

Jintao Gao
Zhancheng Guo

Super Gravity Metallurgy

Separation of Valuable Component
in Metallurgical Slag

 冶金工业出版社
Metallurgical Industry Press

 Springer

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ISBN 978-981-99-4648-8 ISBN 978-981-99-4649-5 (eBook)
<https://doi.org/10.1007/978-981-99-4649-5>

Jointly published with Metallurgical Industry Press

The print edition is not for sale in China (Mainland). Customers from China (Mainland) please order the print book from: Metallurgical Industry Press.

ISBN of the Co-Publisher's edition: 978-7-5024-9117-8

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Preface

The essence of high-temperature metallurgical process is chemical reaction and material separation. From the thermochemical reaction rate point of view, chemical reaction is not the limiting link in high-temperature metallurgical process, while the material transfer and phase separation rate are often the main factors determining the production efficiency of high-temperature metallurgy. Under the action of gravity, the phase density difference $\Delta\rho$ is the basis of natural convection and relative motion, and the gravity difference is the decisive factor of driving force of phase separation $\Delta\rho g$. Therefore, the super gravity field can significantly enhance the material transfer and phase separation in high-temperature metallurgical process.

China is rich in multi-element associated complex ore resources, including vanadium titanomagnetite, high phosphorus hematite, rare earth complex ore, ludwigite, etc. For a long time, China's complex symbiotic ores mainly rely on the main process of blast furnace ironmaking and converter steelmaking to smelt and extract Fe resources, while the utilization of other symbiotic components is very limited, resulting in a large number of symbiotic elements (Ti, V, B, REEs, P, etc.) transferred into the metallurgical slag, and a large number of metallurgical slags containing various symbiotic elements are produced in the high-temperature smelting process. Due to the complex phase structure and composition formed in the solidification process of high-temperature smelting slag, it is difficult to achieve the effective separation and recovery of various valuable components with fine, scattered, and miscellaneous characteristics in the metallurgical slag by traditional beneficiation methods.

This book systematically summarizes the research results of the authors in the field of selective separation of various valuable components in metallurgical slag via super gravity over the years. This book consists of seven chapters. Chapter 1 introduces the principles, apparatus, research methods of super gravity high-temperature metallurgy, and the characteristics for metallurgical slag produced from various complex ores. Chapters 2–7 focus on the selective crystallization and separation of Ti, B, REEs, P, and V from Ti-bearing slag, B-bearing slag, RE-bearing slag, RE-concentrate, P-bearing slag, and V-bearing slag, respectively. Chapters 2–7 contain the thermo-

dynamics and kinetics for selective crystallization of Ti, B, REEs, P, and V and the selective separation of various Ti, B, REEs, P, and V phases from metallurgical slag melts via super gravity.

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Contents

1	General Introduction	1
1.1	Super Gravity High-Temperature Metallurgy	1
1.1.1	Effect of Super Gravity on Phase Separation in High-Temperature Metallurgy	1
1.1.2	Apparatus for Super Gravity High-Temperature Metallurgy	3
1.1.3	Analytical and Characterization Methods for Super Gravity High-Temperature Metallurgy	5
1.2	Super Gravity Metallurgy in Selective Separation of Valuable Component from Metallurgical Slag	6
1.2.1	Introduction for Metallurgical Slag of Complex Ores	6
1.2.2	Selective Crystallization and Separation of Valuable Component in Metallurgical Slag by Super Gravity	13
	References	16
2	Selective Crystallization and Separation of Ti in Ti-Bearing Slag	19
2.1	Selective Crystallization and Separation of Perovskite in Ti-Bearing Slag	22
2.1.1	Thermodynamic Analysis for Crystallization of Ti in CaO–TiO ₂ –SiO ₂ –Al ₂ O ₃ –MgO System	22
2.1.2	Crystallization Behavior of Perovskite in CaO–TiO ₂ –SiO ₂ –Al ₂ O ₃ –MgO System	22
2.1.3	Crystallization and Growth Kinetics of Perovskite in CaO–TiO ₂ –SiO ₂ –Al ₂ O ₃ –MgO System Under Super Gravity	26
2.1.4	Motion Behavior of Perovskite in CaO–TiO ₂ –SiO ₂ –Al ₂ O ₃ –MgO System Under Super Gravity	35

2.1.5	Separation of Perovskite from CaO–TiO ₂ –SiO ₂ –Al ₂ O ₃ –MgO System by Super Gravity	43
2.1.6	Motion Behavior of Perovskite in Ti-Bearing Blast Furnace Slag Under Super Gravity	46
2.1.7	Separation of Perovskite from Ti-Bearing Blast Furnace Slag by Super Gravity	48
2.2	Phase Transformation of Ti and Separation of Rutile in Ti-Bearing Slag	53
2.2.1	Thermodynamic Analysis for Phase Transformation of Ti in CaO–TiO ₂ –SiO ₂ –Al ₂ O ₃ –MgO System	54
2.2.2	Phase Transformation Behavior of Ti to Rutile in CaO–TiO ₂ –SiO ₂ –Al ₂ O ₃ –MgO System	54
2.2.3	Crystallization Behavior of Rutile in CaO–TiO ₂ –SiO ₂ –Al ₂ O ₃ –MgO System	58
2.2.4	Separation of Rutile from CaO–TiO ₂ –SiO ₂ –Al ₂ O ₃ –MgO System by Super Gravity	61
2.2.5	Selective Crystallization of Rutile in Ti-Bearing Blast Furnace Slag	64
2.2.6	Separation of Rutile from Ti-Bearing Blast Furnace Slag by Super Gravity	68
2.3	Separation of Anosovite from Ti-Bearing Slag in Reducing Atmosphere	72
2.3.1	Thermodynamic Analysis for Phase Transformation of Ti in CaO–TiO ₂ –SiO ₂ –Al ₂ O ₃ –MgO System Under Reducing Atmosphere	72
2.3.2	Crystallization Behavior of Anosovite in CaO–TiO ₂ –SiO ₂ –Al ₂ O ₃ –MgO System	73
2.3.3	Separation of Anosovite from CaO–TiO ₂ –SiO ₂ –Al ₂ O ₃ –MgO System by Super Gravity	75
2.3.4	Separation of Anosovite from Ti-Bearing Blast Furnace Slag by Super Gravity	79
2.4	Carbothermal Reduction of Ti and Separation of Ultrafine TiC Powders in Ti-Bearing Slag	82
2.4.1	Thermodynamic Analysis for Carbothermal Reduction of Ti	83
2.4.2	Carbothermal Reduction of Ti to TiC in Ti-Bearing Blast Furnace Slag	84
2.4.3	Crystallization Behavior of Carbonized Ti-Bearing Slag	85
2.4.4	Motion Behavior of Ultrafine TiC Powders in Carbonized Ti-Bearing Slag Under Super Gravity	88

2.4.5	Separation of Ultrafine TiC Powders from Carbonized Ti-Bearing Slag by Super Gravity	91
2.5	Amplification Study for Selective Separation of Ti in Ti-Bearing Slag by Super Gravity	96
2.5.1	Super Gravity Metallurgy Apparatus for Amplification Study	97
2.5.2	Amplification Study for Separation of Perovskite from Ti-Bearing Slag by Super Gravity	97
	References	100
3	Selective Crystallization and Separation of B in B-Bearing Slag	105
3.1	Competitive Crystallization of B, Si, and Mg in B-Bearing Slag ...	107
3.1.1	Thermodynamic Analysis for B, Si, and Mg in $\text{MgO-SiO}_2\text{-B}_2\text{O}_3\text{-CaO-Al}_2\text{O}_3$ System	107
3.1.2	Competitive Crystallization Behavior of B, Si and Mg in $\text{MgO-SiO}_2\text{-B}_2\text{O}_3\text{-CaO-Al}_2\text{O}_3$ System	108
3.2	Two-Stage Separation of Olivine and Suanite in B-Bearing Slag	111
3.2.1	Stage 1: Primary Separation of Olivine and B-Rich Slag by Super Gravity	112
3.2.2	Crystallization Behavior of B and Mg in Separated B-Rich Slag	114
3.2.3	Stage 2: Further Separation of Suanite from B-Rich Slag by Super Gravity	117
3.2.4	Characterization for the Separated Olivine and Suanite	118
3.3	Selective Separation of Last Precipitated Suanite in B-Bearing Slag	121
3.3.1	Thermodynamic Analysis for Crystallization of B in $\text{MgO-SiO}_2\text{-B}_2\text{O}_3\text{-CaO-Al}_2\text{O}_3$ System	122
3.3.2	Selective Crystallization of Last Precipitated Suanite in B-Bearing Slag	122
3.3.3	Sept I: Primary Separation of the Mixture of Suanite and Olivine from B-Bearing Slag by Super Gravity	125
3.3.4	Mineral Evolution of Suanite and Olivine with Temperature	127
3.3.5	Sept II: Further Separation of Molten Suanite and Olivine Crystal	128
3.3.6	Characterization for Separated Suanite	131
3.4	Crystalline Phase Transformation and One-Step Separation of Suanite in B-Bearing Slag	133
3.4.1	Thermodynamic Analysis for Crystalline Phase Transformation in $\text{B}_2\text{O}_3\text{-SiO}_2\text{-MgO-CaO-Al}_2\text{O}_3$ System	133
3.4.2	Primary Crystalline Phase Transformation for Enriching Amorphous B into Suanite	133

3.4.3	Separation of Suanite from B-Bearing Slag by Super Gravity	137
3.4.4	Characterization for the Properties of Separated Suanite	140
References		145
4	Selective Crystallization and Separation of REEs in RE-Bearing Slag	149
4.1	Selective Crystallization of REEs in RE-Bearing Slag	150
4.1.1	Isothermal Phase Diagram of CaO–SiO ₂ –CaF ₂ –Ce ₂ O ₃ System	150
4.1.2	Phase Equilibria of RE-Phase in CaO–SiO ₂ –CaF ₂ –Ce ₂ O ₃ System	160
4.1.3	Isothermal Crystallization and Growth Kinetics of RE-Phase in CaO–SiO ₂ –CaF ₂ –Ce ₂ O ₃ System	163
4.2	Selective Separation of REEs in RE-Bearing Slag	167
4.2.1	Motion Behavior of Cefluosil in RE-Bearing Slag Under Super Gravity	167
4.2.2	Separation of Cefluosil from RE-Bearing Slag by Super Gravity	172
References		176
5	Selective Crystallization and Separation of REEs in RE-Concentrate	179
5.1	Mineral Evolution and Selective Concentration of Cerium Oxyfluoride in RE-Concentrate	181
5.1.1	Mineral Evolution and Enriching of REEs in RE-Concentrate	181
5.1.2	Selective Concentration of Cerium Oxyfluoride in RE-Concentrate Under Super Gravity	184
5.2	Mineral Reconstruction and Selective Separation of Cerium Oxyfluoride in Reductive Atmosphere	188
5.2.1	Mineral Reconstruction and REEs Enrichment in RE-Concentrate Under Reductive Atmosphere	188
5.2.2	Selective Separation of Cerium Oxyfluoride from RE-Concentrate by Super Gravity	190
5.3	Stepwise Crystallization and Separation of REEs (Ce, La, Pr, Nd) in Concentrate	197
5.3.1	Stepwise Crystallization Behavior of REEs (Ce, La, Pr, Nd) in RE-Concentrate	197
5.3.2	Successive Concentration of REEs (Ce, La, Pr, Nd) in RE-Concentrate Under Super Gravity	199
5.3.3	Respective Separation of REEs (Ce, La, Pr, Nd) from RE-Concentrate by Super Gravity	205
References		210

6	Selective Crystallization and Separation of P in P-Bearing Slag	213
6.1	Selective Crystallization of C_2S-C_3P in $CaO-SiO_2-FeO-MgO-P_2O_5$ System	215
6.1.1	Thermodynamic Analysis for P in $CaO-SiO_2-FeO-MgO-P_2O_5$ System	215
6.1.2	Solid Solution Behavior of P in $CaO-SiO_2-FeO-MgO-P_2O_5$ System	215
6.2	Motion and Separation of C_2S-C_3P in $CaO-SiO_2-FeO-MgO-P_2O_5$ System	218
6.2.1	Motion Behavior of C_2S-C_3P in $CaO-SiO_2-FeO-MgO-P_2O_5$ System Under Super Gravity	218
6.2.2	Separation Behavior of C_2S-C_3P in $CaO-SiO_2-FeO-MgO-P_2O_5$ System by Super Gravity	228
6.3	Motion and Separation of C_2S-C_3P in Steelmaking Slag	231
6.3.1	Motion Behavior of C_2S-C_3P in Steelmaking Slag Under Super Gravity	232
6.3.2	Separation Behavior of C_2S-C_3P from Steelmaking Slag by Super Gravity	237
	References	240
7	Selective Crystallization and Separation of V in V-Bearing Slag	243
7.1	Selective Crystallization of V-Containing Spinel in $FeO-SiO_2-V_2O_3-TiO_2-CaO-MgO$ System	245
7.1.1	Thermodynamic Analysis for V in $FeO-SiO_2-V_2O_3-TiO_2-CaO-MgO$ System	245
7.1.2	Crystallization Behavior of V-Containing Spinel in $FeO-SiO_2-V_2O_3-TiO_2-CaO-MgO$ System	245
7.2	Selective Separation of V-Containing Spinel in V-Bearing Slag	247
7.2.1	Motion Behavior of V-Containing Spinel in V-Bearing Slag Under Super Gravity	247
7.2.2	Separation of V-Containing Spinel from V-Bearing Slag by Super Gravity	254
	References	259

Chapter 1

General Introduction



Abstract Reports the general introduction for super gravity high-temperature metallurgy. The principles, apparatus, and research methods for super gravity high-temperature metallurgy are introduced in Sect. 1.1. The characteristics for metallurgical slag produced from various complex ores are introduced, and a new method for selective crystallization and separation of valuable component in metallurgical slag by super gravity is proposed in Sect. 1.2.

1.1 Super Gravity High-Temperature Metallurgy

1.1.1 *Effect of Super Gravity on Phase Separation in High-Temperature Metallurgy*

The essence of high-temperature metallurgical process is chemical reaction and material separation. From the thermochemical reaction rate point of view, chemical reaction is not the limiting link in high-temperature metallurgical process, while the material transfer and phase separation rate are often the main factors determining the production efficiency of high-temperature metallurgy. Under the action of gravity, the phase density difference $\Delta\rho$ is the basis of natural convection and relative motion, and the gravity difference is the decisive factor of driving force of phase separation $\Delta\rho g$. Therefore, the super gravity field can significantly enhance the material transfer and phase separation in high-temperature metallurgical process [1].

Take a basic solid–liquid phase separation in high-temperature metallurgical process, for example. The variation laws of force and motion behavior of solid particles with different sizes and gravity coefficients in a typical metallurgical melt are studied. Considering that the common solid particles in the melt are generally subjected to three lateral forces in the condition of super gravity, including the centrifugal force far away from the centrifugal axis F_c (Eq. 1.1), the frictional resistance F_f (Eq. 1.2), and the buoyancy caused by centrifugation F_B (Eq. 1.3). Hence, the theoretical movement time for solid particles with different sizes in the melt under super gravity compared with that of normal gravity is conducted based on the theory of stratification and movement [2].

$$F_C = m \frac{v^2}{x} = m\omega^2 x = \rho V \omega^2 x \quad (1.1)$$

$$F_f = f \frac{dx}{dt} \quad (1.2)$$

$$F_B = \frac{m}{\rho} \rho_0 \omega^2 x \quad (1.3)$$

When $F_C = F_B + F_f$, the acceleration of the solid particle is zero, and the particle is shown to be an isokinetic motion, and the isokinetic velocity is as Eq. (1.4).

$$\frac{dx}{dt} = \frac{m \left(1 - \frac{\rho_0}{\rho}\right)}{f} \omega^2 x \quad (1.4)$$

According to the Stokes formula [3], the friction coefficient of the spheroidal particles f is as Eq. (1.5), and combined with the gravity coefficient as calculated according to Eq. (1.6), the complete movement time τ could be obtained as Eq. (1.7).

$$f = 6\pi \eta x \quad (1.5)$$

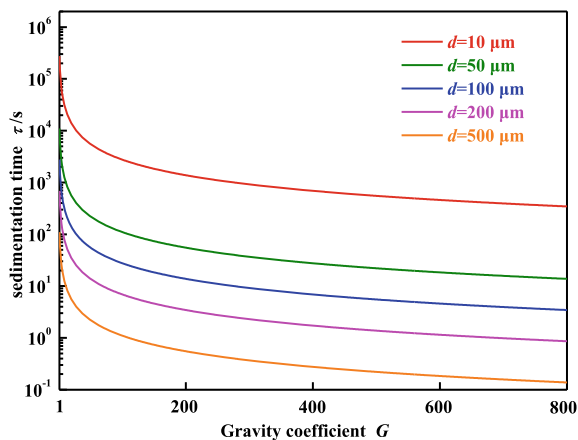
$$G = \frac{\sqrt{g^2 + (\omega^2 x)^2}}{g} = \frac{\sqrt{g^2 + \left(\frac{N^2 \pi^2 x}{900}\right)^2}}{g} \quad (1.6)$$

$$\tau = \frac{L}{\frac{dx}{dt}} = \frac{9\eta L \times 10^{-3}}{2g(\rho - \rho_0)d^2 G} \quad (1.7)$$

where m is the mass of solid particles, kg; v is the linear velocity, m/s; x is the distance from centrifugal axis to the center of sample, m; ω is the angular velocity, rad/s; ρ and ρ_0 are density of the solid particles and melt, g/cm³; V is the volume of solid particles, m³; f is the friction coefficient; $\frac{dx}{dt}$ is the movement velocity, m/s; η is viscosity of the melt, Pa s; L is the active length, m; G is gravity coefficient; g is the normal gravity acceleration, $g = 9.8 \text{ m/s}^2$; and d is equivalent spherical diameter of the solid particles, m.

The theoretical movement time τ for solid particles with different sizes in the melt, using the experimental dimensional parameters and experimental measurement results (a density difference of 5 g/cm³, a sample active length of 3 cm, and a melt viscosity of 0.1 Pa s), as a function of gravity coefficient G and particle diameters d is shown in Fig. 1.1. The theoretical movement time for solid particles with the minimum size of 10 μm is 276,000 s in a normal gravity, which decreases significantly to 345 s when the gravity coefficient increased to $G = 800$. The theoretical results verified further the significant enhancement of super gravity on the motion and separation behavior of solid particles in the melt.

Fig. 1.1 Theoretical movement time τ for solid particles with different sizes in the melt as a function of gravity coefficient



Based on the theoretical results, it can be seen that the increase of gravity coefficient can intensify the relative movement between various phases and significantly strengthen the material transfer and phase separation in high-temperature metallurgical process. Therefore, super gravity technology is expected to make a breakthrough in the field of high-temperature metallurgy. In recent years, the authors have been engaged in the research of super gravity high-temperature metallurgy in order to solve the scientific and technical problems of phase separation in high-temperature metallurgical process.

1.1.2 Apparatus for Super Gravity High-Temperature Metallurgy

Super gravity is essentially a kind of centrifugal force produced by centrifugal field on the ground. The development of super gravity technology began in the 1980s. Professor Ramshaw [4] of ICI Company in the UK firstly introduced super gravity into distillation unit operation in chemical industry and then carried out relevant research work in the UK, the USA, and the medium-sized countries. At present, the super gravity technology is mainly used in the chemical industry under the room temperature and low-temperature conditions. The super gravity field has been used to strengthen the molecular mixing and mass transfer process of gas–liquid, gas–liquid–solid, and liquid–liquid reactions in unit operations such as distillation, degassing, and dust removal.

However, due to the limitation of experimental techniques such as heating, temperature control, and atmosphere control in high-speed rotating reactor, the researches on high-temperature and super gravity metallurgy are rarely reported before 2010. The authors have been persisting in the research and development of experimental equipment and research methods for super gravity metallurgy for many years. In

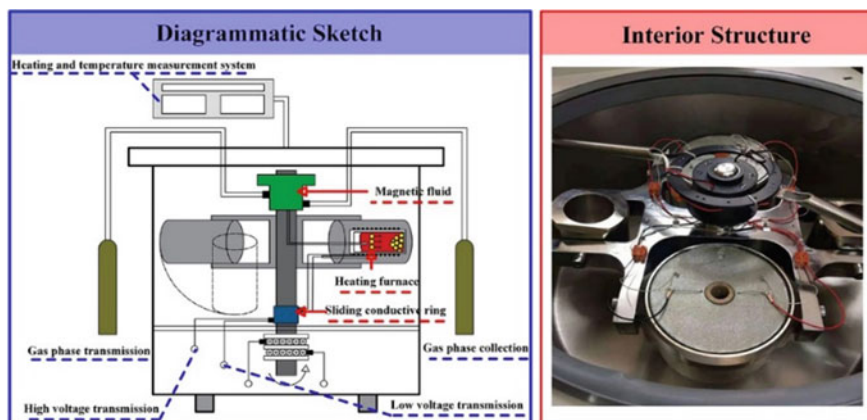


Fig. 1.2 Experimental apparatus for super gravity high-temperature metallurgy

order to apply super gravity to the field of high-temperature metallurgy, the authors integrate super gravity field with high-temperature environment, solve the key technologies such as continuous heating and temperature measurement and control of the reactor under the condition of high-speed rotation, internal atmosphere control of the reactor, and develop the super gravity high-temperature metallurgical experimental equipment (as shown in Fig. 1.2).

Under the condition of high-speed rotation, the resistance heater and temperature thermocouple in the reactor are in “dynamic” state, while the power supply and measurement and control system are in “static” state. The key to realize continuous heating and temperature measurement and control of high-speed rotating reactor is to solve the problem of current conduction at both ends and real-time transmission of temperature signal. The authors develop a low-resistance sliding conductive ring, which integrates multiple sliding conductive rings with the rotating shaft of the centrifuge, solves the “dynamic” and “static” connection problems between the high-temperature resistance furnace and the power supply and the measurement and control system, solves the problems of resistance heating strong current transmission and temperature measurement and control weak signal acquisition under the condition of high-speed rotation, and realizes the continuous heating and temperature measurement and control of the high-speed rotating reactor.

Under the condition of high-speed rotation, the resistance heater in the reactor needs to bear great centrifugal force, especially when the centrifuge starts and resonates, the high-temperature resistance heater is prone to fracture. Although the experimental study of super gravity high-temperature metallurgy at different temperatures below 1300 °C can be realized by using wire resistance, the research object has great limitations, and it is difficult to meet the temperature requirements for the research of iron and steel metallurgy. The authors have developed the filled ceramic resistance heater, solved the fracture problem of high-temperature resistance heater,

and realized the experimental research of super gravity high-temperature metallurgy at different temperatures below 1600 °C.

Different reduction, oxidation, or inert atmospheres should be controlled in the experimental study of high-temperature metallurgy. The atmosphere control in the centrifugal rotating reactor, just like heating power supply, also needs to solve the “dynamic” and “static” connection between the reactor and the gas source. By integrating the rotating guide ring of magnetic fluid seal with the rotating shaft of centrifuge, the control of different atmospheres in the high-speed rotating reactor can be realized, and the gas phase produced in the reactor can also be collected in real time.

The establishment of the experimental device of super gravity in high temperature has laid a foundation for the experimental research of super gravity high-temperature metallurgy at different temperatures below 1600 °C. This book systematically introduces the author’s research about the super gravity metallurgy in selective separation of valuable component from metallurgical slag.

1.1.3 Analytical and Characterization Methods for Super Gravity High-Temperature Metallurgy

For the research of super gravity high-temperature metallurgy reported in this book, the following main analytical methods were used to characterize the physical properties of the samples obtained by super gravity, such as phase composition, chemical composition, and element distribution.

1. X-ray diffraction method (XRD) is applied to detect the mineral phase structures of the samples [SMARTLAB(9)].
2. Scanning electron micrograph and energy-dispersive spectrum (SEM–EDS) is applied to acquire the microstructures and elemental compositions of the samples [MLA250].
3. X-ray fluorescence (XRF) is applied to measure the chemical compositions of the samples [AXIOS max].
4. Electron probe microanalyzer (EPMA) characterizes the elements distributions of the samples.
5. Inductively coupled plasma-optical emission spectrometer (ICP) is applied to determine the chemical compositions of the samples [ICAP PQ].
6. Thermal gravimetric analyzer (TGA) is applied to attain the mass losses of various reactions with various temperatures in the samples [STA 449C].
7. X-ray photoelectron spectroscopy (XPS) is applied to reveal the valence states of each element on the surface in the samples [AXISULTRA-DLD].
8. Transmission electron microscope (TEM) is applied to accurately characterize the crystal structures of the samples [FEIF20].

- 9. High-temperature confocal laser scanning microscope (CLSM) is applied to observe the in-situ morphology evolution of the samples [VL2000DX-SVF17SP].
- 10. Particle size analyzer (PSA) is applied to analyze the volume fractions and particle sizes of the samples [Malvern mastersizer, hydro 2000 μ].

1.2 Super Gravity Metallurgy in Selective Separation of Valuable Component from Metallurgical Slag

1.2.1 Introduction for Metallurgical Slag of Complex Ores

China is short of high-grade iron ore resources, but it is rich in multi-element associated complex ore resources, including vanadium titanomagnetite, high phosphorus hematite, rare earth complex ore, ludwigite, etc. For a long time, China’s complex symbiotic ores mainly rely on the main process of blast furnace ironmaking and converter steelmaking to smelt and extract Fe resources, while the utilization of other symbiotic components is very limited, resulting in a large number of symbiotic elements (Ti, V, B, REEs, P, etc.) transferred into the metallurgical slag produced in the high-temperature smelting process, and a large number of metallurgical slags containing various symbiotic elements are piled up and discarded. The sources of metallurgical slag from complex ores are shown in Fig. 1.3. The inefficient utilization of these metallurgical slags not only results in the waste of a large number of symbiotic resources, but also causes some environmental pollution problem of metallurgical solid waste discharge [5, 6].

In this book, the typical metallurgical slags produced from the high-temperature metallurgical process of complex ores in China are studied, including the titanium (Ti)-bearing slag produced from blast furnace ironmaking process of vanadium

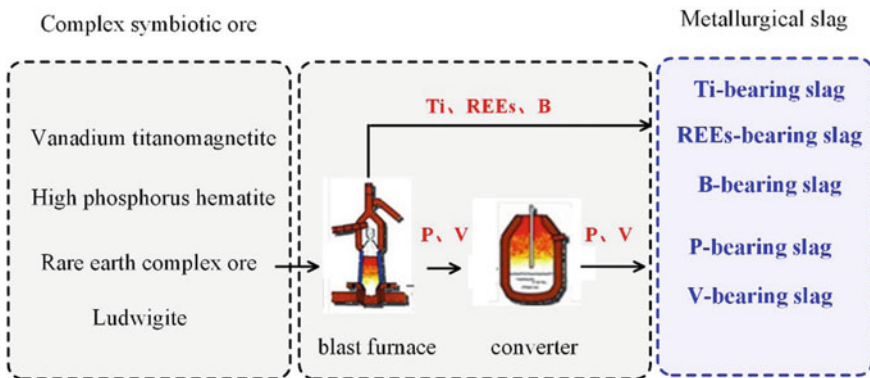


Fig. 1.3 Sources of metallurgical slag from complex ores

Table 1.1 Chemical compositions of the Ti-bearing slag (wt%)

CaO	SiO ₂	TiO ₂	Al ₂ O ₃	MgO	TFe	V ₂ O ₅	MnO ₂	P ₂ O ₅	S	Others
28.64	25.44	23.35	11.09	7.06	2.82	0.20	0.75	0.02	0.12	0.50

titanomagnetite, the vanadium (V)-bearing slag [7, 8] produced from blast furnace ironmaking and converter steelmaking process of vanadium titanomagnetite, the boron (B)-bearing slag [9–12] produced from ironmaking process of ludwigite, the rare earth (RE) bearing slag [13] and rare earth concentrate [14–18] produced from ironmaking and mineral process of rare earth complex ore, and the phosphorus (P)-bearing slag produced from blast furnace ironmaking and converter steelmaking process of high phosphorus hematite. The chemical composition, phase composition, and other basic physical properties of the employed metallurgical slags are shown below.

1.2.1.1 The Ti-Bearing Slag

The titanium-bearing slag employed in this book is produced from the blast furnace process of vanadium titanomagnetite in the Panzhihua Iron and Steel Corporation of China. The chemical compositions and mineralogical compositions of the titanium-bearing slag are shown in Table 1.1 and Fig. 1.4. The mass fractions of TiO₂ and CaO are 23.35 and 28.64 wt%, and the mineral phases mainly include perovskite (CaTiO₃), pyrope (Mg₃Al₂Si₃O₁₂), and diopside (Ca (Mg, Al) (Si, Al)₂O₆). With the help of SEM–EDS analysis shown in Fig. 1.5 and Table 1.2, it is obvious that the titanium (Ti) mainly existed in the form of perovskite and diopside, whereas the fine perovskite grains with dendritic shape uniformly distribute among the pyrope and diopside as well as some residual iron grains.

1.2.1.2 The V-Bearing Slag

The vanadium-bearing slag employed in this book is produced from blast furnace ironmaking and converter steelmaking process of vanadium titanomagnetite in Panzhihua Iron and Steel Corporation of China, and its chemical composition is listed in Table 1.3 [7].

Figure 1.6 shows a typical SEM image of the vanadium-bearing slag, combined with the EDS data for the mineral phases as shown in Table 1.4, where the white phase is the spinel, gray phase is the olivine, and the dark gray phase is the silicate. Based on the SEM–EDS analysis, the V, Ti, and Cr are mainly distributed in the spinel phases, while the Ca and Si are in the silicate phases. The XRD pattern in the Fig. 1.7 indicates further that the spinel and silicate are the main mineral phases in vanadium-bearing slag, and the vanadium is mainly in the form of FeV₂O₄, Fe₂VO₄, and MgV₂O₄ [8].

