

The Slag Formation Mechanism in a Melter-Gasifier for Ironmaking

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Abstract

The slag formation mechanism in a melter-gasifier of the two-step ironmaking process was examined by the meltdown test for DRI-additive-ash mixed bed under load and confirmed by analysis for the slag taken from the actual furnace. For the slag phase analyses chemical analysis, SEM-EDS and XRD pattern analysis were used. The primary slag originated from the gangue in DRI was homogeneous. Partially melted secondary slag composing of dicalcium silicate with dissolved FeO was formed under rather higher CaO/SiO₂ basicity. Then these slags reacted with bottom ash resulting in the homogeneous tertiary slag with the dissolved FeO. Finally the final slag similar to tapped slag was collected in the hearth of the melter-gasifier. The slag had CaO/SiO₂ slightly greater than 1.

Introduction

Two-step ironmaking process using pellet and raw coal has been adopted as an alternative route for hot metal production. Up to now blast furnace has been the main method to produce the hot metal worldwide, which consist of lumpy, cohesive and hearth zones in a reaction vessel. In the blast furnace process the major function of the cohesive zone is to form the melts and to distribute the gas flow upward the lumpy zone in order to enhance the heat exchange between gas and solid. Hence the control of the cohesive zone is very important but difficult for the stable blast furnace operation[1, 2].

In the two-step ironmaking process that adopts a reduction shaft and a melter-gasifier, the operation is rather easier than that of blast furnace because of no liquid-state cohesive zone. Fig. 1 illustrates the schematic process flow from a viewpoint of material flow. The furnace condition, particularly, melter-gasifier condition related to an appropriate slag formation, is sometimes unstable owing to the reduction degree of direct-reduced iron (DRI), the calcination of flux and physicochemical characteristics of coal. A very high basicity slag normally has high melting point. Its viscosity varies significantly under the furnace conditions, resulting in the slag formation problem [3]. Those problems might be related to the heterogeneity of the final slag due to precipitation of second phase such as dicalcium silicate and high viscosity for high basicity slag[4].

Thus the slag formation is a complex. process and it has not been clearly studied yet. In this study, the slag formation mechanism in the melter-gasifier was examined by experimental analysis based upon the meltdown test under load and by slag analysis for the sample taken from the actual furnace.

Experimental Procedure

For examining the slag formation phenomena in the melter-gasifier in which direct-reduced iron, flux and coal as burden materials were charged, several kinds of samples had been prepared. DRI pellets were sampled from the reduction shaft furnace through the down-pipe connected to the melter-gasifier. Limestone and dolomite in the yard were taken and calcined at 850 °C in the air to be used for the flux samples in the test. Char as fixed bed materials in the experiments was sampled from the melter-gasifier through a tuyere. Ash that usually produced by char combustion in front of the tuyeres in the melter-gasifier was prepared by combusting the char in the air. The char was made in advance by volatilization of raw coal at 1200 °C under argon atmosphere.

Two kinds of experimental apparatuses were employed for investigating the slag formation mechanism in the melter-gasifier. Fig. 2 illustrates the main equipment consisting of electrical resistance furnace for the high temperature meltdown test of iron ore under the load to simulate char fixed bed in the melter-gasifier. Fig. 3 shows the detailed picture of the mixed bed composing of char, pellets, fluxes and bottom ash inside the graphite crucible for the test. Table 1 represents the experimental conditions applied for the test. During the test, meltdown temperatures of metal and slag were observed through the window by naked eyes. Bed shrinkage and pressure drop data were continuously recorded. Usually metal dripped after the first peak of pressure drop ahead of slag dripping which occurred after the second peak of pressure drop. Other apparatus adopted was x-ray imaging system using the x-ray fluoroscopy to directly observe the serial reactions and slag forming phenomena during the heating till dripping

under the same conditions as those in the melt-down test. In this experiment, heavy molybdenum rod (density=8.4 g/cm³, melting point=2415 °C) was placed on the top of the mixed bed to exert the load.

For the slag phase analyses after the experiments, three sorts of analyzing methods were employed, i.e., chemical analysis, SEM-EDS and XRD pattern analysis. For the slag collected after the test, the chemical analysis was performed to examine the slag composition and basicity. Then XRD pattern analysis for powdered slag was taken to identify the slag phases for the melting path study. Microanalysis by SEM-EDS was carried out to observe the slag phases and their compositions under the back-scattered electron image.

Finally, slag-bearing materials taken from the actual melter-gasifier through tuyeres were classified into partially melted DRI, residual slag and dripped slag. Then those samples were analyzed by using the same analysis techniques such as chemical analysis, SEM-EDS and XRD pattern analysis to confirm the slag formation mechanism in comparison with the above experimental results.

Results

Fig. 4 represents the shrinkage, pressure drop curves for the meltdown test of the DRI-flux-ash mixed bed under the load. Table 2 shows the meltdown temperatures of the metal and slag. In general, the dripping of the metal preceded that of the slag. Meanwhile rather more viscous slag was squeezed out under the load after the second peak of pressure drop. Then the bed shrinkage remained steady. Table 2 shows that the temperature of metal dripping ranged from 1420 to 1470 °C whereas that of slag dripping occurred around 1500 °C.

Table 3 indicates the chemical compositions of slags obtained from the meltdown tests under the given conditions. The bottom ash in test A means the ash produced by combustion around the tuyeres while the powdered ash in test B accounts for the fly ash penetrated into the voidage of the fixed bed in the melter-gasifier. Test C denotes the result from the interruption test at 1420 °C for the phase analysis formed at that temperature. Therefore, few melt dripping occurred during that test. Basicity (CaO/SiO₂) of the dripped slag generally appeared to be lower than that of the residual slag owing to the partially melted basic fluxes.

