Asian Journal of Chemistry; Vol. 24, No. 11 (2012), 5337-5340

ASIAN JOURNAL OF CHEMISTRY

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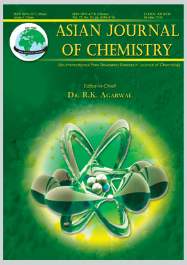

Effect of TiO_2 on the Slag Properties for $CaO-SiO_2-MgO-Al_2O_3-TiO_2$ System

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(*Received*: 25 November 2011; *Accepted*: 16 June 2012) AJC-11630

In the present work, the slag properties were investigated for $CaO-SiO_2-MgO-Al_2O_3-TiO_2$ system. Effects of TiO_2 and temperature on viscosity, melting characteristics and surface tension were analyzed. The results showed that temperature decreases the viscosity within the range studied and all the viscosity values are less than 0.4 Pa.s at high temperature. The viscosity of the slag fluctuates within 0.2 Pa.s at a given temperature above 1350 ºC. However, the viscosity of the slag containing 20 % TiO_2 increases sharply up to even more than 2.9 pa.s at lower temperature (<1350 ºC). The liquidus temperature increases gradually then decreases slightly with increasing titania and all of them are lower than 1300 ºC. Surface tension follows an oppsite trend at a given temperature. It reaches a maximum value when tiatania content in slag is 18 %. The temperature seems to have no obvious effect on surface tension.

Key Words: Titaniferous slag, Viscosity, Melting characteristics, Surface tension.

INTRODUCTION

Blast furnace slag composition has important bearing on its physicochemical characteristics which affects the degree of desulphurization, smoothness of operation, slag handling, coke consumption, hot metal productivity and its quality, *etc*. The slag properties which affect most are viscosity, sulphide capacity, stability and melting performance. These properties have great influence on the overall blast furnace process. Therefore, variation of these slag characteristics with composition and temperature has been a field of active research from 1960s[1-17]. However, most of these studies were carried out over TiO_2-free slag or titaniferous slag with titania normally less than 15 % or more than 25 %. A little experimental data is available in literature for titaniferous slag with titania in the range of 15 to 25 %.

In the present work, the slag viscosity, melting performance and surface tension were experimentally determined for $CaO-SiO_2-MgO-Al_2O_3-TiO_2$ slag system. In the case of the weight ratio CaO/SiO_2 =1.11, titania varied from 16 to 22 % between 1270 and 1500 ºC, as described in Table-1. The effects of TiO_2 on the metallurgical properties of the preceding slag systems were investigated. It is helpful to enrich and perfect a systematical theory of smelting titaniferous ores in blast furnace.

EXPERIMENTAL

The slag samples were prepared with different titania contents by adding pure TiO_2 powders (reagent grade) in desired proportions to the water-quenched slag obtained from the blast furnace, followed by sintering and melting. Afterward, the melt was cooled to form solid (slag) and the solid milled into a fine powder. In order to confirm the reproducibility of experimental data, some experiments for the same composition were carried out three times and the average value was adopted as the correct value at each temperature.

TABLE-1
CHEMICAL COMPOSITION OF THE SLAG STUDIED IN THE PRESENT WORK

Sample	CaO (%)	SiO_2 (%)	MgO (%)	Al_2O_3 (%)	TiO_2 (%)	V_2O_5 (%)	FeO (%)	MnO (%)	Basicity*
1	29.86	26.98	9.02	13.19	15.17	0.14	0.97	0.67	1.11
2	29.11	26.30	8.80	12.86	18.00	0.14	0.95	0.65	1.11
3	28.43	25.67	8.59	12.46	20.00	0.13	0.92	0.63	1.11
4	27.74	25.07	8.38	12.26	22.00	0.13	0.90	0.62	1.11

*Basicity = CaO/SiO_2

A rotating cylinder method was adopted to measure the viscosity of the molten slag. The apparatus used was similar to that used by Lee[8] but with a molybdenum plunger and graphite crucible and other minor changes. The crucible containing the slag sample (about 120 g of slag sample) was placed inside the furnace. The slag samples were heated to the experimental temperature and held at that temperature for 0.5 h and the rotating spindle was immersed into the slag and was located at a middle position in the melt. Ar gas was flowed into the reaction chamber at 0.4 L/min during the viscosity measurement. All the viscosity measurements were made during the cooling cycle until the slag reached its freezing point.

