–5 where the lines are in good agreement with the experimental points. From the comparison of aluminum and oxygen contents between calculations and experiments, the experimental values in silica, liquid oxide and corundum phase mostly corresponded to the calculated values.

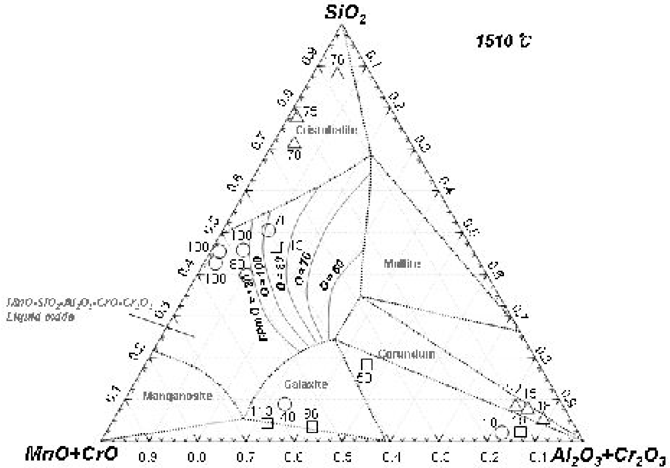


Figure 5. Variation of inclusion composition equilibrated with liquid Fe-16 per cent Cr alloy according to [per cent O] (1510ºC)

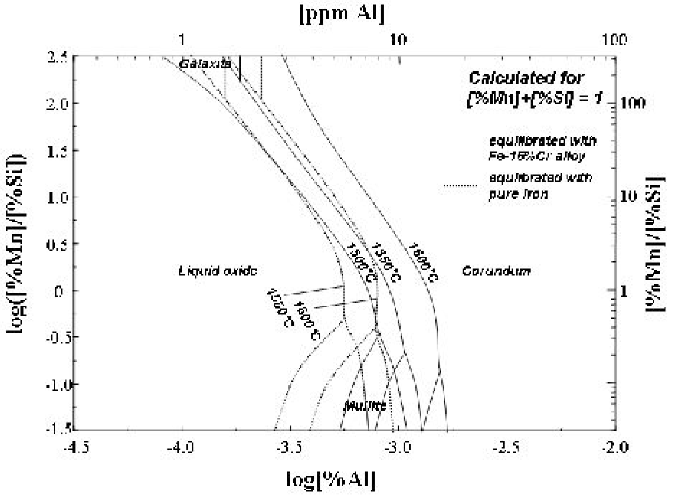
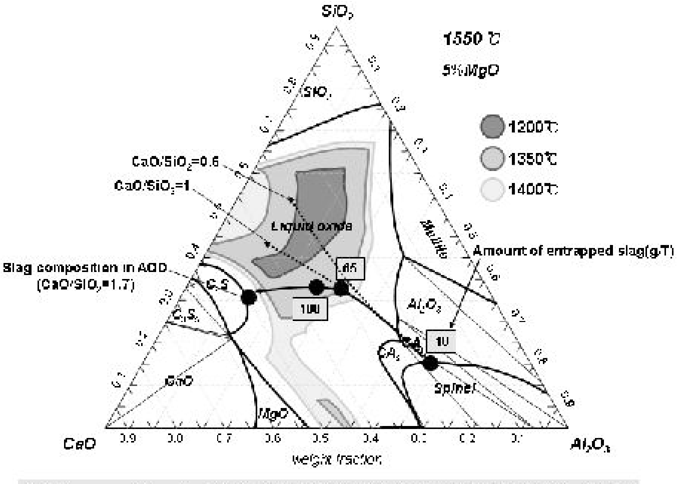


Figure 6. Equilibrium relationship between log[per cent Mn]/[per cent Si] and log [per cent Al] in liquid Fe-16 per cent Cr alloy at various temperatures

It is noted that 10 ppm of Al is critical content in most cases for the effect of Al addition on Si/Mn complex deoxidation in liquid Fe-16 per cent Cr alloy at 1510–1600°C as shown in Figures 3–6.