Fig. 5 shows x-ray images taken for DRI-flux-ash mixed bed under the same conditions as those in the meltdown test. To start with, DRI pellets and flux mixtures were layered on top of the char bed as shown in Fig. 5 (a). In between pellets and char bed, ash mixture was packed as the bottom ash generated in the actual furnace. Above 1300 °C, the mixed bed started to shrink as shown in Fig. 5 (b) due to sintering of DRI particles caused by gangue melting inside the particles. At about 1460 °C, a lot of slags resulted from the low melting point phase formation owing to reaction among FeO in DRI, fluxes and ash were found. Smelting reduction of FeO by solid carbon and carburization in metal occurred simultaneously. Then metal dripped through the char bed around 1470 °C. It was clearly confirmed by the x-ray image as shown in Fig. 5 (c) that the metal dripping occurred at about 1470 °C.

Fig. 6 shows the microstructure of partially melted slag, which was induced by low melting point phases in unmelted flux. Low melting-point slag that normally had higher concentration of FeO, was penetrated into the solid flux. From EDS analysis for both parts basicity turned out to be around 2. It was confirmed by XRD pattern in Fig. 7 that

low melting point phase was gehlenite($2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$, C_2AS). Meanwhile unmelted solid structure turned out to be dicalcium silicate ($2\text{CaO}\cdot\text{SiO}_2$, C_2S).

On the other hand, actual slag samples taken from tuyeres in the melter-gasifier were analyzed in comparison with the results based upon the meltdown test. Slags sampled from the actual furnace normally contained some amount of FeO_x . Table 4 shows the basicity and XRD phases for the homogeneous sampled slags. The basicities of these slags, which could be formed around tuyeres, turned out to be less than 1. From XRD pattern analysis, main slag phases found out to be gehlenite.

In the actual furnace some DRI with partially melted shell descended to the tuyere region owing to operation condition such as the thermal level of furnace. Fig. 8 shows the cross-sectioned microstructure of the partially melted DRI pellet sampled from the melter-gasifier through tuyeres. From Table 5, the slag originated from gangue formed in the outer shell or core indicated almost the same basicity as that of the raw pellet. Here T. Fe means total content of metallic iron and FeO related to the reduction degree. Slag formed previously inside the FeO core part was exuded to the metallic shell part basicity of which was about 1. Then the partially melted DRI pellets were sintered each other under the presence of the liquid phase[5].

Discussion

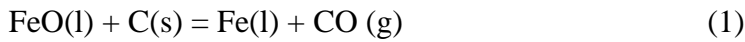
Fig. 9 demonstrates the schematic diagram proposed for the slag formation mechanism in the melter-gasifier. For the two-step ironmaking process, the melting path for slag formation has not been exactly defined yet. Moreover, the slag formation mechanism might be somehow different from that in the blast furnace process. The blast furnace is called one-step ironmaking process because reaction vessel is only one. Inside the furnace, there appear several distinct reaction zones such as lumpy zone, cohesive zone, dripping zone and hearth, etc. The cohesive zone in which ore softens and partially melts, is very much important to maintain upper layer burden load and to distribute the reduction gas from lower combustion zone. Occasionally the cohesive zone could aggravate the furnace condition if it is not stable because the position of the cohesive zone is dependent on the melt formation temperature.

On the other hand, two-step ironmaking process consisting of reduction shaft and melter-gasifier has no cohesive zone. Therefore pellet is prereduced to solid Fe-FeO mixture with about 90% of reduction degree. Furthermore there is only fixed bed consisting of char originated from coal, which charged directly into the melter-gasifier in comparison with the alternate coke layers in the case of the blast furnace. Hence the slag formation mechanism in the two-step ironmaking process might be rather different from that in the blast furnace. Several kinds of low melting-point phases could be formed at the temperature ranged from 1100 to 1400 °C.

DRI pellets and fluxes are separately charged to the melter-gasifier because of no cohesive zone as mentioned earlier. Hence the melting starts by way of two paths at the early stage of the slag formation. In this study the primary and the secondary slags formed in the upper part of char bed are defined in the following way. Firstly the “primary slag” that is homogeneous, is $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ slag with the dissolved FeO originated from the gangue in DRI as mentioned earlier in Fig. 8 and Table 5. Meanwhile, the fluxes consisting of basic components such as CaO and MgO are mostly used for neutralizing the ash comprising of acidic components such as SiO_2 and Al_2O_3 in char[3]. Secondly, partially melted, inhomogeneous “secondary” slag

composing of C_2S and C_2AS with the dissolved FeO , are formed in separate way from the primary slag. The high melting point compound such as C_2S existed under the high basicity. As basicity is greater than one, $(C,W)_2S$ [A region] could be formed at the lower level of Al_2O_3 as shown in Fig. 10 for $CaO-SiO_2-Al_2O_3-FeO_x$ phase diagram[5-8]. However C_2AS [D region] is the main constituent slag phase of secondary slag because of Al_2O_3 content. Molten FeO_x in DRI soaks into porous solid flux in contact with the fly ash consisting mainly of SiO_2 and Al_2O_3 . Therefore low melting point phase such as C_2AS with the dissolved FeO_x is formed with basicity around 2.

In the next stage, the homogeneous primary slag originated from gangue and inhomogeneous secondary slag containing FeO are mixed at about 1300 to 1400 °C. At the similar temperature range, the smelting reduction of liquid FeO occurs simultaneously or competitively to the slag formation according to the following reaction.



Then these slags react with bottom ash originated from the combusted char in the lower part of char bed resulting in the “tertiary” slag. Main phase of tertiary slag is C_2AS [D region] and CAS_2 [E region] with basicity less than 1 as shown in Fig. 10.