The measurements of the liquidus temperature were made by using an optical softening temperature device, which was similar to that used by Jia and Liu[9]. Each end of the reaction tube was properly sealed by water-cooling metal caps to prevent air entering into the system and closed by a quartz window allowing the CCD camera to follow the experiments visually. A thermocouple was inserted into the furnace through the quartz window and the reaction tube was purged with argon gas throughout the duration of experiment. In this experiment, each sample was pressed into a briquette in a cylindrical mould(φ 3 × 3 mm) and was placed on the MgO substrate kept in the ceramic reaction tube. Temperatures were measured by observing the deformation of the slag sample. The definitions of these temperatures are as follows:

Softening temperature: The remaining height of the slag sample is 75 % of the original height.

Hemisphere temperature (liquidus temperature): The remaining height becomes equal to half of the original level.

In the current work, the ring method has been used to measure the surface tension of the slag phases. The tests were conducted by measuring the force required to separate the measuring piece from the liquid surface. The apparatus used was same to that used in viscosity experiment.

RESULTS AND DISCUSSION

Fig. 1 shows the effect of TiO_2 on the viscosity of the $CaO-SiO_2-MgO-Al_2O_3-TiO_2$ slag at different temperatures. It is apparent from Fig. 1(a) that the slag viscosity decreases with increasing temperature. When temperature is below the melting temperature, the viscosity thickens at a faster rate for high TiO_2 bearing slags (20 % or 22 % TiO_2), whereas the viscosity change of low TiO_2 containing slag (16 % or 18 %) has an opposite effect. This indicates that low TiO_2 containing slag can be handled easily in the process of iron making at low temperature.

Most of the viscosities fluctuate within 0.2 Pa.s at a given temperature (>1350 ºC), as shown in Fig. 1(b). However, it should be mentioned here that the viscosity of the slag containing 20 % TiO_2 increases sharply up to even more than 2.9 Pa.s when temprature is below 1350 ºC. This implies that TiO_2 does not have any significant effect on viscosity at higher temperature (>1350 ºC) and all the viscosity values are less than 0.4 Pa.s.

The increase in viscosity at constant temperature could be caused not only by the formation of solid particles of titanium carbonitride dispersed through the slag, but also by the polymerization of orthosilicate ions. Titania effects on viscosity in two forms as an amphoteric oxide: first, TiO_2 acts as a silica network modifiers[18]. Ti^{4+} cation is larger than Si^{4+} cation, then Ti-O-Ti and Ti-O-Al bonds are expected to be weaker than Si-O-Si and Si-O-Al bonds, thus the addition of TiO_2 to highly polymerized aluminosilicate melts will decrease their viscosity. Second, Ti^{4+} ions exist in tetrahedrons as network formers, since Ti^{4+} ions can replace Si^{4+} ions to form $[TiO_4]^{4-}$or occupy the voids in octahedron with the addition of titania[19]. Some sharing of oxygen ions must occur, resulting in the formation of large silicate ions and a rise in viscosity. The influence of titania on the slag viscosity depends on which function is predominant. If the first function has a stronger effect, thus TiO_2 reduces the viscosity. However, it is possible that slag thickening effect dominates with further addition of TiO_2. A similar observation was found in present case for the slag with TiO_2 content in the range of 16 to 20 %. The viscosity decreases instead of increases when TiO_2 is varied between 20 and 22 %, which is in close agreement with the reported work[20]. There are few data available on the viscosity and the structural analysis for the slag with multiple amphoteric oxides coexisting within a wide range of titania content. Further investigation of structural analysis is required.