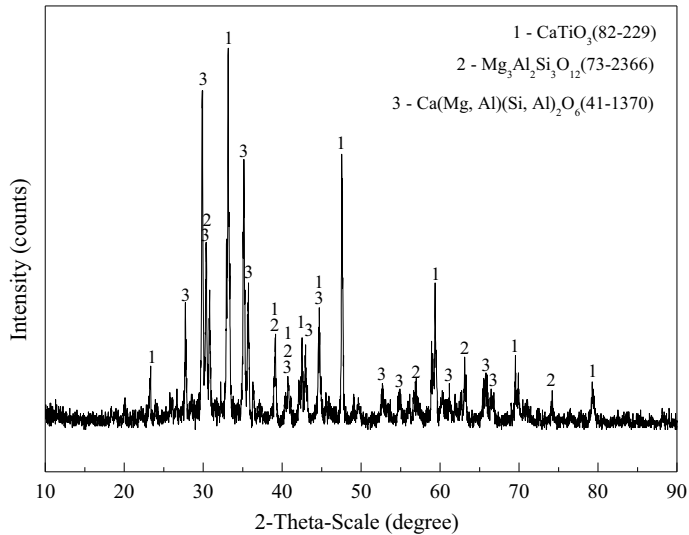


Fig. 1.4 XRD patterns of the Ti-bearing slag

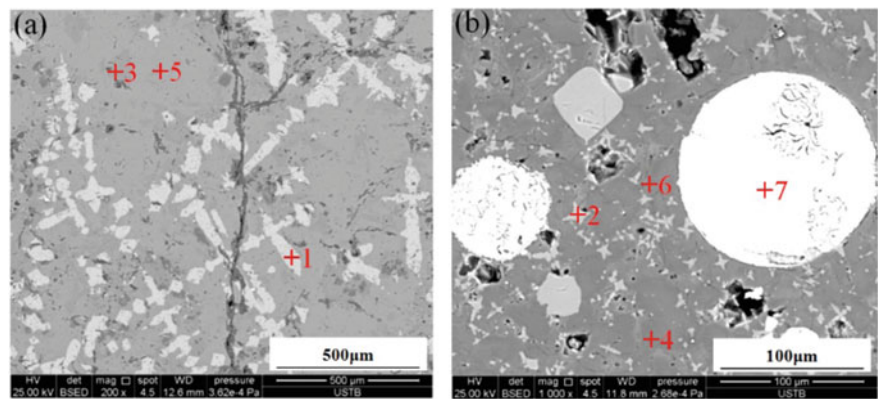


Fig. 1.5 SEM images of the titanium-bearing slag: **a** 500× ; **b** 1000×

Table 1.2 Energy-dispersive spectrum data of the mineral phases in the Ti-bearing slag (wt%)

Positions	No	Ca	Si	Ti	V	Fe	Al	Mg	O
Figure 1.5a	Pt.1	32.80	—	39.24	—	—	—	—	27.96
Figure 1.5b	Pt.2	32.82	—	41.48	0.23	—	—	—	25.48
Figure 1.5a	Pt.3	5.40	23.33	4.21	—	—	10.71	13.02	43.33
Figure 1.5b	Pt.4	5.76	22.35	4.02	—	—	10.04	13.21	44.62
Figure 1.5a	Pt.5	23.76	12.35	13.02	—	—	10.04	6.21	34.62
Figure 1.5b	Pt.6	23.95	14.08	13.37	0.03	—	11.74	5.27	31.57
Figure 1.5b	Pt.7	—	—	—	—	100	—	—	—

Table 1.3 Chemical composition of the V-bearing slag (wt%)

FeO	SiO ₂	V ₂ O ₃	TiO ₂	MnO	Cr ₂ O ₃	Al ₂ O ₃
36.6	15.58	13.04	12.21	9.09	3.82	3.12
MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	SO ₃	NbO
3.05	2.71	0.27	0.24	0.16	0.08	0.03

Fig. 1.6 SEM image of the V-bearing slag

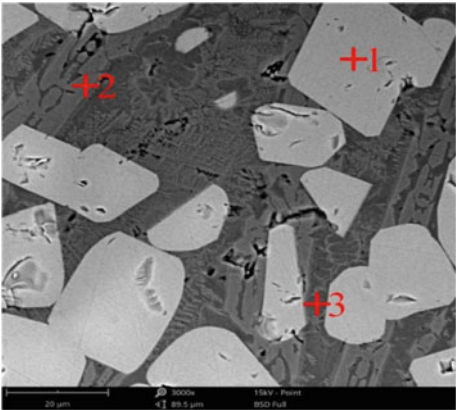


Table 1.4 EDS data of the mineral phases in the V-bearing slag (wt%)

Positions	Phase	O	Mg	Al	Ti	V	Mn	Cr	Fe	Si	Ca
Pt.1	Spinel	7.70	4.90	2.27	9.13	22.36	6.08	9.05	37.35	0.85	0.31
Pt.2	Olivine	26.38	8.37	5.37	0.45	0.89	0.82	0.96	23.06	16.00	0.20
Pt.3	Silicate	12.14	4.67	1.36	1.19	0.98	9.53	0.25	31.97	19.87	18.04

Fig. 1.7 XRD pattern of the vanadium-bearing slag

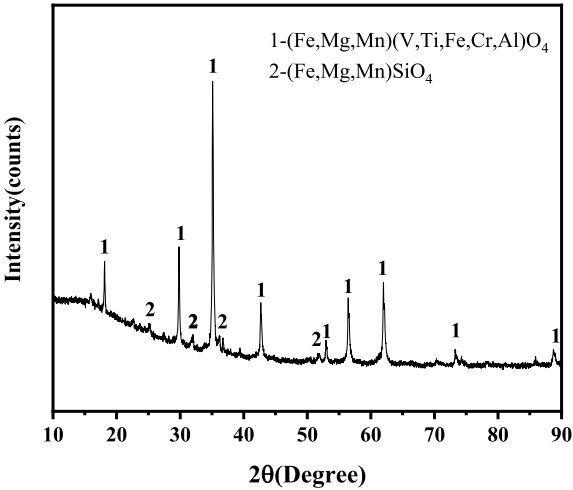
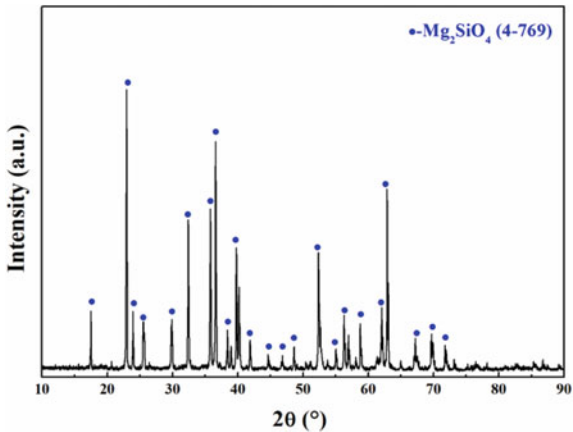


Table 1.5 Main chemical compositions of the B-bearing slag (wt%)

Composition	MgO	SiO ₂	B ₂ O ₃	CaO	Al ₂ O ₃	Others	B ₂ O ₃ /SiO ₂ (B/S)
Boron-bearing slag	42.40	31.12	19.13	3.16	1.98	2.21	0.61

Fig. 1.8 XRD pattern of B-bearing slag



1.2.1.3 The B-Bearing Slag

The boron-bearing slag employed in this book is produced from ludwigite in the iron-making process of Fengcheng Iron and Steel Group Co., Ltd., in Liaoning Province, China [9, 10]. The chemical composition of the boron-bearing slag is shown in Table 1.5. The slag has a relatively high concentration of boron, and the mass fraction of B₂O₃ is up to 19.13 wt%. However, only the significant diffraction peaks of Mg₂SiO₄ appear in the XRD pattern of the slag, as shown in Fig. 1.8. Further from the SEM–EDS results of the boron-bearing slag as shown in Fig. 1.9 and Table 1.6, a number of fine equiaxed crystals of Mg₂SiO₄ are present in the slag, while all the boron appears in the slag phase in an amorphous state [11, 12].

1.2.1.4 The Re-Bearing Slag

The rare earth-bearing slag employed in this book is produced from the ironmaking process of the Bayan Obo ore in Inner Mongolia, China. The morphologies of the RE-bearing slag are shown in Fig. 1.10, while the compositions are listed in Table 1.7. As seen in Table 1.7, the RE-bearing slag contains 12.38 wt% of RE₂O₃ [13].

Fig. 1.9 SEM image of B-bearing slag

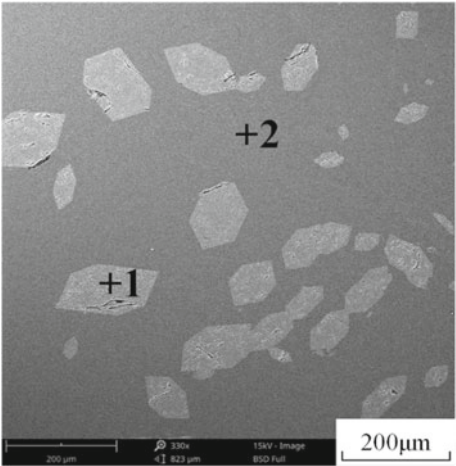


Table 1.6 EDS data of different phases in B-bearing slag (wt%)

Positions	No	Mg	Si	O	Ca	Al	B	Fe	Phases
Figure 1.8	Pt. 1	33.32	20.27	46.41	–	–	–	–	Mg ₂ SiO ₄
Figure 1.9	Pt. 2	21.23	11.94	49.02	3.47	2.48	10.25	1.61	Slag phase

Fig. 1.10 Morphology of the RE-bearing slag



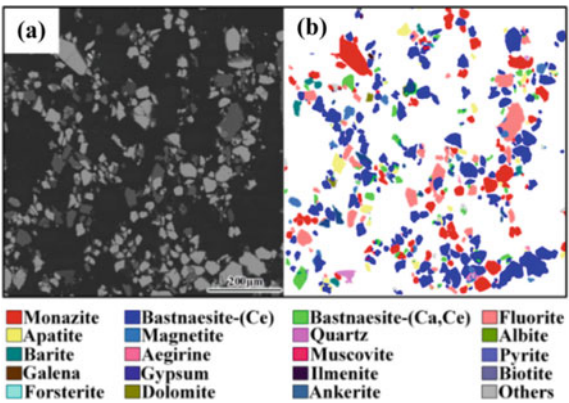
Table 1.7 Composition of the RE-bearing slag (wt%)

CaF ₂	SiO ₂	CaO	RE ₂ O ₃	FeO	BaO	MnO	Sum
42.05	21.22	18.35	12.38	2.66	1.84	1.50	100

Table 1.8 Chemical compositions of RE-concentrate (wt%)

Composition	CaO	P ₂ O ₅	Fe ₂ O ₃	SO ₃	F	SiO ₂	MgO
Content	14.34	9.63	8.09	4.93	8.41	1.09	3.46
Composition	BaO	MnO	Ce ₂ O ₃	La ₂ O ₃	Pr ₆ O ₁₁	Nd ₂ O ₃	
Content	1.59	0.37	26.42	11.84	2.99	2.84	

Fig. 1.11 MLA images of RE-concentrate

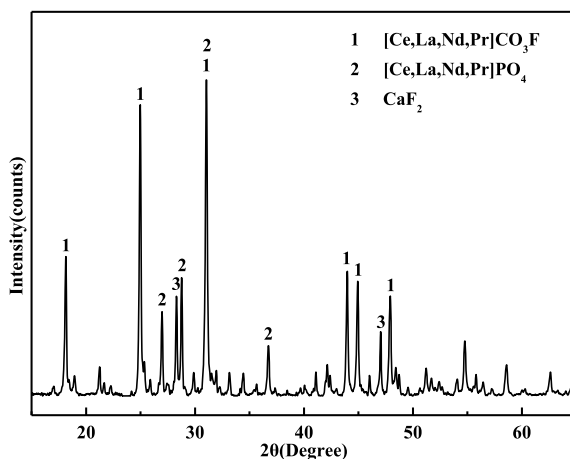


1.2.1.5 The Re-Concentrate

The rare earth concentrate employed in this book is produced through multi-stage beneficiation of the Bayan Obo ore in Inner Mongolia, China [14]. Its chemical compositions that detected by the XRF combined with ICP-AES methods are shown in Table 1.8 [15]. It is found that the rare earth concentrate is a multi-component rare earth system which consists of more than 13 species elements including four REEs of Ce, La, Pr, and Nd, and the total mass fraction of REEs is up to 44.09 wt%. Moreover, there are more than 20 kinds of minerals with various elements composition, which are tightly integrated with each other and dispersed in the RE-concentrate, as the MLA images shown in Fig. 1.11 [16]. Combined with the XRD pattern of the raw material as shown in Fig. 1.12, bastnaesite, monazite, and fluorite are the primary minerals in the Bayan Obo RE-concentrate [17, 18].

1.2.1.6 The P-Bearing Slag

The P-bearing slag employed in this book is produced from the blast furnace iron-making and converter steelmaking process of high phosphorus hematite in Laiwu Iron and Steel Co., Ltd., Shandong Province, China. Its main chemical composition is shown in Table 1.9, where the mass fraction of P₂O₅ is 2.62 wt%. It can be seen from the XRD pattern in Fig. 1.13 that the main mineral phases in the steelmaking

Fig. 1.12 XRD pattern of RE-concentrate**Table 1.9** Chemical composition of the steelmaking slag (wt%)

CaO	Fe ₇ O	SiO ₂	MgO	MnO	P ₂ O ₅	Al ₂ O ₃	TiO ₂
48.23	24.44	14.52	5.21	2.01	2.62	1.74	1.23

slag are mainly the solid solution formed by tricalcium silicate (C_3S), dicalcium silicate (C_2S), calcium aluminate ferrite (C_2AF), iron-magnesium-manganese oxides (RO phase), and a small amount of free calcium oxide (CaO). Figure 1.14 shows the SEM–EDS images of the steelmaking slag. It is clear that steelmaking slag is mainly composed of four different phases A, B, C, and D, which are closely intercalated and distributed, as the SEM image shown in the Fig. 1.14a. Based on the EDS images of the four phases A, B, C, and D as shown in Fig. 1.14b–e, the A and B phases are mainly composed of Ca, Si, O, and a small amount of P elements. The mass ratio of calcium to silicon in phase A is greater than that of phase B, and the content of P element is less than that of phase B. Combined with the XRD pattern, it confirms that the phase A is tricalcium silicate, and the phase B is dicalcium silicate. The C phase containing a large amount of Fe, Ca, Al, and O is calcium aluminate ferrite phase, and the phase D with the Fe, Mg, and Mn is RO phase.

1.2.2 Selective Crystallization and Separation of Valuable Component in Metallurgical Slag by Super Gravity

Scholars at home and abroad have carried out long-term unremitting research on the utilization of metallurgical slag of complex ores and proposed a series of treatment methods, such as physical beneficiation [19], wet leaching [20], carbonization [21], nitridation [22], and chlorination [23], which are of great significance to the

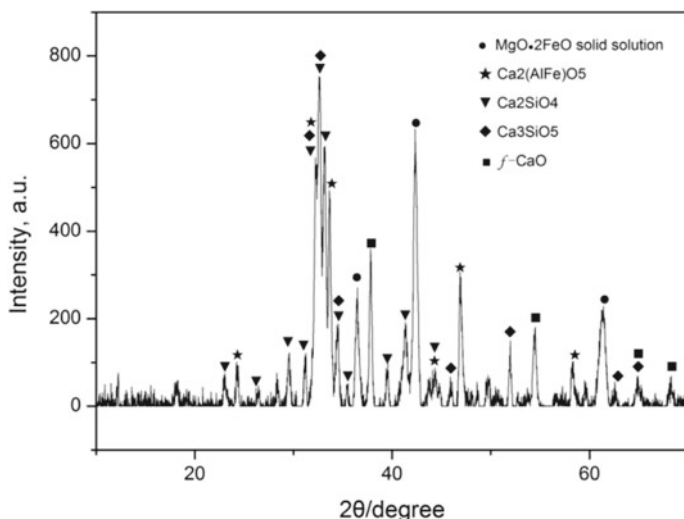


Fig. 1.13 XRD pattern of the steelmaking slag

utilization of the metallurgical slag. However, due to the complex phase structure and composition formed in the solidification process of high-temperature smelting slag, it is difficult to achieve the effective separation and recovery of various valuable components with fine, scattered, and miscellaneous characteristics in the cold slag by traditional beneficiation methods.

In this book, the authors develop a new method for selective crystallization and separation of valuable component in metallurgical slag by applying super gravity to the efficient utilization of the metallurgical slag, and the schematic diagram for the process is shown in Fig. 1.15. Firstly, the paragenetic elements are selectively enriched into the specified phase during the cooling process of molten slag by adjusting the appropriate physical and chemical conditions. And the super gravity field is applied in the single crystallization temperature range of the paragenetic element, where only the crystals of paragenetic elements are solid, while the slag is in molten state. Under the force of super gravity, the directional enrichment and efficient separation of the dispersed crystals of paragenetic elements from the molten slag can be fully complete as driven by the super gravity, based on the differences of physical properties between the different phases. The efficient separation and extraction of valuable components from metallurgical slag of complex ores is not only to solve the problem of sustainable development of metallurgical industry, but also important for the large-scale utilization of complex symbiotic ore resources in China.

Moreover, the high-purity crystals of the symbiotic elements can be efficiently separated online from the molten metallurgical slag at high temperature under the force of super gravity. Therefore, the physical and chemical information for the formation and transformation of symbiotic elements in the molten metallurgical

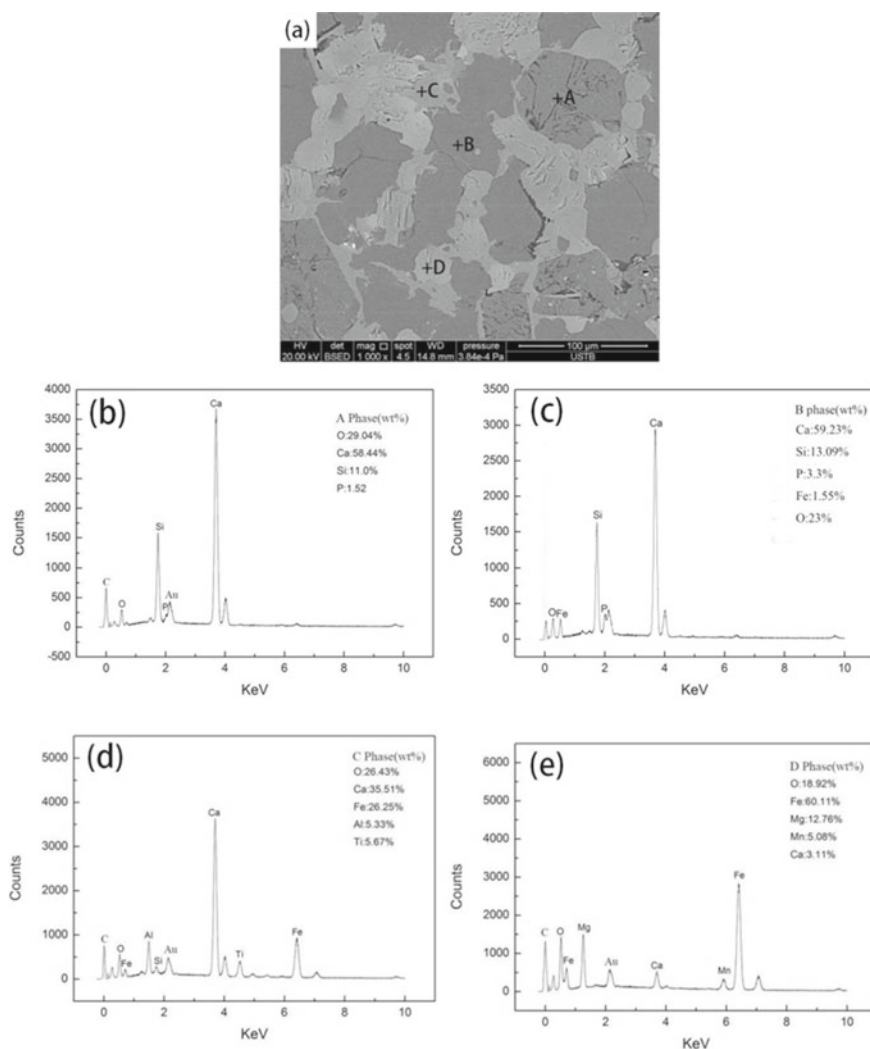


Fig. 1.14 SEM-EDS images of steelmaking slag

slag can be accurately obtained, which can provide the necessary basic data for the physical and chemical properties of the molten metallurgical slag.

This book includes the selective crystallization and separation of various valuable components in metallurgical slag of different complex ores in the following chapters, respectively:

Chapter 2 reports the selective crystallization and separation of Ti in Ti-bearing slag.

Chapter 3 reports the selective crystallization and separation of B in B-bearing slag.

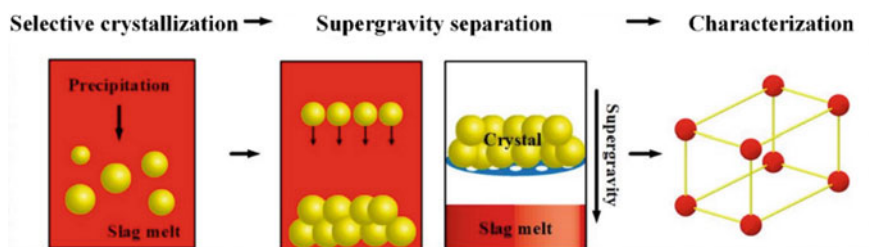


Fig. 1.15 Schematic diagram for selective crystallization and separation of valuable component in metallurgical slag by super gravity

Chapter 4 reports the selective crystallization and separation of REEs in RE-bearing slag.

Chapter 5 reports the selective crystallization and separation of REEs in RE-concentrate.

Chapter 6 reports the selective crystallization and separation of P in P-bearing slag.

Chapter 7 reports the selective crystallization and separation of V in V-bearing slag.

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Chapter 2

Selective Crystallization and Separation of Ti in Ti-Bearing Slag



Abstract It reports the selective crystallization and separation of Ti in Ti-bearing slag. The selective crystallization of Ti into perovskite, the phase transformation of Ti into rutile, the crystallization behavior of Ti into anosovite, and the carbothermal reduction of Ti into TiC in Ti-bearing slag are reported in Sects. 2.1, 2.2, 2.3, and 2.4, respectively. The study on selective separation of various Ti-rich phases of perovskite, rutile, anosovite, and TiC powders in molten Ti-bearing slag is included in the Sects. 2.1, 2.2, 2.3, and 2.4, respectively. The amplification study for selective separation of Ti in Ti-bearing slag is reported in Sect. 2.5.

Vanadium-titanium magnetite is a kind of iron, titanium, and vanadium multiple-element symbiotic composite ore resource in massive reserves, especially in the Panxi region of China [1, 2]. So far, vanadium-titanium magnetite is mainly adopted by blast furnace iron-making process for refining and extracting the iron, whereas utilization of the titanium and vanadium resources is limited. Generally speaking, the mass fraction of TiO_2 in the raw ore is 9.0–12.0 wt%, and about 53% of TiO_2 migrates to the iron ore concentrate after mineral processing. And then the iron ore concentrate further transforms into the vanadium (V)-bearing hot metal and the titanium (Ti)-bearing blast furnace slag containing 20.0–25.0 wt% of TiO_2 during the blast furnace iron-making process [3, 4]. Nevertheless, the Ti-bearing slag can hardly resort to the traditional separating technique resulting from the dispersed distribution of titanium component in various mineral phases, fine grains ($< 10 \mu\text{m}$), and complex interfacial combination of the titanium phase. And so, the Ti-bearing slag has been accumulating 70 million tons, and it is still increasing at a rate of 3 million tons per year [5, 6]. In recent years, many hydrometallurgical [7, 8] and pyrometallurgical [9] methods have been throwing light on the comprehensive utilization of Ti-bearing slag.

Based on the $\text{CaO-TiO}_2\text{-SiO}_2$ phase diagram, perovskite (CaTiO_3) is the primary crystallization phase of titanium in the Ti-bearing blast furnace slag, and most of the investigations on crystallization and separation behaviors of titanium from the Ti-bearing slag laid particular stress on the perovskite phase taking on a similar mineral composition to the original slag [10–13]. Sui [14, 15] proposed a process of crystallization combined with physical separation to recover titanium-bearing phase from the Ti-bearing slag. As for the crystallization process of Ti-bearing phase from

the Ti-bearing slag at high temperature, Zhang [16], Li [17], Sun [4], Wang [18] and Guo [19] reported that oxidizing the slag, appropriate increasing of the slag basicity, and adding some Si-Fe, CaF_2 , MnO , and Fe_2O_3 powders as the additives were beneficial for the crystallization of perovskite in the Ti-bearing slag.

Although perovskite is the primary crystallization phase of Ti-bearing slag, a mole of perovskite ($\text{CaO}\cdot\text{TiO}_2$) is composed of one TiO_2 molecule and one CaO molecule, and the theoretical content of TiO_2 in perovskite is only 58.87 wt% [20, 21]. Compared to the perovskite, the rutile (TiO_2) with a higher titanium content and a simpler composition would be a better choice for recovering titanium from the Ti-bearing slag. Furthermore, rutile is a versatile material which has been widely applied in various fields of pigments [22], gas sensors [23], varistors [24] and dielectric materials [25, 26]. Thus, the phase transformation of Ti from perovskite into rutile and the efficient separation of rutile from the slag need to be investigated. Sun [27], Ren [28], Chen [29] and Samal [30] reported that small amount of acidic oxides additive such as P_2O_5 and B_2O_3 , reducing slag basicity, microwave irradiation, and plasma treatment could facilitate the formation of rutile in Ti-bearing slags, respectively.

Except for rutile, through controlling physical–chemical conditions such as temperature, slag basicity, and atmosphere of Ti-bearing slag, titanium can form another titanium dioxide of anosovite (Ti_3O_5) in the molten Ti-bearing slag [31]. Considering the theoretical content of Ti in the anosovite was much higher than that in the perovskite, and along with its greater density, the anosovite would be also a better choice for separating titanium from the Ti-bearing slag. Li [32] proposed that anosovite appeared in the Ti-bearing slag in case of increasing the SiO_2 content to above 35 wt% and reducing at a high temperature, whereas it was difficult to separate the very fine anosovite crystals from the slag by conventional mineral processing [33, 34]. Ren [13] proposed that adding small amount of B_2O_3 could effectively reduce the activity of Ca^{2+} ; thus, the crystallization of perovskite was inhibited, and titanium in slag can tend to form anosovite. Furthermore, the adding B_2O_3 can observably improve the fluidity of slag, and the crystallization of anosovite crystals can be improved.

Moreover, based on the thermodynamics data between the main components in Ti-bearing slag and carbon (C), the $[\text{TiO}_4]^{4-}$ rather than other components can be reduced to the TiC in the molten state of the slag. TiC is proved to be a remarkable carbide of transition metal with high melting point (3260 °C), high hardness (28–35 GPa), and favorable electronic conductivity ($30 \times 10^6 \text{ S/cm}$). Thus, the ultrafine powders of TiC have wide applications in the cutting tools [35], electrical ceramics [36], and battery anode materials [37]. Recently, the ultrafine TiC powders are mainly prepared by various synthetic methods using high-purity ultrafine powders of metallic titanium or titanium dioxide. Compared to the solid–solid reaction of ultrafine carbon with metallic Ti or TiO_2 powders, the solid–liquid reaction of carbon powders with $[\text{TiO}_4]^{4-}$ in the molten Ti-bearing slag can provide a more favorable kinetic condition for the formation and dispersion of TiC powders. In recent years, the carbothermal reduction has gradually become a research hotspot to utilization of Ti-bearing slag. Panzhihua Iron and Steel (Group) Co. developed a process of high-temperature carbonization and low-temperature chlorination for industrialization of Ti-bearing

slag [38], where the molten Ti-bearing slag was first carbonized in electric furnace for the reduction of TiC at about 1973 K and then chlorinated in fluidized bed furnace at about 873 K for further chlorination of TiCl_4 [39]. While the calcium and magnesium in the Ti-bearing slag could be also chlorinated under the chlorine atmosphere, their chlorides would obstruct the chlorination bed and greatly reduced the chlorination efficiency of titanium. Thus, recovery of ultrafine TiC powders from molten Ti-bearing slag would be another sustainable method for clean utilization of the massive Ti-bearing slag. Compared with perovskite, rutile, and anosovite crystals formed in Ti-bearing slag [40, 41], the TiC powders are ultrafine particles only with several micrometers and the separation of ultrafine TiC powders from Ti-bearing slag will face great difficulties.

For the separation of various titanium-rich phases from the Ti-bearing slag, the beneficiation methods were mainly adopted, such as the fine-grinding, flotation [42] and gravity separation methods [43], while the conventional beneficiation methods face great difficulty to efficiently separate the titanium-rich phases from other minerals at room temperature due to the intimate intermixing and the minor density difference between them. Accordingly, if the titanium-rich phase could be separated from others at its crystallization temperature range, at which titanium crystallizes into the only titanium-rich crystal, whereas other minerals form the slag melt, it would be beneficial to effectively separate the solid particles from the slag melt. However, the existence of a large amount of solid titanium-rich phases is to increase the viscosity of the slag melt, and the driving force generated by the difference in density between the titanium-rich crystals and slag melt is insufficient to effectively overcome the large interfacial tension between the two phases. Therefore, it is difficult to separate the titanium-rich crystals from the molten Ti-bearing slag via free sedimentation under conventional conditions. Based on study about the super gravity technology, the mass migration of different phases can be greatly improved by super gravity force, and the role of interfacial tension between two different phases became insignificant. Therefore, selective separation of various Ti-rich phases from Ti-bearing slag is conducted by super gravity.

In this Chapter, selective crystallization and separation of Ti in Ti-bearing slag are proposed, and the study on various Ti-rich phases is included in the following sections, respectively:

Section 2.1 reports the selective crystallization and separation of perovskite in Ti-bearing slag [40, 44–48].

Section 2.2 reports the phase transformation of Ti and separation of rutile in Ti-bearing slag [41, 49].

Section 2.3 reports the separation of anosovite from Ti-bearing slag in reducing atmosphere [50–53].

Section 2.4 reports the carbothermal reduction of Ti and separation of ultrafine TiC powders in Ti-bearing slag [54].

Section 2.5 reports the amplification study for selective separation of Ti in Ti-bearing slag [48].

2.1 Selective Crystallization and Separation of Perovskite in Ti-Bearing Slag

In this section, the basic slag system of $\text{CaO-TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ is conducted for Ti-bearing slag, the thermodynamic analysis for crystallization Ti, and the crystallization and growth behaviors of perovskite in the Ti-bearing slag system are studied [44]. On this basis, the directional motion and selective separation behaviors of perovskite in both the $\text{CaO-TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ system and the Ti-bearing blast furnace slag produced in Panzhihua Iron and Steel Corporation of China are studied, respectively [44–48].

2.1.1 Thermodynamic Analysis for Crystallization of Ti in $\text{CaO-TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ System

The basic slag system of $\text{CaO-TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ is conducted for Ti-bearing slag, and the equilibrium phase diagram of $\text{CaO-SiO}_2\text{-TiO}_2\text{-6%MgO-12%Al}_2\text{O}_3$ calculated through FactSage 7.2 is shown in Fig. 2.1, where the green point in phase diagram is the original chemical composition of Ti-bearing blast furnace slag. It is obvious that the composition of the original Ti-bearing blast furnace slag is located in the primary phase field of perovskite (CaTiO_3), indicating that the perovskite is the primary crystallization phase in Ti-bearing blast furnace slag.

According to the thermodynamic data of the reaction $\text{TiO}_2 + \text{CaO} = \text{CaTiO}_3(\text{s})$, raising the slag basicity (CaO/SiO_2) can increase the activity of CaO in the slag that promotes the forward reaction of perovskite crystallization. But increasing the slag basicity to over 1.30 will also facilitate the crystallization of calcium silicate according to the experiments of Li [17]. Hence, the slag basicity was adjusted from 1.13 to 1.30 by adding CaO into $\text{CaO-TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ system, and the crystallization behavior of perovskite in the Ti-bearing slag system is studied.