In this study, the ash prepared in advance are directly used for the meltdown test at about 1500 °C to simulate the slag making in the melter-gasifier experiencing the combustion of the char at above 2000 °C. Hence the ash would participate in forming the fully melted slag with the basicity of the tapped slag[9-14]

On the other hand metal produced by the smelting reduction separates from slag and is carburized in contact with char according to the following reaction.



As carburization proceeds, the melting point of metal is lowered, then molten metal drips through the char bed. Lastly, the “final” slag similar to tapped slag, is collected in the hearth of the melter-gasifier. Main phase of the final slag is melilite consisting of C_2AS (gehlenite) and C_2MS_2 ($2CaO \cdot MgO \cdot 2SiO_2$, akermanite).

In summary, Table 6 shows the main phases consisting of slags formed in the melter-gasifier. The primary slag is $CaO-SiO_2-Al_2O_3-MgO$ slag with the dissolved FeO originated from the gangue in DRI. For the secondary slag basicity ranges from 1 to 2 because most of the slag phase turned out to be C_2AS . For the tertiary slag basicity becomes less than 1 owing to the bottom ash composing of SiO_2 and Al_2O_3 . Basicity of the final slag returns to about 1 through slag-metal reaction such as SiO_2 reduction to Si in molten metal.

Conclusions

The slag formation mechanism in the melter-gasifier of the two-step ironmaking process different from that in the blast furnace was examined by the meltdown tests under load and by analysis for the slag taken from the actual furnace. The primary slag originated from the gangue in DRI was homogeneous. Partially melted secondary slag composing of dicalcium silicate with dissolved FeO was formed under the high CaO/SiO_2 . Then these slags react with bottom ash resulting in the homogeneous tertiary slag with the dissolved FeO . The final slag similar to tapped slag was collected on the top of the metal pool. The slag had CaO/SiO_2 basicity slightly greater than 1 in the hearth of the melter-gasifier.

References

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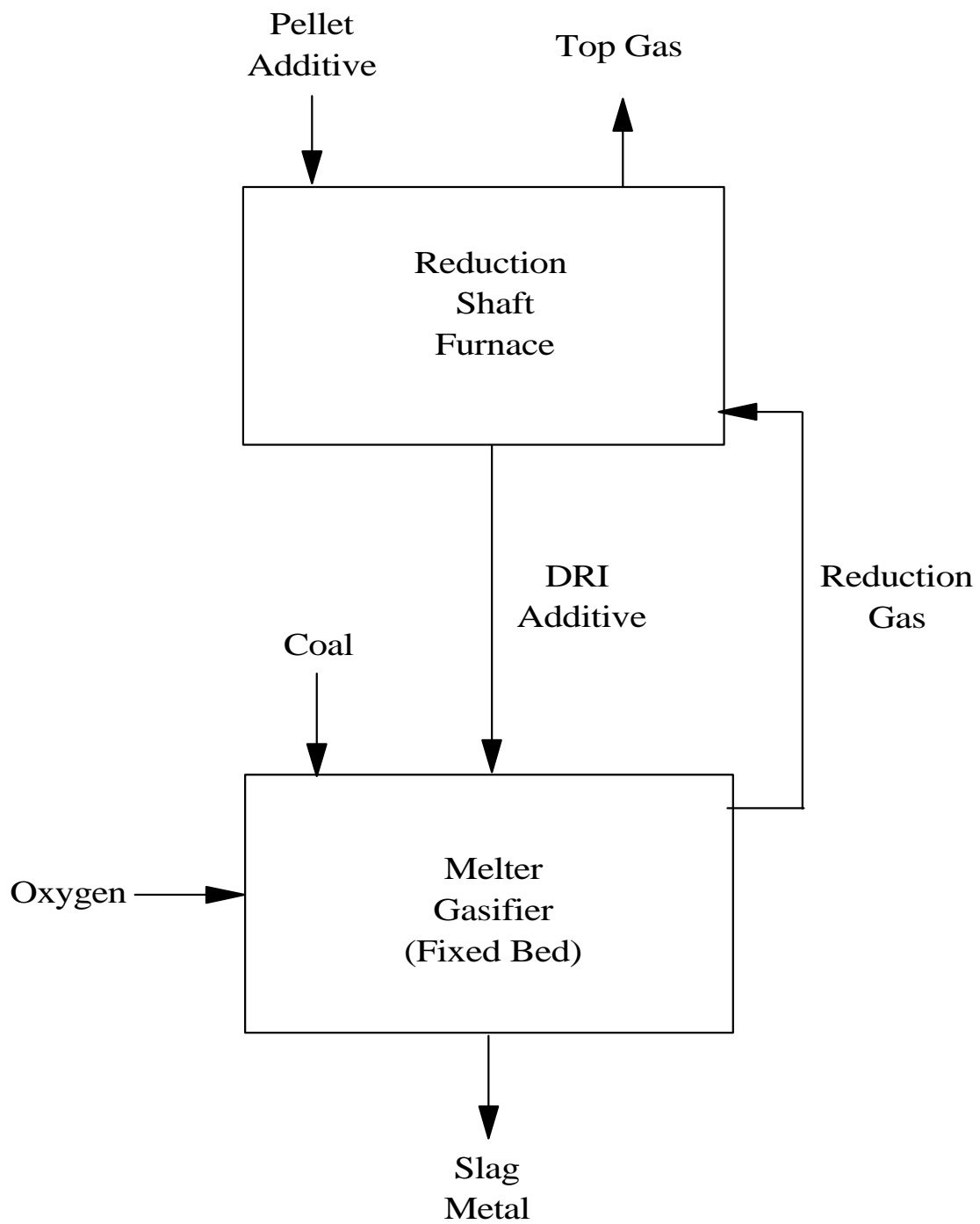


Fig. 1. Schematic material flow diagram for two-step ironmaking process.