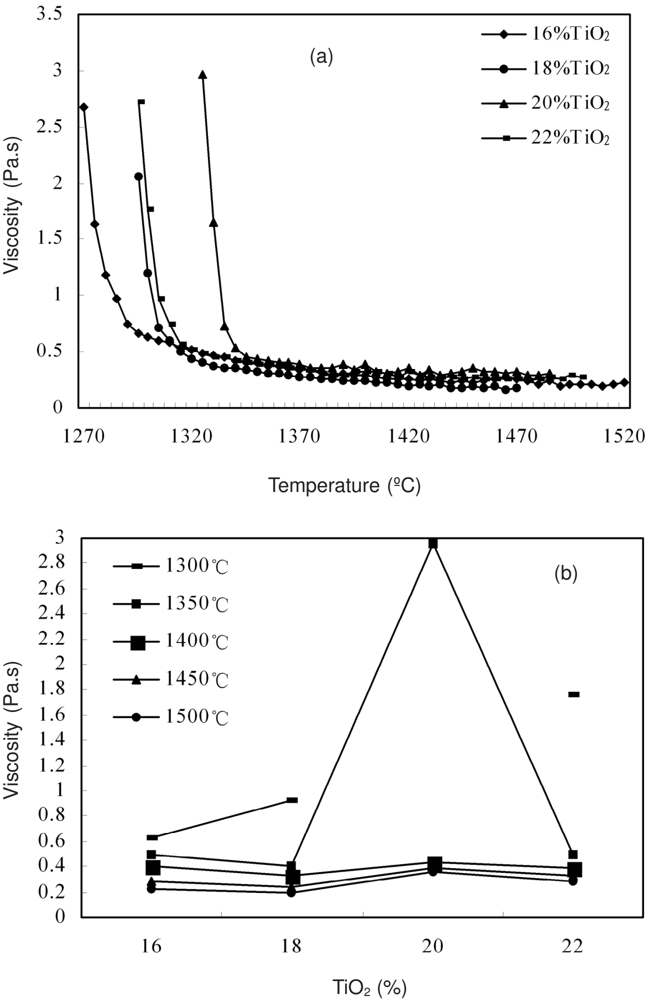

Fig. 1. Variation in viscosity of slag with TiO_2 content and temperature

The melting temperature means the turning point of the curves in Fig. 1(a). The results show that melting temperature increases first and then decreases with increasing titania content in slag and all of them are less than 1400 ºC. In modern balst furnace practice, the fluidization temperature range from temperature when the liquid slag can't flow freely (the viscosity is 2.0 Pa.s) to the melting temperature represents operational difficulties as a very important parameter. The results are presented in Table-2 and Fig. 2. In this study temperature range is narrow for high titania contents, leading to large operation difficulties. For low titania contents, the opposite is true and the stability is better. The result may be due to the formation of a new phase which probably consists of a lower oxide of titanium with lime and silica.

TABLE-2
MELTING TEMPERATURE AND THE FLUIDIZATION TEMPERATURE RANGE FOR TITANIFEROUS SLAG

TiO_2 (%)	16	18	20	22
Melting temperature (ºC)	1288.6	1313.2	1338	1326.3
Fluidization temperature range (ºC)	15.6	21.9	11.7	11.5

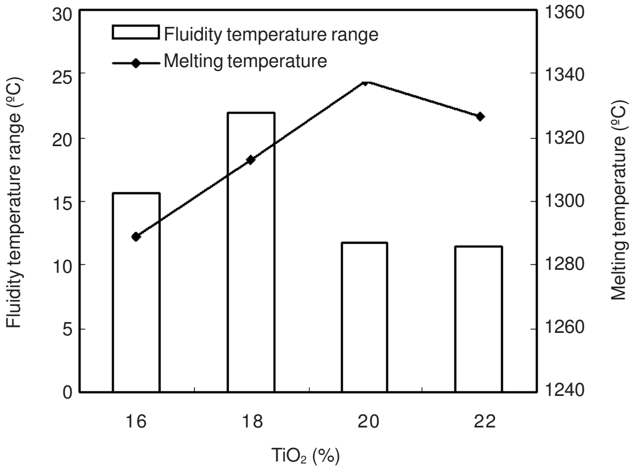

Fig. 2. Effect of TiO_2 on melting temperature and fluidity temperature range

Fig. 3 indicates the variation of the hemisphere temperatures and softening temperatures as a function of the TiO_2 content (16 %-22 %) for each slag composition. Both of them increase gradually then decrease marginally with increasing titania content and all of them are lower than 1300 ºC. A comparison between the data obtained from phase diagram for Al_2O_3-CaO-SiO_2-TiO_2 slag at Al_2O_3=10 %[21] and the data of the present investigation was made in order to ascertain the reliability of the data produced in the present work. The results of the present work are in close agreement with the reported work according to the principle that the liquidus temperature of real slag should be less than that obtained from phase diagram. So it is suggested that the results are more accurate.

