The Conductivity and the Crystallization of Perovskite (CaTiO_3) from Ti-bearing Blast Furnace Slag Studied by A. C. Impedance Method

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The conductivities of a Ti-bearing blast furnace slag (with 23% TiO_2) and the synthetic slag consisting of $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-TiO}_2\text{-MgO}$ were measured accurately in the temperature range of 1 653–1 733 K by A. C. impedance method. The relationships between the conductivity and temperature were obtained as: $\ln \kappa = 14.212 - 24\,820/T$ for the Ti-bearing blast furnace slag and $\ln \kappa = 8.557 - 15\,860/T$ for the synthetic slag (unit of κ : $\Omega^{-1}\cdot\text{cm}^{-1}$) in the temperature range of 1 703–1 733 K. Perovskite phase (CaTiO_3) could precipitate from these slags during slag cooling process. The temperature at which CaTiO_3 started to crystallize was determined as 1 693 K. Rate constants and activation energy for the formation reaction of CaTiO_3 were calculated based on the data of conductivity and the first order kinetic equation. Dissociation reactions of Al_2O_3 and TiO_2 could take place due to the crystallization of perovskite phase and the variation of the basicity of the slag. The rate constants and the activation energy for the dissociation reactions were also calculated.

KEY WORDS: Ti-bearing blast furnace slag; electrical conductivity; A.C. Impedance; Perovskite (CaTiO_3); crystallization.

Introduction

There is about 23–25% (wt) TiO_2 in the Panzhihua (Panzhihua Iron and Steel Group Corporation) Ti-bearing blast furnace slag which is obtained in the process of making Vanadium-bearing pig iron from the vanadium-bearing titanomagnetite in blast furnace. It is worth to recover titanium from the slag on the view of economics and full utilization of valuable resources. Several mineral phases will crystallize during the slag cooling process. Perovskite (CaTiO_3) is the mineral phase which crystallize initially when the slag is cooled.¹⁾ About 60% of the TiO_2 in the slag will crystallize as CaTiO_3 which grows to large size if the cooling process is well controlled.²⁾ Therefore by mineral separation method perovskite phase can be separated from the processed slag. Owing to the ionic nature of molten slag, the slag cooling process can be studied electrochemically. A. C. impedance method can be used in the studies of ionic conductor, semiconductor and dielectric materials in solid or liquid state. S. L. Schiefelbein and D. R. Sadoway³⁾ determined the conductivity of the $\text{CaO-SiO}_2\text{-MgO}$ slag by A. C. impedance measurement. The crystallization behavior of mineral phase in slag has not been studied by A. C. impedance measurement up till now. The present work investigated the conductivity and structure change of the Ti-bearing blast furnace slag and the synthetic slag of $\text{CaO-SiO}_2\text{-MgO-Al}_2\text{O}_3\text{-TiO}_2$ by A. C. impedance measurement.

1. Experimental Apparatus

1.1. Experimental Apparatus

There are several methods for the measurement of conductivity of slag. The method with four electrodes is the one with the highest accuracy.⁴⁾ The four electrodes are working electrode (WE), reference electrode 1 (RE1), reference electrode 2 (RE2), and counter electrode (CE), respectively. When current is passed through WE and CE, the voltage difference between RE1 and RE2 is measured. Because the current passed to the high impedance voltage meter through the two reference electrodes is very small and can be neglected so that no polarization occurs on them, the resistance between RE1 and RE2 can be calculated accurately based on the four electrode arrangement. The electrodes are made of Mo wires with 1 mm in diameter. The four electrodes were isolated by two Al_2O_3 tubes with double holes for insulating purpose. The two Al_2O_3 tubes are fixed on the holder by nuts as shown in Fig. 1. Crucibles are made of iron with high purity in size of $\varnothing 45 \times 40 \times 30$ mm.

1.2. Raw Material and Experimental Procedure

The Ti-bearing blast furnace slag is obtained from Panzhihua Iron and Steel Group Corporation, China. Its composition is shown in Table 1. The total weight of the mixed slag for each experiment is 130 g, with 5% CaF_2 in it. The composition of the synthetic slag is also listed in Table 1. All oxides used in preparing the synthetic slag are analytical reagents. They were melted into

Fig. 1. Experimental arrangement.