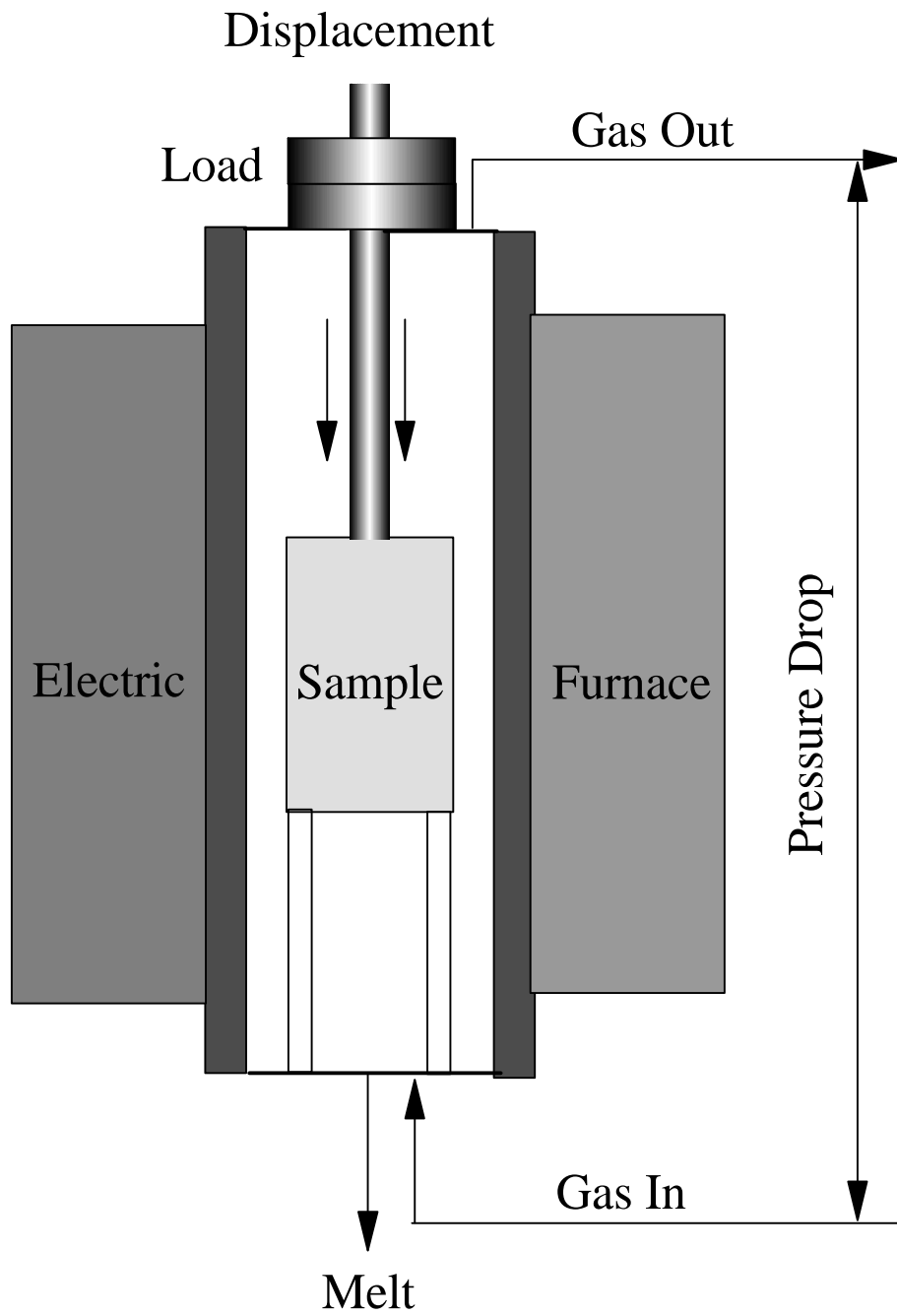


Fig. 2. Schematic sketch of apparatus for high temperature meltdown test under the load.

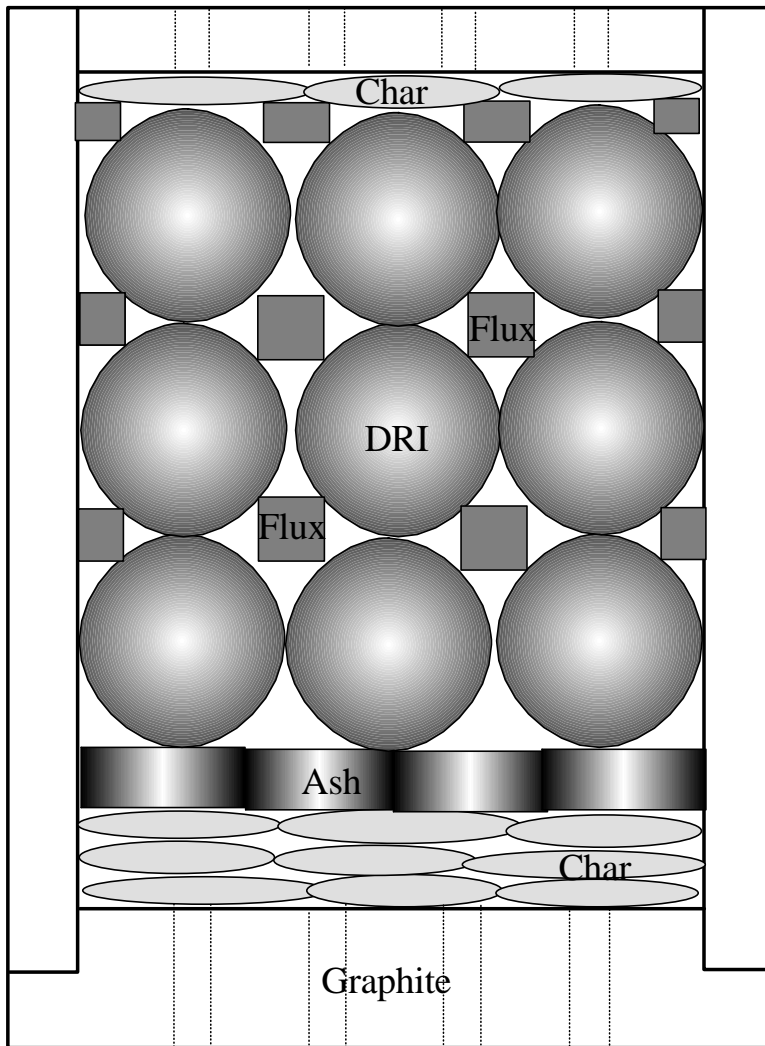


Fig. 3. Detailed picture of the DRI-flux-ash mixed bed.

