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Kinetics of non-isothermal precipitation process of perovskite phase in oxidized Ti-bearing blast furnace slag

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Abstract: Kinetics of non-isothermal precipitation process and crystal growth of perovskite phase in oxidized Ti-bearing slag were investigated. The oxidized slag was obtained by blowing the air into the molten Ti-bearing blast furnace slag through a lance. The experimental results show that the cooling rate has important effect on precipitation and growth of perovskite phase in oxidized slag; the lower cooling rate is in favor of not only the increase of the volume fraction of perovskite phase, but also the growth of perovskite phase grain sizes. The particle coarsening in non-isothermal process has important effect on the crystal growth of perovskite phase. The relative volume fraction of perovskite phase could be approximately described by JMAK equation, and the experiential expression of the average crystal radius of perovskite phase was also obtained.

Key words: Ti-bearing slag; oxidation; crystallization; kinetics

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1 Introduction

China is rich in mineral resources of titanium, 92.4% of which is vanadium-titanium bearing magnetite, deposited mostly around the southwestern part. About 53% titanium is in the iron concentrate after mineral processing, after smelting process the blast furnace slag containing 20%−22% TiO_2 is produced[1]. Several mineral processing and metallurgical processes have been proposed for treating the slag[2−4], however, owing to the dispersed distribution of titanium component in various mineral phases, and very fine grains (<10 μm) and complex interfacial combination, the applications of these processes to separate and extract titanium from the slag may result in poor recovery and high cost.

If the molten slag could be treated after it effused from blast furnace, most of the titanium component could be concentrated in only one mineral phase which could grow up enough, and then this mineral phase was separated from the slag by mineral dressing method. Therefore, the slag would become the raw material for extracting titanium instead of a waste product. Fortunately, based on the several studies and practices in a pilot plant on the slag[5−7], by blowing air into the molten slag, most of the titanium component could be enriched into the perovskite phase which could grow and coarsen through the oxidation together with heat treatment. It is well known that the cooling rate of molten system plays a key role in precipitating characteristics of the crystalline phase, in other words, the cooling rate also influences the precipitation and growth of perovskite phase in molten slag. LI et al[8] have studied the kinetics of non-isothermal precipitation process of the perovskite phase in the $CaO\text{-}TiO_2\text{-}SiO_2\text{-}Al_2O_3\text{-}MgO$ system. LI et al[9] have investigated the selective enrichment of Ti component in Ti-bearing blast furnace slag and precipitation behavior of perovskite phase. LOU et al[10] have studied the kinetics of perovskite phase precipitate in slag bearing titanium. However, all of the aforementioned studies have mainly been aimed at the deoxidized Ti-bearing slag, and the kinetics of perovskite phase in oxidized Ti-bearing slag has rarely been reported.

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Industrial processes often depend on the kinetic behavior of systems undergoing phase transformations under non-isothermal conditions. In order to obtain further information about the precipitation process of the perovskite phase, it is necessary to study the kinetics of non-isothermal precipitate process of perovskite phase in slag oxidized by air.

2 Experimental

2.1 Slag preparation

The slag in this study was the bottom slag of a blast furnace in Xichang Iron and Steel Company. About 1.2 t molten slag was injected into a designed slag ladle and then a lance was used to blow air into the molten slag for 15 min. Air flow to the slag was controlled and kept at 5×10^{-4} m^3/s by rotor meter situated between the ladle and the gas supply equipment. During this process, the temperature of slag was measured by disposable thermocouples. The cooling slag obtained after these treatments was called oxidized slag.

2.2 Remelting treatment of oxidized slag

The remelting experiments were carried out in a vertical $MoSi_2$ furnace fitted with a type R thermocouple, which was controlled by the Shimaden SR–53 temperature programmed control instrument. The temperature accuracy was within ±3 K. The oxidized slag (the chemical composition is listed in Table 1) was remelted in a platinum crucible under purified argon atmosphere at 1 723 K for 40 min in order to make it fully melt and then make it cool at required cooling rates. In this process, the samples were obtained by water quench method at the designed temperature so as to know the in situ phase status.

Table 1 Chemical composition of oxidized slag (mass fraction, %)

CaO	MgO	TiO_2	Al_2O_3	SiO_2	V_2O_5	Fe_2O_3	MnO	Others
28.98	6.21	21.17	11.05	27.15	0.22	4.35	0.49	0.38

After being polished, the microstructures of the slag samples were characterized by metallographic microscopy. The average grain size and volume fraction of perovskite phase were determined on a Quantime520 image analyzer by the line intercept method (average of 15 fields).