2.1.2 Crystallization Behavior of Perovskite in $\text{CaO-TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ System

2.1.2.1 Experimental Procedure

To investigate the crystallization behavior of different phases in the molten Ti-bearing slag, the $\text{CaO-TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ system was first prepared by mixing chemical agents powders based on the main compositions of Ti-bearing slag as given in Table 2.1. Subsequently, the Ti-bearing slags were put into some graphite crucibles with an inner diameter of 19 mm and a height of 60 mm and heated to 1773 K

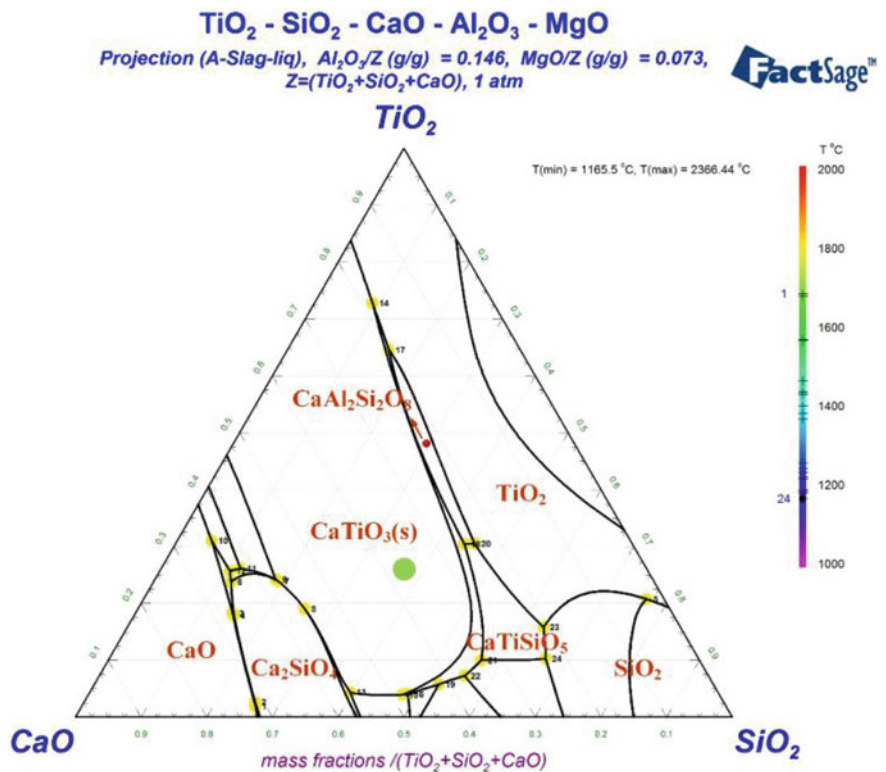


Fig. 2.1 Equilibrium phase diagram of CaO–SiO₂–TiO₂–6wt%MgO–12wt%Al₂O₃ system

in high-purity argon in muffle furnace to avoid the possible reduction of titanium-bearing minerals. After heating at the constant temperature for 30 min to make the slag fully melted, the temperatures were rapidly decreased at a cooling rate of 20 K/min, and then the melted Ti-bearing slags were slowly cooled at 1743–1713 K, 1713–1683 K, 1683–1653 K, 1653–1623 K, 1623–1593 K, 1593–1563 K, 1563–1533 K, 1533–1503 K, 1503–1473 K, 1273–1243 K, 1243–1213 K, or 1213–1183 K with a cooling rate of 0.5 K/min for 60 min, respectively. After that, the graphite crucibles were taken out and water-quenched. The samples obtained by cooling liquation at different temperature ranges were sectioned longitudinally along the center axis and measured by SEM and XRD to gain the microstructures and mineral compositions of the precipitated phases in Ti-bearing slag.

Table 2.1 Chemical composition of CaO–TiO₂–SiO₂–Al₂O₃–MgO system (wt%)

Composition	CaO	TiO ₂	SiO ₂	Al ₂ O ₃	MgO	Basicity
Content	33.07	23.35	25.44	11.09	7.06	1.30

2.1.2.2 Crystallization Behavior of Perovskite

The mineral compositions of the molten Ti-bearing slag with a basicity of 1.30 after cooling at different temperature ranges with a cooling rate of 0.5 K/min are shown in Fig. 2.2. Obviously, perovskite is the first crystallized phase from the molten Ti-bearing slag, whose diffraction peak intensity increases with temperature decreasing from 1743 to 1563 K, and the peak value appears significantly in 1593–1563 K. When temperature decreases to 1563–1553 K, the second crystallized phase of pyrope starts to appear and the diffraction peak intensity increases with decreasing temperature. When temperature further decreases to 1473–1443 K, the third crystallized phase of diopside also appears. However, with the successive crystallization of pyrope and diopside, the viscosity of molten Ti-bearing slag increases, and the migration rate of Ca^{2+} and TiO_3^{2-} in the melt decreases, so the nucleation and growth of perovskite is blocked, so the diffraction peak intensity of perovskite decreases with the temperature further decreasing from 1563 to 1383 K.

Furthermore, the microstructures of above Ti-bearing slags are shown in Fig. 2.3. As shown in Fig. 2.3a and b, white perovskite changes from fine floc or needle-shaped crystals to larger equiaxed crystals with the temperature decreasing from 1743 to 1563 K, and the larger size of perovskite appears in 1593–1563 K. When it comes to the temperature below 1563 K as shown in Fig. 2.3c and d, the dark gray pyrope and light gray diopside appear successively at 1563–1533 K and 1473–1443 K, which uniformly include among the first perovskite. According to the XRD patterns and microstructures of perovskite precipitated at different temperature ranges, it is

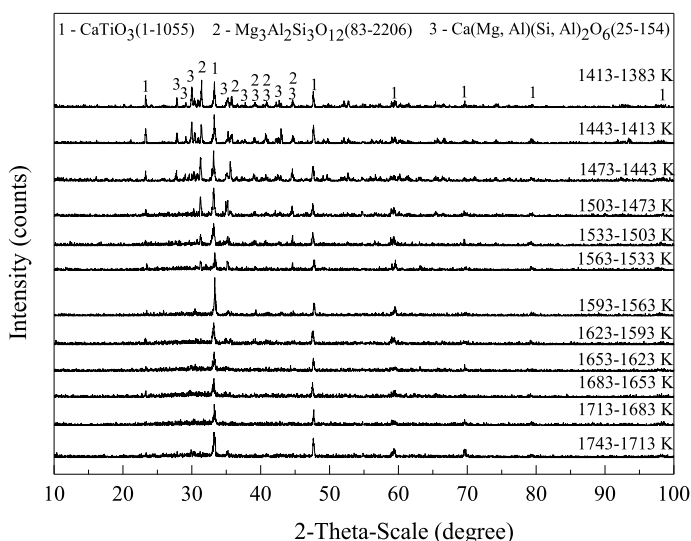


Fig. 2.2 XRD patterns of the molten Ti-bearing slag after cooling at different temperature ranges

indicated that the 1593–1563 K is the advantageous crystallization temperature of perovskite from the molten Ti-bearing slag.

The variations in volume fraction and equivalent diameter of the perovskite precipitated in Ti-bearing slag with temperature are shown in Fig. 2.4. Obviously, they both increase first and then decrease with temperature decreasing from 1743 to 1383 K, and the more crystallization quantity and larger crystal size of perovskite both appear in 1593–1563 K. According to the study of Eagan [55], when the temperature is above 1563 K, only perovskite exists in the molten Ti-bearing slag, and the migration rate

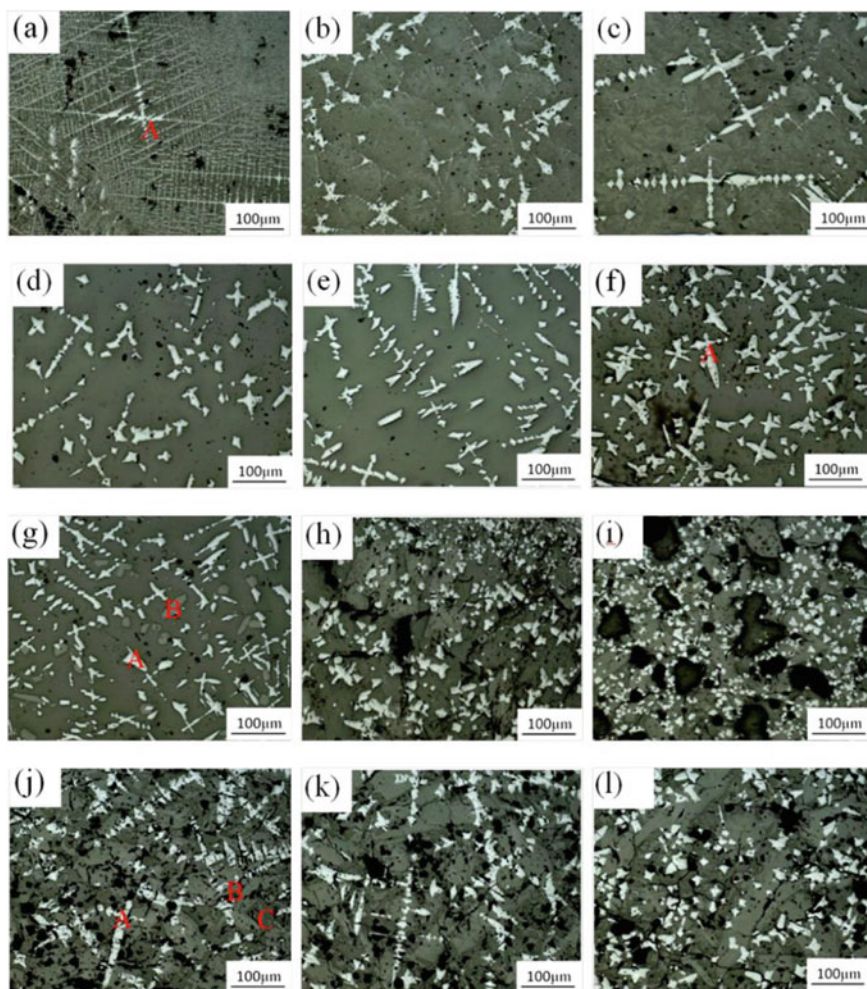


Fig. 2.3 Variation in microstructures of the Ti-bearing slag melt after cooling at different temperatures: **a** 1743–1713 K; **b** 1713–1683 K; **c** 1683–1653 K; **d** 1653–1623 K; **e** 1623–1593 K; **f** 1593–1563 K; **g** 1563–1533 K; **h** 1533–1503 K; **i** 1503–1473 K; **j** 1473–1443 K; **k** 1443–1413 K; **l** 1413–1383 K

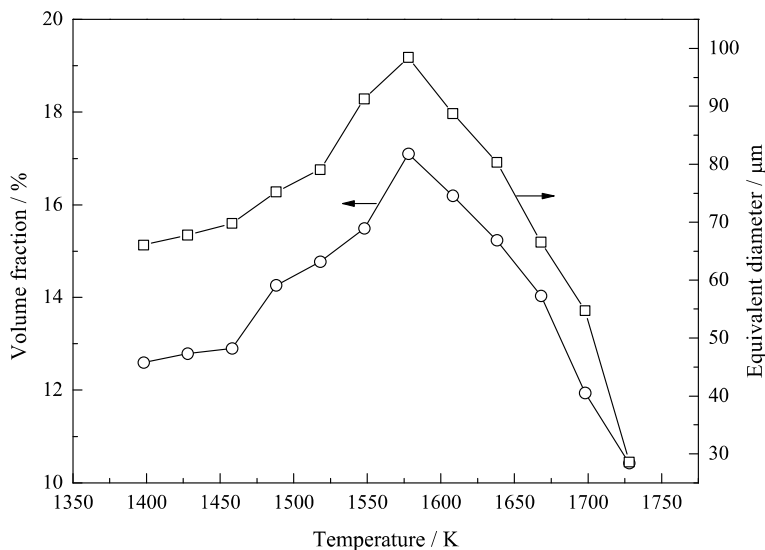


Fig. 2.4 Variations in volume fractions and equivalent diameters of perovskite in Ti-bearing slag with temperature

of Ca^{2+} and TiO_3^{2-} in the melt is faster, which is beneficial for the nucleation and growth of perovskite. However, as the temperature decreases to below 1563 K, the viscosity of the melt increases with the successive crystallization of pyrope and diopside, and the migration rate of Ca^{2+} and TiO_3^{2-} decreases. As a result, the nucleation and growth of perovskite are blocked.

2.1.3 Crystallization and Growth Kinetics of Perovskite in $\text{CaO-TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ System Under Super Gravity

The crystallization of perovskite in $\text{CaO-TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ system under the super gravity field with different gravity coefficients at various cooling rates is conducted further. The volume fractions and equivalent diameters of perovskite against gravity coefficients and cooling rate are obtained by simplifying the layered samples into three areas, and the effects of super gravity field on the crystallization and growth kinetics of perovskite in Ti-bearing slag are studied.

2.1.3.1 Experimental Procedure

The chemical agents of CaO, TiO₂, SiO₂, Al₂O₃, and MgO were well mixed based on the compositions of CaO–TiO₂–SiO₂–Al₂O₃–MgO system as given in Table 2.1, which was put into a graphite crucible with an inner diameter of 19 mm, and heated at 1773 K for 30 min under argon gas in a muffle furnace to make the Ti-bearing slag fully melted. Thereafter, the melted Ti-bearing slag was rapidly cooled to 1593 K at a cooling rate of 20 K/min, and the crucible was quickly transferred into the heating furnace of centrifugal apparatus that has been preheated to 1593 K simultaneously. After temperature was constant, the centrifugal apparatus was started immediately and adjusted to different angular velocity of 1036 r/min, 1465 r/min, or 1794 r/min ($G = 300$, $G = 600$ or $G = 900$), and the slag was cooled slowly from 1593 to 1563 K at different cooling rates ($\alpha = 1$ K/min, $\alpha = 2$ K/min, $\alpha = 3$ K/min, or $\alpha = 6$ K/min), respectively. Afterward, the crucible was taken out, and the sample was water-quenched. Simultaneously, the parallel experiments were carried out at the same cooling rates in a normal gravity field.

The samples obtained by super gravity with different gravity coefficients and different cooling rates were sectioned longitudinally along the center axis. Afterward, the samples were measured by the scanning electron micrograph and energy-dispersive spectrum (SEM–EDS) for analyzing the microstructures and mineral compositions of perovskite and measured further on the image analyzer (LEICA Qwin 500) by line intercept method (average of 20 fields) [56, 57] for the volume fraction and equivalent diameter of perovskite in different areas of different samples, respectively.

Due to the layered structures appeared in the samples obtained by super gravity, the layered sample was simplified into three areas along the super gravity direction: slag-rich area (S), interface area (I), and perovskite-rich area (P). And the volume fractions and equivalent diameters of perovskite in the layered samples with different gravity coefficients and different cooling rates were obtained further by weighting the volume fractions and equivalent diameters of perovskite in their respective areas via Eqs. (2.1) and (2.2).

$$V = \frac{(V_{P-S} \cdot V_S) + (V_{P-I} \cdot V_I) + (V_{P-P} \cdot V_P)}{V_S + V_I + V_P} \quad (2.1)$$

$$d = \frac{(d_{P-I} \cdot V_I) + (d_{P-P} \cdot V_P)}{V_I + V_P}, \quad (2.2)$$

where V , V_{P-S} , V_{P-I} , and V_{P-P} are the volume fractions of perovskite in the layered sample, slag-rich area, interface area, and perovskite-rich area; d , d_{P-I} , and d_{P-P} are the equivalent diameter of perovskite in the layered sample, interface area, and perovskite-rich area, m; V_S , V_I , and V_P are the volume fractions of slag-rich area, interface area, and perovskite-rich area.

2.1.3.2 Crystallization and Growth Kinetics of Perovskite

The vertical section and microstructures of the samples obtained in normal gravity field at different cooling rates are illustrated in Figs. 2.5 and 2.6, respectively. In a macroscopic view, a uniform structure appears in the sample. Combined with the EDS data given in Table 2.2, the gray-white perovskite uniformly distributes among the slag from a microscopic view. Moreover, with the decrease of cooling rate, the fine perovskite with characteristic of dispersing spicule gradually changes to the larger dendrites and equiaxed crystals, and the crystallization amount of perovskite also increases significantly, which is consistent with the results of Zhang and Eagan. This indicates that the reaction time of Ca^{2+} and TiO_3^{2-} extends with the decrease of cooling rate, and thus, both the self-growth and the grain coarsening of perovskite are promoted.

Compared with the uniform structures presented in the samples obtained in a normal gravity field, the layered structures appear significantly in the samples obtained by super gravity as illustrated in Fig. 2.7. Combining the microstructures with the variations of volume fractions and equivalent diameters of perovskite in different areas of the layered samples as shown in Figs. 2.8 and 2.9, the larger perovskite moves along the direction of super gravity and concentrates as the perovskite-rich phase in the bottom area, whereas the slag melt migrates along the opposite direction and forms the slag-rich phase in the upper area, as well as some smaller perovskite concentrates in the interface area between the two phases.

With respect to the Stokes' law via Eq. (2.3) [55], the crystallization and growth process of perovskite in a super gravity field are described as shown in Fig. 2.10. The first crystallized perovskite migrates quickly along the super gravity direction due to the density difference between the slag melt and gradually concentrates and grows into larger crystals in the bottom area driven by super gravity. Meanwhile, the new perovskite keeps crystallizing and concentrating toward the bottom area, while some last crystallized fine perovskite stops in the interface area before reaching the bottom area.

$$Vr = \frac{dr}{dt} = \frac{d^2 \Delta \rho}{18\eta} w^2 R, \quad (2.3)$$

Fig. 2.5 Vertical section of the sample obtained in normal gravity field at a cooling rate of 1 K/min



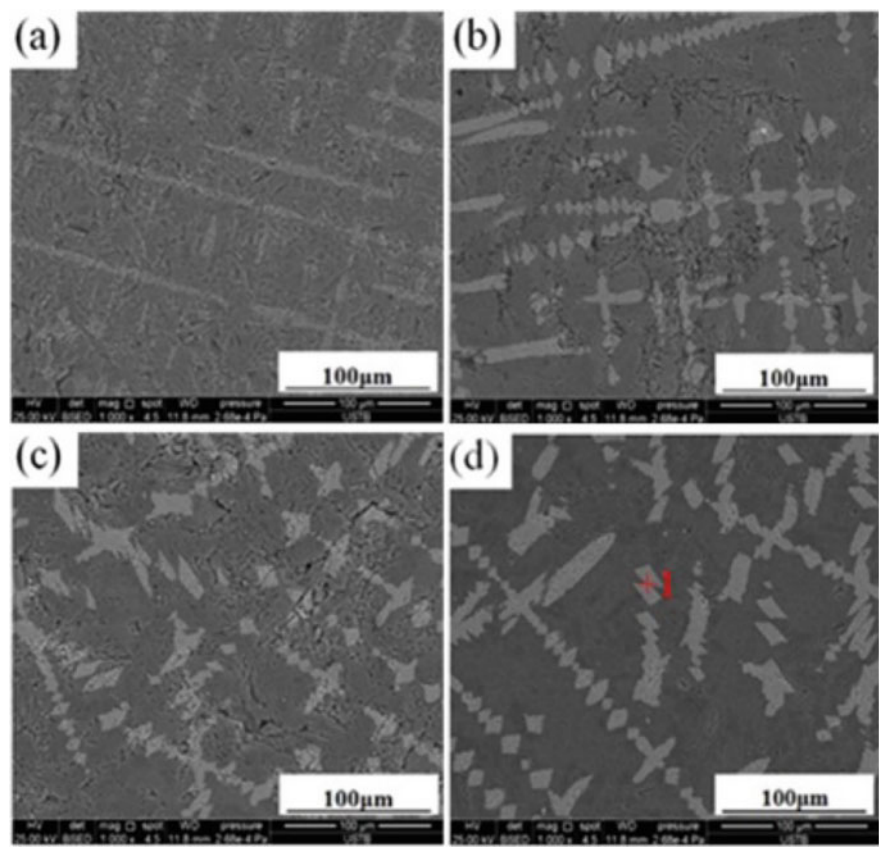


Fig. 2.6 Micrographs of the samples obtained in a normal gravity field at different cooling rates: **a** $v = 6$ K/min; **b** $v = 3$ K/min; **c** $v = 2$ K/min; **d** $v = 1$ K/min

Table 2.2 Energy-dispersive spectrum data of perovskite (wt%)

Area	Ca	Ti	O
Figure 2.6d	31.52	37.13	31.35

where V_r is the migration velocity of perovskite, m/s; d is the diameter of perovskite, m; $\Delta\rho$ is the density difference between perovskite and slag, kg/m^3 ; η is the viscosity of slag melt, N s/m^2 .

Moreover, the microstructures of perovskite-rich phases in the layered samples obtained by super gravity with different gravity coefficients at different cooling rates are illustrated in Fig. 2.11. Obviously, both the content and crystal size of perovskite in the perovskite-rich phases increase gradually with the increase of gravity coefficient and the decrease of cooling rate. It is evidenced that increasing gravity coefficient is definitely beneficial for the concentration and growth of perovskite along the super gravity direction.

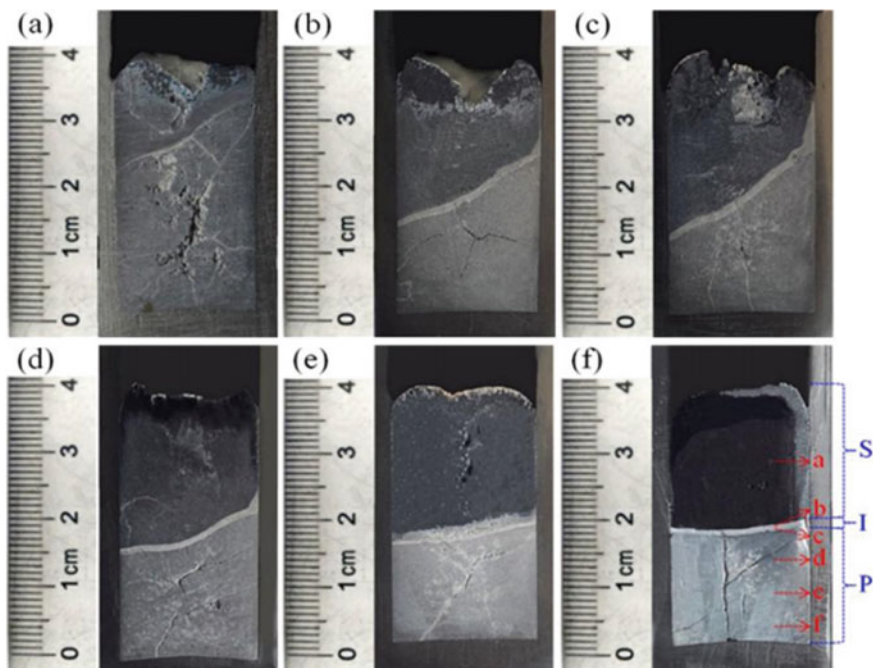


Fig. 2.7 Vertical sections of the samples obtained by super gravity with different gravity coefficients at different cooling rates: **a** $G = 300$, $v = 6$ K/min; **b** $G = 300$, $v = 3$ K/min; **c** $G = 300$, $v = 2$ K/min; **d** $G = 300$, $v = 1$ K/min; **e** $G = 600$, $v = 1$ K/min; **f** $G = 900$, $v = 1$ K/min

To investigate further the effect of super gravity on the crystallization and growth kinetics of perovskite in the Ti-bearing slag melt, the layered sample obtained by super gravity is simplified into three areas along the super gravity direction based on the minor discrepancies of the content and crystal size of perovskite in their respective areas as shown in Fig. 2.7. They are slag-rich area, interface area, and perovskite-rich area. Afterward, the volume fraction and equivalent diameter of perovskite in the whole samples with different gravity coefficients and different cooling rates are obtained by weighting the values of the three areas.

Figure 2.12 presents the variations of volume fraction of perovskite in the whole samples obtained by super gravity with different gravity coefficients as a function of cooling rate. Generally speaking, the volume fraction of perovskite increases gradually with the decrease of cooling rates. Moreover, as cooling rate approaches zero ($v \rightarrow 0$), the crystallization reaction of perovskite reaches an equilibrium state, and the volume fraction of perovskite in the equilibrium state of super gravity increases significantly compared with that of normal gravity. The increase of crystallization amount of perovskite with the increase of gravity coefficient can be explained as following reasons. In the normal gravity field, with the crystallization of perovskite, the concentration of Ca^{2+} and TiO_3^{2-} decreases, while the concentration of other ions increases gradually around the first crystallized crystals, and thus, the crystallization

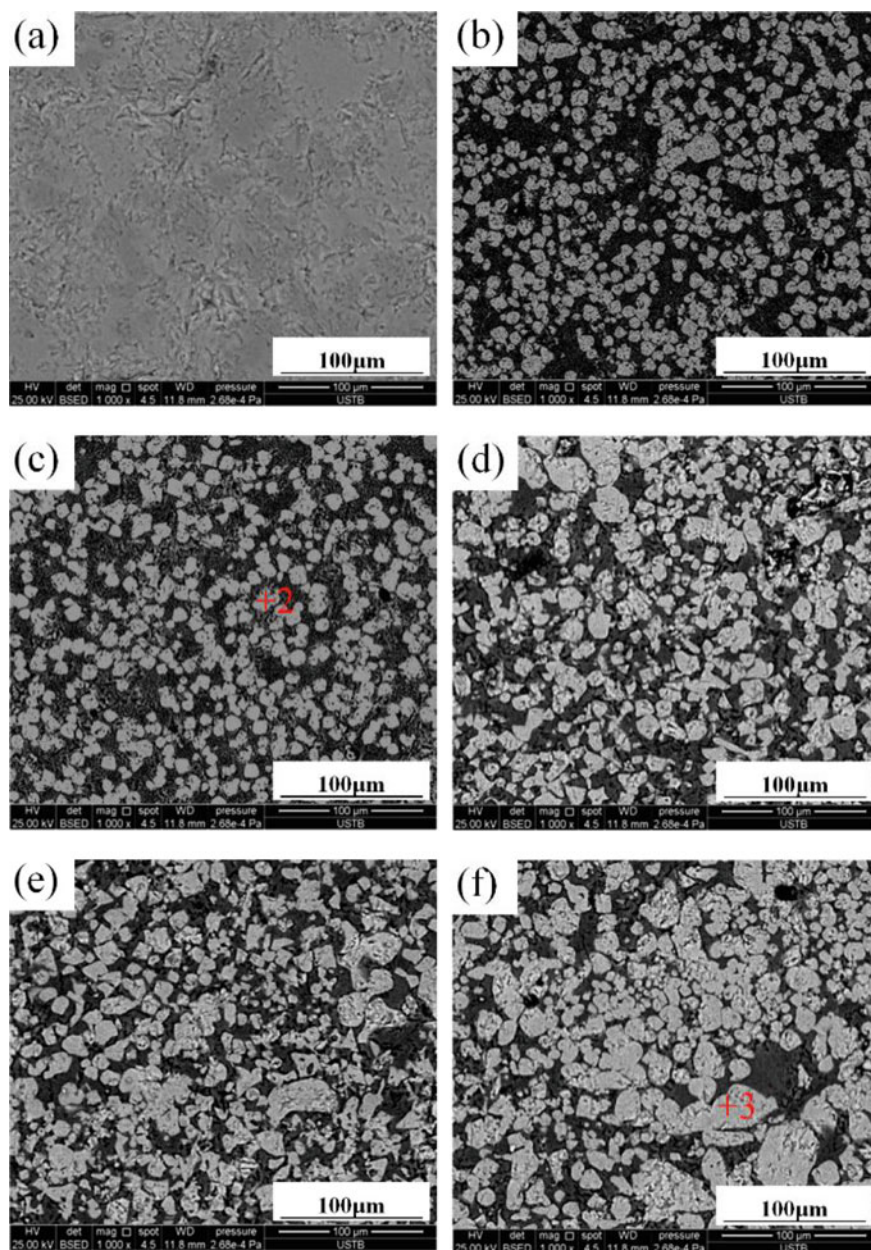


Fig. 2.8 Micrographs of different areas in the layered sample obtained by super gravity with gravity coefficient of $G = 900$ and cooling rate of 1 K/min: **a** slag-rich area; **b** and **c** interface area; **d–f** perovskite-rich area

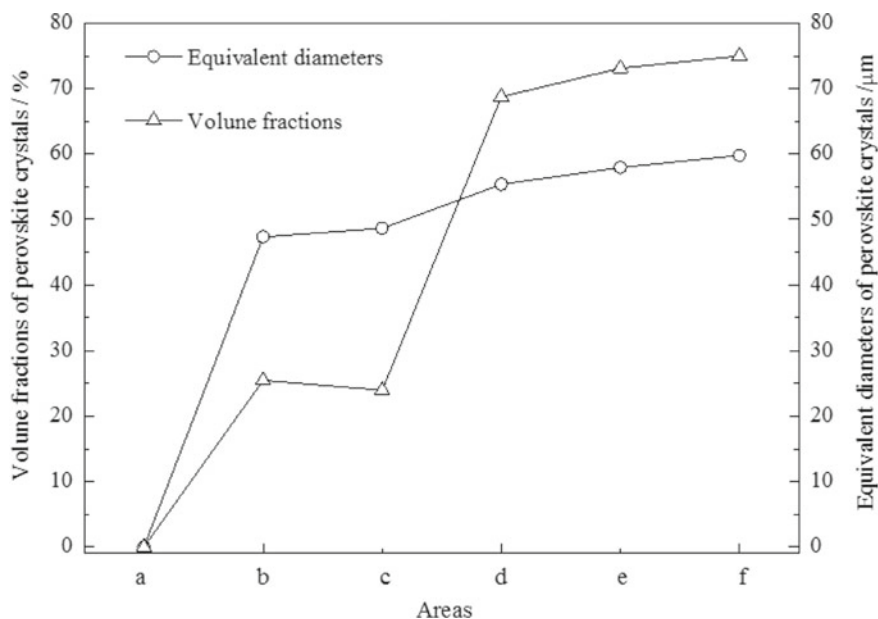


Fig. 2.9 Variations of volume fractions and equivalent diameters of perovskite in different areas of the layered sample obtained by super gravity with gravity coefficient of $G = 900$ and cooling rate of 1 K/min

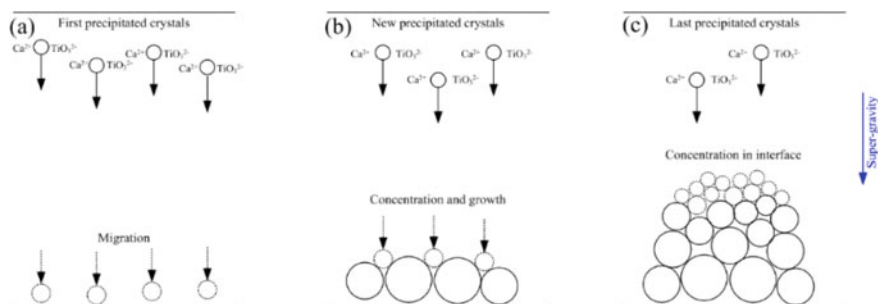


Fig. 2.10 Systematic diagram of crystallization and growth process of perovskite in a super gravity field: **a** migration of first crystallized crystals; **b** concentration and growth of the perovskite; **c** concentration of last crystallized perovskite

and nucleation of perovskite are blocked. In contrast, the first crystallized perovskite migrates quickly and separates from the slag melt driven by super gravity based on the density difference between the two phases. Thus, the concentration of Ca^{2+} and TiO_3^{2-} in the slag melt can maintain a higher level, and thus, the new perovskite can keep crystallizing and nucleating from the slag melt. Furthermore, the viscosity of

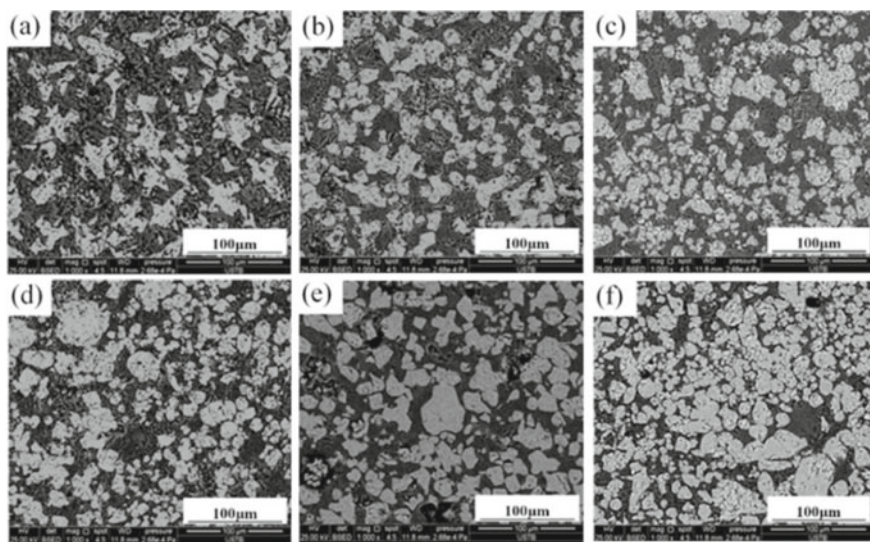


Fig. 2.11 Micrographs of perovskite-rich phases in the layered samples obtained by super gravity with different gravity coefficients at different cooling rates: **a** $G = 300$, $v = 6$ K/min; **b** $G = 300$, $v = 3$ K/min; **c** $G = 300$, $v = 2$ K/min; **d** $G = 300$, $v = 1$ K/min; **e** $G = 600$, $v = 1$ K/min; **f** $G = 900$, $v = 1$ K/min

slag melt increases with the successive crystallization of perovskite, and the diffusion rate of Ca^{2+} and TiO_3^{2-} decreases in normal gravity field. However, increasing the gravity coefficient can enhance the diffusion rates of Ca^{2+} and TiO_3^{2-} and thus fasten the rate of crystallization reaction.