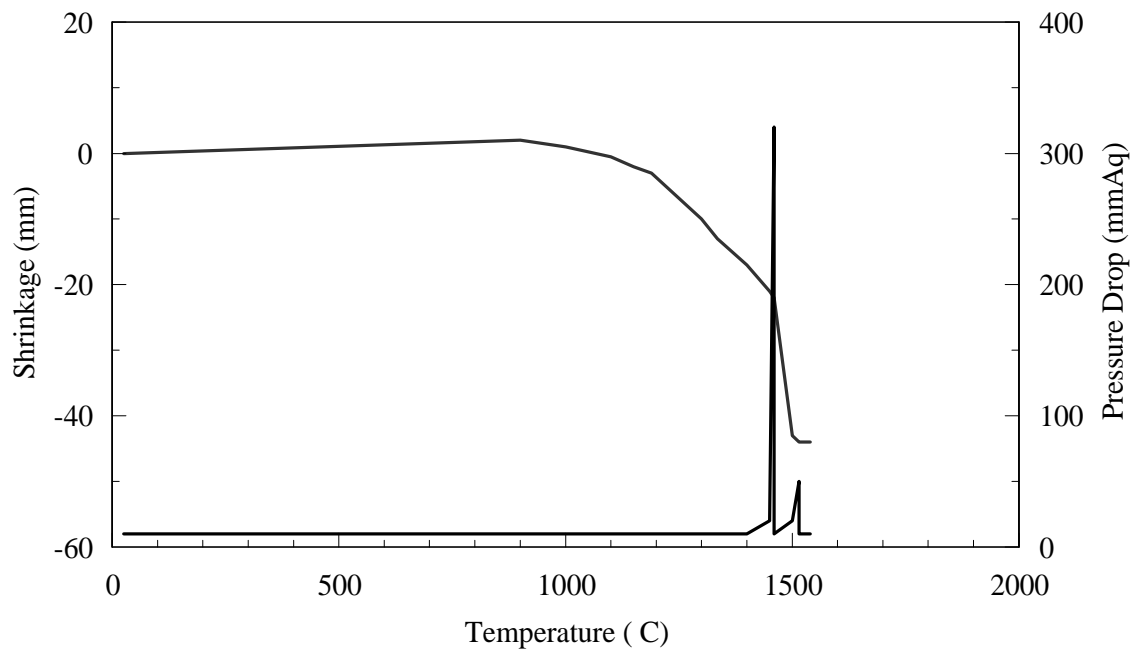


Fig. 4. Shrinkage and pressure drop curves obtained from the meltdown test.

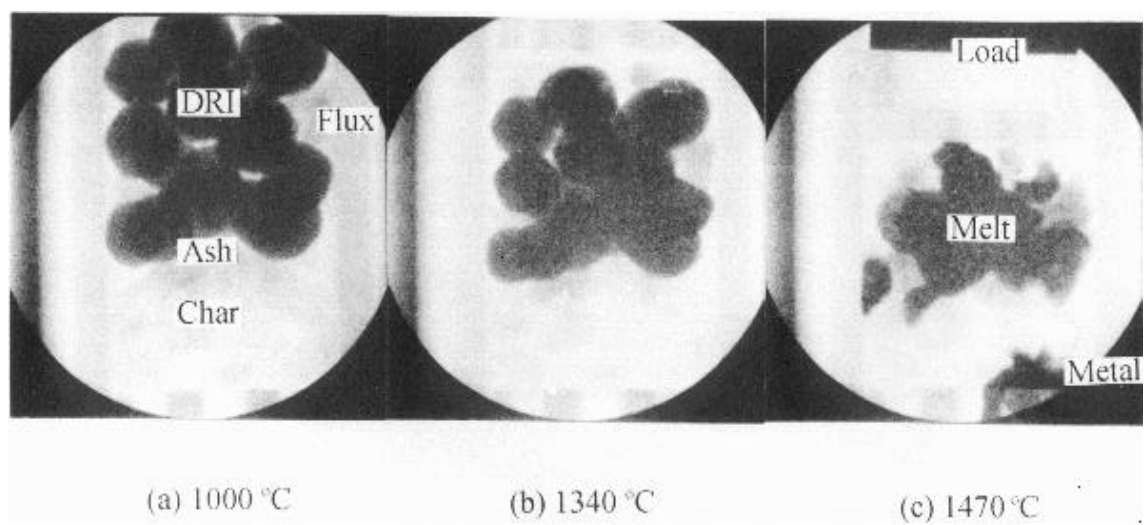


Fig. 5. X-ray image for the DRI-flux-ash mixed bed during the meltdown test.