3 Results and discussion

3.1 Oxidization behavior of molten slag

Ti-bearing slag is deoxidized slag, in which a large amount of low valency titanium exists, which accounts for 1/4−1/5 of the total titanium concentration. When air was blown in, the low valency titanium ions and Ti(C, N) could be oxidated into Ti^{4+}, at the same time, the other reduced components in slag such as C, FeO and S also could be oxidized. The released heat during oxidization process would raise the temperature of molten slag. Fig.1 shows the relationship between the temperature of molten slag and oxidizing time. It can be seen that with the oxidizing time increase, the temperature of molten slag increases to the maximum at oxidizing time of 4−6 min, after that the temperature decreases with the increase of oxidizing time. The rising of molten slag temperature through oxidizing treatment provides a crucial condition for extracting titanium component from Ti-bearing slag economically.

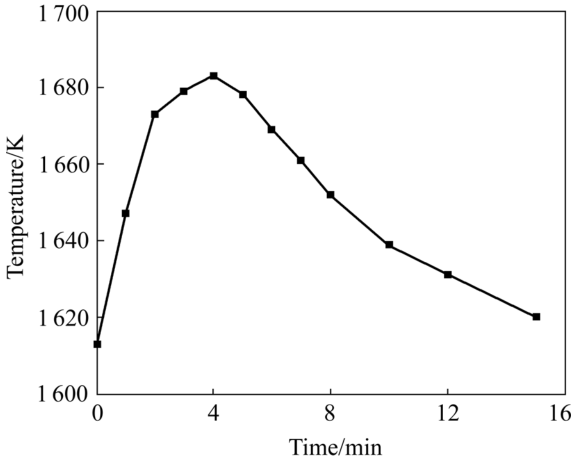

Fig.1 Relationship between temperature of molten slag and oxidizing time

After oxidizing, the titanaugite phase, Ti-rich diopside phase, and Ti(C, N) phase disappear; only the perovskite phase as a main Ti-containing crystalline phase and the $MgAl_2O_4$ spinel phase can exist, in other words, the titanium component in slag can be selectively enriched into the perovskite phase through oxidation[11].

3.2 Transformation kinetics of perovskite phase

Fig.2 shows the morphology of perovskite phase at a cooling rate of 0.5 K/min. Through the morphology of the quenched samples, it can be seen obviously that the early precipitating perovskite phase crystals are fine dispersing floc or spicule. These small crystals melt down and grow into column crystals along with the prolonging of time as well as the descending of temperature.

Fig.3 illustrates the volume fraction of perovskite phase as a function of temperature from image analysis results at cooling rates of 0.5−5 K/min. It can be seen that perovskite phase in oxidized Ti-bearing slag begin to precipitate at about 1 663 K. With the cooling rate decrease, the volume fraction increases. As it is

