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Isothermal precipitation and growth process of perovskite phase in oxidized titanium bearing slag

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Abstract: The isothermal precipitating behavior of perovskite phase in oxidized titanium bearing slag was studied by quenching method. The kinetics of precipitating process and crystal growth of perovskite phase was analyzed. The results show that the precipitating and growth of perovskite are non-equilibrium process at the beginning of isothermal treatment. There are two factors influencing the growth rate of perovskite phase on non-equilibrium condition, one is the supersaturation concentration of perovskite and the other is the coarsening arising from the growth of larger perovskite at the expense of smaller ones. The precipitation kinetics of perovskite phase can be nearly described by the JMAK equation.

Key words: titanium bearing slag; perovskite phase; kinetics; non-equilibrium process

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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]. This titanium bearing blast furnace slag is an important man-made resource. Several mineral and metallurgical processes have been tested for treating the slag, such as gravity separation, flotation separation combined with magnetic separation, melting reduction and hydro-metallurgy[2−5]. However, due to the dispersed distribution of Ti component in various fine grained (<10 μm) mineral phases with the complex interfacial combination, the application of these processes to separate and extract titanium from the slag may results in poor recovery and high cost. This slag has been already accumulated 50 million tons so far, resulting in a waste of titanium resources and environment pollution.

Based on several studies and practices in a pilot plant on the slag[6−13], when the molten slag was oxidized, most of the Ti component in slag could be enriched into the perovskite phase. The key to exploit and use the slag lies in separation of perovskite efficiently. The precipitation of perovskite phase in molten slag is a complex dynamics process, and attracts more attention with its gradually important application. LI et al[14] studied the kinetics of non-isothermal precipitation process of the perovskite phase in slag. The effect of heat-treatment on precipitation behavior of perovskite phase was investigated by LI et al[15]. LOU et al[16] studied the isothermal growth of perovskite phase in the titanium bearing slag. However, all of the aforementioned studies mainly aimed at the deoxidized titanium bearing slag, and the precipitation behavior of perovskite phase in oxidized slag was rarely reported. In this work, the transformation of the perovskite phase at isothermal process in the oxidized slag was studied.

2 Experimental

The oxidized titanium bearing slag was made by the following procedures. The experiment was completed in

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Xichang Iron and Steel Company of China. About 1.2 t molten bottom slag effused from a blast furnace was injected into a designed slag ladle and then a lance was used to blow air into the molten slag for 15 min. Then the slag was cooled at a rate of 4 K/min. The chemical composition of the oxidized slag is listed in Table 1.

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

CaO	MgO	TiO_2	Al_2O_3	SiO_2
28.98	6.21	21.17	11.05	27.15

V_2O_5	Fe_2O_3	MnO	Others
0.22	4.35	0.49	0.38

The reheating experiments were carried out in a vertical $MoSi_2$ furnace fitted with an R-type thermocouple, which was controlled by a Shimaden SR-53 temperature programmed control instrument. The temperature accuracy was within ±3 K. 200 g oxidized slag was reheated in a molybdenum crucible under purified argon atmosphere at 1 723 K for 30 min in order to make it fully melted, and then the slag was rapidly cooled down at a rate of 20 K/min to the required temperature for isothermal treatment. The samples were obtained by water quench method at different time so as to know the in situ phase status.

After being polished, the microstructures of the slag samples were characterized by metallographic microscope. 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 Precipitation behavior of perovskite phase

The morphologies of quenched slag isothermally treated at 1 593 K are shown in Fig.1. It can be seen that a lot of perovskite crystal embryos have formed after isothermal treatment for 5 min. The early precipitating perovskite phase crystals are fine dispersing floc or spicule. These small crystals grow into column crystals along with the prolonging of time, and the number of crystal of perovskite phase decreases, the grain size enlarges as well as the perovskite precipitation content increases.