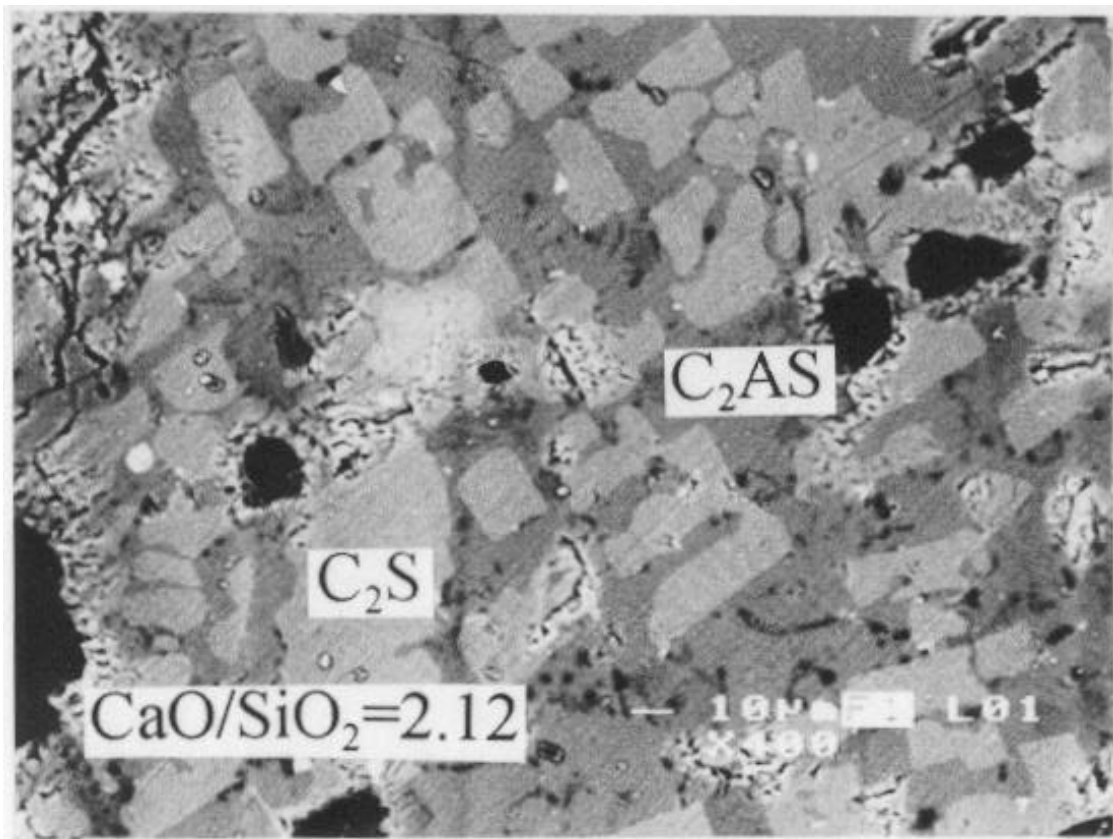


Fig. 6. The microstructure of the partially melted slag.

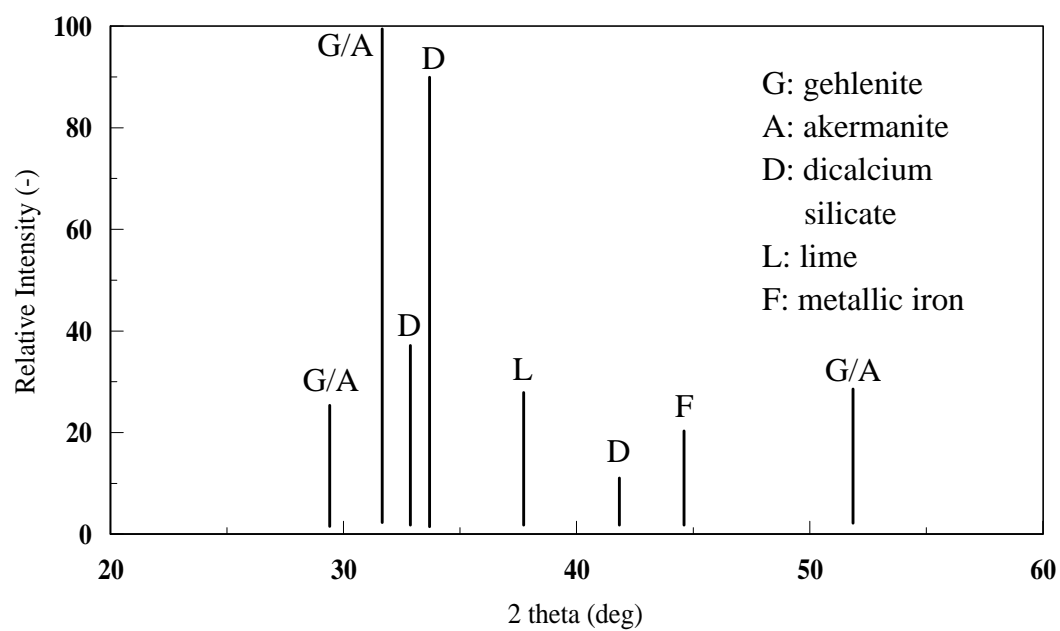


Fig. 7. X-ray diffraction pattern for the partially melted slag.