Surface tension of slag exerts a considerable impact on the kinetics of the reactions taking place at the boundaries of the liquid slag-liquid metal phases, when a gaseous phase is released. The phenomena occurring on the interface may be decisive for the speed of the entire process[22]. Fig. 4 illustrates the effect of tiatania content and temperature on slag surface tension. The increase in the titania content in the slag of constant basicity ratio up to about 18 % TiO_2 level brings about a substantial surface tension (about 2 or 3 times greater than the others), then surface tension decreases with further additions at a given temperature. There is a slight increase in surface tension when the TiO_2 content changes from 20 to 22 %. Whereas the temperature seems to have no obvious effect on surface tension.

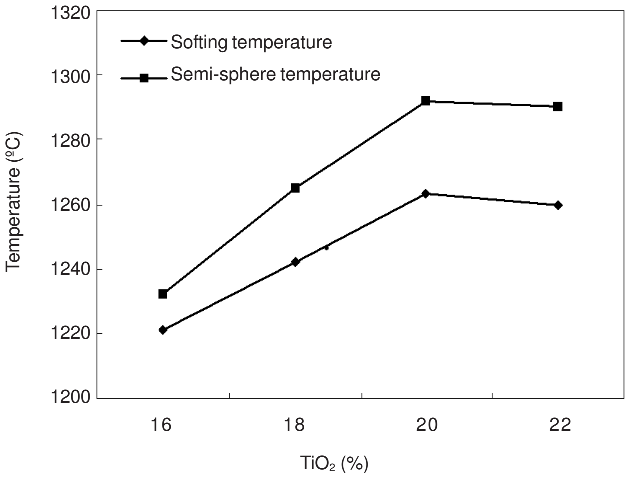

Fig. 3. Variation of temperatures as a function of titania content

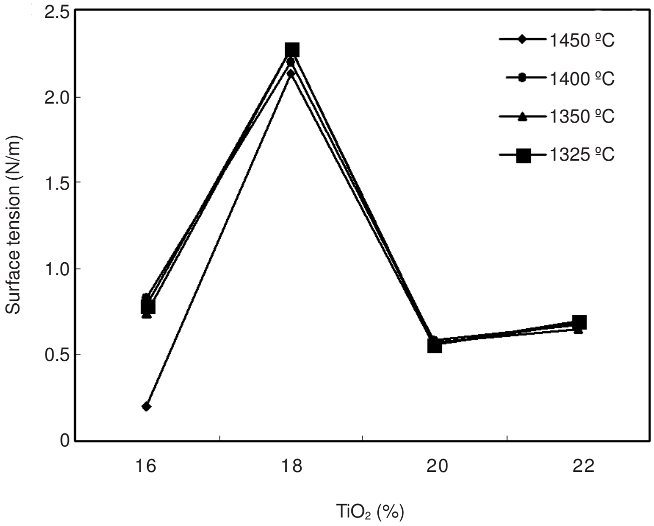

Fig. 4. Titania content dependency of surface tension of the slag

TiO_2 is a surface active substance. It was generally acknowledged that surface tension is related to the percentage of Ti^{4+} ions in octahedral symmetry to that of total Ti^{4+} ions and ion volume. Diao *et al.*[23] has proposed that Ti^{4+} ions exist in tetrahedrons can reduce surface tension of the slag and Ti^{4+} ions in octahedral symmetry have the opposite effect. This explains why surface tension fluctuates in this study. Further investigation is considered necessary because a fairly large diversity was found between different investigations.

Conclusion

As discussion and observed from the results, the finding can be summarized as follows:

(i) The viscosity decreases with increasing tempreture within the range studied. When temperature is above the melting temperature, all the viscosity values are less than 0.4 Pa.s and the slags have good fluidity.

(ii) The influence of TiO_2 in slag on viscosity was found insignificant at higher temperature (>1350 ºC), whereas below the melting temperature, the viscosities of titaniferous slag increase quickly, especially that of the slag containing 20 % titania.

(iii) The liquidus temperature increases gradually then decreases with increasing titania content and all of them are lower than 1300 ºC.

(iv) Surface tension brings to a maximum value with titania content of 18 %. Whereas the temperature seems to have no obvious effect on surface tension.

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