Note

Characterization of Melting of Some Slags in the $\text{Al}_2\text{O}_3\text{--CaO--MgO--SiO}_2$ Quaternary System

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Ladle treatment plays increasingly important role in making clean steels nowadays. In many industrial practices, synthetic ladle slags are based on the $\text{Al}_2\text{O}_3\text{--CaO--MgO--SiO}_2$ quaternary system. Usually, the compositions of the slags are targeted on the single liquid region of the phase diagram. On the other hand, the phase diagram information of the $\text{Al}_2\text{O}_3\text{--CaO--MgO--SiO}_2$ quaternary involves considerable uncertainties. The available sections of the phase diagrams in this system in Slag Atlas¹⁾ are after Osborn *et al.*,^{2,3)} Gutt and Russel⁴⁾ as well as Cavalier and Sandreo-Dendon.⁵⁾ Unfortunately, many liquidus temperatures are given as dotted lines. Disagreements between the phase diagram and the reality have been found by both the present research laboratory and the steel industry.⁶⁾ Since ladle refining is very often operated at temperatures between 1 823 K and 1 923 K, the present communication aims at a study of a number of slag compositions to examine whether these slags are single liquids or multiphase mixtures at 1 858 K.

While the differential thermal analysis (DTA) is well established to determine the temperature of phase transformation, the measurements of the liquidus temperatures of slags using this technique are difficult because of the invariable supercooling of the slags. The exothermic peak associated with the solid separation at the liquidus temperature occurs at much lower temperatures. During the heating mode, the compositional inhomogenities would result in considerable uncertainties. Hence, a quenching technique was employed in the present study

The Al_2O_3 , CaO, MgO and SiO_2 oxide powders were calcined at 1 073 K for 24 h before being thoroughly mixed in an agate mortar. The oxide mixtures were pressed into small pellets of about 1.3 g and sealed in a glass bottle. The bottle was kept in a desiccator before the experiment.

A horizontal furnace was employed for most of the experiments. The experimental setup is schematically shown in Fig. 1. The furnace had KANTHAL SUPER 1800 (molybdenum silicide) heating elements with a maximum working temperature of 1 973 K. The furnace having an even temperature zone of 40 mm was controlled with an accuracy of ± 3 K by a programmable EORUTHERM 2408 P4 regulator using a Pt–30%Rh/Pt–6%Rh thermocouple. The alumina reaction tube had the dimensions of 60 mm o.d. and 50 mm i.d. Platinum crucibles were used to hold

the samples. The crucibles were carefully shaped to avoid creeping-out of the slag during the experiments. An alumina holder was used to support two crucibles along with the samples. In a typical run, the samples on the alumina holder were carefully introduced into the reaction chamber and placed in the even temperature zone. Argon gas was passed through the reaction tube at low flow rate. A constant argon flow was maintained through out the experiment. The samples were heated up to 1 858 K and kept there for more than 5 h. After equilibration of the samples, the sample holder was rapidly pulled out of the furnace. After a quick visual examination, to see if the sample was completely molten, the samples were quenched in liquid nitrogen. Efforts were made to carry out the experiments with identical quenching speed. The quenching time for the horizontal setup experiments was less than 2 s. In order to confirm the reproducibility of the experimental method, each slag composition was investigated four times.

In many ladle treatments, slags of high basicities are employed. Hence, several slag compositions of high CaO contents were further studied. In order to examine whether these high basicity slags were still single liquid at lower temperatures that might be encountered in ladle refining, these slags were quenched from 1 793 K. To avoid the slight possibility of solidification of the sample during quenching, a vertical furnace was employed. The vertical furnace also had KANTHAL SUPER 1800 heating elements.

As shown in Fig. 2, an alumina reaction tube was used as the reaction chamber. The slag sample was placed in a platinum crucible welded in both ends. The platinum crucible was hanged by a piece of platinum wire in the even temperature zone of the furnace. Two Pt–30%Rh/Pt–6%Rh thermocouples were used. One was placed in contact with the reaction chamber to control the furnace and the other one was positioned directly under the crucible to measure the sample temperature. The sample was heated under constant argon flow and kept at the experimental temperature, 1 793 K for 7 h. The platinum wire was cut off and the sample was quenched in liquid nitrogen. The crucible was opened for visual examination. The samples were embedded in bakelite under vacuum for microscopic examination. It should be pointed out that the use of the vertical furnace setup for quenching these samples was due to the consideration that the liquidus temperatures of the samples would

Fig. 1. Schematic figure of the horizontal furnace. 1. silicone rubber stopper; 2. alumina reaction tube; 3. furnace; 4. gas inlet; 5. thermocouple; 6. alumina crucible holder; 7. platinum crucible containing the sample; 8. gas outlet.