Table 1. Compositions of slag. (mass%)

	TiO ₂	CaO	MgO	SiO ₂	Al ₂ O ₃	V ₂ O ₅	V ₂ O ₃	FeO	others
Synthetic slag	26.00	30.00	9.04	21.40	13.50				
Ti-bearing blast furnace slag	23.26	25.12	8.41	23.19	13.41	0.32		4.86	
Steelmaking slag	2.38	48.53	7.05	5.91	23.26		2.53	18.13	1.52
Mixed slag*	20.67	27.80	8.29	21.34	14.27			6.35	

*Mixed slag was prepared by mixing Ti-bearing blast furnace slag with steel making slag in proportion of 8:1.

mother slag first. The crucible and slag were put into the hot zone of a MoSi₂ furnace. Argon gas was flowed through the furnace to exchange air in it and was kept flowing during the whole experimental period. The heating rate was 10 K/min. The temperature of the slag was kept at 1733 K for 1 hr at first for the slag to be melted completely. The electrodes were lowered into the slag by adjusting the holder down or up and kept at a suitable position. The depth of electrodes dipped into slag was confirmed as 15 mm by reading the scale on the holder. The resistance between RE1 and RE2 was monitored with a Solar 3486A multi-meter and it decreased sharply when the electrodes contact with the surface of the slag. Then the impedance of the slag between two electrodes RE1 and RE2 was measured with 1255HF frequency response analyzer and 1286 electrochemical interface (Solartron Instruments, Schlumberger). The measurement was made in two directions, increasing and decreasing temperature. The interval of temperature between the two successive measuring points is 10 K. The time used for holding constant temperature at each point is 10 min. Temperature range of the experiment was 1653 to 1733 K. The sweeps were performed in the frequency range of 100 Hz–100 kHz with equal interval of logarithmic frequency and the magnitude of A. C. signal is 30 mV.

Although slag is a pure resistance, the equivalent circuit is series of a resistance and a capacity. Real part of the impedance with the smallest capacity was taken as the resistance of the slag.³⁾ Standard KCl aqueous solution was used to determine the cell constant.

Fig. 2. Relationships between conductivity and temperature.

Fig. 3. Image of the perovskite crystals (magnify: 200 times) initially crystallized from the Ti-bearing blast furnace slag sampled at 1693 K.

2. Results and Discussions

2.1. The Conductivity of Ti-bearing Blast Furnace Slag

The measured results of conductivity of Ti-bearing blast furnace slag can be seen from Fig. 2. Linear relations were obtained when the logarithm of conductivity of the slag was plotted against the reciprocal of temperature. It is found from Fig. 2 that the rate of conductivity decreasing with the decrease of temperature is lower than before from 1693 K. This phenomena shows that some change happened in the slag which affected the conductivity of the slag. It is also found from the microscopy observation of the quenched sample (see Fig. 3) that the fine crystals of CaTiO₃ appeared at 1693 K in the slag. It should be noted that this kind of perovskite crystal is different from that crystallized during the quenching process. In that case a few small crystals appeared with some coarsened one together. X-ray results of the slag at 1703, 1693 and 1673 K further shown that there was only glass phase in the slag at 1703 K, as shown in Fig. 4, no peak of crystal existed in it; and existed several peaks of crystal CaTiO₃ at 1693 and 1683 K. The crystallization of CaTiO₃ decreased the number of Ca²⁺ ions, which is main electrical charge carrier, and also the existing of CaTiO₃ grains in the slag made the apparent viscosity of the slag higher than before. Both can cause the conductivity decreasing. Therefore the rate of conductivity decreasing became faster. The temperature of the slag was decreased from 1733 to 1663 K and kept at 1663 K for 2.5 hr to observe the variation of conductivity of the slag with time. The results are shown

Fig. 4. X-ray results of slag at different temperature.

Fig. 5. Conductivity change with time at constant temperature.

in Fig. 5. From Fig. 5 it is found that at 1663 K the conductivity of the slag decreases first (A–B section) and then increases (B–C section) and finally keeps constant (C–D section).

The measured values of conductivity of the slag between 1703 to 1733 K have been fit by the least square regression to an Arrhenius equation. The results are as follows: $\ln \kappa = 14.212 - 24820/T$, where κ is in $\Omega^{-1} \cdot \text{cm}^{-1}$ and T in Kelvin.