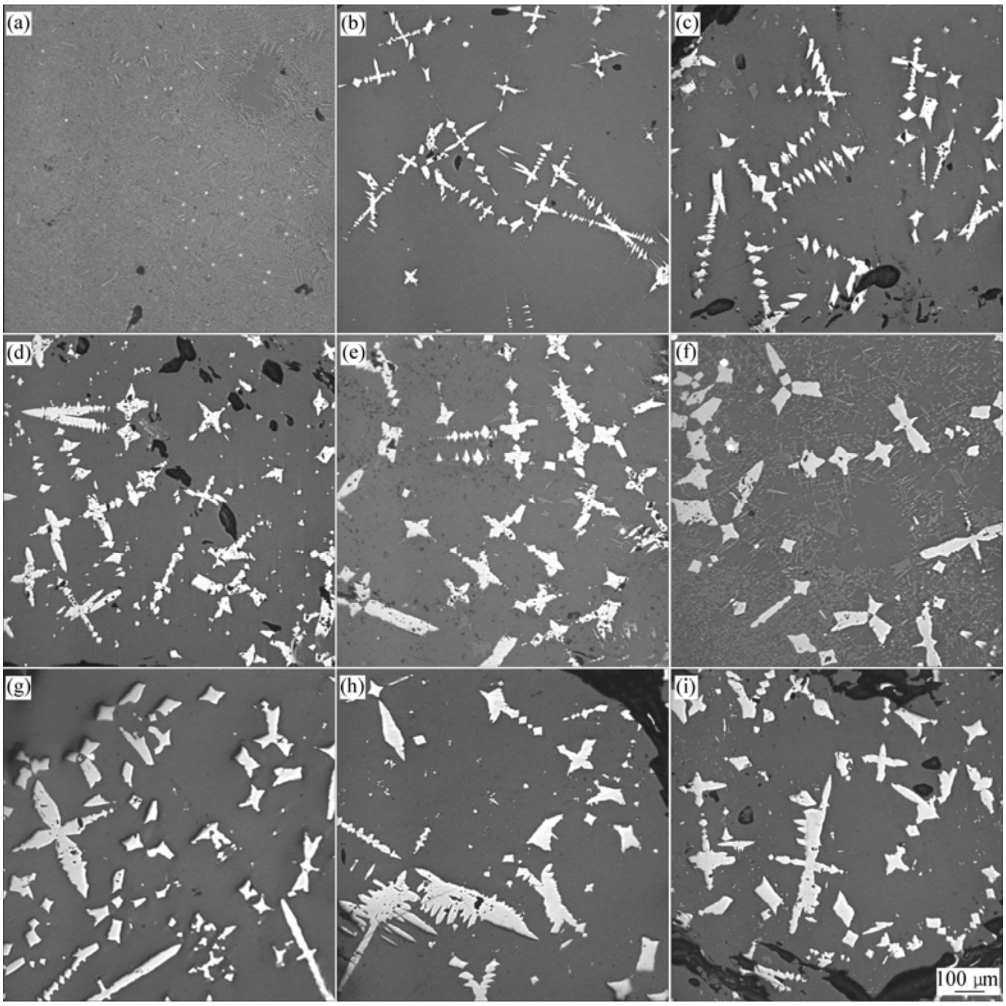

Fig.1 Micrographs of samples of slag heated at 1 593 K for 5 min (a); 10 min (b); 15 min (c); 20 min (d); 30 min (e); 50 min (f); 70 min (g); 90 min (h) and 110 min (i)

Fig.2 shows the variations of volume fraction of perovskite phase with the isothermal time. Obviously, with increasing isothermal treatment time, the volume fraction of perovskite phase increases rapidly, however, when the isothermal time reaches 70 min, the perovskite precipitation content is unchangeable. Furthermore, it is also indicated that the higher the isothermal temperature, the lower the volume fraction of perovskite phase is. In fact, at the beginning of isothermal process, the precipitation of perovskite is a non-equilibrium process which is caused by the supersaturation concentration of perovskite in the molten slag.

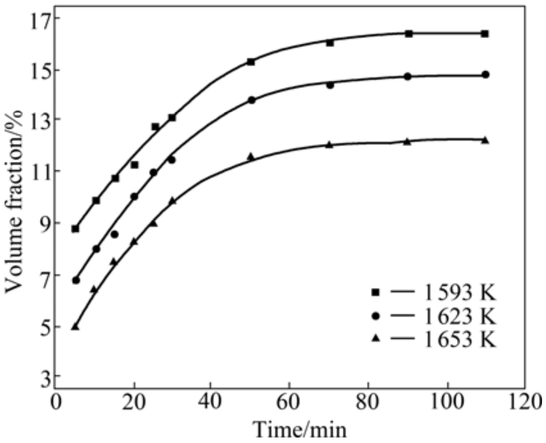

Fig.2 Variation of volume fraction of perovskite phase with isothermal time

Fig.3 shows the variation of x with the aging time, where x is a ratio of perovskite phase volume fraction at a certain isothermal time to the perovskite phase volume fraction at equilibrium state. When $x < 1$, the precipitation of perovskite phase is in the dynamic region and when $x=1$, the precipitation is in the quasi-equilibrium state region. It can be seen from Fig.3 that the transformed fraction of perovskite phase for the three different isothermal treatment processes all approach to 1 when the aging time is beyond 70 min. To obtain further information on the precipitation kinetics, the JMAK equation is applied[17]:

$$x(t)=1-\exp(-kt^n) \quad (1)$$

where k is the dynamics constant, n is the time factor. From Eqn.(1), the following equation can be derived:

$$\ln[-\ln(1-x(t))]=n\ln t+\ln k \quad (2)$$

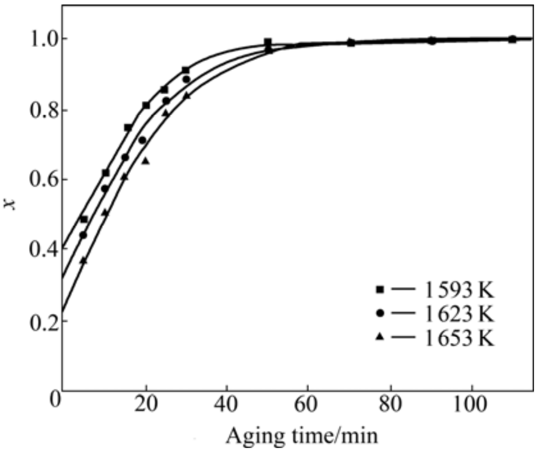

Fig.3 Variation of transformed fraction of perovskite phase with aging time

Fig.4 shows the experimental results of $\ln[-\ln(1-x(t))]$ against $\ln t$ at temperatures of 1 593, 1 623 and 1 653 K. It can be seen that the curves are straight lines and the slopes are almost the same, which illustrates that the precipitating process of perovskite can be described by Eqn.(1).