Figure 6 shows the equilibrium relationship between the Mn/Si ratio and Al content in liquid Fe-16 per cent Cr alloy at 1510º–1600ºC. The boundary lines between liquid oxide and $(Al,Cr)_2O_3$ corundum phase are formed at a little higher Al contents than those of pure iron and shifted to the right side (higher Al) with increasing temperature. The whole area in the condition above 15 ppm of Al content is taken by a corundum phase, in which the Mn/Si ratio is not very effective on the inclusion composition. An Al_2MnO_4 galaxite phase generates where the Mn/Si ratio is higher than 100 and Al content is lower than 2 ppm at 1510ºC. On the other hand, a mullite phase exists where the Mn/Si ratio is lower than 0.3 and Al content is in the range between 5.6 and 12.5 ppm.



Initial composition: Fe 16%Cr 0.3%Si 0.5%Mn 0.0025%Al 0.0065%O, 1550 ℃

Figure 7. Trace line of composition change of inclusion with respect to the amount of slag entrapped in liquid Fe-16 per cent Cr alloy at 1550ºC

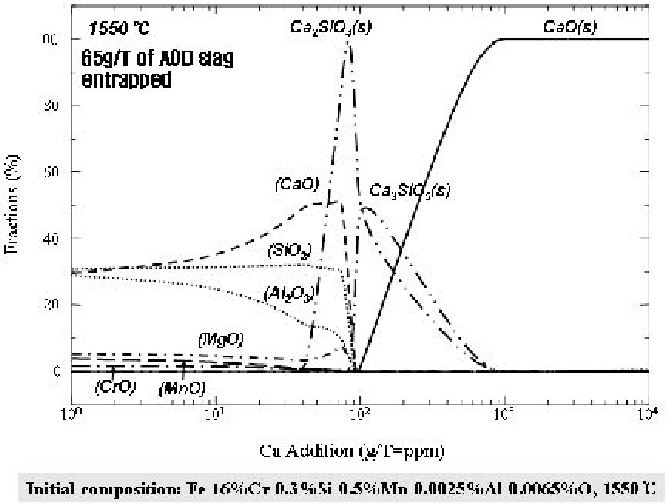


Figure 8. Fractions of each oxide in inclusion with respect to amount of Ca addition in liquid Fe-16 per cent Cr alloy at 1550ºC

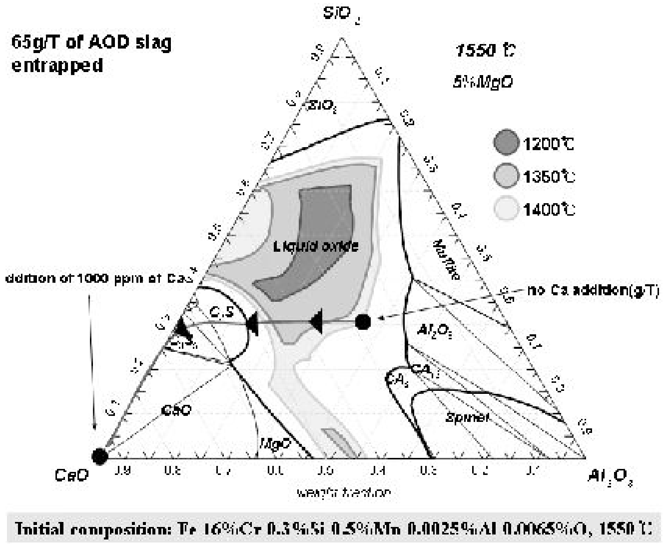


Figure 9. Trace line of composition change of inclusion according to Ca addition in liquid Fe-16 per cent Cr alloy at 1550ºC

Prediction of complex deoxidation inclusions in Fe-16 per cent Cr alloy with slag entrapment and Ca treatment