2.2. The Relation between the Variation of Conductivity and the Structure of Ti-bearing Blast Furnace Slag

The results of the conductivity measurement and the microscope observation of quenched slag samples showed that the crystals of CaTiO_3 have formed at 1693 K in the slag.

The ionic reaction of crystallization of CaTiO_3 is as follow:

According to ionic theory of molten slag, SiO_2 is an acidic component and will combine with O^{2-} in molten slag to form anion cluster with larger ionic radius such as SiO_4^{4-} and $\text{Si}_2\text{O}_7^{6-}$ etc. CaO is a basic one and will

give out O^{2-} to form positive ion Ca^{2+} with smaller ionic radius and fast moving rate. Al_2O_3 and TiO_2 are neutral components, they show acidic behavior in basic slag and basic one in acidic slag. Although there exist various kinds of ions in the slag, the main conducting ions are free ions, especially the Ca^{2+} , Mg^{2+} and Al^{3+} etc with smaller ionic radius and faster moving rate.⁵⁾

It is known from reaction (1) that Ca^{2+} had been consumed during the crystallization of CaTiO_3 , which must cause the decrease of the conductivity of the slag. When the amount of CaTiO_3 crystallized in the slag reaches its maximum, the number of Ca^{2+} in the slag is the minimum so that the conductivity reaches its lowest value. This corresponds with point B in Fig. 5. Conductivity variation with time from A to B in Fig. 5 corresponds with the crystallization of the perovskite. The original slag was basic one because the ratio of CaO over SiO_2 was over 1:1. As CaTiO_3 crystallized, CaO was consumed, the slag revealed acidic behavior gradually. Neutral oxides TiO_2 remained after the crystallization of CaTiO_3 and Al_2O_3 in acidic slag went through following reactions:

When the above reactions reached their equilibrium status, the slag was the richest in the free ions of Ti^{4+} and Al^{3+} . The conductivity of the slag would reach to its maximum in this case. This corresponds to the point C in Fig. 5. Therefore section B–C may account for the dissociation reactions of Al_2O_3 and TiO_2 . In section C–D, no changes occurred in the slag which kept the conductivity of the slag constant. It can be seen from Fig. 5 that although the numbers and kinds of the main electrical charge carrier had changed during this constant temperature process at 1663 K, the final conductivity of the slag almost did not change compared with that at the beginning of constant temperature process. This may be because that the decrease of conductivity caused by the formation of perovskite is cancelled by the increase the dissociation of Al_2O_3 and TiO_2 . The conductivity variation with time of the slag at 1653 K is almost same as that at 1663 K. The time needed for the conductivity to reach maximum value at 1663 K is 65 min.

2.3. Rate Constant for Dissociation Reactions of TiO_2 and Al_2O_3

From above analysis it can be seen that at 1663 K from point B TiO_2 and Al_2O_3 in the slag began to dissociate according to Eqs. (2) and (3) and reached equilibrium at point C. The concentrations of TiO_2 and Al_2O_3 in the slag at point B were at their maximum values and minimum at point C. In order to calculate the rate constants for the dissociation reactions of the two components it is assumed that the dissociation reactions are complete. Let κ_0 and κ_∞ represent the conductivity of the slag at point B and C in Fig. 5. According to the reference,⁶⁾ there exists following relation between concentration of reactant and the conductivity of the slag:

Table 2. Rate constant k for dissociation reactions of TiO_2 and Al_2O_3 in Ti-bearing blast furnace slag.

Temperature (K)	κ_∞ ($\Omega^{-1}\cdot\text{cm}^{-1}$)	κ_0 ($\Omega^{-1}\cdot\text{cm}^{-1}$)	t (min)	κ_t ($\Omega^{-1}\cdot\text{cm}^{-1}$)	k (min^{-1})
1663	0.76	0.01	120	0.60	0.026
1653	0.60	0.004	80	0.17	0.004

Table 3. Rate constant k for the formation reaction of CaTiO_3 in Ti-bearing blast furnace slag.