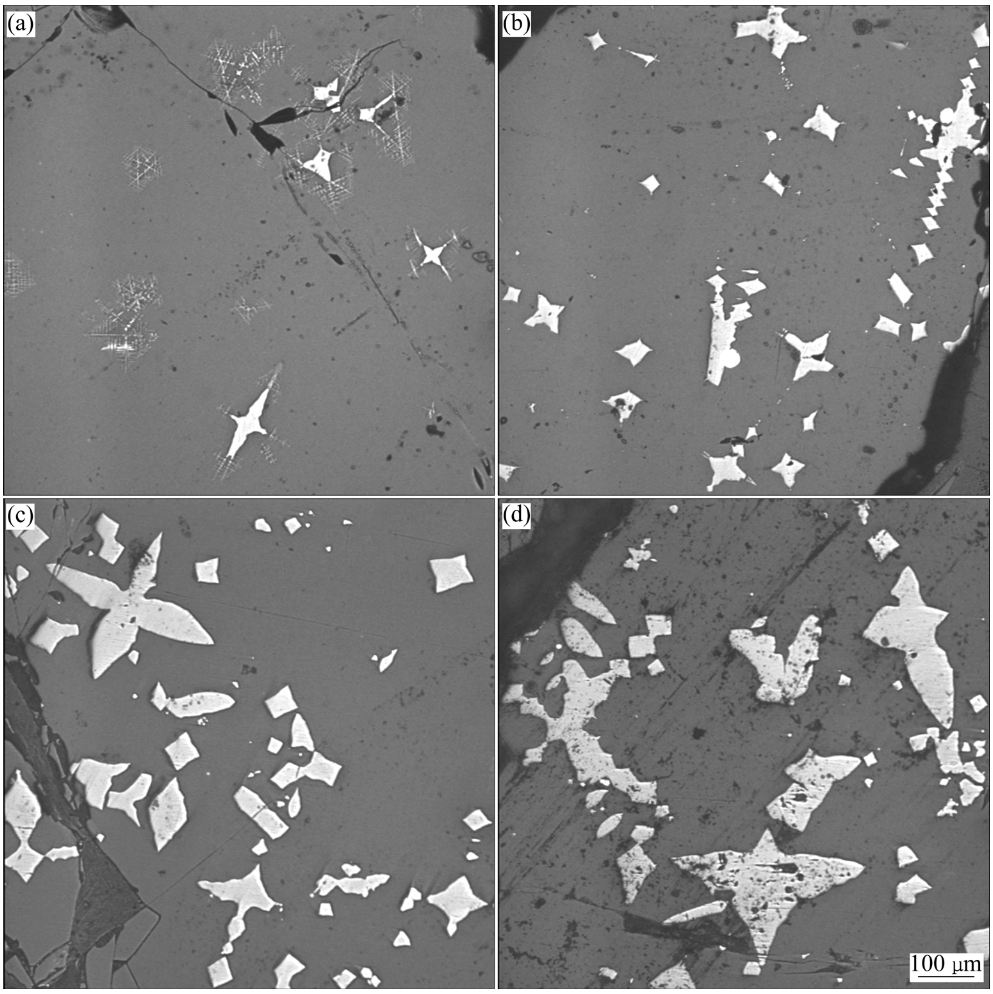

Fig.2 Micrographs of quenched oxidized slag with cooling rate of 0.5 K/min at different temperatures: (a) 1 643 K; (b) 1 623 K; (c) 1 563 K; (d) 1 503 K

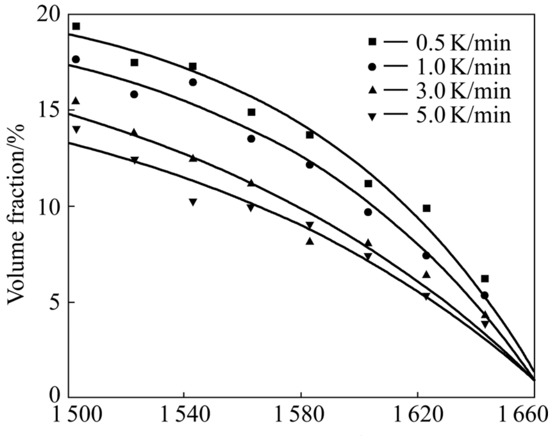

Fig.3 Relation between temperature and volume fraction of perovskite phase

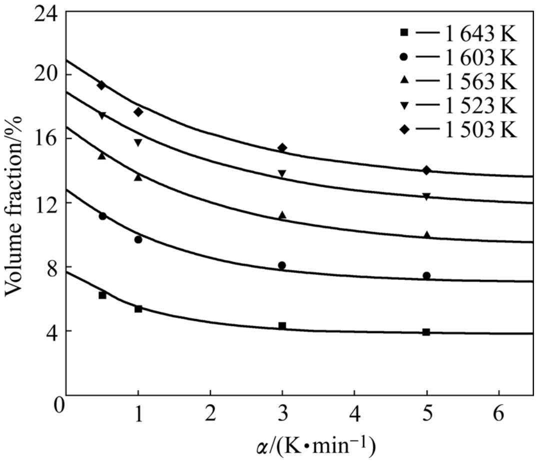

Fig.4 Variations of volume fraction against cooling rate

well-known, in diffusion controlled transformation, lower cooling rate is in favor of the system achieving equilibrium state and making the volume fraction achieving the maximum value. Fig.4 shows the variations of perovskite phase volume fraction with the cooling rate. It can be seen that the volume fraction of perovskite phase closes to a maximal value when *α* closes to zero, which indicates the slag system is achieving equilibrium state. It is also indicated that at the same cooling rate, the lower the temperature, the higher the volume fraction of the perovskite phase is.

To obtain further information on the crystallization kinetics, the following JMAK experience equation is applied, which is often used for precipitation kinetics process in molten slag[12−14].

$$X=\frac{f(\alpha,T)}{f(0,T)}=1-\exp(-\frac{c}{a^{n}}) \quad (1)$$

where X is relative transformed fraction, %; $f(\alpha, T)$ is the volume fraction of perovskite phase at temperature T when the cooling rate is α; $f(0, T)$ is the volume fraction of perovskite phase at temperature T when the cooling rate is zero; n is a numerical constant; $c=C\exp\cdot\{-1.052nE/[R(T_0-T)]\}$, where C is a numerical constant; T_0 is the temperature of perovskite phase starting to precipitate in slag, K; E is the activation energy for crystal growth, J/mol. The value c and n can be calculated by the following equation:

$$\ln[-\ln(1-X)]=-n\ln\alpha+\ln c \quad (2)$$

The experimental results show that the curves of $\ln[-\ln(1-X)]$ against $\ln\alpha$ are straight lines and the slopes are approximately the same[15], which illustrates that the precipitate process of perovskite phase can be described by JMAK equation. From the experimental results, the value c and n can be got, n=0.356, $c=2.07\exp[-10.72/(1\,663-T)]$.

