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Kinetics of non-isothermal precipitation process of the perovskite phase in CaO-TiO$_2$-SiO$_2$-Al$_2$O$_3$-MgO system

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Kinetics of non-isothermal precipitate process and crystal growth of perovskite (CaO·TiO$_2$) phase in CaO-TiO$_2$-SiO$_2$-Al$_2$O$_3$-MgO system were studied. The experimental results show that the relative volume fraction can be described by the equation given by Matusita *et al.* and the experiential expression of average crystal radius was obtained. The particle coarsening in non-isothermal process has important effects on the crystal growth of perovskite phase. © *2000 Kluwer Academic Publishers*

1. Introduction

More than 3 million tons of blast furnace slag containing about 25% TiO$_2$ are produced by smelting V-Ti bearing magnetite every year in Panzhihua Iron and Steel Company. The Ti-bearing slag is a very important man-made resource. Because of the dispersed distribution of Ti component in various mineral phase, very fine grains ($<$10 μm) and complex interfacial combination, it is very difficult to recovery Ti component from the slag by traditional separating technique. So far the slag has not been efficiently utilized those results in a waste of the resource and the pollution of environment.

The main chemical components of titanium bearing blast furnace slag are CaO, TiO$_2$, SiO$_2$, Al$_2$O$_3$ and MgO. The main titanium-containing mineral phase is perovskite (CaO·TiO$_2$). If perovskite phase fully grow and coarsen, it can be separated from the slag by mineral dressing method. In order to obtain further information about the precipitation process of perovskite phase in the slag, it is necessary to study the kinetics of non-isothermal precipitate process of perovskite phase in CaO-TiO$_2$-SiO$_2$-Al$_2$O$_3$-MgO system.

Phase transformation which proceed via nucleation and growth by isothermal experimental technique have widely been studied [1–3] and the last decades have been a strong theoretical and experimental interest in the application of non-isothermal experimental analysis techniques to the study of phase transformations [4, 5]. Non-isothermal experiments can be used to extend the temperature range of measurement beyond that accessible to isothermal experiments. Industrial processes often depend on the kinetic behavior of systems undergoing phase transformations under non-isothermal conditions. Phase transformations involving nucleation and growth, and particular to the crystallization kinetics of glass forming liquids have been studied [6–8]. Most of the studies afore mentioned have mainly been aimed on solid state nucleation and growth transformations, and the crystallization kinetics in molten oxide system have rarely been reported.

2. Experimental procedure

Chemical composition of the experimental material is given in Table I.

The experimental material was melted in electric furnace under argon gas at 1743 K for 30 minutes in order to make it fully melted and then make it cool at required cooling rates to 1473 K. In this process, the samples were obtained by water quench method at designed temperatures.

The temperature was measured by Pt-Rh thermal couple and controlled by SR53 type program thermal control apparatus.

Volume fraction and radii of perovskite phase was measured by image analysis apparatus. The microstructure of the sample examined by SEM at an operating voltage of 20 kV.

3. Results and discussion

3.1. Kinetics of transformation

Fig. 1 illustrates the volume fraction, *x*, of perovskite phase as a function of temperature from image analysis

TABLE I Chemical composition of the experimental material

CaO	SiO$_2$	TiO$_2$	Al$_2$O$_3$	MgO	MnO	V$_2$O$_5$	Total Fe	Others
25.2	23.6	23.3	13.4	8.4	1.0	0.32	3.44	1.34

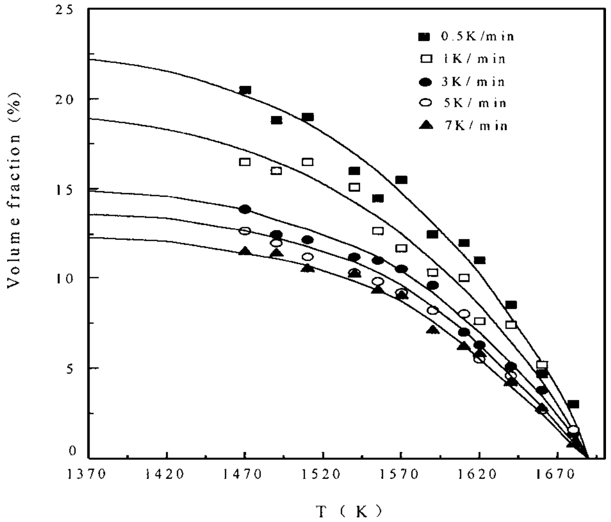


Figure 1 Volume fraction of perovskite against temperature.

results at cooling rates of 0.5–7 K/min. It can be seen that perovskite phase begin to precipitate at 1693 K. With the cooling rate decrease, volume fraction increases. Well-known, in diffusion controlled transformation, lower cooling rate is in favor of the system achieving equilibrium state and making the volume fraction achieve the maximum value.