Figure 2.13 presents the variations of equivalent diameter of perovskite in the whole samples obtained by super gravity with different gravity coefficients as a function of cooling rates. Obviously, the equivalent diameter of perovskite increased gradually with the decrease of cooling rates [57]. Moreover, the equivalent diameter of perovskite increased significantly with the increase of gravity coefficient, and the reasons can be attributed to the combination of self-growth and directional concentration of perovskite. In a super gravity field, the concentration of Ca^{2+} and TiO_3^{2-} in the slag melt increases compared with that of normal gravity, which is beneficial for the self-growth of perovskite. On the other hand, super gravity forced the new crystallized perovskite move toward bottom area, which increases the interfacial free energy between the crystals and melt, and so the fine perovskite was concentrated into the larger crystals.

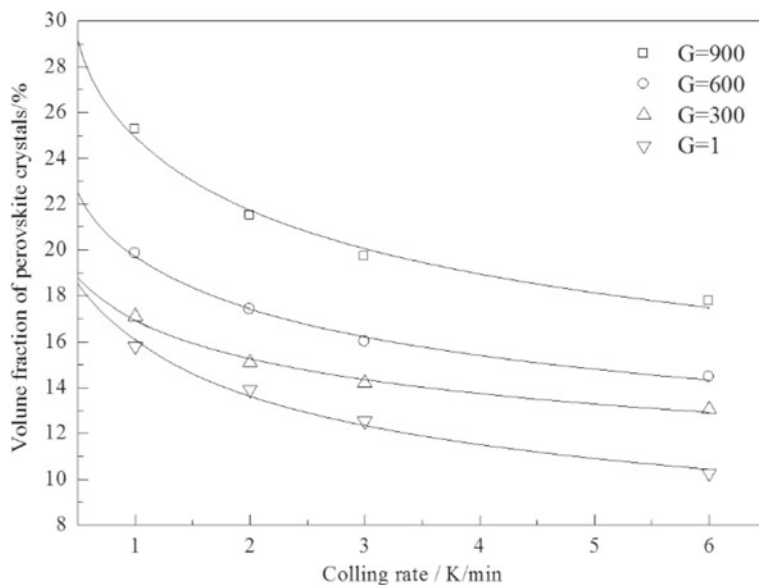


Fig. 2.12 Variations of volume fractions of perovskite obtained by super gravity with different gravity coefficients as a function of cooling rate

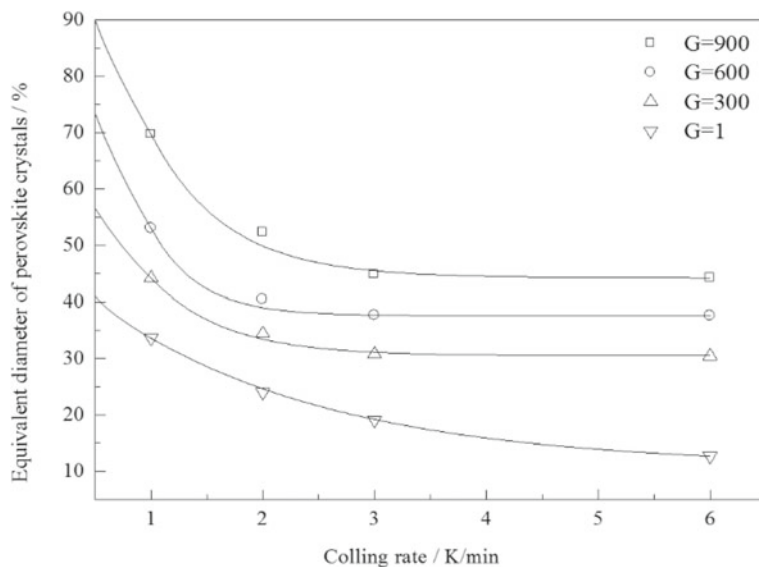


Fig. 2.13 Variations of equivalent diameter of perovskite in the whole samples obtained by super gravity with different gravity coefficients as a function of cooling rates

2.1.4 Motion Behavior of Perovskite in $\text{CaO-TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ System Under Super Gravity

Based on the crystallization and growth behaviors of perovskite, the favorable condition and temperature range for crystallization and growth of perovskite in Ti-bearing slag are obtained. On this basis, the motion and separation behaviors of perovskite in Ti-bearing slag at its single crystallization temperature are conducted under super gravity field.

2.1.4.1 Experimental Procedure

Firstly, the chemical agent powder based on Table 2.1 was well mixed and put into a graphite crucible and heated in the muffle furnace that was controlled by a program controller with an R type thermocouple, within the observed precision range of ± 3 K. The Ti-bearing slag was melted in the muffle furnace under argon gas at 1773 K for 30 min to make it fully melted and then rapidly cooled to 1623 K at a cooling rate of 20 K/min. Then the molten Ti-bearing slag was slowly cooled at a cooling rate of 0.5 K/min for 120 min for the fully crystallization of perovskite and finally water-quenched the slag.

An amount of 40 g of the quenched Ti-bearing slag was put into a graphite crucible with the inner diameter of 19 mm and heated to target temperature in the heating furnace of the centrifugal apparatus, and then the centrifugal apparatus was started and adjusted to the specified angular velocity. The centrifugal apparatus was not shut off until the target time, and then the graphite crucible was quenched into water. The sample was sectioned longitudinally along the center axis. One part was crossly divided along the interface between the white area and black area as illustrated in Fig. 2.14b into two parts, which were characterized by XRD and XRF in order to obtain the respective mineral composition and chemical component. The other part was measured on the SEM and image analyzer by the average of 20 fields in order to gain the volume fraction and equivalent diameter of perovskite. Simultaneously, the parallel experiment was carried out at 1578 K for 30 min under the normal gravity.

2.1.4.2 Motion Behavior of Perovskite Under Super Gravity

Figure 2.14 shows cross section of the samples obtained under super gravity with the gravity coefficient of $G = 600$, $t = 20$ min, and $T = 1578$ K compared with the parallel sample under normal gravity. As illustrated in Fig. 2.14b, a layered structure appears significantly in the sample obtained by super gravity with the gravity coefficient of $G = 600$, with the upper area black, the middle area white, and the bottom area gray, respectively, while the parallel sample obtained with $G = 1$ presents the uniform structure as shown in Fig. 2.14a.

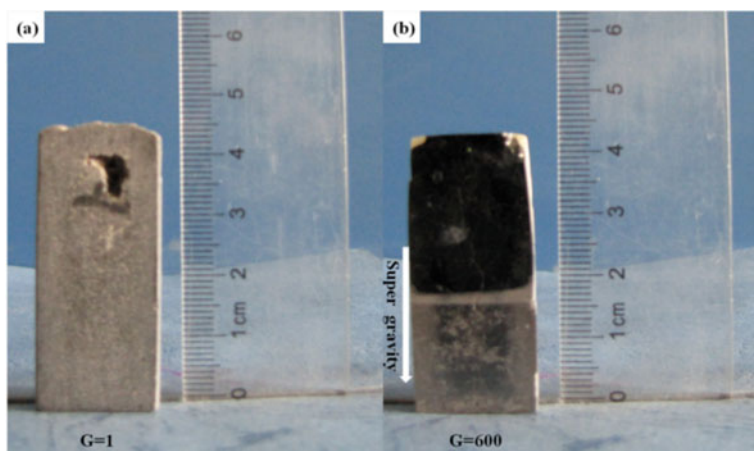
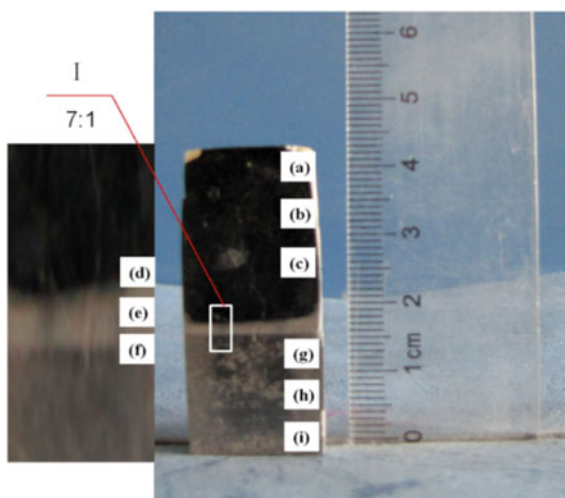


Fig. 2.14 Cross section of the sample obtained by super gravity compared with the normal gravity: **a** $G = 1$, $t = 20$ min, $T = 1578$ K; **b** $G = 600$, $t = 20$ min, $T = 1578$ K

Nine areas were divided in the layered sample as shown in Fig. 2.15 and characterized by the metallographic microscopy for their microstructures, and the corresponding results are given in Fig. 2.16. Overall, the crystal size of perovskite increases with the area approaching to the bottom of the sample; that is, the gradient distribution of perovskite presents in the layered sample along the direction of super gravity.

SEM images of the nine areas in the layered sample under super gravity are shown in Fig. 2.16. As shown in Fig. 2.16a–c, the slag melt moves to the upper areas based on the density differences between perovskite and slag melt, where it is practically impossible to find any perovskite in the upper areas ranged from area (a) to area (c).

Fig. 2.15 Positions of nine areas in the layered sample obtained under super gravity at $G = 600$, $t = 20$ min, and $T = 1578$ K



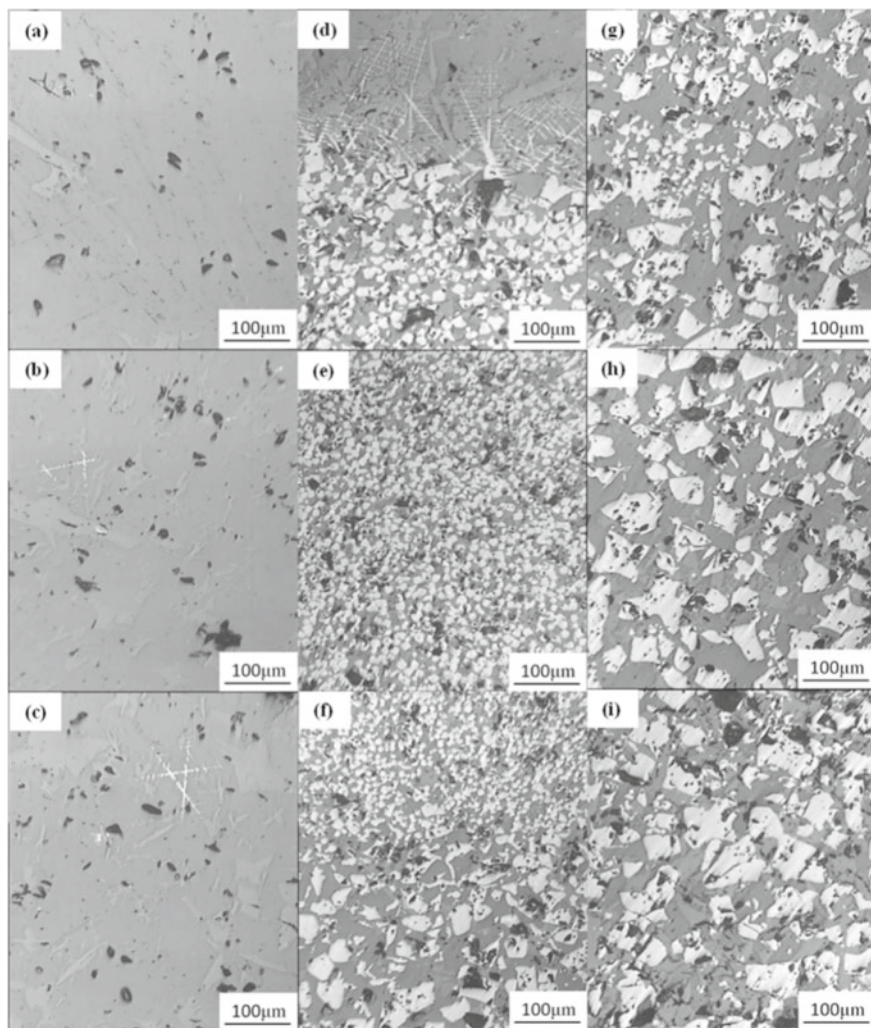


Fig. 2.16 SEM images of nine areas in the layered sample under super gravity at $G = 600$, $t = 20$ min, $T = 1578$ K

There is an obvious interface appearing in the middle areas (d)–(f) of the layered sample as shown in Fig. 2.16d–f, and the lower side of the interface area is full of fine equiaxed crystals of perovskite, as shown in Fig. 2.16e. Almost all of the large crystals of perovskite concentrate into the lower areas of (g)–(i) as shown in Fig. 2.16g–i, where the size of the equiaxed crystals increases significantly with the area approaching to the bottom of the sample along the direction of super gravity, and the peak value lies in the bottom area (i) of the sample.

Tables 2.3, 2.4, and 2.5 present the variations of volume fraction of perovskite in different areas of the layered samples with different gravity coefficient, different time, and different temperature, respectively. The volume fraction of perovskite is approaching zero from the upper area (a) to area (c) with the conditions of $G \geq 600$, $t \geq 20$ min, and $T \geq 1578$ K. By contrast, the volume fraction of perovskite increases slightly from the middle area (g) to area (i), and the peak value appears in area (e). The peak value is presented in the interface area (e) rather than the bottom area (i), mainly because of a great number of mall perovskite accumulating in area (e).

Table 2.3 Variations of volume fraction of perovskite in different areas of the layered samples with different gravity coefficient at $t = 10$ min and $T = 1578$ K

Gravity coefficient	Areas						
	(a)	(b)	(c)	(e)	(g)	(h)	(i)
150	8.29	10.06	13.96	37.72	22.48	28.17	31.26
300	0	9.02	13.58	38.61	25.5	30.4	34.06
450	0	0	9.43	39.9	28.51	31.72	36.77
600	0	0	0	44.86	30.29	32.42	36.5
750	0	0	0	46.17	31.81	33.15	36.44

Table 2.4 Variations of volume fraction of perovskite in different areas of the layered samples with different time at $G = 600$ and $T = 1578$ K

Time/min	Areas						
	(a)	(b)	(c)	(e)	(g)	(h)	(i)
5	7.54	10.36	14.46	40.13	33.89	37.17	40.47
10	0	6.89	12.58	42.17	34.5	37.4	40.56
20	0	0	0	43.26	35.74	38.85	41.29
30	0	0	0	44.86	36.29	39.42	41.93
40	0	0	0	46.17	36.81	40.15	42.44

Table 2.5 Variations of volume fraction of perovskite in different areas of layered the samples with different temperature at $G = 600$ and $t = 20$ min

Temperature/K	Areas						
	(a)	(b)	(c)	(e)	(g)	(h)	(i)
1518	2.25	4.77	5.06	47.89	37.42	39.17	41.37
1548	0	6.89	12.58	42.59	34.5	37.4	40.56
1578	0	0	0	39.97	32.15	38.54	40.98
1608	0	0	0	36.31	31.08	37.45	41.05
1638	0	0	0	34.89	30.81	38.75	40.44

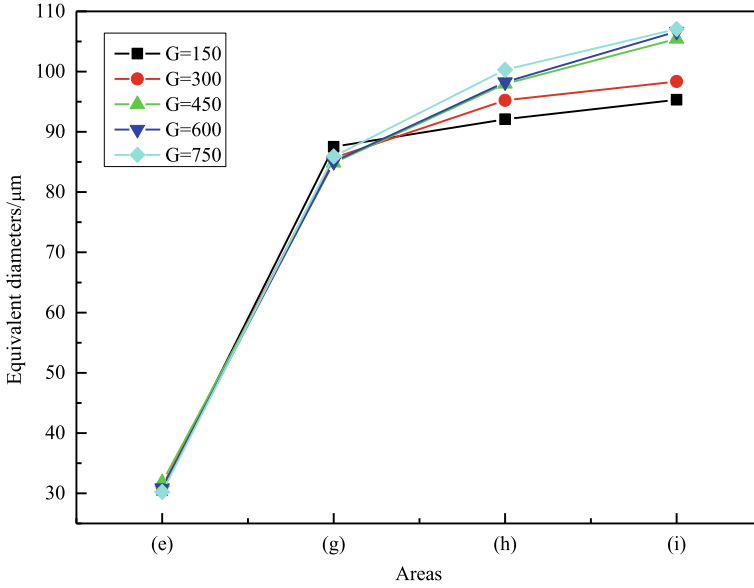


Fig. 2.17 Variations of equivalent diameters of perovskite in different areas of the layered samples with different gravity coefficient at $t = 10$ min and $T = 1578$ K

Figures 2.17, 2.18, and 2.19 show further that the particle distribution of perovskite varies in different areas of the layered sample obtained under super gravity. It indicates that the equivalent diameter of perovskite increases significantly along the direction of super gravity.

When perovskite is assumed to be spherical in shape, the motion equation of perovskite in the Ti-bearing slag melt can be calculated by Stokes' law:

$$\frac{\pi}{6}d^3(\rho_p - \rho_l)r\omega^2 - 3\pi\eta d\frac{dr}{dt} = \frac{\pi}{6}d^3\rho_p\frac{d^2r}{dt^2}. \quad (2.4)$$

If the inertial terms on the right-hand side of Eq. (2.4) is neglected, then

$$\frac{dr}{dt} = \frac{d^2(\rho_p - \rho_l)}{18\eta}\omega^2 r. \quad (2.5)$$

Thus:

$$Vr = \frac{d^2\Delta\rho}{18\eta}\omega^2 r. \quad (2.6)$$

If assuming ω is a constant,

$$r = r'e^{A\omega^2 t}. \quad (2.7)$$

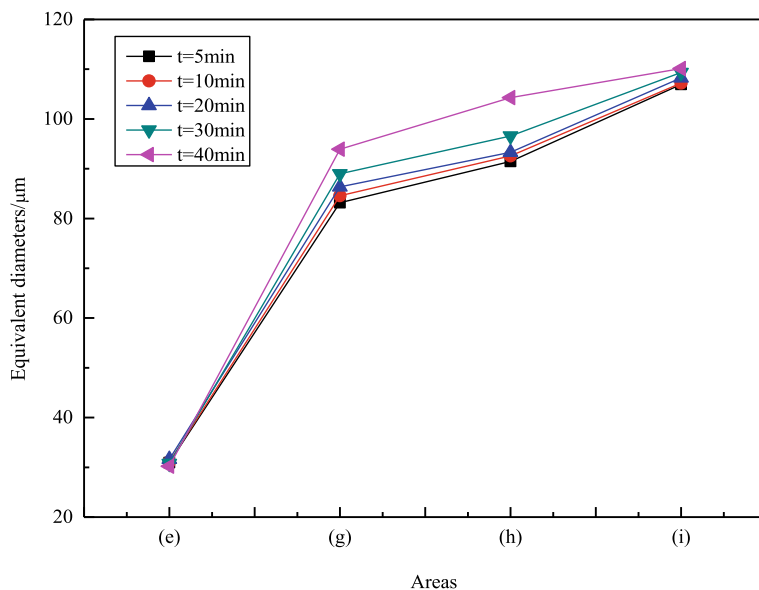


Fig. 2.18 Variations of equivalent diameters of perovskite in different areas of the layered samples with different time at $G = 600$ and $T = 1578$ K

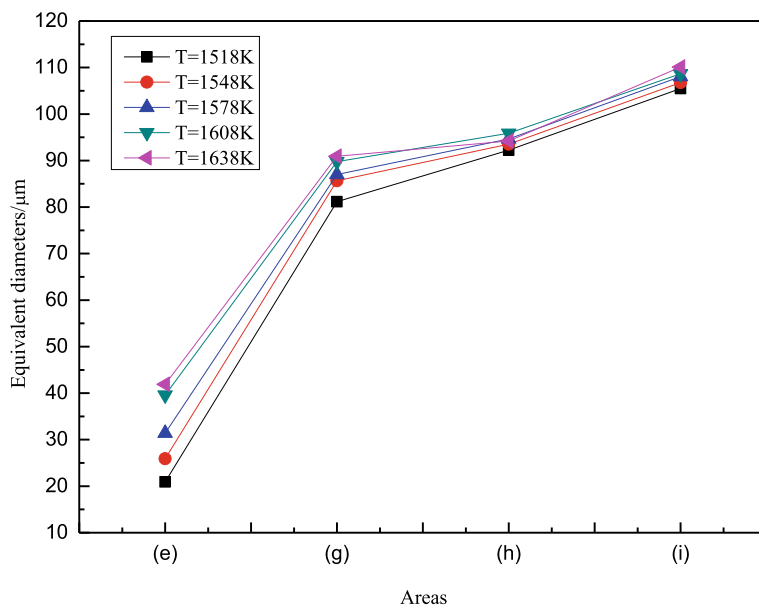


Fig. 2.19 Variations of equivalent diameters of perovskite in different areas of the layered samples with different temperature at $G = 600$ and $t = 20$ min

Thus:

$$t = \frac{1}{A\omega^2} \ln \frac{r}{r'} = \frac{900}{A\pi^2 N^2} \ln \frac{r}{r'}, \quad (2.8)$$

where $A = \frac{d^2 \Delta \rho}{18\eta}$, $\Delta \rho = \rho_p - \rho_l$.

Substituting the density of perovskite $\rho_p = 4.10 \times 10^3 \text{ kg/m}^3$, the density of Ti-bearing slag melt $\rho_l = 3.10 \times 10^3 \text{ kg/m}^3$, and the viscosity of the Ti-bearing slag melt $\eta = 1 \text{ N s/m}^2$, $N = 1465 \text{ r/min}$, $r = 0.27 \text{ m}$, and $r' = 0.23 \text{ m}$ into Eq. 2.8:

Hence:

$$t = 1.38 \times 10^{-7} \frac{1}{d^2}.$$

When $d = 100 \text{ }\mu\text{m}$, thus $t = 13.82 \text{ s}$

When $d = 30 \text{ }\mu\text{m}$, thus $t = 153.6 \text{ s} = 2.56 \text{ min}$

When $d = 10 \text{ }\mu\text{m}$, thus $t = 1382.4 \text{ s} = 23.04 \text{ min}$.

That is the moving speed of perovskite in the Ti-bearing slag melt, which is proportional to the size of perovskite as shown in Eq. 2.6. As a result, the larger perovskite gathers at the bottom of the sample, while some small ones accumulate in the middle of the sample, and the gradient size distribution of perovskite appears in the sample along the direction of super gravity.

What is more, Eq. 2.6 shows the arrival time to certain positions as a function of the size of perovskite. When substituting the density between perovskite and slag melt, the viscosity of the Ti-bearing slag melt, and the angular velocity with the constant into Eq. 2.8, it needs 13.82 s for the perovskite with the equivalent diameter of 100 μm moving from the position of 0.23 m to 0.27 m under the force of super gravity, while it needs 2.56 min and 23.04 min for the perovskite with the equivalent diameter of 30 μm and 10 μm , respectively. It seems that the arrival time is smaller than the experiments done in this study, which is mainly due to the assumption that perovskites are spherical in shape. In fact, perovskite is mainly equiaxed crystals, which will experience more viscous resistance than the spherical perovskite. In addition, the volume fraction of perovskite is more than 30% in the Ti-bearing slag melt, which would also increase the interparticle collision and delay the movement of perovskite.

Figure 2.20 shows the XRD patterns of the separated perovskite and slag phases obtained under super gravity compared with normal gravity. There are various diffraction peaks of perovskite, diopside, and pyrope that appear significantly in the parallel sample obtained under normal gravity. In contrast, an overwhelming majority of perovskite accumulates in the bottom of the sample as driven by super gravity, while the slag phase including diopside and pyrope occupies the upper side of the sample.

Under the conditions of $G = 600$, time $t = 20 \text{ min}$, and temperature $T = 1578 \text{ K}$, the mass fraction of TiO_2 in the perovskite phase is up to 34.97 wt%, while that of the slag phase is just 11.16 wt% as listed in Table 2.6. The recovery ratio of Ti in the

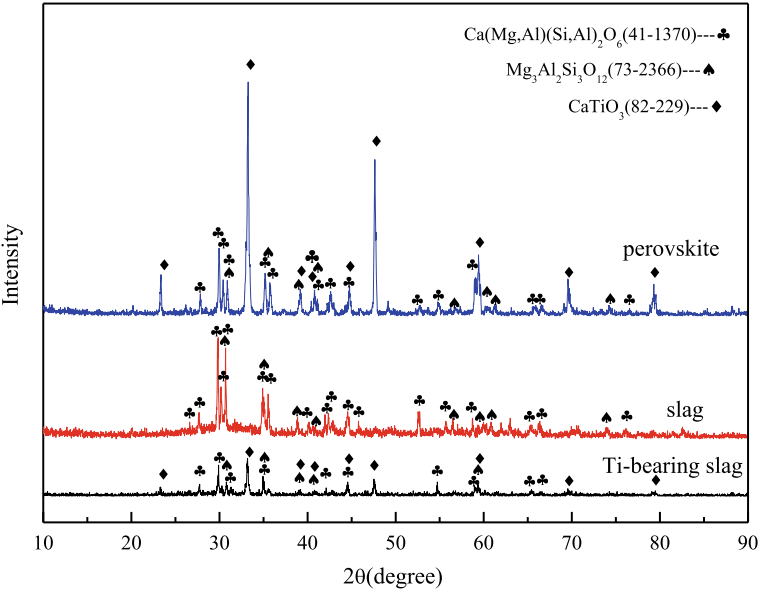


Fig. 2.20 XRD patterns of the perovskite and slag phases under super gravity

perovskite phase is up to 74.16% under super gravity, as calculated via Eqs. 2.9 and 2.10. The recovery ratio of Ti in the perovskite phase under super gravity is listed in Table 2.7.

$$\varepsilon_{\text{Ti-P}} = \frac{m_{\text{P}} \times \omega_{\text{Ti-P}}}{m_{\text{P}} \times \omega_{\text{Ti-P}} + m_{\text{S}} \times \omega_{\text{Ti-S}}} \times 100\% \tag{2.9}$$

$$\varepsilon_{\text{Ti-S}} = \frac{m_{\text{S}} \times \omega_{\text{Ti-S}}}{m_{\text{S}} \times \omega_{\text{Ti-P}} + m_{\text{S}} \times \omega_{\text{Ti-S}}} \times 100\%, \tag{2.10}$$

Table 2.6 Chemical compositions of the perovskite and slag phases under super gravity (wt%)

Phases	CaO	TiO ₂	SiO ₂	Al ₂ O ₃	MgO
Perovskite phase	37.42	34.97	15.09	7.55	4.98
Slag phase	26.85	11.16	35.62	17.43	8.94
Parallel sample	30.88	22.34	25.28	13.08	7.19

Table 2.7 Recovery ratio of Ti in the perovskite phase under super gravity

Phases	Mass fraction (%)	Mass fraction of TiO ₂ (wt%)	Recovery ratio of Ti (%)
Perovskite phase	47.81	34.97	74.16
Slag phase	52.19	11.16	25.84

where $\varepsilon_{\text{Ti-P}}$ and $\varepsilon_{\text{Ti-S}}$ are the recovery ratio of Ti in the perovskite phase; m_{P} and m_{S} are the mass fractions of the perovskite and slag phases; and $w_{\text{Ti-P}}$ and $w_{\text{Ti-S}}$ are the mass fractions of Ti in the perovskite and slag phases.

2.1.5 Separation of Perovskite from $\text{CaO-TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ System by Super Gravity

2.1.5.1 Experimental Procedure

Based on the crystallization and growth behaviors of perovskite in Ti-bearing slag, 20 g of the Ti-bearing slag in which the perovskite was fully crystallized was put onto a graphite fiber felt of 10 mm height with the pore size less than 0.01 mm and held on a graphite filter (I.D. 19 mm) with the pore size of $d = 0.5$ mm. The composite graphite crucible was heated to 1563 K in the heating furnace of the centrifugal apparatus, and then the centrifugal apparatus was started and adjusted to the specified angular velocity of 1465 r/min ($G = 600$) at the constant 1563 K for 5 min. Afterward, the centrifugal apparatus was shut off, and the graphite crucible was taken out and water-quenched. The samples held on the filter and flow through the filter were sectioned longitudinally along the center axis. One was characterized by XRD and XRF to obtain the respective mineral composition and chemical component, and the other was measured by SEM and EDS to gain the microstructure and element distribution of the separated samples. Simultaneously, the parallel experiment was carried out at 1563 K for 5 min under normal gravity.

2.1.5.2 Separation Behavior of Perovskite

Figure 2.21 shows vertical profiles of the sample obtained by super gravity ($G = 600$, $t = 5$ min, and $T = 1563$ K) compared with the parallel sample under normal gravity. The Ti-bearing slag is separated into two parts by super gravity, where the sample held back on the filter appears white, with a number of porosities, while the sample went through the filter presents black, with a glassy state, as shown in Fig. 2.21b. In contrast, the uniform structure presents in the parallel sample under the normal gravity, as shown in Fig. 2.21a. Combined with the X-ray diffraction analysis as shown in Fig. 2.22, almost all of the perovskite were held back on the filter, while the slag melt went through the filter which transformed into the diopside and pyrope phases during cooling process.