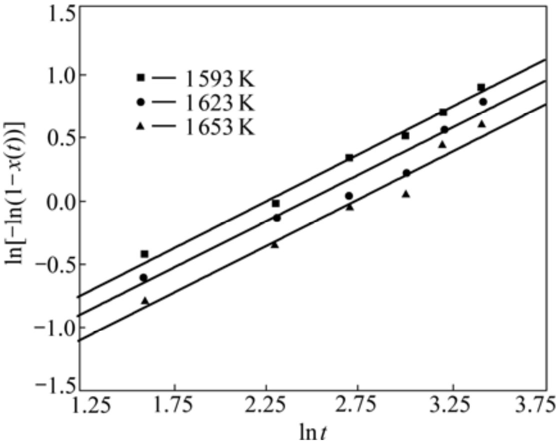

Fig.4 Plot of $\ln[-\ln(1-x(t))]$ against $\ln t$

3.2 Growth behavior of perovskite phase

Fig.5 shows the variation of average grain size of perovskite with aging time. It can be seen from Fig.5 that the growth of perovskite grain is quicker at the beginning of isothermal treatment than that after isothermal treating process. At the beginning stage, the system is in non-equilibrium state. There are two factors influencing the

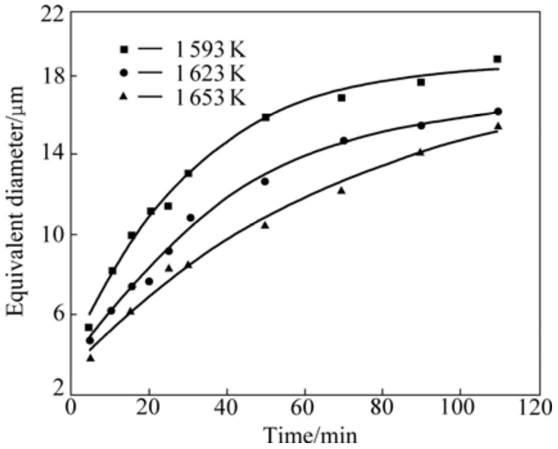

Fig.5 Variation of grain diameters with aging time

average growth rate of perovskite grain size. One is the rate of nucleation and the variation of the transformed fraction to perovskite, the other is the coarsening arising from the growth of larger perovskite grain at the expense of smaller ones.

The growth of average crystal radii in non-equilibrium system can be described by the following equation[16]:

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\bar{r}^3}{x}\right)=\frac{k_1}{x}-k_2 \qquad (3)$$

where k_1 and k_2 are constant; $\bar{r}$ is the average perovskite crystal radii; x is the relative transformed fraction.

The experimental results of the variation of $\bar{r}^3/x$ with $1/x$ are shown in Fig.6, which reveals that the curves are straight lines. Obviously, the growth of perovskite in the non-equilibrium system in oxidized titanium bearing slag can also be described by Eqn.(3).

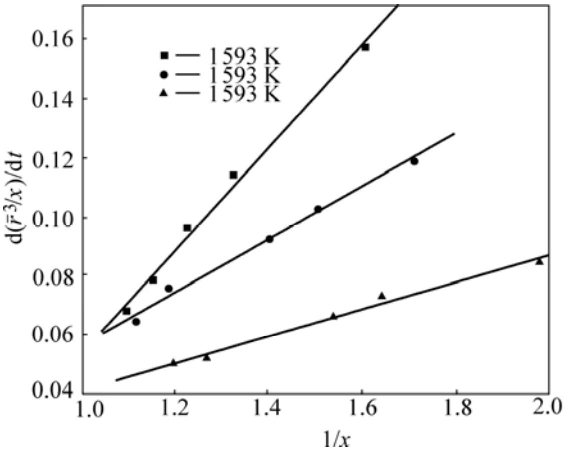

Fig.6 Variation of $\bar{r}^3/x$ with $1/x$

4 Conclusions

1) The precipitation and the growth of perovskite are in the non-equilibrium process at the beginning of isothermal treatment.

2) The supersaturation concentration and coarsening influence the growth rate of perovskite phase in non-equilibrium condition.

3) The precipitation kinetics of perovskite phase can be nearly described by the JMAK equation. The variation of $\bar{r}^3/x$ to the relative transformed fraction of perovskite phase is illustrated as straight line during the non-equilibrium process.

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