To obtain further information on the crystallization kinetics, the following equation was applied, which is derived by Matusita *et al.* [9] used for non-isothermal crystallization process in amorphous materials.

$$-\ln(1-x) = \frac{c}{\alpha^n}\exp\left[-\frac{1.052nE}{RT}\right] \tag{1}$$

where x is crystal volume fraction, c is a numerical constant, α is the constant heating rate, R is Boltzmann constant, E is the activation energy for crystal growth and T is the absolute temperature. Thinking about the present work is to study the phase transformation in cooling process and the system is different from amorphous materials, the above equation can be change into following statement,

$$-\ln(1-x') = \frac{c}{\alpha^n}\exp\left[-\frac{1.052nE}{R(T_0-T)}\right] \tag{2}$$

where x' is a relative transformed fraction and $x' = \frac{f(\alpha,T)}{f(0,T)}$. Here $f(\alpha, T)$ is the volume fraction of perovskite at temperature, T when the cooling rate is α. $f(0, T)$ is the volume fraction of perovskite at temperature, T when the cooling rate is zero. T_0 is the temperature of perovskite phase starting to precipitate. Equation 2 can be rewritten as,

$$x' = 1 - \exp\left(-\frac{k}{\alpha^n}\right) \tag{3}$$

where k is a function of temperature and it can be described by the following equation,

$$k = c \times \exp\left(-\frac{b}{1693-T}\right) \tag{4}$$

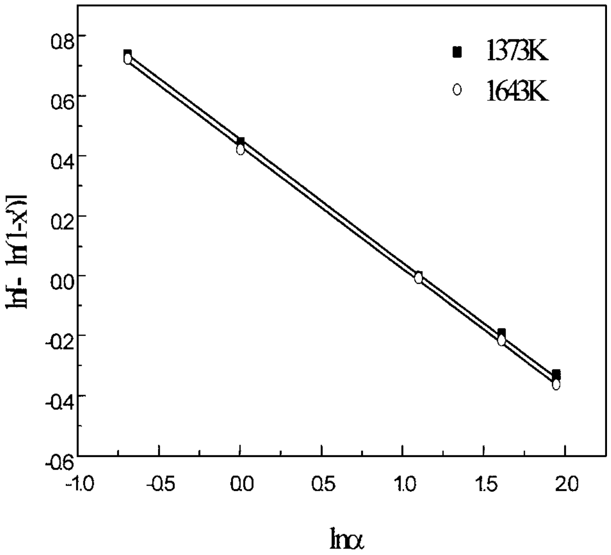


Figure 2 $\ln[-\ln(1-x')]$ against $\ln\alpha$.

where c, b is constants. From Equation 3, the following equation can be derived,

$$\ln[-\ln(1-x')] = -n\ln\alpha + \ln k \tag{5}$$

Fig. 2 is the experimental results of $\ln[-\ln(1-x')]$ against $\ln\alpha$ at temperatures of 1373 K and 1643 K. It can be seen that the curves are straight lines, which illustrate that the precipitate process of perovskite can be described by Equation 3. The n-value is the slope of the straight lines, which is 0.407. $k = 1.58\exp[-\frac{1.32}{(1693-T)}]$.

3.2. Kinetics of growth

Fig. 3 shows the morphology of perovskite phase at the cooling rates of 0.5 K/min and 5 K/min. It can be seen that lower cooling rate is in favor of the growth and coarsening of perovskite.

Fig. 4 shows the variations of $\alpha\cdot\bar{r}^3$ against α. It is shown that when α close to zero, $\alpha\cdot\bar{r}^3$ close to a limited value, while α increase, $\alpha\cdot\bar{r}^3$ decrease promptly. This result can be approximately described by the following equation,