With the help of SEM and random EDXA analysis, the microstructures of the separated perovskite and slag phases are displayed in Fig. 2.23, and the EDS analysis data for the perovskite and slag phases are shown in Table 2.8. It is clear that the perovskite held on the filter is dendriform, and the primary dendrite is well developed

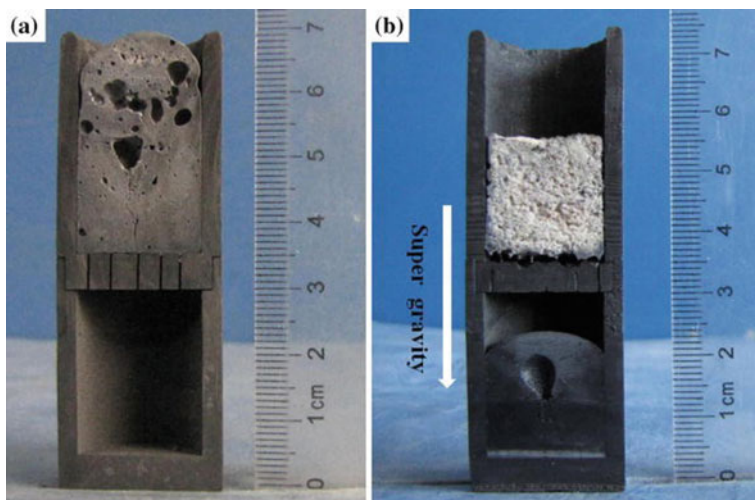


Fig. 2.21 Vertical profile of the samples obtained by super gravity compared with the normal gravity: **a** $G = 1$, $t = 5$ min, $T = 1563$ K; **b** $G = 600$, $t = 5$ min, $T = 1563$ K

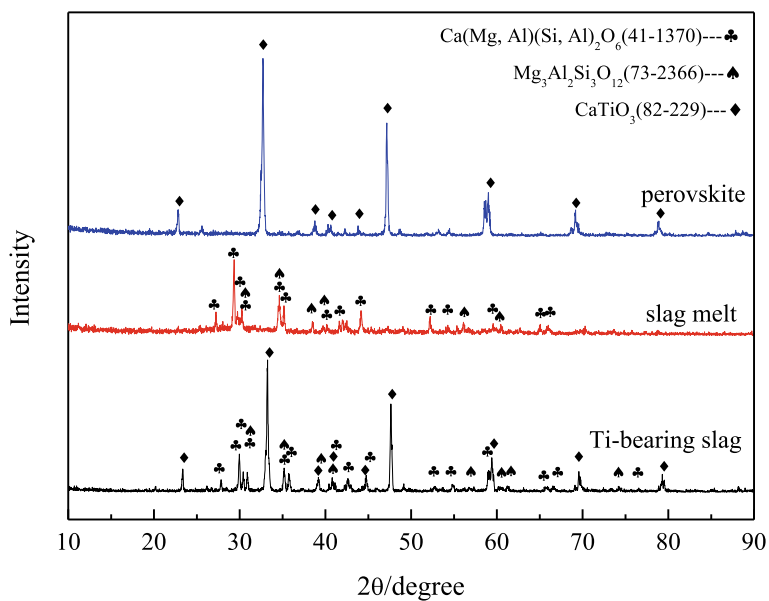


Fig. 2.22 XRD patterns of the samples obtained by super gravity

with an interdendritic angle of 90° and secondary dendrite spacing $d_2 \approx 10\text{ }\mu\text{m}$. In constant, it is hard to find any perovskite particles in the slag phase.

The chemical compositions of the separated samples are listed in Table 2.9. It is confirmed that the Ti is mainly enriched into the perovskite, while the Mg, Al, and Si are mainly formed the slag melt, which is fully separated from the perovskite by super gravity and then transform into the diopside and pyrope phases during cooling process. The mass fraction of TiO_2 in the perovskite phase is up to 52.94 wt%, while the mass fraction of TiO_2 in the slag phase is just 5.88 wt%. Accordingly, the recovery ratio of Ti in the separated perovskite phase is up to 81.28% by super gravity, as listed in Table 2.10.

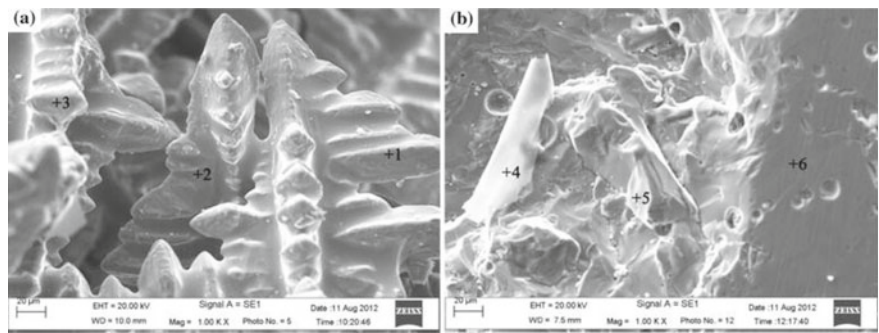


Fig. 2.23 SEM images of the separated sample by super gravity: **a** perovskite; **b** slag phase

Table 2.8 EDS data of the perovskite and slag phases (wt%)

No	Ca	Si	Ti	Al	Mg	O
Pt1	42.05		30.28			27.67
Pt2	42.35		28.66			28.99
Pt3	38.62		35.71			25.67
Pt4	3.39	20.78	2.78	12.64	15.25	45.16
Pt5	16.7	15.77	3.77	17.89	7.19	38.68
Pt6	15.68	15.34	3.17	18.14	7.62	40.05

Table 2.9 Chemical compositions of separated samples by super gravity (wt%)

Phases	CaO	TiO ₂	SiO ₂	Al ₂ O ₃	MgO
Perovskite phase	39.88	52.94	4.08	2.07	1.03
Slag phase	29.98	5.88	37.16	16.39	10.59
Parallel sample	30.88	22.34	25.28	13.08	7.19

Table 2.10 Recovery ratio of Ti in the separated perovskite and slag phase by super gravity

Phases	Mass fraction (%)	Mass fraction of TiO ₂ (wt%)	Recovery ratio of Ti (%)
Perovskite phase	32.53	52.94	81.28
Slag phase	67.47	5.88	18.72

2.1.6 Motion Behavior of Perovskite in Ti-Bearing Blast Furnace Slag Under Super Gravity

On the basis of the motion and separation behaviors of perovskite in the CaO–TiO₂–SiO₂–Al₂O₃–MgO system under the force of super gravity, the industrial Ti-bearing blast furnace slag produced from blast furnace process of Panzhihua Iron and Steel Corporation of China is conducted, and the selective crystallization and separation of perovskite from the Ti-bearing blast furnace slag by super gravity are carried out.

2.1.6.1 Experimental Procedure

The natural cooled Ti-bearing blast furnace slag produced from the Panzhihua Iron and Steel Corporation of China is used as the raw materials. As listed in Table 1.1, the mass fractions of TiO₂ and CaO are 23.35 wt% and 28.64 wt%, respectively. According to the XRD analysis shown in Fig. 1.5, the main minerals of the Ti-bearing blast furnace slag include the perovskite (CaTiO₃), pyrope (Mg₃Al₂Si₃O₁₂), and diopside (Ca(Mg,Al)(Si,Al)₂O₆).

The Ti-bearing blast furnace slag was first melted at 1773 K and cooled slowly from 1593 to 1563 K at a cooling rate of 0.5 K/min in the muffle furnace for the fully crystallization of perovskite and then quenched in water. Afterward, an amount of 40 g of the Ti-bearing blast furnace slag above was put into a graphite crucible with an inner diameter of 19 mm and heated up to 1578 K in the heating furnace of centrifugal apparatus. And then the centrifugal apparatus was started and adjusted to the angular velocity of 1638 r/min ($G = 750$). After concentrating at 1578 K for 25 min, the centrifugal apparatus was shut off, and the graphite crucible was quenched in water. Simultaneously, the parallel experiment was carried out at the same temperature for 25 min in the normal gravity field.

2.1.6.2 Motion Behavior of Perovskite in Ti-Bearing Blast Furnace Slag

The vertical sections of the sample obtained under super gravity with gravity coefficient of $G = 750$ compared with normal gravity ($G = 1$) are illustrated in Fig. 2.24. In a macroscopic view, a uniform porosity structure is presented in the sample obtained in the normal gravity field. By constant, the layered structure appears significantly in the sample obtained in a super gravity field. The upper part in a yellowish-gray is glassy state, and the bottom part in a gray-white is compact structure. Combined

with the XRD pattern as shown in Fig. 2.25, the upper part of the layered sample is only comprised of pyrope and diopside. In contrast, the bottom part of the layered sample is mainly comprised of perovskite and some pyrope and diopside, whereas the diffraction peak intensity of perovskite is much higher than that of pyrope and diopside. It is evident that perovskite remains in a solid state, while the other minerals transformed into the molten slag after heating at 1578 K, and some porosity is resulted from the slow movement of perovskite in the slag melt under normal gravity, as shown in Fig. 2.24a. In constant, all of the perovskite moves to the bottom of the sample along the super gravity direction due to the density difference with the slag melt and concentrated at the bottom of the layered sample, whereas the slag melt concentrated at the upper of the sample along the opposite direction, as shown in Fig. 2.24b.

To investigate further the motion behavior of perovskite in the Ti-bearing blast furnace slag melt under the super gravity field, the layered sample was divided into

Fig. 2.24 Vertical sections of the sample obtained by super gravity compared with normal gravity: **a** $G = 1$; **b** $G = 750$

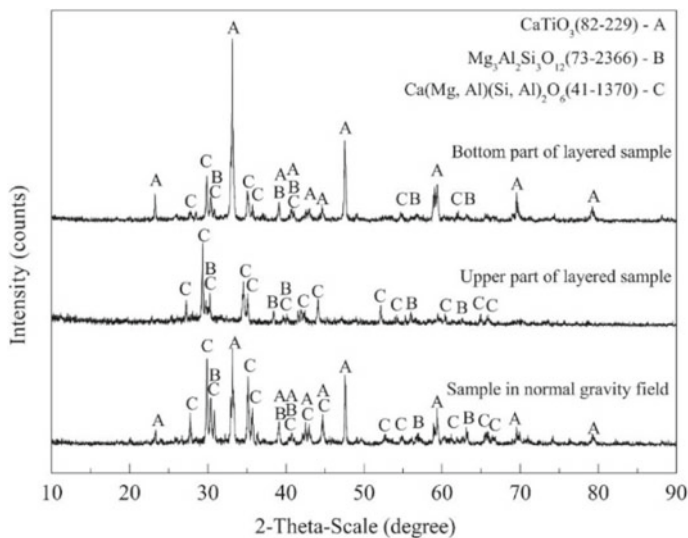
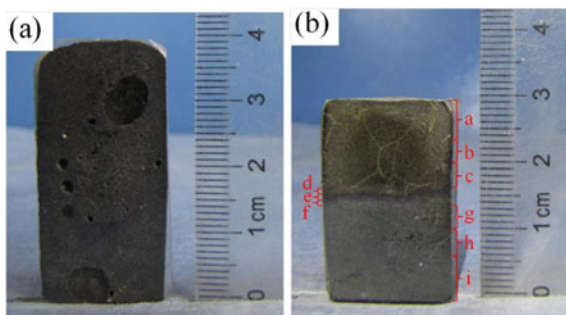


Fig. 2.25 XRD patterns of different areas in the layered sample obtained by super gravity

nine areas along the super gravity direction and characterized, respectively, by the metallographic microscopy, as shown in Fig. 2.26. In the upper areas (a)–(c) of the layered sample, it is practically impossible to find any perovskite. Nevertheless, the fine dendrites crystals, fine equiaxed crystals, and larger equiaxed crystals of perovskite appeared successively in the upper, middle, and bottom of the interface areas (d)–(f) in the layered sample. The larger equiaxed crystals of perovskite concentrate in the bottom areas (g)–(i) of the layered sample, and the crystals size increases significantly with the area approaching to the bottom along the direction of super gravity.

According to the variations in volume fraction and equivalent diameter of the perovskite in different areas of the layered sample as shown in Fig. 2.27, it is obvious that the equivalent diameter and volume fraction of perovskite in the upper areas (a)–(c) are approaching to zero. Instead, the equivalent diameter of perovskite increases significantly from area (d) to area (i) along the super gravity direction, and the peak value appears in the bottom area (i), which is up to 110 μm . Similarly, the volume fraction of perovskite also increases from the bottom areas (g)–(i) along the super gravity direction, but the peak value is presented in the interface area (e) due to the small size of perovskite resulting in a great number of that accumulating in this area. It gives further evidence that all of the perovskite crystals move along the super gravity direction and collide with each other, grows into larger equiaxed crystals, and then concentrates in the bottom area of the layered sample.

The chemical compositions of the perovskite and slag phases in the layered sample obtained by super gravity compared with normal gravity are given in Table 2.11. The mass fraction of TiO_2 in the perovskite phase is up to 34.65 wt%, whereas those of SiO_2 , Al_2O_3 , and MgO are decreased to 17.85 wt%, 5.97 wt%, and 4.83 wt%, respectively. In contrast, the mass fraction of TiO_2 in the slag phase decreases to 12.23 wt%, whereas those of SiO_2 , Al_2O_3 , and MgO are up to 31.23 wt%, 15.52 wt%, and 11.37 wt%, respectively. It is indicated that the super gravity field is definitely beneficial for the directional migration of perovskite in the Ti-bearing slag melt. Under the force of super gravity, an overwhelming majority of perovskite can be separated from the Ti-bearing slag melt, and the recovery ratio of Ti in the perovskite phase is up to 75.28%.

2.1.7 Separation of Perovskite from Ti-Bearing Blast Furnace Slag by Super Gravity

2.1.7.1 Experimental Procedure

The Ti-bearing blast furnace slag with a basicity of 1.30 was melted at 1773 K and then cooled slowly at 1593–1563 K for 60 min to promote the fully crystallization of perovskite, which was used for the separation of perovskite from the Ti-bearing blast furnace slag by super gravity. 20 g of the Ti-bearing blast furnace slag was put

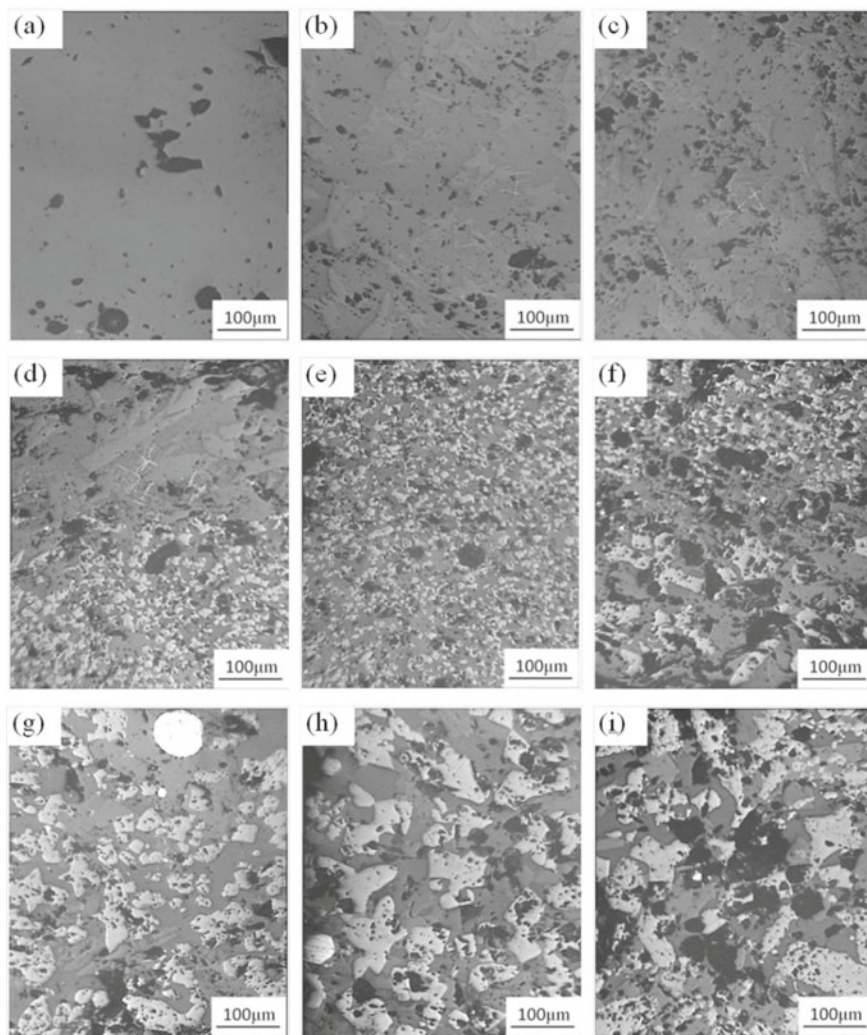


Fig. 2.26 SEM images of the nine areas in the layered sample obtained by super gravity

onto a graphite fiber felt of 10 mm height with the pore size less than 0.01 mm, held on a graphite filter (I.D. 19 mm) with the pore size of $d = 0.5$ mm, and then put into the upper part of composite graphite crucible. The Ti-bearing blast furnace slag was heated to 1578 K in the heating furnace of centrifugal apparatus to make the other minerals form the molten slag, while the perovskite remains in solid state. And then, the centrifugal apparatus was started and adjusted to the specified angular velocity of 1638 r ($G = 750$) at the constant temperature for 10 min. After that, the centrifugal apparatus was shut off, and the graphite crucible was taken out and water-quenched.

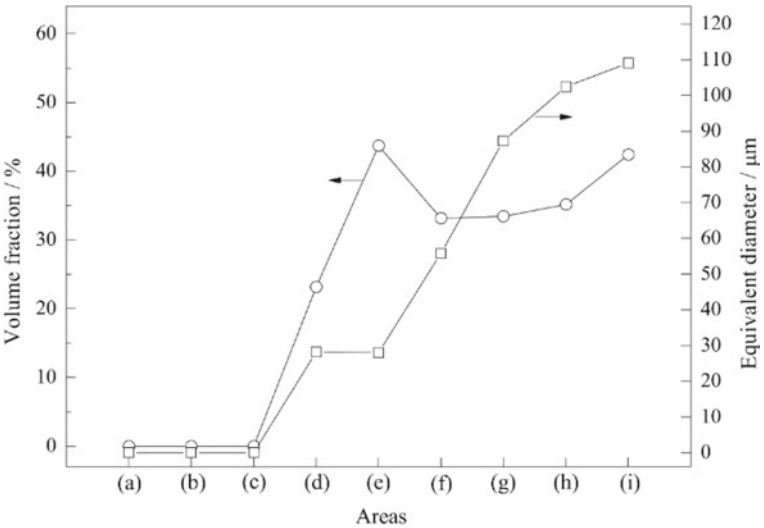


Fig. 2.27 Volume fractions and equivalent diameters of perovskite in different areas of the layered sample obtained by super gravity

Table 2.11 Chemical compositions of the perovskite and slag phases obtained by super gravity (wt%)

Phases	CaO	TiO ₂	SiO ₂	Al ₂ O ₃	MgO	Fe ₂ O ₃
Perovskite phase	34.28	34.65	17.85	5.97	4.83	2.41
Slag phase	29.01	12.23	31.23	15.52	11.37	0.64
Ti-bearing blast furnace slag	30.92	23.31	24.82	10.34	8.17	2.44

Simultaneously, the parallel experiment was carried out at 1578 K for 10 min under the normal gravity.

After the super gravity separation, the samples that held on and went through the filter were sectioned longitudinally into two parts along the direction of super gravity. One part was measured by SEM–EDS method for analyzing the microstructures of the separated samples. The other part was crossly divided along the filter and characterized by XRD and XRF methods to determine the mineral compositions and chemical components of the separated samples. After that, the recovery ratio of Ti was calculated via Eq. 2.8.

2.1.7.2 Separation Behavior of Perovskite from Ti-Bearing Blast Furnace Slag

The vertical sections of the sample obtained by super gravity with gravity coefficient of $G = 750$ compared with the parallel sample with gravity coefficient of $G = 1$ are

illustrated in Fig. 2.28. It is obvious that the layered structure appears significantly in the sample obtained by super gravity. In a macroscopic view, the sample that held on the filter appears as a black, porous structure, whereas the sample went through the filter shows a gray, glassy state, as shown in Fig. 2.28b. In contrast, the whole sample with a uniform structure is completely held on the filter under normal gravity, as shown in Fig. 2.28a.

With the help of XRD analysis, the mineral compositions of samples that held on and went through the filter obtained by super gravity with the gravity coefficient of $G = 750$ compared with the parallel sample under normal gravity are shown in Fig. 2.29. Compared with the mixed diffraction peaks of perovskite, pyrope and diopside appeared in the parallel sample, the only diffraction peak of perovskite appeared significantly in the sample held on the filter, while only the diffraction peaks of pyrope and diopside appeared in the sample went through the filter. It is indicated that the Ti fully transformed into perovskite, while the other minerals form the molten slag, whereas the two phases with the different physical states can hardly be separated from each other under the condition of normal gravity. Under the force of super gravity, the slag melt moves along the super gravity direction and goes through the filter and then concentrated as slag phase in the bottom crucible, while the perovskite crystals with the size of 0.05–0.12 mm are fully intercepted by the filter with the pore size less than 0.01 mm and separate from the slag melt efficiently.

The SEM–EDS analysis for the separated samples that held on and went through the filter by super gravity was carried out. According to the EDS data given in Table 2.12, the perovskite phase is only comprised of calcium (26.69–27.84 wt%), titanium (32.61–33.82 wt%), and oxygen (38.31–40.15 wt%), whereas the slag phase mainly consists of pyrope and diopside. As the SEM images shown in Fig. 2.30,

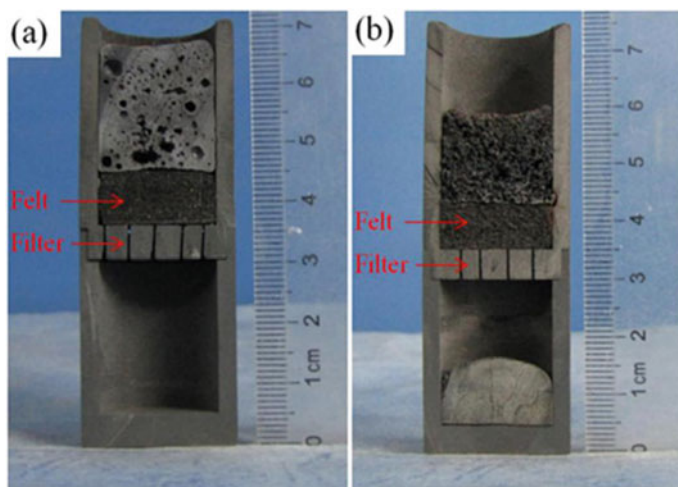


Fig. 2.28 Vertical sections of the sample obtained by super gravity compared with normal gravity: **a** $G = 1$; **b** $G = 750$

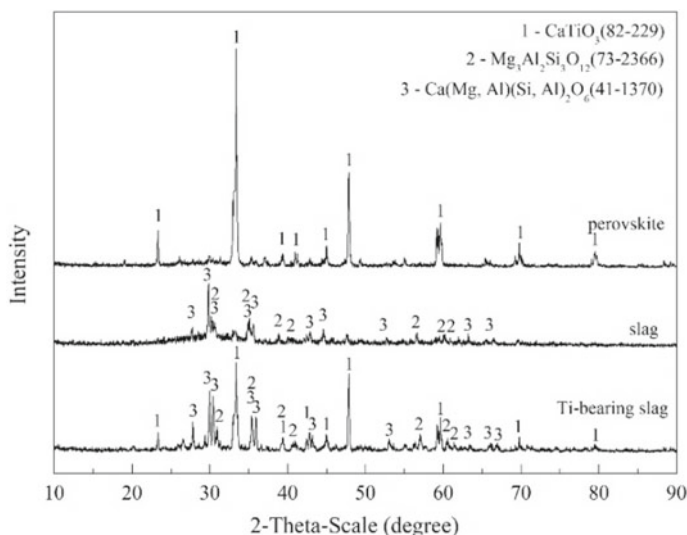


Fig. 2.29 XRD patterns of the separated perovskite and slag phases obtained by super gravity

the separated perovskite phase appeared as the typical dendrite structure from a microscopic view, and the secondary dendrite is well developed with some fine iron grains distributed on it. In contrast, the separated slag phase presents in a compact structure, in which it is practically impossible to find any perovskite. It confirms that all of the perovskites are effectively separated from the molten Ti-bearing blast furnace slag as derived by super gravity.

The chemical compositions of the separated samples obtained by super gravity compared with the parallel sample are given in Table 2.13. After the separation of perovskite and slag phases from Ti-bearing blast furnace slag by super gravity with the gravity coefficient of $G = 750$ at 1578 K for 10 min, the mass fraction of TiO_2 in the perovskite phase is up to 46.36 wt%, whereas that of the slag phase is only 8.77 wt%. Simultaneously, the mass fractions of other minerals (SiO_2 , Al_2O_3 , and MgO) in the slag phase are up to 35.9 wt%, 14.86 wt%, and 10.67 wt%, whereas that of the perovskite phase are only 7.13 wt%, 4.22 wt%, and 3.28 wt%, respectively.

Table 2.12 EDS data of various phases in the separated samples (wt%)

Position	Ca	Si	Ti	V	Fe	Al	Mg	O
Figure 2.30 Pt.1	26.69	—	32.61	0.55	—	—	—	40.15
Figure 2.30 Pt.2	27.48	—	33.82	0.39	—	—	—	38.31
Figure 2.30 Pt.3	4.95	—	2.24	—	90.29	—	—	2.52
Figure 2.30 Pt.4	18.63	15.64	3.32	—	—	15.37	7.45	39.59
Figure 2.30 Pt.5	4.44	20.54	4.83	—	—	11.47	13.44	45.28

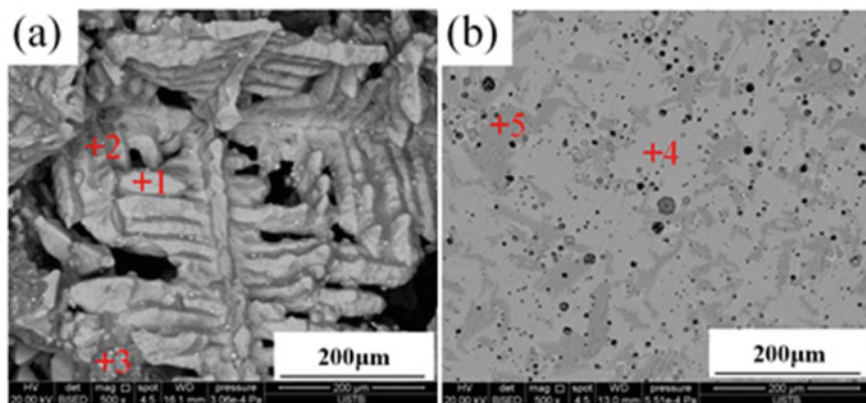


Fig. 2.30 SEM images of the separated samples by super gravity: **a** perovskite; **b** slag

Table 2.13 Chemical compositions of the separated samples obtained by super gravity (wt%)

Phases	TiO ₂	CaO	SiO ₂	Al ₂ O ₃	MgO	Fe ₂ O ₃
Perovskite phase	46.36	36.13	7.13	4.22	3.28	2.88
Slag phase	8.77	28.85	35.9	14.86	10.67	0.95
Ti-bearing blast furnace slag	23.38	31.05	25.56	11.21	7.13	1.67

Table 2.14 Recovery ratio of Ti in the separated samples obtained by super gravity

Phases	Mass fraction (%)	Mass fraction of TiO ₂ (wt%)	Recovery ratio of Ti (%)
Perovskite phase	40.4	46.36	78.17
Slag phase	59.6	8.77	21.83

In the case of $G = 750$, $T = 1578$ K, and $t = 10$ min, the recovery ratio of Ti in the separated perovskite phase is up to 78.17% as listed in Table 2.14.

2.2 Phase Transformation of Ti and Separation of Rutile in Ti-Bearing Slag

Compared to the perovskite ($\text{CaO} \cdot \text{TiO}_2$), a mole of perovskite is composed of one TiO_2 molecule and one CaO molecule, where the theoretical content of TiO_2 in perovskite is only 58.87 wt%, the rutile (TiO_2) with a higher titanium content, and a simpler composition would be a better choice for recovering titanium from the Ti-bearing slag. In this section, selective separation of rutile from the Ti-bearing slag

through phase transformation and super gravity separation is proposed. The thermodynamic analysis and phase transformation behavior for Ti to rutile, selective crystallization, and selective separation behaviors of rutile from the $\text{CaO-TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ system and the Ti-bearing blast furnace slag are studied, respectively [41, 49].

2.2.1 Thermodynamic Analysis for Phase Transformation of Ti in $\text{CaO-TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ System

The equilibrium phase diagram of $\text{CaO-SiO}_2\text{-TiO}_2\text{-6wt\%MgO-12wt\%Al}_2\text{O}_3$ calculated through FactSage 7.2 is shown in Fig. 2.31, and the equilibrium phase of Ti in the $\text{CaO-SiO}_2\text{-TiO}_2\text{-MgO-Al}_2\text{O}_3$ system as a function of basicity and TiO_2 content is shown in Fig. 2.32. Based on the thermodynamic analysis, it is found that perovskite ($\text{CaO}\cdot\text{TiO}_2$) is the main equilibrium phase of Ti under the condition basicity of 1.1–0.7 in $\text{CaO-TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ system. The amount of perovskite decreases obviously with the basicity decreasing from 1.1 to 0.7 in thermodynamics. With the decrease of basicity to 0.5, the primary equilibrium phase of Ti transforms from the perovskite to rutile thermodynamically. Moreover, the amount of rutile increases thermodynamically with the increase of TiO_2 content from 22.5 to 28.5%, as calculated in Fig. 2.32.

2.2.2 Phase Transformation Behavior of Ti to Rutile in $\text{CaO-TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ System

2.2.2.1 Experimental Procedure

On account of the $\text{CaO-SiO}_2\text{-TiO}_2\text{-6wt\%MgO-12wt\%Al}_2\text{O}_3$ equilibrium phase diagram as calculated in Fig. 2.31, the slag basicity and TiO_2 content of Ti-bearing slag were varied from $R = 1.1$ to 0.9, 0.7, 0.5, and $w(\text{TiO}_2) = 22.5\%$ to 24.5%, 26.5%, and 28.5%, respectively, to investigate the phase transformation behavior of Ti. Firstly, 10 g of the Ti-bearing slags were filled into an alumina crucible, which were melted at 1773 K in a muffle furnace, and followed by slow cooling at 1773–1473 K at the rate of 1 K/min for crystallization of Ti in the slags. Subsequently, the crucibles were taken out from the muffle furnace and water-quenched immediately. After that, all the samples were divided into two halves along the longitudinal center line and analyzed by the XRD, SEM-EDS, and EPMA methods for investigating the phase variation of Ti in various Ti-bearing slags and determining the favorable conditions for transformation of Ti from perovskite to rutile.