Solid $(Al,Cr)_2O_3$ type oxides are formed as the deoxidation products in the AOD of stainless steelmaking such as Fe-16 per cent Cr alloy. It may react with CaO in the slag entrapped in the alloy and most of these inclusions also contain MgO. In the view that CaO and MgO are supposed to coexist with the deoxidation products, unlike the thermodynamic calculation in the previous section, the effects of the slag entrapment and Ca addition were studied as follows. In order to make a prediction of complex deoxidation product in equilibrium with Fe-16 per cent Cr alloy with respect to the amount of entrapped CaO-SiO_2-Al_2O_3-MgO-MnO-CrO_x slag, the calculations using the optimized database for Fe-16 per cent Cr alloy and FactSage database for molten oxide (slag) were done.

The calculations for Si deoxidation were performed at 1550ºC and the composition of metal was referred to the sample produced by POSCO. The compositions of the alloy containing 0.3 per cent Si-0.5 per cent Mn-0.0025 per cent Al-0.0065 per cent O in mass equilibrated with the slag of 50per cent CaO-30 per cent SiO_2-10 per cent Al_2O_3-10 per cent MgO in mass were supposed to demonstrate the situation of metal and slag in the ladle after Si deoxidation in the AOD process. According to the report of Rinaldi *et al.*[14], about 300 g per ton (g/T=ppm) of slag penetrated into steel in the ladle and 65 g/T in the final product. In order to vary the inclusion composition with the flow of the processes, the calculation was performed by changing the amount of slag from 1 ppm to 10,000 ppm.

The inclusion composition with respect to the amount of entrapped slag chases the trace line on the ternary phase diagram of SiO_2-CaO-Al_2O_3 (-5per cent MgO) system as shown in Figure 7. The liquid inclusions with low melting points are not formed even if more than 100 g/T of slag are entrapped in the alloy. In addition, if the amount of entrapped slag is less than 65 g/T, solid inclusions containing corundum phase will be precipitated in the alloy below 1400ºC, which requires Ca addition in the ladle process.

In a similar manner of slag entrapment, the calculations were carried out for 65 g/T of slag entrapment at the same temperature with the variation of the amount of Ca addition, where it was assumed that Ca added in the alloy fully reacted with surrounds and sulphur was ignored to simplify the calculations. The inclusion composition containing solid Al_2O_3 in a corundum phase is changed with a Ca addition, as shown in Figure 8, where a solid corundum phase in inclusions disappeared easily with a very small amount of Ca addition at 1550ºC. By increasing Ca addition, the quantity of CaO in liquid oxide increases and that of Al_2O_3 in liquid oxide decreases. The amount of SiO_2 is almost not changed in mass and per cent, regardless of the increase of the amount of Ca addition.

Solid Ca_2SiO_4 and Ca_3SiO_5 phases begin to precipitate at 30 g/T and 100 g/T of Ca addition, respectively. In addition, the figure shows that the inclusion in the alloy is saturated with solid CaO by the injection of Ca above 100 g/T at 1550ºC in the ladle. The inclusion composition follows the path of the solid thick line in Figure 9 with respect to Ca addition. As can be seen, the modification of the inclusions to obtain the liquid oxide phase having a low melting point is not possible under this condition. It is due to an unchanged amount of SiO_2 in the composition of the inclusion.

This phenomenon is thought to be explained by the abnormal decrease in activity of SiO_2 in the area where the trace line passes through, as represented in Figure 10. There are two paths to reach the region saturated with CaO, in which either the oxygen in Al_2O_3 or SiO_2 would be consumed by Ca, resulting in the choice of path I or path II.

In the view of the affinity of the element with oxygen, Ca should react with the oxygen of SiO_2 and follow path II, which, however, decreases the activity of SiO_2 abnormally so that the equilibrium between Si in the alloy and SiO_2 in inclusion is suddenly broken. This equilibrium is recovered by increasing the amount of SiO_2 in inclusions. On the other hand, in the case that Ca reacts with the oxygen of Al_2O_3, following path I, the activities of Al_2O_3, SiO_2 and CaO can be changed gradually, which is essential to maintain the equilibrium between alloy and inclusions.