Temperature (K)	κ_∞ ($\Omega^{-1}\cdot\text{cm}^{-1}$)	κ_0 ($\Omega^{-1}\cdot\text{cm}^{-1}$)	t (min)	κ_t ($\Omega^{-1}\cdot\text{cm}^{-1}$)	k (min^{-1})
1663	0.01	0.9	35	0.7	0.0092
			55	0.61	
			90	0.28	
1653	0.004	0.8	45	0.59	0.0068

$$C_0/(C_0 - x) = (\kappa_\infty - \kappa_0)/(\kappa_\infty - \kappa_t) \dots\dots\dots(4)$$

Where C_0 is the initial concentration of reactant, $(C_0 - x)$ the concentration of reactant at time t , κ_t the conductivity of the slag at time t . In the case that reaction obeys the first order kinetic equation:

$$k = 1/t \ln\{C_0/(C_0 - x)\} = 1/t \ln\{(\kappa_\infty - \kappa_0)/(\kappa_\infty - \kappa_t)\} \dots\dots\dots(5)$$

Where k is the sum of rate constant for the dissociation reactions of TiO_2 and Al_2O_3 .

Taking an arbitrary point between point B and C into Eq. (5), k can be calculated. The results of rate constant k together with κ_∞ and κ_0 at 1663 and 1653 K are listed in **Table 2**. According to the Arrhenius formula, the activation energy of the dissociation reactions was also calculated as 4270 kJ/mol. High activation energy means large resistance of the dissociation reactions.

2.4. Rate Constant for the Formation Reaction of CaTiO_3

Perovskite (CaTiO_3) was formed at 1693 K during the cooling process of Ti-bearing blast furnace slag. From Fig. 5 it can be seen that at 1663 K the rate of formation reaction of Perovskite (CaTiO_3) was low till it was held nearly 40 min. Therefore the conductivity data can be used to calculate the rate constant for the formation reaction of CaTiO_3 approximately. The calculation is as follows: the conductivity at point A in Fig. 5 at 1663 K was taken as κ_0 , and that at point B as κ_∞ . The approximate linear relation between $\ln(\kappa_\infty - \kappa_t)$ and t proved that the formation reaction of CaTiO_3 is the reaction with first order. The results of rate constant at 1663 and 1653 K are listed in **Table 3**. The activation energy is 680 kJ/mol. and much less than that of the dissociation reactions. In fact it is easier for the formation of perovskite (CaTiO_3) in the slag than the dissociation of TiO_2 and Al_2O_3 .

2.5. The Conductivity of Synthetic Slag

At the same conditions with the Ti-bearing blast furnace slag, the conductivity of synthetic slag at different temperatures was also studied. Either the results of conductivity (see Fig. 2) or the microscopy observation for the quenched samples showed that the crystals of

CaTiO_3 have begun to form at 1693 K in the slag. In the temperature range of 1703–1733 K, the relation between the conductivity and the temperature for the synthetic slag is $\ln \kappa = 8.557 - 15860/T$ (unit of κ is $\Omega^{-1}\cdot\text{cm}^{-1}$). At each temperature, the conductivity of synthetic slag was lower than that of the Ti-bearing blast furnace slag. The 5% CaF_2 in the Ti-bearing blast furnace slag made the fluidity of slag better and there was also 6.35% FeO in the Ti-bearing blast furnace slag which has special conducting mechanism and higher ability of electrical conducting⁵⁾ so that the Ti-bearing blast furnace slag had higher conductivity.

Conclusions

(1) The conductivity of Ti-bearing blast furnace slag and synthetic $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-TiO}_2\text{-MgO}$ slag were measured accurately in the temperature range of 1653–1733 K by A. C. impedance method. The results obtained are $\ln \kappa = 14.212 - 24820/T$ for Ti-bearing blast furnace slag and $\ln \kappa = 8.557 - 15860/T$ (unit of κ : $\Omega^{-1}\cdot\text{cm}^{-1}$) for synthetic slag in the range of 1703–1733 K.

(2) The temperature at which CaTiO_3 began to crystallize from molten Ti-bearing blast furnace slag was determined as 1693 K through conductivity measurement using A. C. impedance method.

(3) The rate constants and activation energy for the formation reaction of CaTiO_3 were calculated based on the first order kinetic equation.

(4) When perovskite crystallized from the Ti-bearing blast furnace slag the basicity of the slag decreased because of the consumption of CaO . Neutral oxides Al_2O_3 and TiO_2 in the slag revealed basic behavior gradually and dissociated to generate free O^{2-} and metal ions. Time needed for the dissociation reactions to reach equilibrium at 1653 and 1663 K is determined by analyzing conductivity change with time. The sum of rate constant and the activation energy for the dissociation reactions at 1653 and 1663 K is calculated based on first order kinetic equation.

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