3.3 Growth kinetics of perovskite phase

Fig.5 shows the equivalent diameter of perovskite against temperature at different cooling rate. It can be seen that the low cooling rate is in favor of the growth and coarsening of perovskite phase grain size.

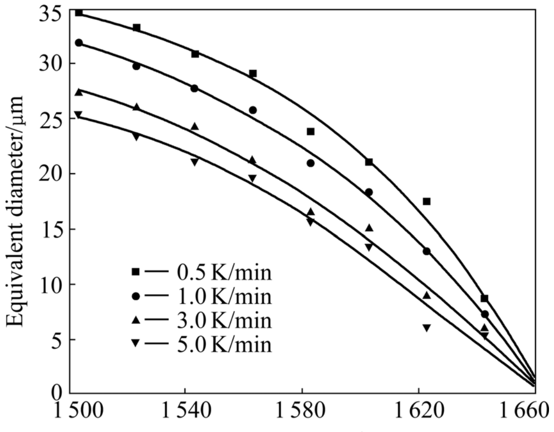

Fig.5 Equivalent diameter of perovskite against temperature

Fig.6 shows the variations of $\alpha\bar{r}^3$ against α at different temperatures, α is the cooling rate (K/min) and $\bar{r}$ is the average crystal radius of perovskite (μm). It can be seen that when $\alpha\rightarrow 0$, $\alpha\bar{r}^3$ is close to a limited value, while α increases, $\alpha\bar{r}^3$ increase promptly. This result can be approximately described by the following equation:

$$\alpha\bar{r}^3=A(T)[1+\exp(-\frac{b}{a^{p}})] \quad (3)$$

where $A(T)$ is the value of $\alpha\bar{r}^3$ when α=0. p and b can be obtained from the experimental results, p=−0.645, $b=-0.987\exp[-10.78/(1\,663-T)]$.

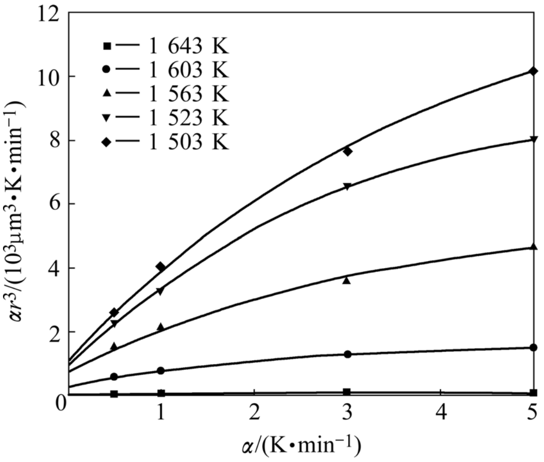

Fig.6 Variations of $\alpha\bar{r}^3$ against α

It is found based on the experimental results and phenomenon that there are two factors that influence the growth rate of perovskite particles in oxidized Ti-bearing slag. One is the rate of nucleation and variation of the fraction transformed to perovskite, and the other is the coarsening arising from the growth of larger perovskite at the expense of smaller ones.

For non-isothermal process, the relation of average radius of precipitate phase $\bar{r}$ and the cooling rate α can be described by the following equation[8]:

$$\alpha\bar{r}^3=\int_{T_0}^{T}k(T)\mathrm{d}T \quad (4)$$

where $k(T)$ is a coarsening parameter, which is related to temperature only; T_0 is the temperature of precipitate phase starting to precipitate. From Eqn.(4), it can be seen that the integral item is relative to temperature only, which shows that $\alpha\bar{r}^3$ is close to a limited value irrelative to α when α is close to zero. This result agrees with the experimental results shown in Fig.6.

4 Conclusions

1) Cooling rate has important effect on the precipitation and growth of the perovskite phase. Lower cooling rate is in favor of not only the increase of the volume fraction of the perovskite phase, but also the growth of perovskite phase grain sizes.

2) The precipitation kinetics of perovskite in oxidized Ti-bearing slag can be approximately described by the JMAK equation, $X=1-\exp(-c/\alpha^{n})$, where n=0.356,

$c=2.07\exp[-10.72/(1\,663-T)]$.

3) The average crystal radius of perovskite in oxidized Ti-bearing slag can be approximately described by the equation, $\alpha\bar{r}^3=A(T)[1+\exp(-b/\alpha^p)]$, where $p=-0.645$, $b=-0.987\exp[-10.78/(1\,663-T)]$.

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