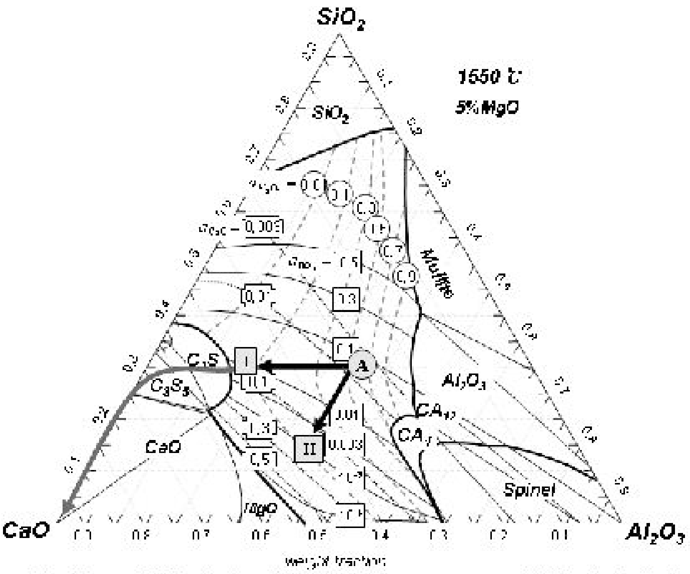


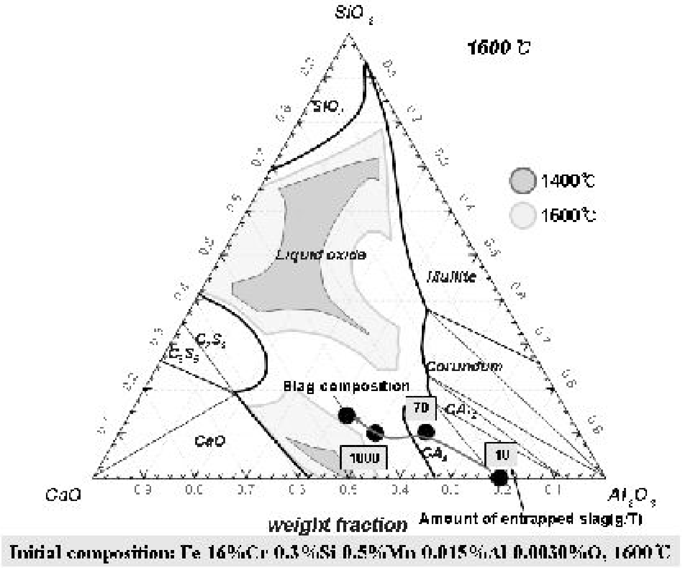
Figure 10. Iso-activity lines of SiO_2, CaO and Al_2O_3 in ternary system of SiO_2-CaO-Al_2O_3 with 5 per cent MgO at 1550ºC

Therefore, the only practical method for decreasing the precipitation of deleterious inclusions in Si-deoxidized Fe-16 per cent Cr alloy is to equilibrate the alloy with a ladle slag of an adequate composition. In order not to exceed a critical content of aluminium, while keeping the O content as low as possible, it is necessary to aim for a CaO-Al_2O_3-SiO_2 slag composition corresponding to a CaO/SiO_2 ratio below 1.5 with Al_2O_3 contents in the range of from 10 per cent to 25 per cent, as represented in Figure 7.