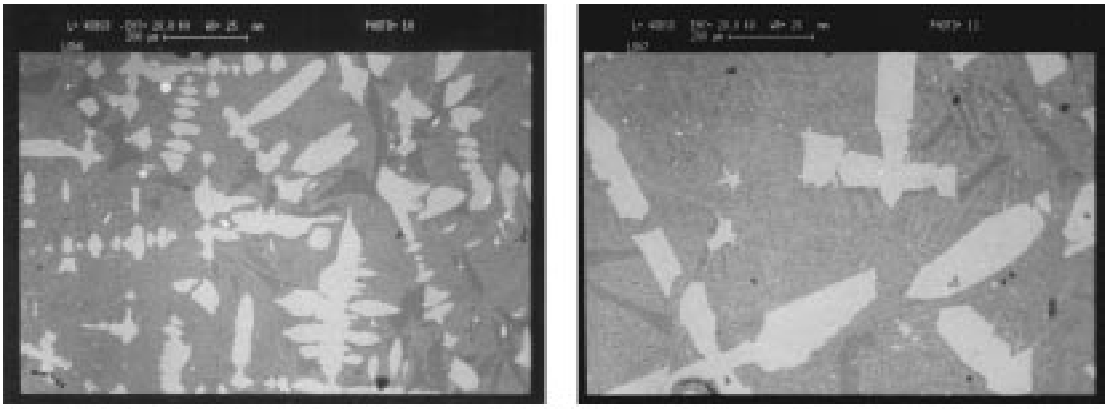
$$\alpha\bar{r}^3 = A(T)\left(1 - e^{-b/\alpha^p}\right) \tag{6}$$

where $A(T)$ is the value of $\alpha\cdot\bar{r}^3$ when $\alpha = 0$. The b and p can be obtained from the experimental results shown in Fig. 3,

$$b = 1.34\exp[-1.44/(1693-T)] \tag{7}$$

$$p = 0.675 \tag{8}$$

Coarsening of precipitate particle is a commonly observed microstructure phenomenon in precipitate process [10]. For equilibrium process, Coarsening occurs by the growth of larger precipitates at the expense of smaller ones with the total precipitate volume being conserved. Average radius of precipitate phase, $\bar{r}$ can be described by the following equation [11],



(a)

(b)

Figure 3 The effects of cooling rates on the morphology of perovskite. (a) 5 K/min; (b) 0.5 K/min. (Backscattered electron images; the bright dendrites are the perovskite phase).

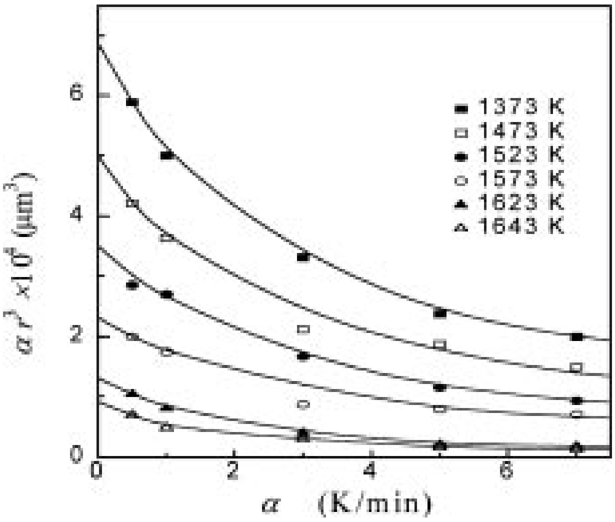


Figure 4 The variations of $\alpha \cdot \bar{r}^3$ against α.

$$\frac{\mathrm{d}\bar{r}^3}{\mathrm{d}t} = k(T) \tag{9}$$

where t is aging time and k(T) is a coarsening parameter, which is related to temperature only.

For non-isothermal process, the system close to equilibrium states when $\alpha \to 0$. The following equation can be derived

$$\alpha\bar{r}^3 = \int_{T_0}^{T} k(T_1)\,\mathrm{d}T_1 \tag{10}$$

where T_0 is the temperature of perovskite phase starting to precipitate. The above integral item is relative to temperature only. It is shown that $\alpha\bar{r}^3$ does close to a limited value irrelative to α when α close to zero. This result is accordance with the experimental results (shown in Fig. 3) and the conclusion of Equation 10.

4. Conclusion

Precipitate and growth kinetics of perovskite phase in CaO-TiO_2-SiO_2-Al_2O_3-MgO system show that cooling rate have important effect on precipitate and growth of perovskite phase. Lower cooling rate is in favor of precipitate of perovskite phase and make the crystal size increase by the growth of larger precipitates at the expense of smaller ones. The relative volume fraction of perovskite phase can be described by the following equation: $x' = 1 - \exp(-k/\alpha^n)$ Where n = 0.407, $k = 1.58\exp[-1.32/(1693 - T)]$; Average crystal radius can be approximately described by the equation, $\alpha\bar{r}^3 = A(T)[1 - \exp(-b/\alpha^p)]$, where p = 0.675, $b = 1.34\exp[-1.44/(1693 - T)]$.

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