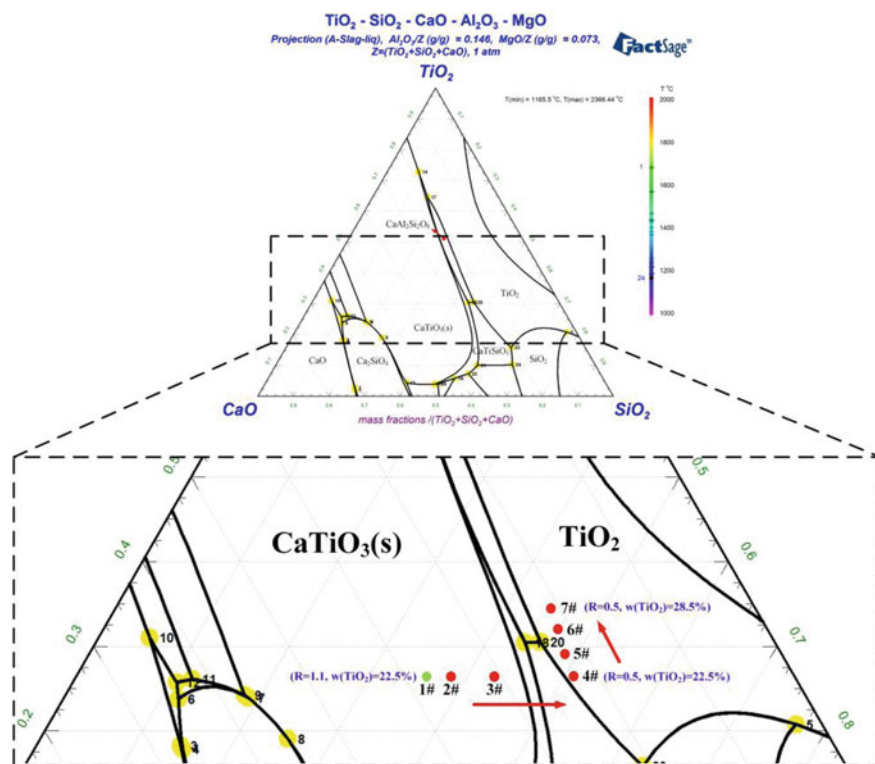


Fig. 2.31 Equilibrium phase diagram of $\text{CaO-SiO}_2\text{-TiO}_2\text{-6wt\%MgO-12wt\%Al}_2\text{O}_3$ system

2.2.2.2 Phase Transformation Behavior of Ti to Rutile

The phase transformation behaviors of Ti in Ti-bearing slag as a function of slag basicity are indicated by the XRD patterns and SEM images, as shown in Fig. 2.33. Apparently, the perovskite ($\text{CaO} \cdot \text{TiO}_2$) and diopside ($\text{Ca}(\text{Mg}, \text{Al})(\text{Al}, \text{Si})_2\text{O}_6$) are the primary crystallization phases in the original Ti-bearing slag with the basicity of 1.1, and the Ti elements are mainly distributed in perovskite phase, as presented in Fig. 2.33b. Through comparing the standard Gibbs free energy changes for reactions of Ca^{2+} with various anions in the molten Ti-bearing slag according to Eqs. (2.11)–(2.13), since the activity of Ca^{2+} in the slag is decreased with the decreasing of slag basicity, the Ca^{2+} reacts preferentially with $[\text{SiO}_4]^{4-}$, Mg^{2+} , and $[\text{AlO}_4]^{5-}$ rather than $[\text{TiO}_4]^{4-}$. Thus, the diffraction peaks of perovskite are dramatically decreased with the decrease of slag basicity from 1.1 to 0.9, while those of the anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) appears with the disappearance of diopside in the slag with the basicity of 0.9. As the slag basicity decreases further from 0.9 to 0.7, the diffraction peaks of perovskite and anorthite continue to decrease, and their amounts and lengths both decrease significantly in the slag, as presented in Fig. 2.33c–d. When the slag basicity decreases to 0.5, the perovskite and anorthite are completely disappeared from the slag, while

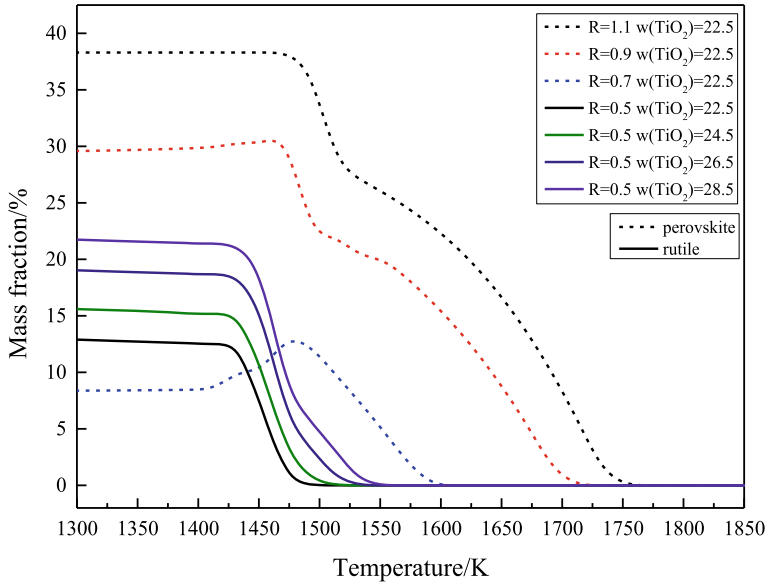
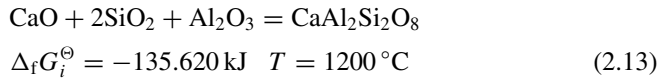
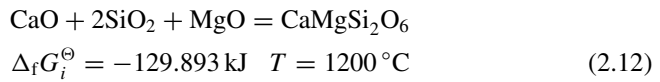
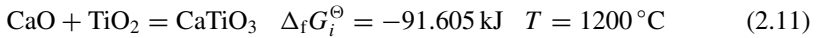


Fig. 2.32 Equilibrium phase of Ti in $\text{CaO-SiO}_2\text{-TiO}_2\text{-6wt\%MgO-12wt\%Al}_2\text{O}_3$ system as a function of basicity and TiO_2 content

the only rutile in size of 80–150 μm appears obviously in the slag, as presented in Fig. 2.33e. So far, the primary crystallization phase of Ti is completely transformed from perovskite into rutile in the Ti-bearing slag.



Based on the $\text{CaO-SiO}_2\text{-TiO}_2\text{-6wt\%MgO-12wt\%Al}_2\text{O}_3$ equilibrium phase diagram, TiO_2 content is another influence factor which is contributed to the phase transformation of Ti besides the slag basicity. Therefore, the phase transformation behaviors of Ti with varying of TiO_2 content in Ti-bearing slag are investigated further, and the XRD patterns and SEM images are shown in Fig. 2.34. It is indicated that decreasing of the slag basicity to $R = 0.5$ creates a favorable condition for single crystallization of rutile, and the only rutile is crystallized in the Ti-bearing slag. Moreover, the diffraction peak intensity of the single rutile increases significantly

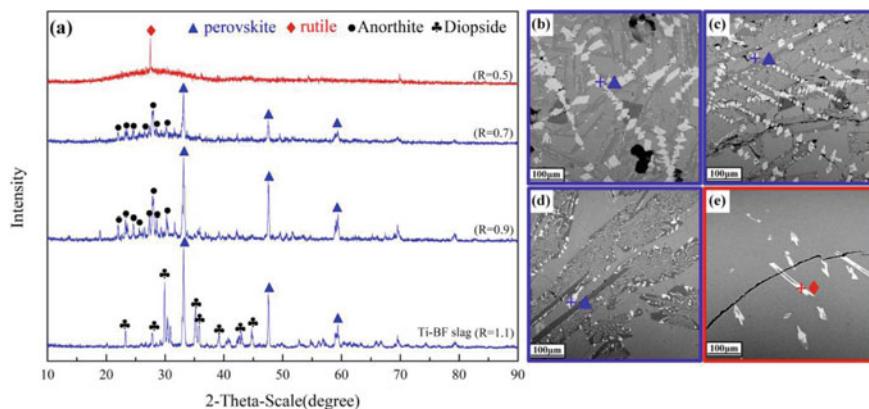


Fig. 2.33 Phase transformation of Ti as a function of slag basicity: **a** XRD patterns; **b–e** SEM images of $R = 1.1, 0.9, 0.7$, and 0.5 , respectively

with the $w(\text{TiO}_2)$ increasing from 22.5 to 26.5%, and its length increases obviously from 80–150 to 500–600 μm , as shown in Fig. 2.34b–d. However, the amount and length of rutile decrease significantly with increasing the $w(\text{TiO}_2)$ further from 26.5 to 28.0%, as the formation of anorthite which inhibits the crystallization of rutile, as presented in Fig. 2.34e.

Moreover, the EPMA results for phase transformation of Ti in Ti-bearing slag under varying conditions are shown in Fig. 2.35. As further verified, the Ti elements are efficiently enriched from its primary crystallization phase of perovskite into rutile in the Ti-bearing slag through decreasing the slag basicity from 1.1 to 0.5, and the Ti is adequately crystallized into the single rutile crystal with a larger length as the $w(\text{TiO}_2)$ increased from 22.5 to 26.5%.

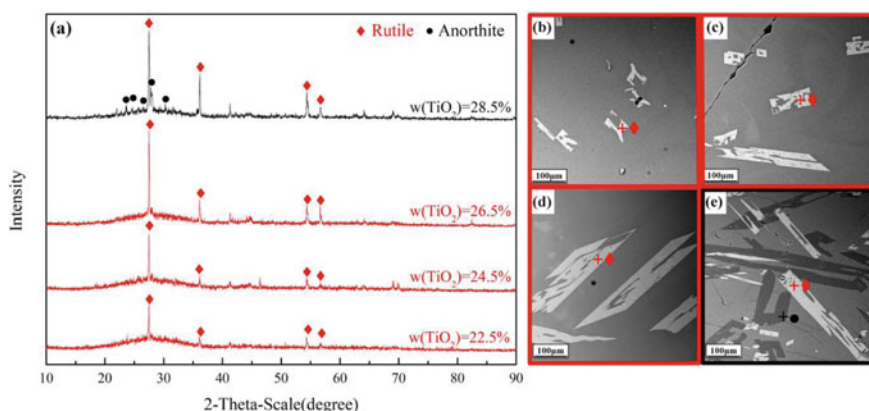


Fig. 2.34 Phase transformation of Ti as a function of TiO_2 content: **a** XRD patterns; **b–e** SEM images of $w(\text{TiO}_2) = 22.5\%, 24.5\%, 26.5\%$, and 28.5% , respectively

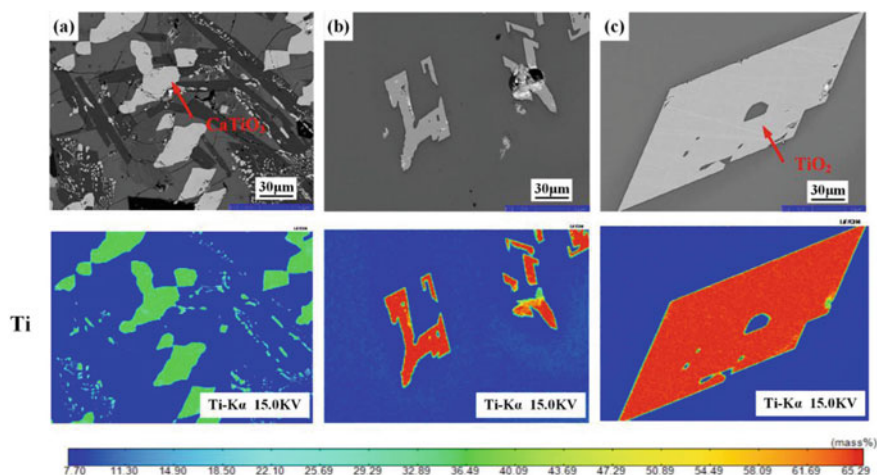


Fig. 2.35 EPMA results for phase transformation of Ti from perovskite into rutile: **a** $R = 1.1$ $w(\text{TiO}_2) = 22.5\%$; **b** $R = 0.5$ $w(\text{TiO}_2) = 22.5\%$; **c** $R = 0.5$ $w(\text{TiO}_2) = 26.5\%$

2.2.3 Crystallization Behavior of Rutile in $\text{CaO-TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ System

2.2.3.1 Experimental Procedure

The crystallization behavior of $\text{CaO-TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ system with decreasing temperature was investigated first. Each 20 g of Ti-bearing slag sample with basicity of 0.5 and TiO_2 content of 22.5 wt% was put into an alumina crucible with an inner diameter of 19 mm and a height of 60 mm, which were heated to 1773 K under argon atmosphere in a muffle furnace to ensure complete melting of binary system. After heating at the constant temperature for 30 min, the samples were slowly cooled at 1773–1723 K, 1723–1673 K, 1673–1623 K, 1623–1573 K, 1573–1523 K, 1523–1473 K, 1473–1423 K, or 1423–1373 K with a cooling rate of 1 K/min, respectively. After holding the sample at each target temperature range for 50 min, the alumina crucibles were removed from the furnace and water-quenched immediately. Subsequently, the samples were analyzed using XRD and SEM-EDS methods to investigate the variations in mineral compositions and microstructures of various crystallized phases with decreasing temperature.

2.2.3.2 Crystallization Behavior of Rutile

Variations in mineral compositions of the $\text{CaO-TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ system ($\text{CaO/SiO}_2 = 0.5$, $w(\text{TiO}_2) = 22\%$) with decreasing temperature are shown in

Fig. 2.36, and the SEM–EDS images and corresponding EDS data of various crystals that crystallized at different temperature ranges from the slag melt are shown in Fig. 2.36 and Table 2.15, respectively. The Ti-bearing slag is in a fully molten state at a high-temperature range of 1773–1573 K, in which there are not any crystals appeared as shown in Fig. 2.37a, b. With decreasing temperature to 1573–1523 K, the rutile (TiO_2) first crystallized from the slag, and only its diffraction peak appears significantly in this temperature range. Moreover, the rutile presents as an obvious quartet structure with a size of 50–100 μm , as shown in Fig. 2.37c. With decreasing temperature further to 1523–1473 K, the diffraction peak intensity of the rutile increases significantly, and the rutile transformed into a hollow quartet structure with a smaller size of 200–300 μm , as shown in Fig. 2.37d.

As temperature decreases to 1473–1423 K, the titanite (CaTiSiO_5) with a white diffuse flocculent structure, and the anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) with a dark gray striped

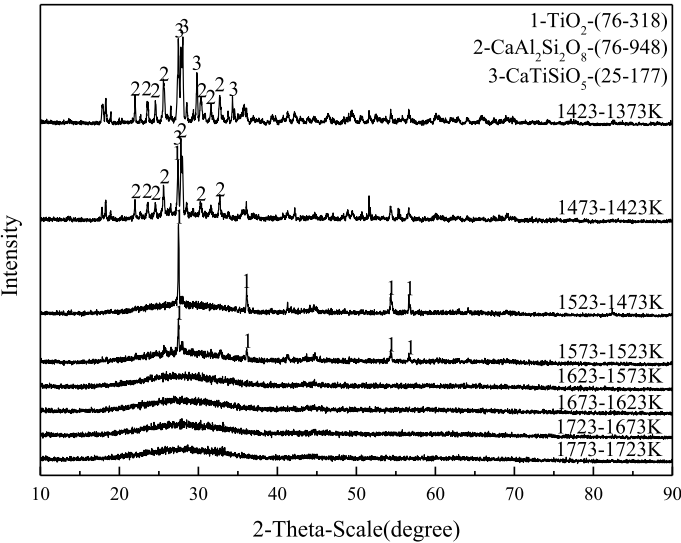


Fig. 2.36 Variation in XRD patterns of $\text{CaO-TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ system ($\text{CaO/SiO}_2 = 0.5$, $w(\text{TiO}_2) = 26.5\%$) with decreasing temperature

Table 2.15 EDS data for various crystallized phases (wt%)

Positions	Phases	Ti	O	Ca	Si	Al	Mg
Figure 2.37g Pt.1	Rutile	60.87	39.13	–	–	–	–
Figure 2.37h Pt.2	Titanite	22.92	35.63	20.74	16.15	4.56	–
Figure 2.37i Pt.3	Anorthite	–	37.62	18.96	21.12	22.30	–

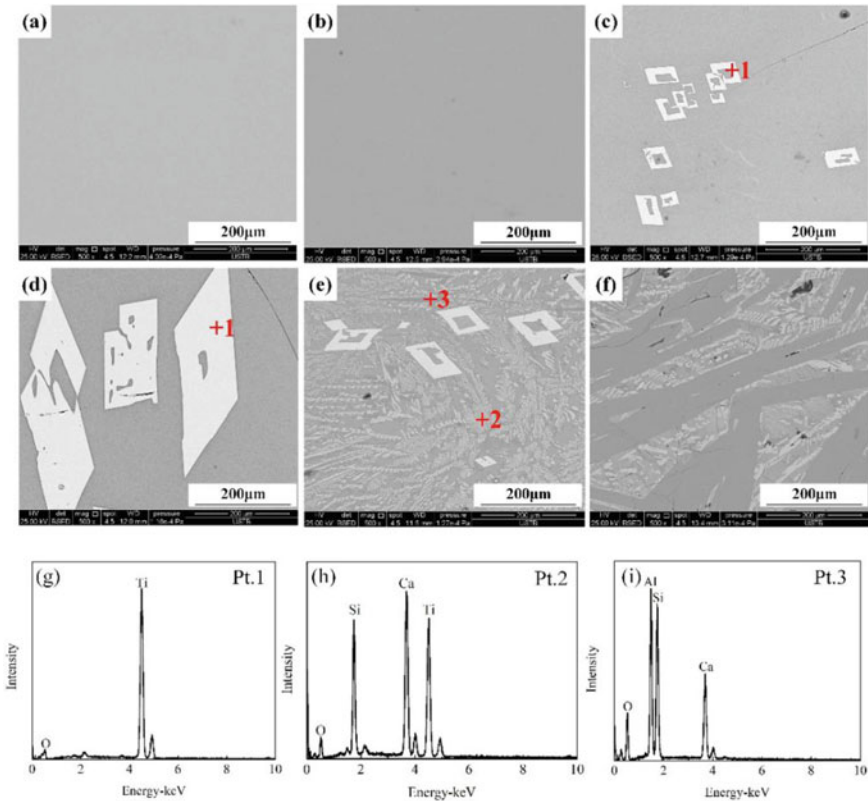


Fig. 2.37 Variations in SEM–EDS images of CaO–TiO₂–SiO₂–Al₂O₃–MgO system (CaO/SiO₂ = 0.5, w(TiO₂) = 22%) after slow cooling at different temperature ranges: **a** SEM of 1673–1623 K; **b** SEM of 1623–1573 K; **c** SEM of 1573–1523 K; **d** SEM of 1523–1473 K; **e** SEM of 1473–1423 K; **f** SEM of 1423–1373 K; **g** EDS of rutile; **h** EDS of titanite; **i** EDS of anorthite

structure also start to crystallize successively from the slag, which discretely distribute among the first crystallized rutile, as shown in Fig. 2.37e. Thus, the diffraction peak intensity of titanite and anorthite increases, whereas that of the rutile decreased obviously in this temperature range. With the temperature decreasing further to 1423–1373 K, the crystal sizes of titanite and anorthite are increased significantly, whereas the rutile disappears completely, as shown in Fig. 2.37f. The existence of a large amount of titanite and anorthite particles at the temperature below 1473 K is to increase the viscosity of slag melt and blocks the migration and coalescence of rutile in the slag. Consequently, 1573–1473 K is the optimum crystallization temperature range for rutile crystals from the CaO–TiO₂–SiO₂–Al₂O₃–MgO system with decreasing temperature, at which titanium crystallizes into the only rutile crystals, whereas other minerals form the molten slag.

2.2.4 Separation of Rutile from $\text{CaO-TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ System by Super Gravity

2.2.4.1 Experimental Procedure

After the sufficient crystallization of rutile, selective separation of the rutile crystal from the Ti-bearing slag melt was conducted at its crystallization temperature in a super gravity field. 10 g of the Ti-bearing slag with basicity of 0.5 and TiO_2 content of 25 wt% was placed on an alumina filter with 0.5 mm pore size, which were fixed onto an alumina crucible (I.D. 19 mm). The composite crucibles were heated to 1553 K in the heating furnace of centrifugal apparatus to make the slag phase change to molten state, while the rutile crystals remain in solid state. Subsequently, the centrifugal apparatus was initiated and adjusted to an angular velocity of 846, 1196, 1465, or 1691 r/min to achieve the gravity coefficients of 200, 400, 600, and 800. After centrifugal rotating at the constant temperature for 5 min, the rotation was stopped and the crucible was water-quenched, respectively. Simultaneously, the parallel experiments were conducted at 1553 K for 5 min under normal gravity.

After separation of rutile from the Ti-bearing slag melt by super gravity, the samples were sectioned longitudinally along the center axis and then analyzed using SEM-EDS, XRD XRF, and TEM methods to investigate the microstructure, mineralogical constitution, chemical composition, and crystal structure of the samples held on and went through the filter. The recovery ratio of Ti in the separated rutile phase was calculated via Eq. (2.14).

$$\varepsilon_{\text{Ti}} = \frac{m_{\text{R}} \times \omega_{\text{Ti-R}}}{m_{\text{R}} \times \omega_{\text{Ti-R}} + m_{\text{S}} \times \omega_{\text{Ti-S}}} \times 100\%, \quad (2.14)$$

where ε_{Ti} is recovery ratio of Ti in the separated rutile phase; m_{R} and m_{S} are the mass fractions of the separated rutile and slag phases; and $\omega_{\text{Ti-R}}$ and $\omega_{\text{Ti-S}}$ are mass fractions of Ti in the separated rutile and slag phases, respectively.

2.2.4.2 Separation Behavior of Rutile

The vertical sections of samples attained under super gravity with gravity coefficient of 600 compared with the parallel sample under normal gravity are shown in Fig. 2.38. Apparently, the entire sample is blocked by the filter, and a uniform structure is observed for the sample attained in a normal gravity field, as shown in Fig. 2.38a. In comparison, the sample is separated into two parts by the filter in a super gravity field. The obvious different macroscopic structures are clearly observed in the separated samples, as shown in Fig. 2.38b. From a macroscopic perspective, the sample above the filter appears as a yellow rod-shape crystal structure as shown

in Fig. 2.38c, whereas the sample below the filter presents in an orange-red glassy state, respectively.

Compared with the XRD patterns of the separated samples attained by super gravity with gravity coefficient from $G = 200$ to $G = 800$ as shown in Fig. 2.39, the only significant diffraction peak of rutile appears in the upper sample, whereas the diffraction peak of the lower sample presents as a typical dispersion peak. It is evidenced that the rutile exists as the only solid phase, whereas other minerals transform into the molten slag at the crystallization temperature range of rutile. However, due to the higher viscosity of the solid-liquid mixture at the low temperature, the driving force generated by difference in density between rutile crystals and slag melt is insufficient to drive the rutile to move and separate from the slag melt in a normal gravity field, as presented in Fig. 2.38a. In contrast, the slag melt evidently moves and subsequently goes through the filter as driven by the super gravity, whereas all the rutile is intercepted by the filter and effectively separated from the slag melt, as presented in Fig. 2.38b.

The SEM and EDS data of the separated samples attained by super gravity with $G = 600$ are shown in Fig. 2.40 and Table 2.16, respectively. From a microscopic perspective, the separated rutile only consists of two elements of titanium (Ti) and oxygen (O), and the mole ratio of Ti to O in the rutile crystals is very close to 1:2. Moreover, the separated rutile appears as a rod-shaped structure, and its crystal size is

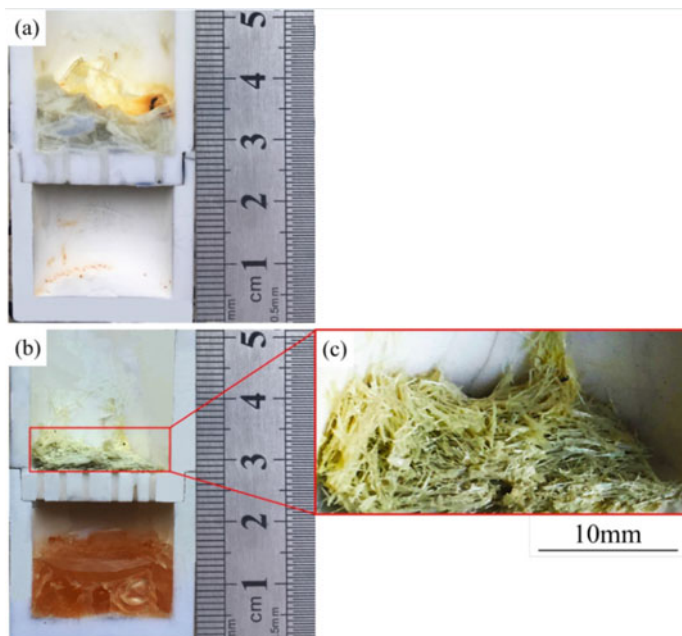


Fig. 2.38 Vertical sections of the samples attained by super gravity compared with the normal gravity: **a** $G = 1$; **b** $G = 600$; **c** macrostructure of the sample above filter

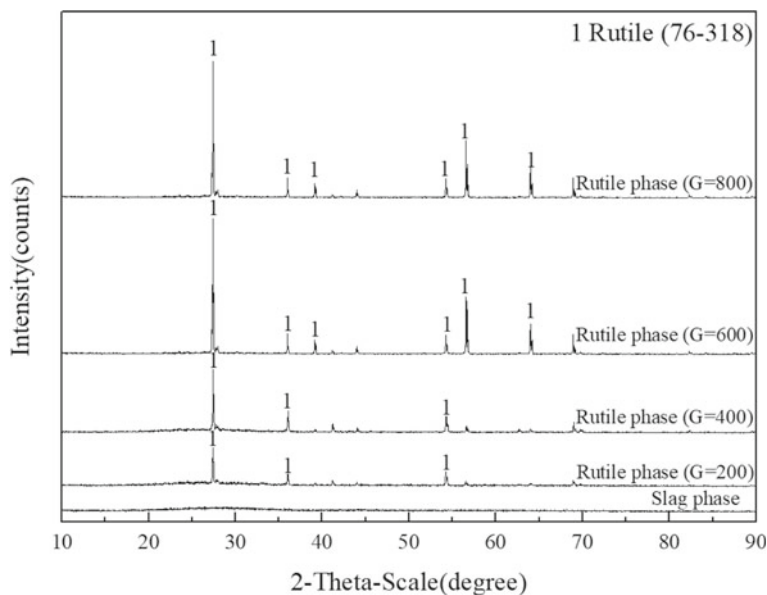


Fig. 2.39 XRD patterns of the separated samples by super gravity ($G = 200$, $G = 400$, $G = 600$, and $G = 800$, $T = 1553$ K)

up to 500–2000 μm as shown in Fig. 2.40a, b. Thus, the large rutile is effectively intercepted by the filter, and each rutile crystal is structurally independent. Conversely, the CaO , SiO_2 , Al_2O_3 , and MgO transformed into the slag melt and subsequently go through the filter and efficiently separated from the rutile by a driving force of super gravity, in which it is practically impossible to find any rutile, as shown in Fig. 2.40d.

Figure 2.41 presents the variations in mass fractions of TiO_2 and the recovery ratios of Ti in the separated rutile as a function of gravity coefficient. The corresponding SEM–EDS images of the separated rutile attained with gravity coefficient from $G = 200$ to $G = 800$ are shown in Fig. 2.42. Increasing gravity coefficient from $G = 1$ to $G = 600$, the mass fraction of TiO_2 in the separated rutile increases significantly with the gradual removal of slag inclusions from the rutile as shown in Fig. 2.42a–c, and the diffraction peak intensity of the rutile phase increased obviously as shown in Fig. 2.39, while the recovery ratio of Ti decreases gradually. With gravity coefficient increasing further from $G = 600$ to $G = 800$, the slag inclusions were almost completely removed from the rutile phase as shown in Fig. 2.42c, d; thus, the mass fraction of TiO_2 and the recovery ratio of Ti in the separated rutile both tend to flat. As according verified, increasing gravity coefficient could enhance the driving force that generated the buoyancy factor ($\Delta\rho g$) between rutile and slag melt, overcoming the resistance between the two phases, and significantly accelerate the migration of rutile in the slag melt. Hence, the separation efficiency between rutile and slag phases and the purity of separated rutile phase are both enhanced significantly with increasing gravity coefficient. Consequently, after separating by super gravity with

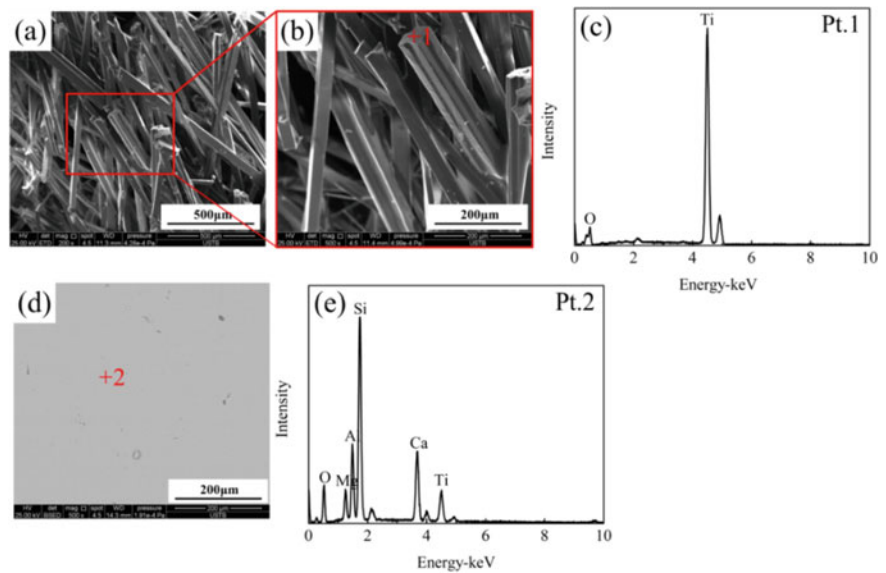


Fig. 2.40 SEM–EDS images of the separated samples attained by super gravity ($G = 600$, $T = 1553$ K): **a** and **b** SEM of rutile phase; **c** EDS of rutile phase; **d** SEM of slag phase; **e** EDS of slag phase

Table 2.16 EDS data of the separated samples (wt%)

Positions	Samples	Ti	O	Ca	Si	Al	Mg
Figure 2.40a Pt.1	Rutile	60.70	39.30	—	—	—	—
Figure 2.40d Pt.2	Slag	8.66	37.33	14.57	23.64	10.85	4.96

$G = 600$ at 1553 K for 5 min, the mass fraction of TiO_2 in the separated rutile phase is high up to 95.56 wt%, whereas that of the slag phase is reduced to 14.77 wt%. In addition, the recovery ratio of Ti in the separated rutile phase is up to 48.43%.

2.2.5 Selective Crystallization of Rutile in Ti-Bearing Blast Furnace Slag

Based on the phase transformation, the crystallization and separation behaviors of rutile in the $\text{CaO-TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ slag system, selective crystallization, and separation of rutile from the Ti-bearing blast furnace slag produced from Panzhihua Iron and Steel Corporation of China are carried out.