In the case of Al deoxidation, the content of Al_2O_3 in inclusions increases compared with Si deoxidation. Therefore, the deoxidation is carried out by adding Mn, Si first and, after adding Al in the AOD process to reduce the quantity of Al_2O_3 in the alloy, an amount of Ca was injected into it during the ladle process to change Al_2O_3 inclusions into CaO-Al_2O_3 type inclusions. The calculations were performed at 1600ºC and the composition of metal is supposed to contain 0.3 per cent Si-0.4 per cent Mn-0.015 per cent Al-0.003 per cent O in mass. The composition of slag equilibrated with the metal is supposed to be 40 per cent CaO-40 per cent Al_2O_3-10 per cent SiO_2-10 per cent MgO in mass. Similarly to Si deoxidation, the calculation was performed by changing the amount of slag entrapped in the alloy from 1 ppm to 10,000 ppm.

The inclusion composition with respect to the amount of entrapped slag follows the path marked on the ternary phase diagram of the SiO_2-CaO-Al_2O_3 system as shown in Figure 11. The inclusion composition changes to liquid oxide phase with increasing the amount of entrapped slag in the alloy. However, these inclusions will be precipitated at 1500°, that is, Ca addition is indispensable for the modification of inclusions to liquid oxide having low melting points.

The calculations on Ca addition were carried out at the same temperature in the case of 70 g/T of inclusions entrapped in the alloy. The inclusion composition saturated with $CaAl_4O_7$ in the initial stage changes according to Ca addition as shown in Figure 12 where solid $CaAl_4O_7$ inclusions disappear with a small amount of Ca addition and participate in liquid oxide phase as CaO and Al_2O_3. According to increasing Ca addition, CaO in liquid oxide increases and Al_2O_3 in liquid oxide decreases. The amount of SiO_2 increases by 15 per cent when 50 g/T of Ca is added.



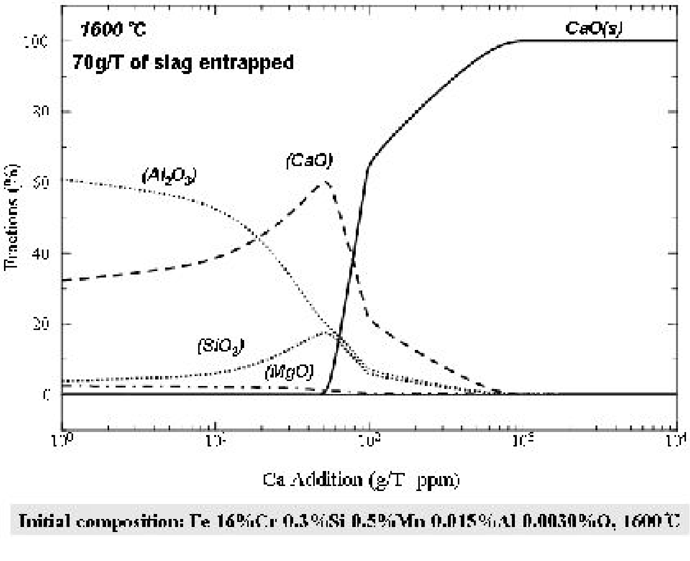
Initial composition: Fe 16%Cr 0.3%Si 0.5%Mn 0.015%Al 0.0030%O, 1600 ℃

Figure 11. Trace line of composition change of inclusion with respect to the amount of slag entrapped in liquid Fe-16 per cent Cr alloy at 1600ºC

As shown in Figure 13, the inclusion composition follows the trace line with increasing the quantity of Ca addition. It is realized from the figure that the inclusion composition does not pass through the liquid oxide area at 1400ºC. It is due to the abnormal decrease of SiO_2 activity in the area as already explained.

It can be seen in Figure 14 that the trace line moves through the gap between 0.003 and 0.001 in the iso-activity lines of SiO_2 in the direction to minimize the activity change of each oxide.

It is expected that the inclusion composition can be reached in the liquid oxide area at 1400ºC by decreasing Si content as low as 0.15 per cent in the alloy, as shown in Figure 15. In spite of the lower Si level, minute control of Ca treatment is also needed since the liquid oxide area of low melting points in a high CaO/SiO_2 ratio (middle of bottom in ternary phase diagram) is much narrower than that in a low CaO/SiO_2 ratio (upper part in the phase diagram).