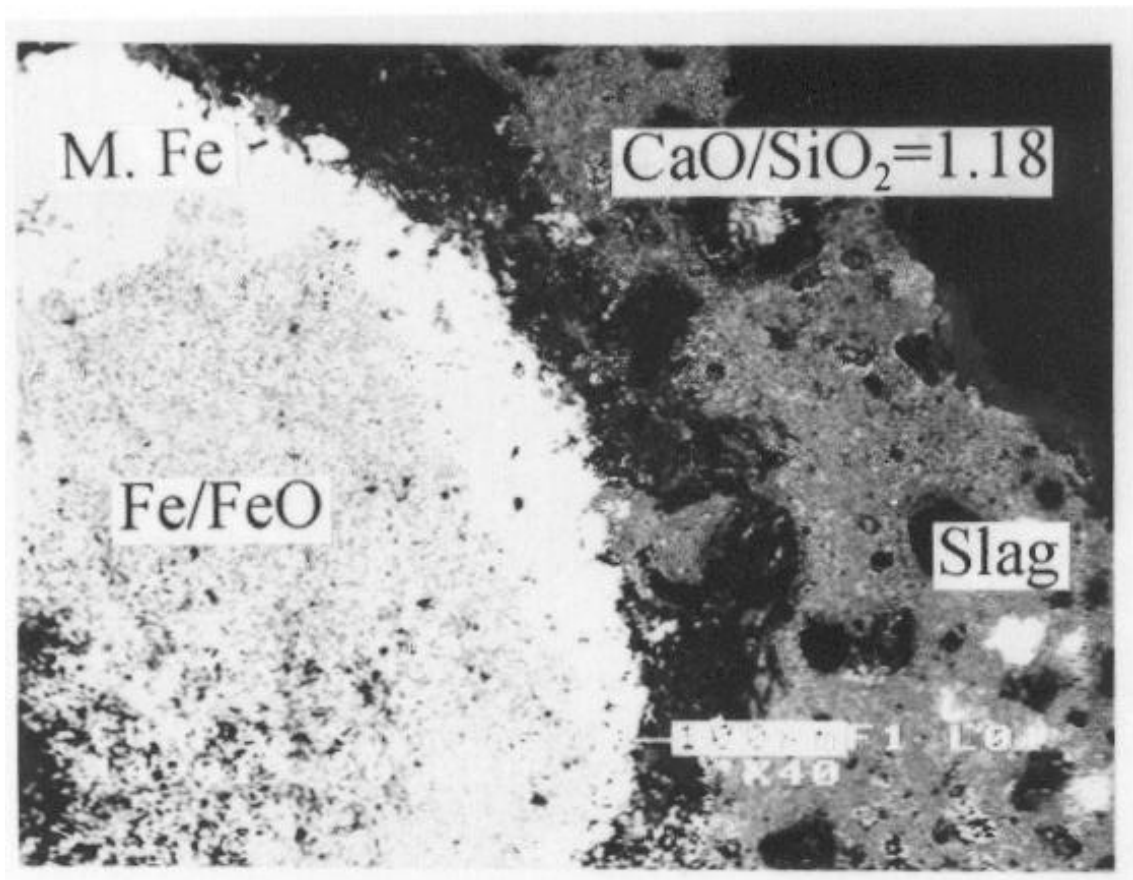


Fig. 8. The cross-section of the partially melted DRI sampled from the actual furnace.

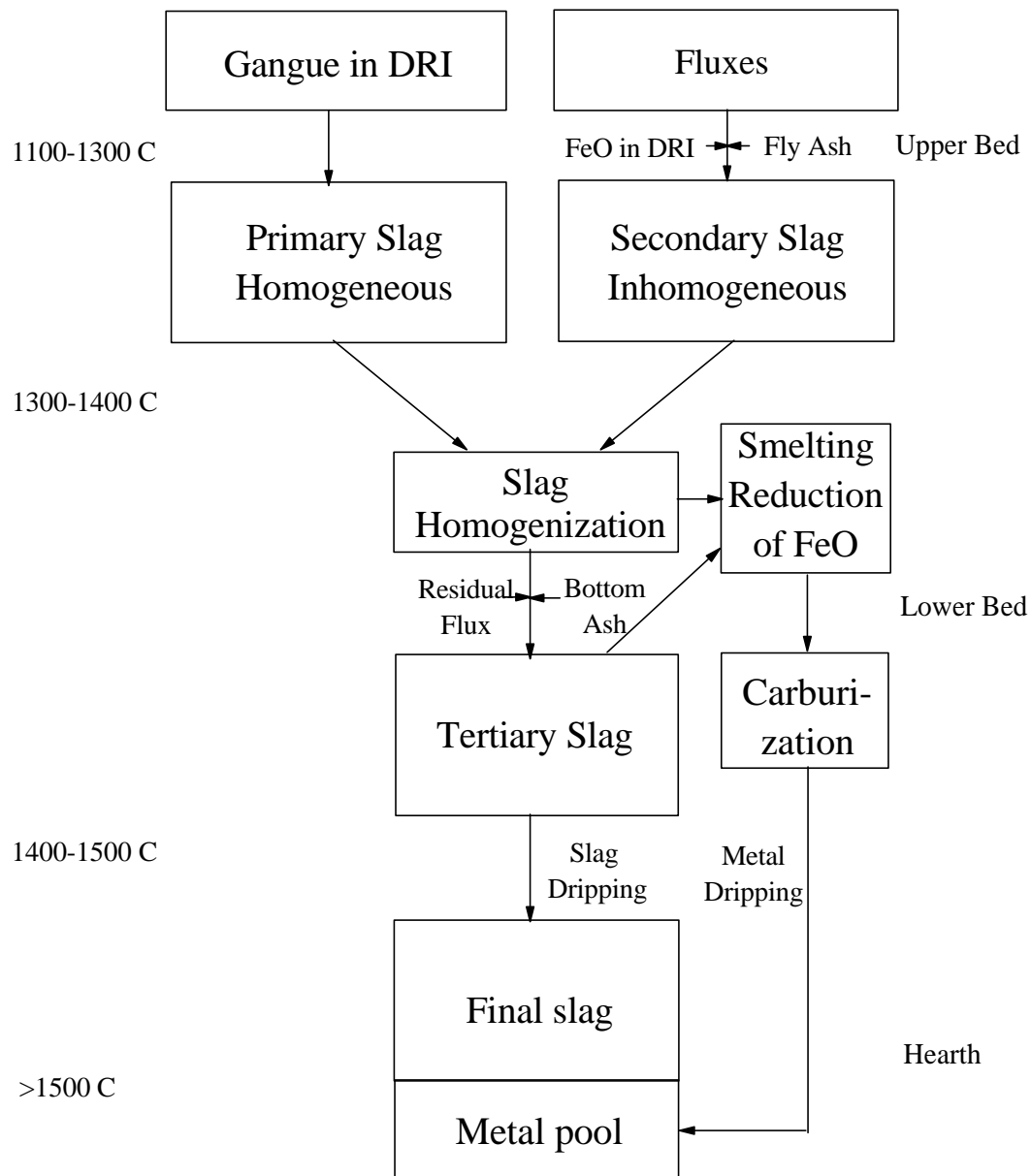


Fig. 9. The slag formation mechanism in the two-step ironmaking process..