Fig. 2. Schematic figure of the vertical furnace. 1 gas outlet; 2 silicone rubber stopper; 3 platinum wire; 4 samples; 5 alumina reaction tube; 6 silicone rubber stopper; 7 thermocouple; 8 gas inlet.

be very close to 1 793 K. The vertical furnace setup would be able to quench the sample within a second, so that the phase(s) present in the sample at 1 793 K could be retained.

Visual examination showed that a sample consisting only a single liquid phase was completely transparent. On the other hand, a multiphase mixture would be semi-transparent or opaque with solid particles present. **Figures 3(a)** and **3(b)** present the quenched samples having a single liquid phase and multiphase mixture, respectively. The difference in their appearances is clearly brought out by these two figures. **Figures 4(a)** to **4(d)** present the photos of the four slags quenched from 1 793 K. The glassy nature of these samples is evidently seen. After visual examination, the samples consisting of only single liquid phase were further subjected to light optical microscopic examination (LOM) for confirmation. **Figure 5** shows an example of the LOM microphotograph of a slag sample with only single liquid phase.

The compositions of the investigated slags along with the results of the experiments are presented in **Table 1**.

A comparison of the present results with the phase dia-

Fig. 3. (a) Photo of a sample with a single liquid phase (nr. 20); (b) photo of a sample of multi-phase mixture (nr. 22).

Fig. 4. (a–d) Photos of the four slags (with single liquid phase) quenched from 1 793 K.

Fig. 5. LOM picture of sample number 9.

Table 1. Compositions of the samples and the experimental results.

Slag no.	mass%Al ₂ O ₃	mass%CaO	mass%MgO	mass%SiO ₂	Result	
					1858 K	1793 K
1	30	50	13	7	multi phase	
2	45	35	13	7	multi phase	
3	25	55	13	7	multi phase	
4	40	40	13	7	multi phase	
5	35	45	13	7	multi phase	
6	35	45	10	10	multi phase	
7	40	40	10	10	liquid	
8	37	43	10	10	liquid	
9	30	54	7	9	liquid	liquid
10	10	40	10	40	liquid	
11	35	50	5	10	liquid	
12	20	30	5	45	liquid	
13	25	45	10	20	liquid	
14	30	45	10	15	liquid	
15	35	50	10	5	multi phase	
16	40	45	10	5	multi phase	
17	20	47	10	23	multi phase	
18	38	47	10	5	liquid	
19	33	47	10	10	liquid	
20	30	55	5	10	liquid	liquid
21	35	55	5	5	multi phase	
22	34	54	5	7	multi phase	
23	35	52	7	6	multi phase	
24	40	50	5	5	liquid	liquid
25	38	50	7	5	liquid	liquid
26	35	45	7	13	liquid	
27	25	45	13	17	multi phase

 Fig. 6. Investigated compositions in the quaternary phase diagram Al₂O₃-CaO-MgO-SiO₂ with 10 mass% MgO. The closed squares represent compositions of single liquids and the open ones represent the compositions of multi-phase mixtures.

grams suggested by Slag Atlas¹⁾ shows that there is considerable disagreement. As an example, Fig. 6 compares the present results with the section having 10% MgO reproduced from Slag Atlas.¹⁾ According to the phase diagram all of the investigated samples should have been melted at the experimental temperature. However, the quenched samples 5, 15, 16 and 17 are all multi-phase mixtures. Likewise, samples 2 and 21–23 should have been melted according to the phase diagram in Slag Atlas,¹⁾ but according to our investigation these samples consist of multi-phase mixtures.

The phase diagrams of the Al₂O₃-CaO-MgO-SiO₂ quaternary system in Slag Atlas¹⁾ include many dotted lines, indicating the uncertainties. Nevertheless, the present communication would still present the experimental results to draw the attention of the researchers and engineers regarding the uncertainties of these phase diagrams. The results might be useful information to the steel industry and to the later reconstruction of the phase diagrams.

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