Initial composition: Fe 16%Cr 0.3%Si 0.5%Mn 0.015%Al 0.0030%O, 1600 ℃

Figure 12. Fractions of each oxide in inclusion with respect to amount of Ca addition in liquid Fe-16 per cent Cr alloy at 1600ºC

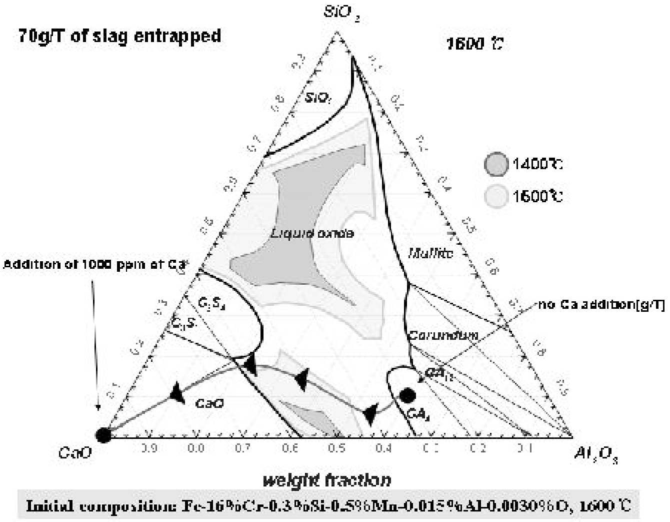


Figure 13. Trace line of composition change of inclusion according to Ca addition in liquid Fe-16 per cent Cr alloy at 1600ºC

From these effects of slag entrapment and Ca addition on Si or Al deoxidation of liquid Fe-16 per cent Cr alloy, the following conclusions are drawn. CaO in deoxidation products affects deoxidation equilibrium by slag entrapment and Ca addition, simultaneously. The higher level of Si and several tens of gram/T of Ca addition are recommended to obtain the liquid inclusions having the melting points of 1350ºC for Si deoxidation. On the other hand, it is important to maintain Si content in the alloy as low as hundreds ppm for Al deoxidation. On the assumption that some amount of slag entrapment is indispensable, Ca injection is needed for Al deoxidation.

Conclusions

An improved database utilizing interaction parameters for molten metal determined in this study and FactSage slag database of MnO-SiO_2-Al_2O_3-CrO_x-MgO system were used for thermodynamic calculations. These were carried out under various thermodynamic conditions, and results were compared with experimental data of Si/Al, Mn/Si, and Mn/Si/Al deoxidation equilibria.

Various interaction parameters in the system of liquid Fe-16 per cent Cr alloy were determined, and these are: $e^{Cr}_{Al(Fe)} = 0.19/T$, $r^{O,Cr}_{Al(Fe)} = -0.01$, $r^{O,Cr}_{Al(Fe)} = -0.00013$, $e^{Cr}_{S1(Fe)} = -0.38/T$, $r^{O,Cr}_{Si(Fe)} = 0.007$, $r^{Si,Cr}_{O(Fe)} = 0.0044$, $r^{Si,Cr}_{A1(Fe)} = -0.0075$, $r^{A1,Cr}_{Si(Fe)} = -0.0078$, $r^{Mn,Cr}_{Si(Fe)} = 0.005$, and $r^{Si,Cr}_{Mn(Fe)} = 0.01$. In addition, existing data were verified with the experimental results carried out in the present study.

Based on the experimental and calculated results, [Mn] and [Si] contents in liquid Fe-16 per cent Cr, which warrant formation of liquid inclusions were identified. In this condition, [Al] in liquid Fe-16 per cent Cr alloy that forms a solid inclusion of corundum phase ($(Al,Cr)_2O_3$), was as low as 10 ppm, which cannot be permitted in the deoxidation process. Therefore, it is expected that corundum phase ($(Al,Cr)_2O_3$) inclusion is inevitably generated under the condition beyond 10 ppm of [Al] after deoxidation.