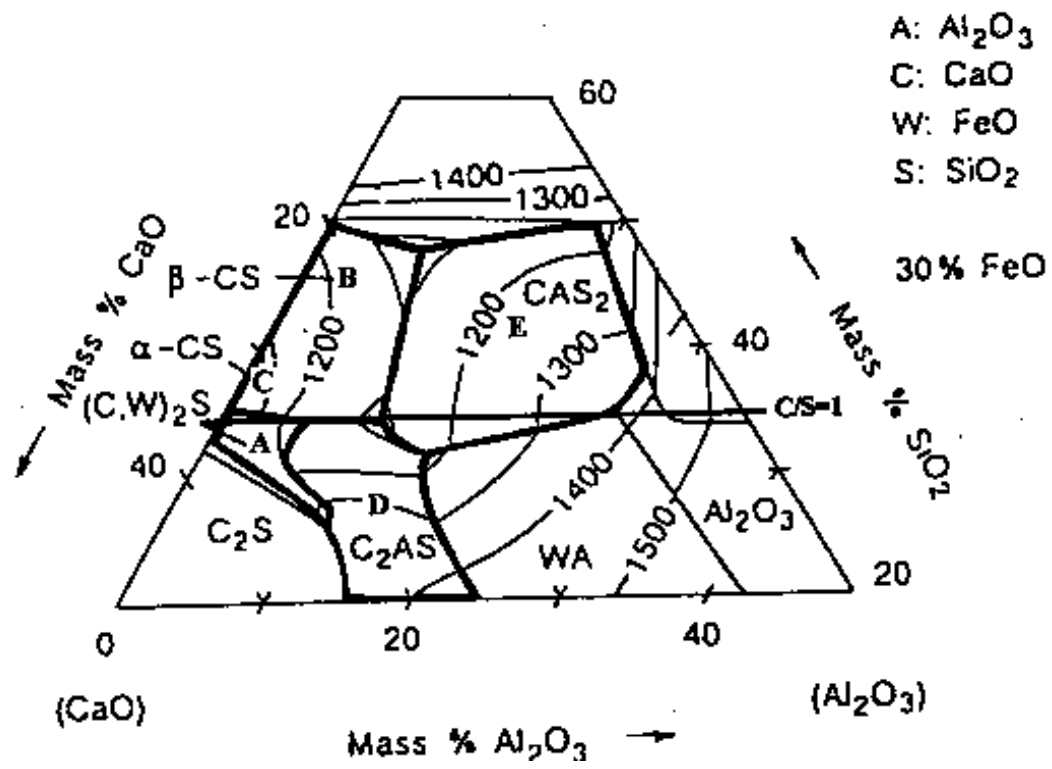


Fig. 10. $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-FeO}_x$ phase diagram [5].

Table 1. Experimental conditions for the meltdown test under load.

item	condition
Load	0.5 kg/cm ²
Atmosphere	100 % CO
Gas flowrate	1.6 l/min
Heating pattern	R.T.*-1000 °C: 7 °C/min, N ₂
	1000-1550 °C: 5 °C/min, CO
	1550 °C-R.T. : Furnace cooling, N ₂
DRI size	9.5-15 mm

* **R.T.:** Room Temperature

Table 2. Meltdown temperatures of the metal and slag under the load.

Test	Condition	Metal(°C)	Slag(°C)
A	Bottom ash	1460	1515
B	Powdered ash	1430-1475	1510-1520
C	Bottom ash Interrupted at 1420 °C	1420	-

Table 3. Chemical compositions of the slag obtained from the meltdown test.

Test	Slag	CaO	SiO ₂	Al ₂ O ₃	MgO	CaO/ SiO ₂
A	Residual	39.38	36.75	10.01	11.43	0.93
	Dripped	37.69	39.80	10.00	11.66	1.06
B	Residual	40.24	36.94	9.70	11.51	0.92
	Dripped	36.17	39.99	9.40	13.04	1.11
C	Residual	44.55	27.47	15.62	6.62	0.62

Table 4. Basicity and main XRD peaks for the slag sampled from the melter-gasifier .

Sample No.	CaO/SiO ₂	XRD peaks
1	0.92	Gehlenite
2	0.90	N. A.
3	0.97	Gehlenite/Metallic Iron

Table 5. Chemical compositions of the shell and core parts of DRI sampled from the melter-gasifier.

part	SiO ₂	CaO	Al ₂ O ₃	MgO	T. Fe	M. Fe*	CaO/SiO ₂
Shell	15.18	16.84	5.01	5.63	44.76	33.57	1.11
Core	4.01	4.40	1.31	0.86	71.03	42.92	1.10

*** M. Fe: Metallic iron**

Table 6. Main constituent phases of slags in the melter-gasifier.

Slag	C/S Basicity Range	Main Phases
Primary	≈ 1	C-A-S-M, W
Secondary	1 – 2	CS, (C,W) ₂ S, C ₂ AS, W
Tertiary	<1	C ₂ AS, CAS ₂ , Fe
Final	≈ 1	C ₂ AS, C ₂ MS ₂

C:CaO, W:FeO, S:SiO₂, A:Al₂O₃, M:MgO