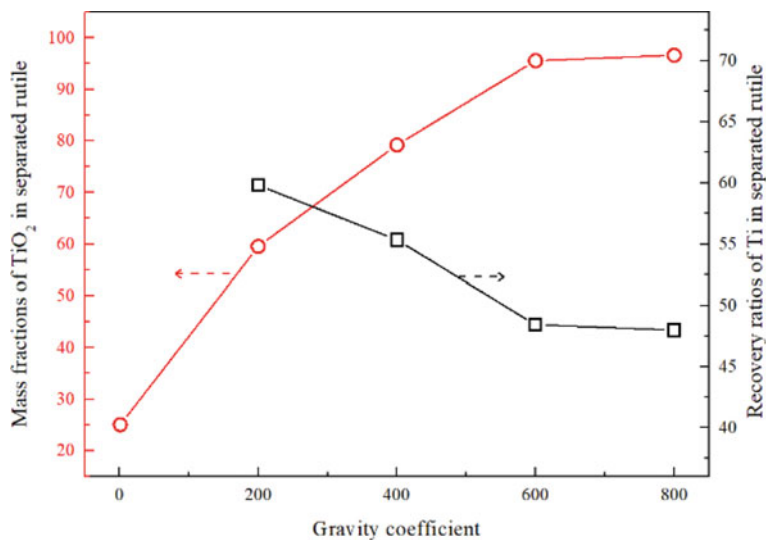


Fig. 2.41 Variations in mass fractions of TiO_2 and recovery ratios of Ti in the separated rutile as a function of gravity coefficient

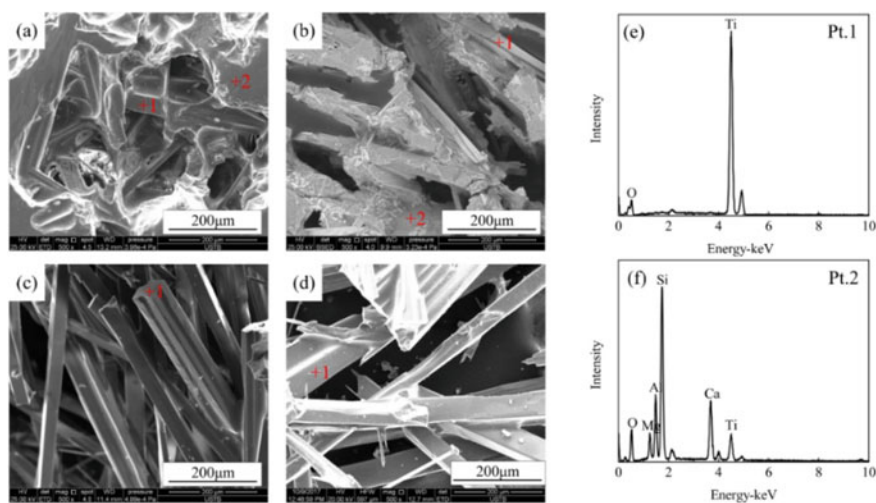


Fig. 2.42 SEM-EDS images of the separated rutile crystals as a function of gravity coefficient: **a** SEM of $G = 200$; **b** SEM of $G = 400$; **c** SEM of $G = 600$; **d** SEM of $G = 800$; **e** EDS of rutile crystal; **f** EDS of slag inclusion

2.2.5.1 Experimental Procedure

In order to acquire the selective separation temperature range for solid and liquid phases of rutile and slag in coexistence, the phase change of rutile and slag in Ti-bearing blast furnace slag was investigated firstly through the in situ observation by high-temperature confocal laser scanning microscope (CLSM, VL2000DX-SVF17SP, Japan). 1.2 g of Ti-bearing blast furnace slag with the condition of $R = 0.5$ and $w(\text{TiO}_2) = 26.5\%$ were polished and put into a platinum crucible (7.8 mm in diameter and 3.2 mm in height), which was placed in the furnace (± 0.1 K accuracy) under the center of scanning microscope. After that, the in situ observation was conducted from room temperature to 1753 K with a heating rate of 30 K/min in an argon atmosphere with a flow rate of 20 ml/min and then cooled down with a cooling rate of 100 K/min. DVD was used to record the images captured with the temperature rising, which were used for analyzing the morphology evolution of Ti-bearing blast furnace slag. Meanwhile, the DTA method was used to verify the phase change of rutile and slag in the Ti-bearing blast furnace slag with temperature rising. 100 mg of the Ti-bearing blast furnace slag were put into an alumina crucible (5 mm in diameter, 4 mm in height), which was measured in a differential thermal analyzer (± 0.5 K accuracy) ranging from 323 to 1773 K with a heating rate of 10 K/min in an argon atmosphere with a flow rate of 300 ml/min.

2.2.5.2 Coexistence Condition for Rutile and Slag in Ti-Bearing Blast Furnace Slag

Firstly, the in situ observation on morphology evolution of the Ti-bearing blast furnace slag combined with the DTA analysis with temperature rising is carried out to investigate the condition for solid and liquid phases of rutile and slag in coexistence in the Ti-bearing blast furnace slag. It is found from Fig. 2.43a that the white rutile crystal with the length larger than $500\text{ }\mu\text{m}$ is included in the black slag at room temperature. As the temperature rises to 1473 K, the liquid slag phase starts to form as shown in Fig. 2.43c. It is confirmed by the obvious endothermic peak that occurred at about 1496 K in the DTA curve due to the formation of molten slag, as shown in Fig. 2.44. When the temperature increases from 1533 to 1567 K, the original slag phase is completely melted to form liquid phase which shows a favorable fluidity, as shown in Fig. 2.43d–e. However, the length of rutile gradually reduces with the temperature increasing further to 1610 K as shown in Fig. 2.43f, arising from the remelting of the rutile crystal to $[\text{TiO}_4]^{4-}$ into the molten slag.

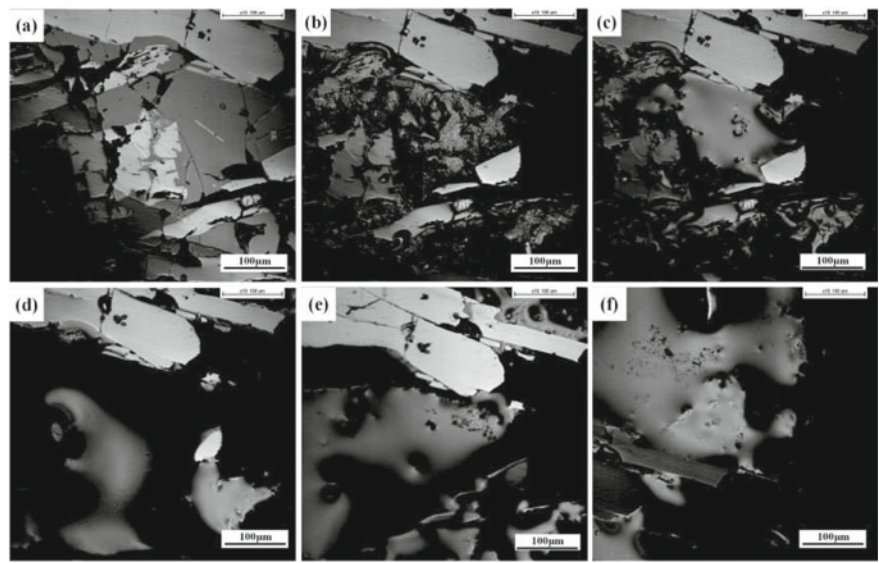
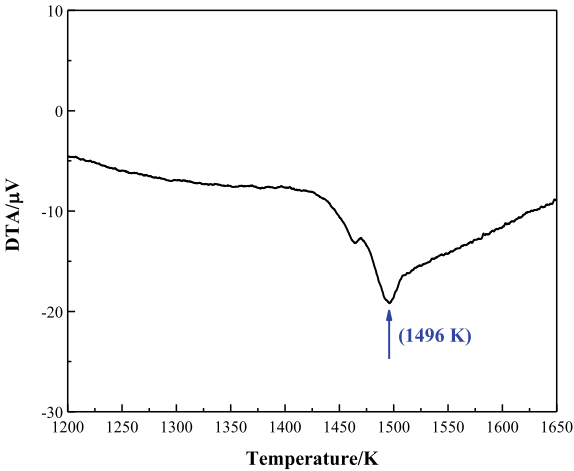


Fig. 2.43 In situ observation on morphology evolution of Ti-bearing blast furnace slag with temperature rising by high-temperature CSLM ($R = 0.5$, $w(\text{TiO}_2) = 26.5\%$): **a** 303 K; **b** 1453 K; **c** 1493 K; **d** 1533 K; **e** 1567 K; **f** 1610 K

Fig. 2.44 DTA curves of Ti-bearing blast furnace slag with temperature rising ($R = 0.5$, $w(\text{TiO}_2) = 26.5\%$)



2.2.6 Separation of Rutile from Ti-Bearing Blast Furnace Slag by Super Gravity

2.2.6.1 Experimental Procedure

Based on the acquired condition for solid and liquid phases of rutile and slag in coexistence, selective separation of rutile from the Ti-bearing blast furnace slag was carried out through super gravity separation in the centrifugal device. 10 g of the Ti-bearing blast furnace slag were put in the upper part of a two-layer alumina crucible with the pore size of 0.01 mm, which was heated to 1493, 1533, 1573, or 1613 K in the heating furnace of centrifugal device for the solid rutile and slag melt in coexistence in Ti-bearing blast furnace slag. Subsequently, the centrifugal device was started and adjusted to an angular velocity of 1675 r/min, to achieve the gravity coefficient of $G = 800$. The slag was centrifuged for 2, 4, 6, or 8 min and then rapidly quenched in water.

After that, the macro and microstructures, the mineral and chemical compositions of the rutile that separated from the Ti-bearing blast furnace slag by the filter through super gravity separation were analyzed by methods such as SEM-EDS, XRD, XRF, and Raman, respectively. In addition, the Ti recovery ratio in rutile from the Ti-bearing blast furnace slag was calculated according to Eq. (2.14).

2.2.6.2 Separation Behavior of Rutile from Ti-Bearing Blast Furnace Slag

Based on the acquired temperature range for solid and liquid phases of rutile and slag in coexistence in the Ti-bearing blast furnace slag, super gravity separation of rutile from the Ti-bearing blast furnace slag is conducted in this condition. The SEM images of rutile separated from the Ti-bearing blast furnace slag as a function of separation temperature are shown in Fig. 2.45a–d. It is found that most of slag melt can be effectively separated from the rutile as driven by super gravity with $G = 800$ for 2 min. Moreover, the separated rutile shows a tridimensional rod-shape in length of 500 μm , in which the slag inclusions are gradually removed with the separation temperature increasing from 1493 to 1573 K as shown in Fig. 2.45a–c, as the decreasing of slag viscosity with the increase of temperature [50]. When the separation temperature increases to 1613 K, although more slag inclusions are removed from the rutile, while the amount and length of rutile are decreased obviously due to the remelting of rutile crystal to $[\text{TiO}_4]^{4-}$ into the molten slag as shown in Fig. 2.45d, which confirms the in situ observation result in Fig. 2.45f.

Figure 2.45e–h shows further the SEM images of rutile separated from the Ti-bearing blast furnace slag through super gravity separation at 1573 K as a function of separation time. As shown in Fig. 2.45e, a small number of slag inclusions are still attached to the surface of rutile through super gravity separation for 2 min. As the separation time increases from 2 to 6 min, the slag inclusions that attached to the

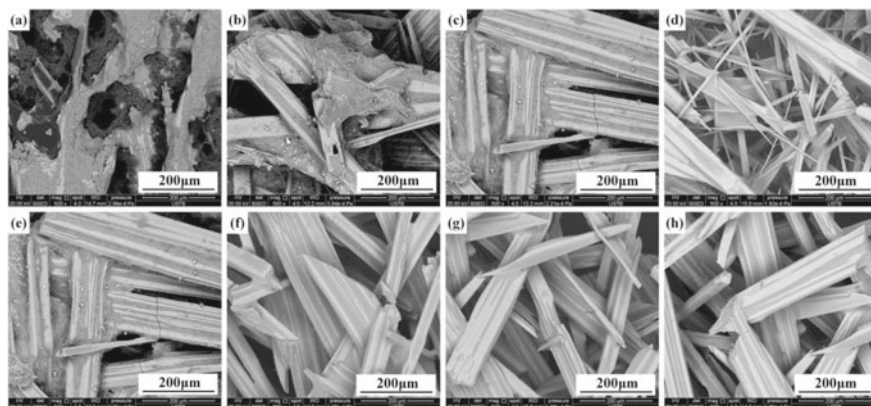


Fig. 2.45 SEM images of rutile separated from Ti-bearing blast furnace slag through super gravity separation with $G = 800$ as functions of separation temperature and time: **a** $T = 1493$ K, $t = 2$ min; **b** $T = 1533$ K, $t = 2$ min; **c** $T = 1573$ K, $t = 2$ min; **d** $T = 1613$ K, $t = 2$ min; **e** $T = 1573$ K, $t = 2$ min; **f** $T = 1573$ K, $t = 4$ min; **g** $T = 1573$ K, $t = 6$ min; **h** $T = 1573$ K, $t = 8$ min

surface of rutile crystals are removed significantly from the rutile under the action of super gravity with the time extend, as shown in Fig. 2.45e–g. When the separation time increases further from 6 to 8 min, almost all of the slag inclusions are completely removed from the rutile, and the rutile separated from the Ti-bearing blast furnace slag shows a uniform and independent structure, as shown in Fig. 2.45g, h.

Variations of TiO_2 content in rutile separated from the Ti-bearing blast furnace slag through super gravity separation as a function of separation temperature and time are presented further in Fig. 2.46. It is indicated that the TiO_2 content in rutile increases significantly with the increase of the separation temperature from 1493 to 1613 K, which is consistent with the phenomenon of removal of slag inclusions from rutile as the SEM images in Fig. 2.45a–d. Moreover, the TiO_2 content in rutile increases further with the increase of separation time from 2 to 6 min, which maintain stability as the separation time increasing further from 6 to 8 min. As further verified, almost all of the slag inclusions are completely removed from rutile, and the rutile is efficiently separated from the Ti-bearing blast furnace slag through super gravity separation with $G = 800$ at 1573 K for 6 min. Through calculating via Eq. (2.13), 55.89% of Ti are effectively recovered from the Ti-bearing blast furnace slag into the rutile with a high TiO_2 content of 95.37 wt% in this condition.

Macro and microstructures of the rutile separated from the Ti-bearing blast furnace slag through super gravity separation with $G = 800$ at 1573 K for 6 min are shown in Fig. 2.47. As the vertical profile of the entire sample shown in Fig. 2.47a, the residual slag is completely separated from the Ti-bearing blast furnace slag and flows into the bottom crucible under the action of super gravity. While all the rutile is efficiently separated by the filter from the residual slag, and the rutile appears to be yellow acicular crystal from a macrocosmic view, as presented in Fig. 2.47b. From the SEM image of rutile presented in Fig. 2.47c, the single rutile with a dendritic

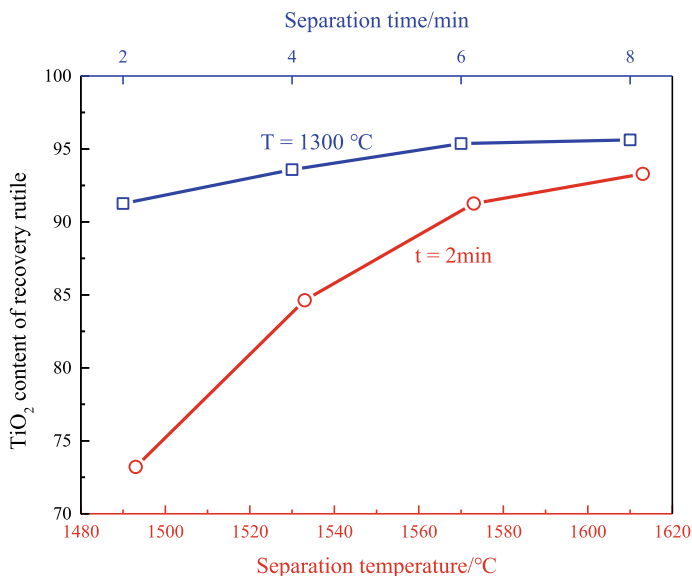


Fig. 2.46 Variations of TiO_2 content in rutile separated from Ti-bearing blast furnace slag through super gravity separation with $G = 800$ as a function of separation temperature and time

shape is separated from the residual slag, and almost no inclusions are adhered to the surface or included between the rutile, which confirms its high purity from a microcosmic view. Moreover, there are not any elements other than Ti and O from the rutile as indicated by the EDS image in Fig. 2.47d. As accordingly verified, the Ti elements are efficiently enriched into the single rutile and be effectively separated from the Ti-bearing blast furnace slag through phase transformation and super gravity separation.

The separated rutile attained by super gravity with $G = 600$ at 1553 K is further analyzed using the TEM to accurately characterize the crystal structure of the rutile. The TEM image of the grated rutile and the corresponding selected-area electron diffraction (SAED) pattern are shown in Fig. 2.48a, b, respectively. Based on the analysis of SEAD pattern results and JCPDF number (76–318), the separated rutile is confirmed to be characterized by a tetragonal structure with a high crystallinity and the single-crystal feature, whose crystalline axis index is [1], as presented in Fig. 2.48b. Additionally, the single-crystal structure of the nanowires and the (200) lattice fringes with an interplanar spacing of approximately 0.23 nm are clearly observed in the HRTEM image, as presented in Fig. 2.48c.

Moreover, the XRD patterns and Raman spectra of the rutile separated from the Ti-bearing blast furnace slag are shown further in Fig. 2.49. The unique diffraction peaks of rutile in Fig. 2.49a confirm its high crystallinity and high purity. Through comparing the exhibited vibrational features for the rutile as the Raman spectra shown in Fig. 2.49b, its bands are appeared significantly at 142.61 cm^{-1} , 239.49 cm^{-1} , 447.97 cm^{-1} , and 609.60 cm^{-1} , which are assigned to the wagging vibrations, the

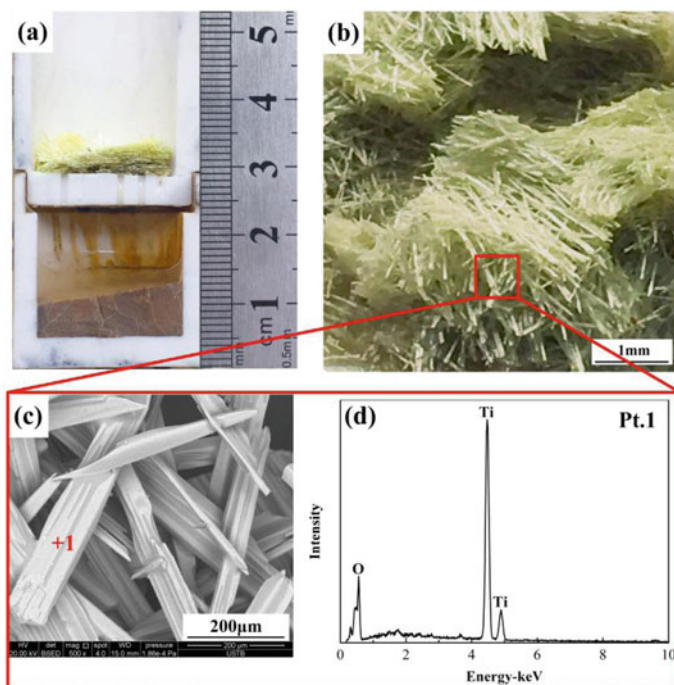


Fig. 2.47 Macro and microstructures of rutile separated from Ti-bearing blast furnace slag through super gravity separation with $G = 800$ at 1573 K for 6 min: **a** vertical profile of entire sample; **b–d** macrostructure, SEM and EDS images of rutile, respectively

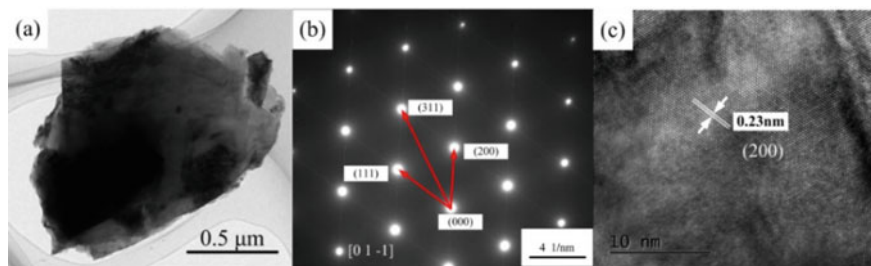


Fig. 2.48 TEM analysis of separated rutile attained by super gravity ($G = 600$, $T = 1553$ K): **a** TEM image, **b** SAED pattern, and **c** HRTEM pattern

complex vibrations, the twisting vibrations, and the symmetric stretching vibrations of the O–Ti–O bonds for rutile TiO_2 , respectively. The Raman spectra of the separated rutile are completely consistent with that of the rutile prepared by the synthetic methods using pure TiCl_4 reagent [51, 52], which confirms the high purity of the rutile recovered from Ti-bearing blast furnace slag.

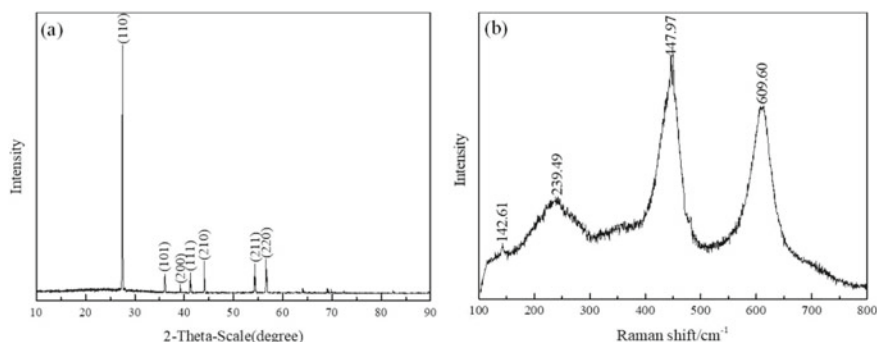


Fig. 2.49 XRD pattern and Raman spectra of rutile separated from Ti-bearing blast furnace slag: **a** XRD pattern; **b** Raman spectra

2.3 Separation of Anosovite from Ti-Bearing Slag in Reducing Atmosphere

Moreover, the titanium can form another different phase of anosovite (Ti_3O_5) in the molten Ti-bearing slag under a reducing atmosphere. Considering the theoretical content of Ti in the anosovite is much higher than that in the perovskite (CaTiO_3), the anosovite would be another choice for separating Ti from the Ti-bearing slag. In this section, selective crystallization and separation of anosovite from the $\text{CaO-TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ system and Ti-bearing blast furnace slag in a reducing atmosphere by super gravity are studied [53].

2.3.1 Thermodynamic Analysis for Phase Transformation of Ti in $\text{CaO-TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ System Under Reducing Atmosphere

The equilibrium phase diagram of $\text{CaO-SiO}_2\text{-22wt\%TiO}_2\text{-12wt\%Al}_2\text{O}_3\text{-6wt\%MgO}$ under reducing atmosphere is calculated through FactSage 7.2 as shown in Fig. 2.50. The green point in equilibrium phase diagram is the original chemical composition of Ti-bearing blast furnace slag, which indicates that perovskite is the primary equilibrium phase of Ti. When the slag basicity decreases to 0.7 (red point), the primary equilibrium phase of Ti transforms from the perovskite to anosovite thermodynamically under the reducing atmosphere. Moreover, the phase transformation of Ti in Ti-bearing slag is greatly influenced by the temperature.

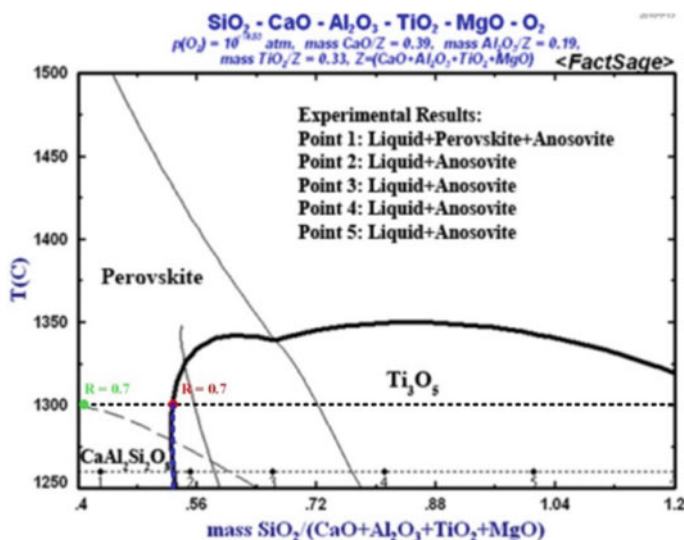


Fig. 2.50 Equilibrium phase diagram of CaO–SiO₂–22wt%TiO₂–12wt%Al₂O₃–6wt%MgO

2.3.2 Crystallization Behavior of Anosovite in CaO–TiO₂–SiO₂–Al₂O₃–MgO System

2.3.2.1 Experimental Procedure

The crystallization behavior of CaO–TiO₂–SiO₂–Al₂O₃–MgO system in a reducing atmosphere with decreasing temperature was investigated first by hot-quenching method combined with various characterization techniques. Each 20 g of Ti-bearing slag sample was put into a graphite crucible with an inner diameter of 19 mm and a height of 60 mm, which were heated to 1773 K with a gas flow of 0.2 L/min CO and 0.1 L/min Ar in a MoSi₂ tube furnace to ensure complete melting of CaO–TiO₂–SiO₂–Al₂O₃–MgO system. After heating at the constant temperature for 30 min, the samples were slowly cooled at 1773–1723 K, 1723–1673 K, 1673–1623 K, 1623–1573 K, 1573–1523 K, 1523–1473 K, 1473–1423 K, or 1423–1373 K with a cooling rate of 1 K/min, respectively. After holding the sample at each target temperature range for 50 min, the graphite crucibles were removed from the furnace and water-quenched immediately. Subsequently, the samples were analyzed using XRD and SEM–EDS to investigate the variations in mineral compositions and microstructures of various crystallized phases with decreasing temperature.

2.3.2.2 Crystallization Behavior of Anosovite

Variations in XRD patterns of $\text{CaO-TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ system in reducing atmosphere with decreasing temperature are shown in Fig. 2.51, and the SEM-EDS images and corresponding EDS data of various crystals that crystallized at different temperature ranges from the Ti-bearing slag melt are shown in Fig. 2.52, respectively. It is clear that the Ti-bearing slag is in a fully molten state at a high-temperature range of 1773–1673 K, in which there are not any crystals appeared as shown in Fig. 2.52a–c.

With decreasing temperature to 1673–1623 K, the anosovite crystals first crystallize from the Ti-bearing slag melt, and only its diffraction peaks appear significantly in this temperature range. Moreover, the rutile crystals present as an obvious quartet structure with a size of 50–100 μm , as shown in Fig. 2.52d. With decreasing temperature further to 1523–1473 K, the diffraction peak intensity of the rutile gradually increases, and the anosovite crystals transform into a rod structure and start to grow to 300 μm , as shown in Fig. 2.52f. As temperature decrease to 1523–1473 K, the diopside phase also starts to crystallize from the slag melt, which discretely distribute among the first crystallized anosovite crystals, as shown in Fig. 2.52g. As temperature decreases to 1473–1423 K, the diffraction peak intensity of diopside increases, whereas that of the anosovite is decreased obviously in this temperature range. The existence of a large amount of diopside at the temperature below 1523 K is to increase the viscosity of slag melt and block the migration and coalescence of anosovite crystals in the Ti-bearing slag melt.

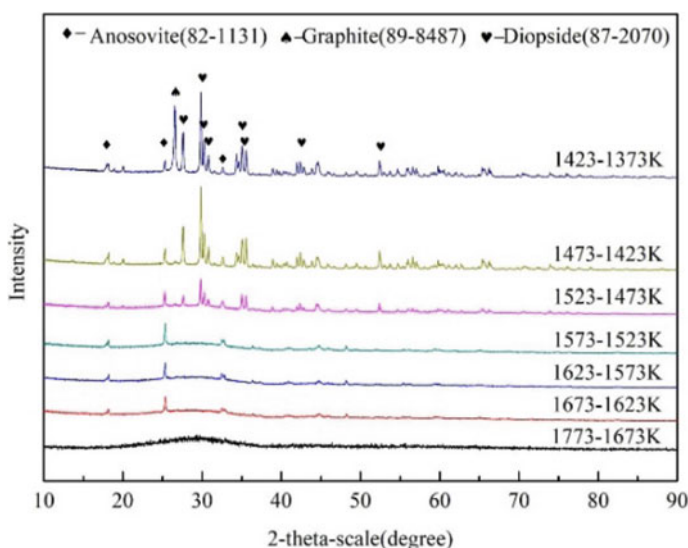


Fig. 2.51 Variation in XRD patterns of $\text{CaO-TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ system in reducing atmosphere with decreasing temperature

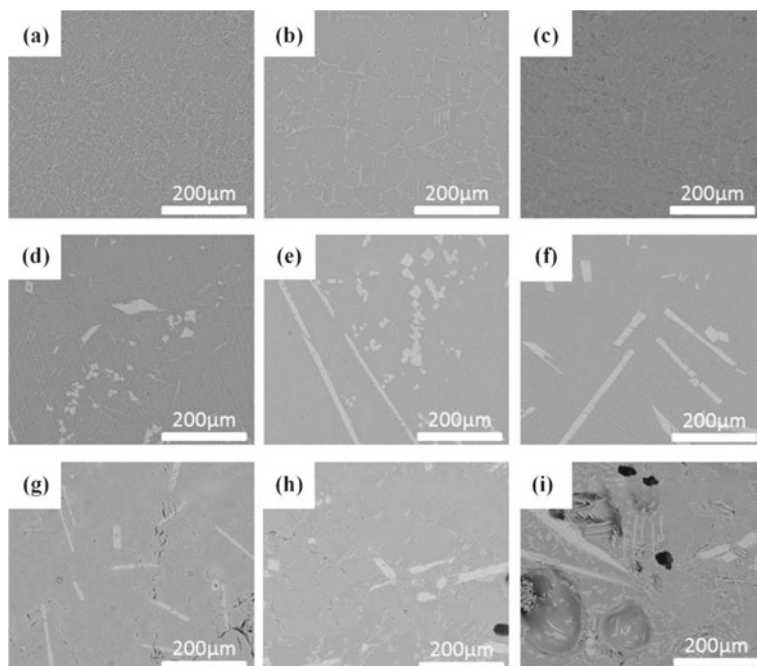


Fig. 2.52 Variations in SEM-EDS images of $\text{CaO-TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ system in reducing atmosphere: **a** 1773 K; **b** SEM of 1773–1723 K; **c** SEM of 1723–1673 K; **d** SEM of 1673–1623 K; **e** SEM of 1623–1573 K; **f** SEM of 1573–1523 K; **g** SEM of 1523–1473 K; **h** SEM of 1473–1423 K; **i** SEM of 1423–1373 K

Consequently, 1673–1523 K is the optimum crystallization temperature range for anosovite crystals from the $\text{CaO-TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ system in reducing atmosphere with decreasing temperature, at which titanium crystallizes into the only anosovite crystals, whereas other minerals form the molten slag.

2.3.3 Separation of Anosovite from $\text{CaO-TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ System by Super Gravity

2.3.3.1 Experimental Procedure

Based on the crystallization behavior of $\text{CaO-TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ system in a reducing atmosphere, separation of anosovite from $\text{CaO-TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ system was conducted by super gravity. The Ti-bearing slag with a basicity of 0.7 was filled in some graphite crucibles with an inner diameter of 19 mm and a height of 60 mm and heated to 1773 K under the gas flow of 0.2 L/min CO and 0.1 L/

min Ar in a MoSi₂ tube furnace to generate a reducing atmosphere. After heating for 30 min to make the Ti-bearing slag fully melted, the temperature was rapidly decreased to 1703 K, and the sample was reduced at the constant temperature for 60 min. Thereafter, the Ti-bearing slag melt was slowly cooled to 1533 K at a cooling rate of 1 K/min for promoting the crystallization of the anosovite crystals. After that, the graphite crucibles were taken out and water-quenched, respectively.

15 g of the Ti-bearing slag in which the anosovite was fully crystallized was put onto a graphite felt with the pore size of 0.01 mm that embedded in a graphite filter with an inner diameter of 19 mm, which was further put onto another graphite crucible. The Ti-bearing slag was heated to 1553 K for 10 min in the heating furnace, after which the centrifugal apparatus was adjusted to the angular velocity of 1036 r/min, 1465 r/min, 1794 r/min, or 2072 r/min ($G = 300$, $G = 600$, $G = 900$, or $G = 1200$) at the constant temperature for 5 min, respectively. After that, the centrifugal apparatus was shut off, and the sample was water-quenched. Moreover, the sample was obtained at 1553 K for 15 min under normal gravity.