Applications of the databases to the prediction of Mn/Si complex deoxidation with Al in high Cr alloys were demonstrated in succession.

In the case of Si-deoxidized Fe-16 per cent Cr alloy, the higher level of Si with a CaO-Al_2O_3-SiO_2 slag of adequate composition corresponding to a CaO/SiO_2 ratio below 1.5 with Al_2O_3 contents in the range of from 10 per cent to 25 per cent is required. In the case of Al deoxidation in Fe-16 per cent Cr alloy, it is important for Si content in the alloy to be lower than 0.1 per cent. Ca injection is needed for Al deoxidation.

Acknowledgement

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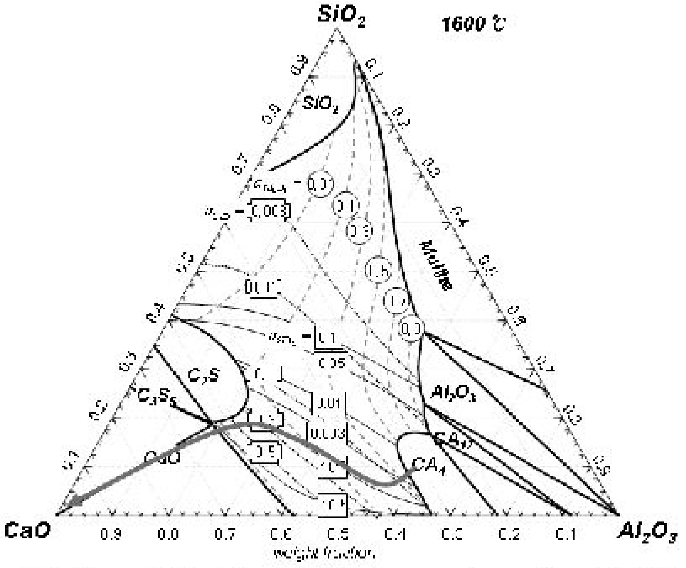

Figure 14. Iso-activity lines of SiO_2, CaO and Al_2O_3 in ternary system of SiO_2-CaO-Al_2O_3 at 1600ºC

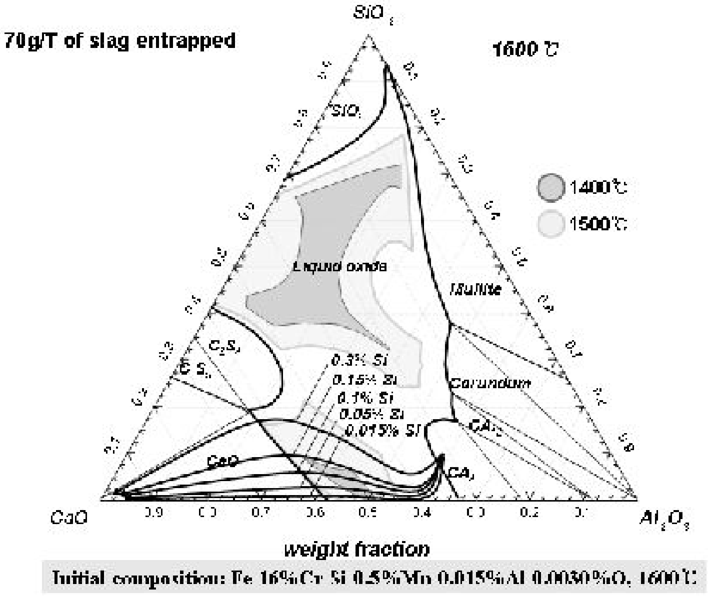

Figure 15. Effect of Si content on trace line of inclusion composition with respect to Ca addition in liquid Fe-16 per cent Cr alloy at 1600ºC

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