After super gravity separation, the samples that intercepted and went through the filter were sectioned into two parts along the longitudinal center axis. One part was measured by SEM-EDS for analyzing the microstructures of the separated samples, while the other was crossly divided along the filter and characterized by XRD and XRF to determine the mineral compositions and chemical components in the separated samples. The recovery ratio of Ti in the separated anosovite phase was calculated via Eq. (2.15)

$$R_{\text{Ti}} = \frac{m_a \times \omega_a}{m_a \times \omega_a + m_s \times \omega_s} \times 100\%, \quad (2.15)$$

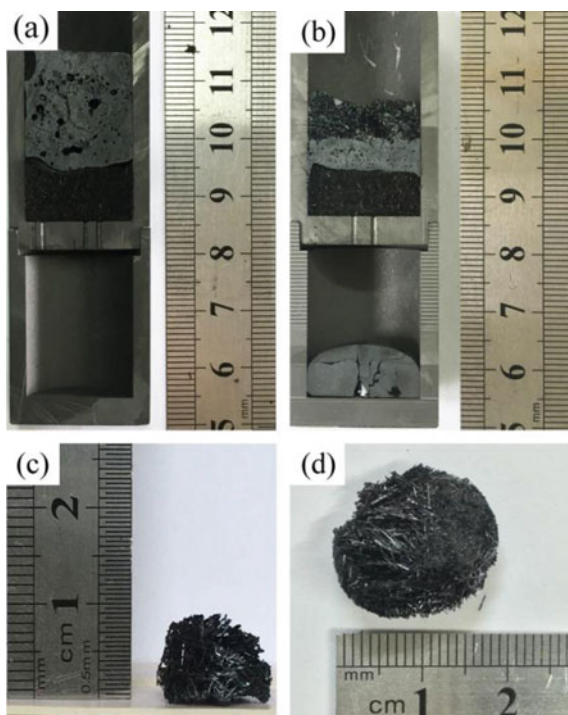
where R_{Ti} is the recovery ratio of Ti in the separated anosovite phase; m_a and m_s are the mass of separated anosovite and slag phases; ω_a and ω_s are the mass fraction of TiO₂ in the separated anosovite and slag phases.

2.3.3.2 Separation Behavior of Anosovite

The vertical profiles of the sample obtained by super gravity with gravity coefficient of $G = 600$ in comparison with parallel sample under normal gravity are illustrated in Fig. 2.53. It is obvious that the whole sample is blocked by the filter as shown in Fig. 2.53a, and a uniform structure presents in the sample obtained in normal gravity field. In contrast, the layered structure appeared significantly after super gravity separation as shown in Fig. 2.53b, and the sample above the filter appeared as a black adamantine luster, rod-shaped structure from a macroscopic view as shown in Fig. 2.53c, d, whereas the sample below the filter presents in a black glassy state.

Compared with the XRD patterns of the separated samples obtained by super gravity as shown in Fig. 2.54, there is only the diffraction peak of anosovite with a high intensity appeared in the upper sample, whereas the diffraction peak of the lower sample presents as a typical dispersion peak. It is in evidence that the super gravity

Fig. 2.53 Macrostructures of the sample obtained by super gravity compared with normal gravity: **a** and **b** vertical profiles of the samples with $G = 1$ and $G = 600$; **c** and **d** macrostructures of the separated anosovite



forces the slag melt goes through the filter and concentrates in the bottom crucible along the super gravity direction, whereas the anosovite crystals are intercepted effectively by the filter and separated from the slag melt.

By means of SEM-EDS analysis, the microstructures of the separated anosovite and slag phases are shown in Fig. 2.55, respectively. Combined with the EDS data given in Table 2.17, most titanium enriches into the anosovite with the mass fraction of 63.77–65.95 wt%, the separated anosovite appears as a typical light gray, prism, and rod-shaped intertexture structure from a microscopic view, and the crystals size of anosovite was high up to 200–4000 μm , as shown in Fig. 2.55a, b. In contrast, the Ca, Si, Mg, Al, and O form the slag melt, and the separated slag presents in a compact structure as shown in Fig. 2.55c, in which it is scarcely possible to find any anosovite grains. It is evidenced that all of the anosovite crystals are effectively separated from the Ti-bearing slag melt under the force of super gravity.

Figure 2.56 presents the variations in mass fractions of TiO_2 and the recovery ratios of Ti in the separated anosovite obtained by super gravity with different slag contents and different gravity coefficients. Obviously, with the decrease of calcium content while the increase of titanium content in the Ti-bearing slag, the recovery ratio of Ti in the separated anosovite is gradually increased due to the enhancement of the equilibrium transforming of titanium from Ti^{4+} to Ti^{3+} and thus promoting the crystal quality of the anosovite. While the mass fraction of TiO_2 in the separated anosovite is

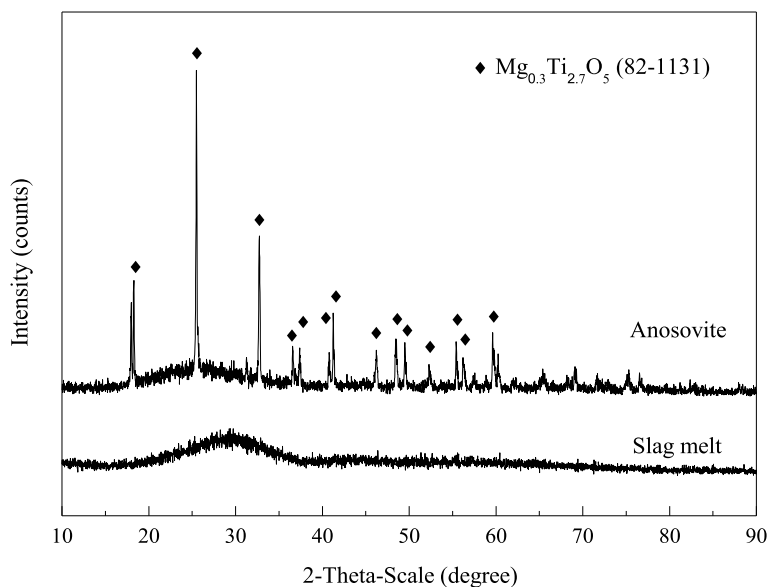


Fig. 2.54 XRD patterns of the separated samples obtained by super gravity

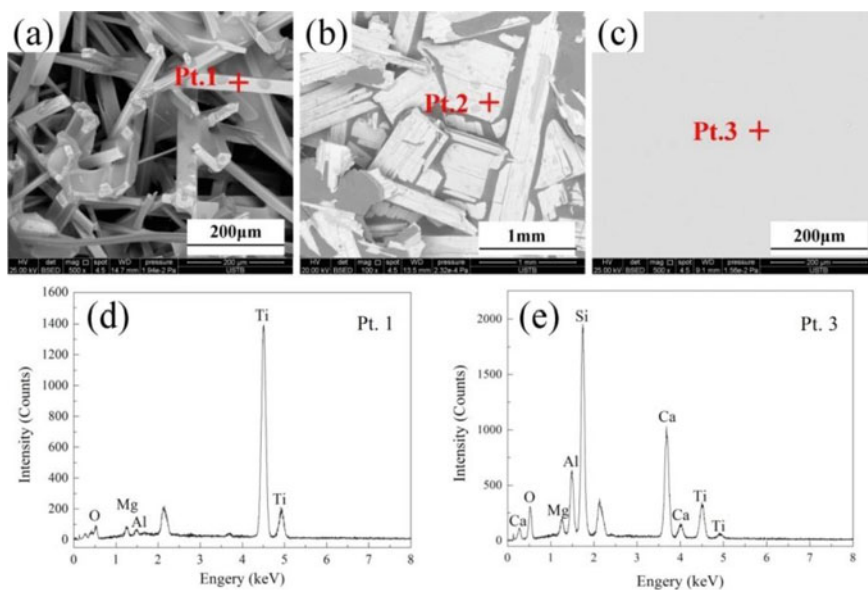


Fig. 2.55 SEM-EDS photographs of the separated anosovite and slag phases: **a** and **b** SEM of anosovite; **c** SEM of slag melt; **d** EDS of anosovite; **e** EDS of slag melt

Table 2.17 EDS data of the separated anosovite obtained by super gravity (wt%)

Positions	Ti	O	Mg	Al
Figure 2.55a Pt.1	65.95	28.44	3.81	1.80
Figure 2.55b Pt.2	63.77	32.03	3.18	1.02

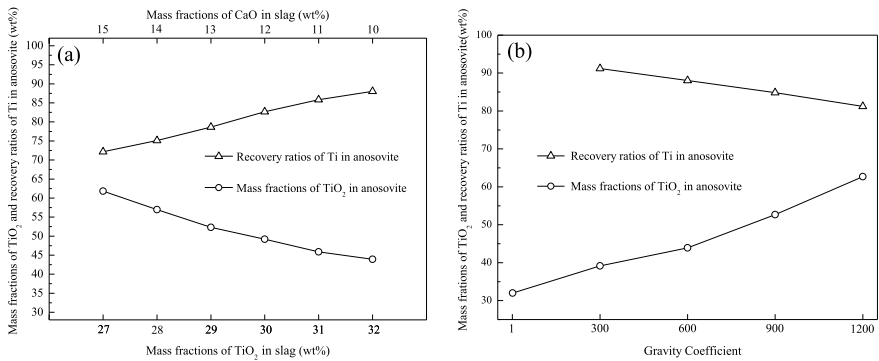


Fig. 2.56 Variations in mass fractions of TiO₂ and the recovery ratios of Ti in the separated anosovites obtained by super gravity with different slag contents and gravity coefficients: **a** variations with the mass fractions of TiO₂ and CaO, **b** variations with gravity coefficient

decreased accordingly resulting from that some slag melt is not effectively separated from the anosovite but stuck in the bottom of the gaps among the anosovite crystals, as shown in Fig. 2.55b. Consequently, increasing the gravity coefficient is definitely beneficial for the reinforced separation between the two phases. Under the condition of 1553 K, $G = 1200$, and $t = 5$ min, the mass fraction of TiO₂ in the separated anosovite is up to 62.68 wt%, and the recovery ratio of Ti is up to 81.21%.

2.3.4 Separation of Anosovite from Ti-Bearing Blast Furnace Slag by Super Gravity

2.3.4.1 Experimental Procedure

On basis of the selective crystallization and separation of anosovite from CaO–TiO₂–SiO₂–Al₂O₃–MgO system under reducing atmosphere, separation of anosovite from the Ti-bearing blast furnace slag by super gravity was conducted further. The Ti-bearing blast furnace slag from Panzhuhua Iron and Steel Corporation of China is employed, and the chemical compositions of the slag are given in Table 1.1. Firstly, the slag basicity of Ti-bearing blast furnace slag was adjusted to 0.6 promoting the transformation of perovskite to anosovite in Ti-bearing blast furnace slag. 10 g of the Ti-bearing blast furnace slag were put in the upper part of a two-layer graphite

crucible with the pore size of 0.01 mm, which was heated to 1573 K under the gas flow of 0.3 L/min CO and 0.1 L/min Ar. After reducing at 1573 K for 60 min in the heating furnace for promoting the crystallization of anosovite, the centrifugal device was started and adjusted to an angular velocity of 846, 1196, 1465, 1691, and 1895 r/min to achieve the gravity coefficient of $G = 800$. The slag was centrifuged for 6 min and then rapidly quenched in water.

After that, the macro and microstructures, the mineral and chemical compositions of the anosovite and slag that separated from the Ti-bearing blast furnace slag by the super gravity were analyzed by methods of SEM-EDS, XRD, and XRF, respectively. In addition, the Ti recovery ratio in the separated anosovite phase from the Ti-bearing blast furnace slag was calculated according to Eq. (2.14).

2.3.4.2 Separation Behavior of Rutile from Ti-Bearing Blast Furnace Slag

The vertical profiles and SEM-EDS images of sample obtained under super gravity and normal gravity are shown in Fig. 2.57. As shown in Fig. 2.57a, when $G = 1$, all of the Ti-bearing blast furnace slag is blocked in the upper crucible by the filter, with a gray uniform state. By contrast, the Ti-bearing blast furnace slag is separated by the filter into two parts under with condition of $G = 600$ as shown in Fig. 2.57b. The lower part presents a black glassy state, whereas the upper part appears in a black rod-shaped structure. The XRD patterns of two parts separated from Ti-bearing blast furnace slag are shown in Fig. 2.58. The upper rod-shaped structure presents a single diffraction peak of anosovite (PDF card No. 76-2373), whereas the lower uniform black glassy structure is without any other diffraction peaks. This indicates that the anosovite crystals are the single solid phase formed in the molten Ti-bearing blast furnace slag, which are fully separated from the slag melt under the force of super gravity, whereas all the slag melt passes through the filter and filled into the lower crucible.

The SEM image of separated anosovite is presented in Fig. 2.57c. It is indicated that the separated anosovite presents an independent rod shape, with no slag melt included. Combined with the EDS image of anosovite shown in Fig. 2.57d, the separated anosovite mainly consists of two elements of Ti and O, with small amount of Mg and Al. It is indicated that anosovite cannot be separated from Ti-bearing blast furnace slag under the gravity due to the high viscosity of solid-liquid mixture. In contrast, the driving force of $\Delta\rho g$ is significantly increased under the super gravity, and the solid-liquid separation between anosovite and slag melt is greatly enhanced by the super gravity. Thus, the slag melt fully passes through the filter and flowed to the bottom crucible as derived by super gravity, while the anosovite is efficiently intercepted by the filter and separated from the slag melt.

Variations in the mass fractions and recovery ratios of Ti in separated anosovite phase as a function of gravity coefficient are shown in Fig. 2.59. The mass fractions of TiO_2 in separated anosovite phase increase significantly with the gravity coefficient increasing from $G = 1$ to $G = 600$, while the recovery ratio of Ti decreases

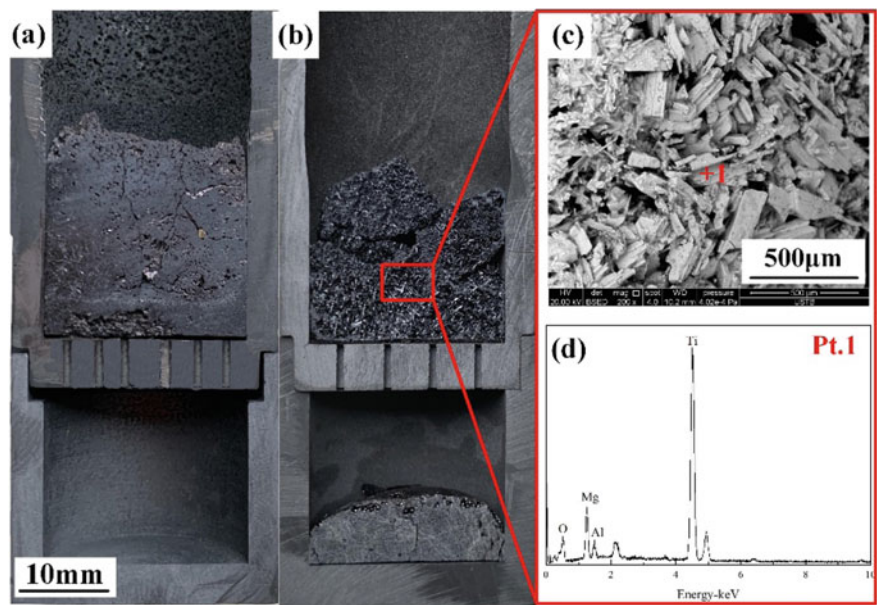


Fig. 2.57 Vertical profiles and SEM–EDS images of anosovite attained under super gravity and normal gravity: **a** $G = 1$; **b** $G = 600$; **c** SEM image of anosovite; **d** EDS image of anosovite

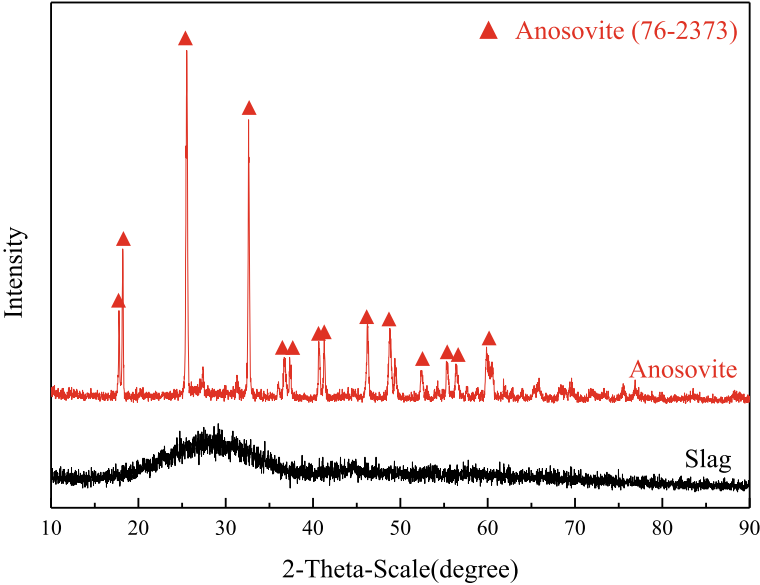


Fig. 2.58 XRD patterns of separated anosovite and slag phases under super gravity

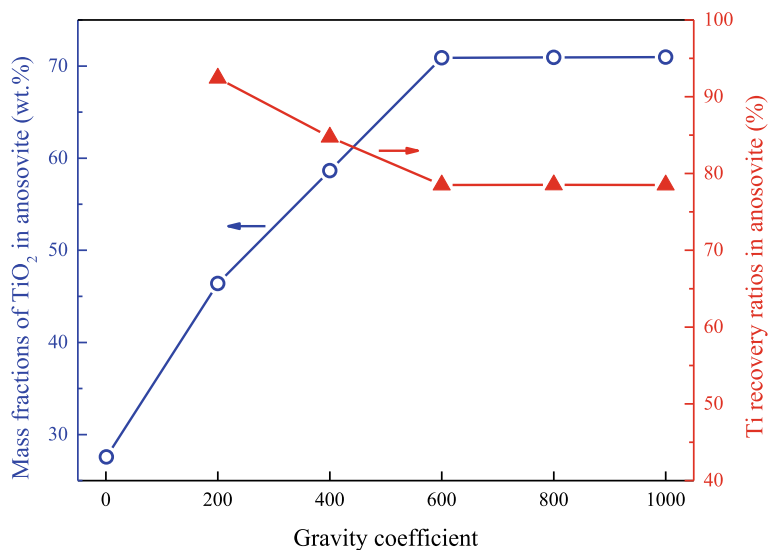


Fig. 2.59 Variations in mass fractions and recovery ratios of Ti in the separated anosovite phase as a function of gravity coefficient

gradually, which indicates that the phase separation of anosovite and slag melt is significantly enhanced with the increase of gravity coefficient. After the gravity coefficient reaching $G = 600$ to $G = 1000$, almost all of the slag inclusions are fully separated from anosovite, and the mass fraction and recovery ratio of Ti in the separated anosovite phase are to 70.89 wt% and 78.51%, respectively.

2.4 Carbothermal Reduction of Ti and Separation of Ultrafine TiC Powders in Ti-Bearing Slag

Titanium carbide (TiC) is proved to be a remarkable carbide of transition metal, and the ultrafine TiC powders were mainly prepared by various synthetic methods using high-purity ultrafine powders of metallic titanium (Ti) or titanium dioxide (TiO_2). Based on the thermodynamics data between the main components in Ti-bearing slag and carbon (C), the $[\text{TiO}_4]^{4-}$ rather than other components can be reduced to the TiC in the molten state of the slag and provides a favorable kinetic condition for the formation and dispersion of TiC powders. In this section, separation of ultrafine TiC powders from molten Ti-bearing slag by super gravity is proposed, to provide another way to produce ultrafine metal carbides from the massive Ti-bearing slag. The thermodynamic analysis and carbothermal reduction of Ti to TiC in Ti-bearing blast furnace slag, the crystallization behavior of carbonized Ti-bearing

slag, and the motion and separation behaviors of ultrafine TiC powders from Ti-bearing blast furnace slag by super gravity are studied, respectively. The mineral and chemical compositions, structure, and morphology of the separated TiC powders from Ti-bearing blast furnace slag are studied [54].

2.4.1 Thermodynamic Analysis for Carbothermal Reduction of Ti

Molten Ti-bearing blast furnace slag is mainly composed of $[\text{TiO}_4]^{4-}$, Ca^{2+} , Mg^{2+} , $[\text{SiO}_4]^{4-}$, and $[\text{AlO}_4]^{5-}$. The ionic activities (α), carbothermal reaction formulas, and standard Gibbs free energy changes for carbothermal reactions of these main components are determined by FactSage 7.1 and listed in Table 2.18. The start temperatures of carbothermal reduction for the main components in the Ti-bearing blast furnace slag are calculated via Eq. (2.16). It can be seen that only the start temperature of $[\text{TiO}_4]^{4-}$ is in the temperature range of molten Ti-bearing blast furnace slag, which indicates that $[\text{TiO}_4]^{4-}$ can be selectively carbothermal reduced to TiC by utilizing the physical heat energy of molten Ti-bearing blast furnace slag.

$$\Delta G = \Delta G^\ominus + RT \ln \frac{(P_{\text{CO}}/P^\ominus)^2 \cdot \alpha_{\text{MC}}}{\alpha \cdot \alpha_{\text{C}}^3}, \quad (2.16)$$

where ΔG is Gibbs free energy changes of carbothermal reaction, J/mol; $\Delta G^\ominus$ is standard Gibbs free energy changes of carbothermal reaction, J/mol; R is the universal gas constant; T is the start temperature of carbothermal reaction, K; P_{CO} is the gas pressure of CO; $P^\ominus$ is the standard gas pressure, $P_{\text{CO}}/P^\ominus \approx 1$; α , α_{MC} , and α_{C} are the activities of ions, metal carbide, and carbon, $\alpha_{\text{MC}} \approx 1$, $\alpha_{\text{C}} \approx 1$.

Table 2.18 Thermodynamic data for carbothermal reduction of main components in molten Ti-bearing blast furnace slag

Composition	α	Reaction	$\Delta G^\ominus$ (J/mol)	T (K)
$[\text{TiO}_4]^{4-}$	8.997×10^{-2}	$\text{TiO}_2 + 3\text{C} = \text{TiC} + 2\text{CO}$	$263,700 - 168.29 T$	1778.5
Ca^{2+}	0.141×10^{-2}	$\text{CaO} + 3\text{C} = \text{CaC}_2 + \text{CO}$	$465,500 - 220.62 T$	2803.4
$[\text{SiO}_4]^{4-}$	7.986×10^{-2}	$\text{SiO}_2 + 3\text{C} = \text{SiC} + 2\text{CO}$	$594,950 - 332.15 T$	1912.2
$[\text{AlO}_4]^{5-}$	1.750×10^{-2}	$2\text{Al}_2\text{O}_3 + 9\text{C} = \text{Al}_4\text{C}_3 + 6\text{CO}$	$685,500 - 349.51 T$	2170.2
Mg^{2+}	1.487×10^{-2}	$\text{MgO} + \text{C} = \text{Mg} + \text{CO}$	$486,830 - 193.36 T$	3265.3

2.4.2 Carbothermal Reduction of Ti to TiC in Ti-Bearing Blast Furnace Slag

2.4.2.1 Experimental Procedure

Firstly, the investigation for the carbothermal reduction of hot Ti-bearing blast furnace slag was carried out. 20 g of the Ti-bearing blast furnace slag produced from Panzhihua Iron and Steel Corporation of China was fully mixed with 2.7 g of carbon powders (99.9% purity), which was put into the alumina crucible with an inside diameter of 19 mm and a height of 70 mm and heated to 1783 K in a tube furnace in argon gas atmosphere. After carbothermal reduction for different time of 0.5 h, 1.0 h, 2.0 h, 4.0 h, and 6.0 h, each sample was taken out and rapidly cooled, respectively. Subsequently, SEM-EDS and XRD methods were employed to analyze the mineral composition and microstructure of the carbonized slag. The conversion ratio of Ti to TiC (C_{Ti}) was calculated via Eq. (2.17).

$$C_{\text{Ti}} = \frac{m_{\text{Ti-TiC}}}{m \cdot w_{\text{Ti}}}, \quad (2.17)$$

where $m_{\text{Ti-TiC}}$ is the mass of Ti in TiC as determined by chemical titration determined by methane dianitpyrine spectrophotometric method [58]; m is the mass of sample after reduction for different time; and w_{Ti} is the mass fraction of Ti in sample, which is determined by ICP-OES method.

2.4.2.2 Carbothermal Reduction Behavior of Ti to TiC

Figure 2.60 shows the XRD patterns of the Ti-bearing blast furnace slag after carbothermal reduction at 1783 K for different time. It is clear that the obvious diffraction peak of TiC (PDF card 65-8805) has appeared in the carbonized Ti-bearing slag after reduction for 0.5 h. This indicates that the kinetic condition for solid-liquid reaction of $[\text{TiO}_4]^{4-}$ and carbon is favorable, and TiC powders are rapidly formed in molten slag. While the carbothermal reduction of Ti is insufficient within 0.5 h, the diffraction peaks of the left carbon are also appeared in the slag. With the increase of reduction time, more Ti was fully reacted with C, and the amount of TiC powders formed in the molten slag increases significantly, while the left carbon is decreased. After carbothermal reduction for 4.0 h, almost all of Ti in the molten slag is fully transformed to TiC, and only the significant diffraction peak of TiC with an extremely high intensity is existed in the slag.

Figure 2.61 shows the SEM-EDS images of the carbonized Ti-bearing slag obtained by carbothermal reduction for different time. The fine light-white TiC powders with a particle size of 2–5 μm are independently appeared in the carbonized Ti-bearing slag after reduction. With the increase of reduction time from 0.5 to

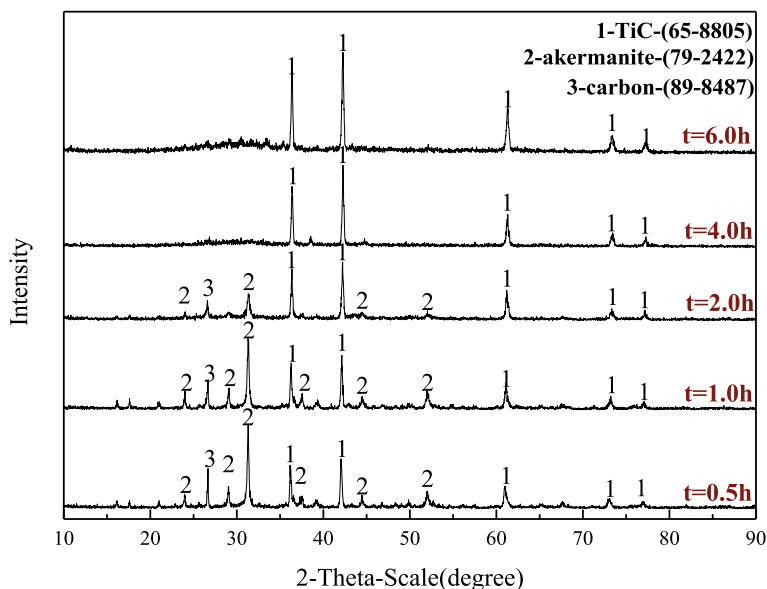


Fig. 2.60 Variations in XRD patterns of Ti-bearing blast furnace slag after carbothermal reduction for different time

6 h, more TiC powders are formed, which are uniformly dispersed in carbonized Ti-bearing slag as exhibited in Fig. 2.61b–f.

The conversion ratio of Ti to TiC with reduction time is shown in Fig. 2.62. This curve confirms that the molten $[\text{TiO}_4]^{4-}$ was easily reacted with C and transformed to TiC, and the conversion ratio of Ti to TiC reaches 43.35% within a short time of 0.5 h. With the reduction time increasing from 0.5 to 4.0 h, the conversion ratio of Ti to TiC increases significantly from 43.35 to 95.83%. As accordingly verified, almost all can be transformed to TiC in the molten carbonized Ti-bearing slag within 4 h, while the formation of large amounts of ultrafine TiC powders causes the extremely high viscosity of the molten slag, which greatly limited the movement and separation of TiC powders in the carbonized Ti-bearing slag.

2.4.3 Crystallization Behavior of Carbonized Ti-Bearing Slag

2.4.3.1 Experimental Procedure

Firstly, the crystallization behavior of the carbonized Ti-bearing slag was investigated, to acquire the solid–liquid coexistence state for single TiC powders in molten slag and create the necessary condition for solid–liquid separation of TiC powders from the molten slag. Each 20 g of the carbonized Ti-bearing slag was filled into

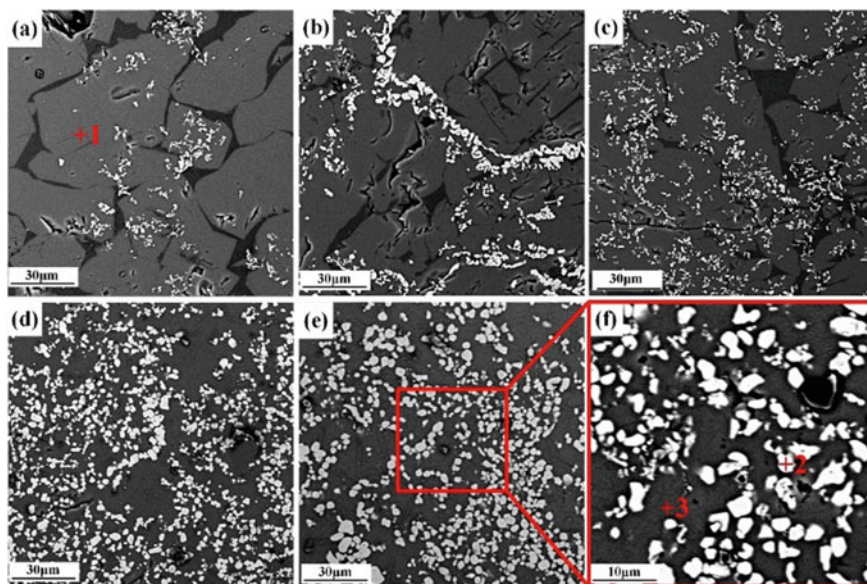
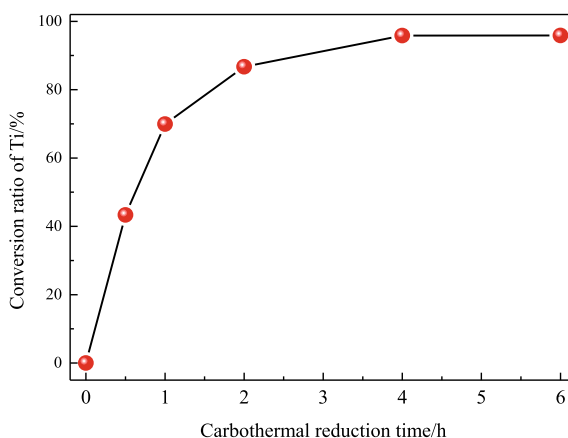


Fig. 2.61 SEM images of the carbonized Ti-bearing slag with reduction time: **a** 0.5 h; **b** 1.0 h; **c** 2.0 h; **d** 4.0 h; **e**, **f** 6.0 h

Fig. 2.62 Conversion ratio of Ti to TiC in Ti-BF slag with reduction time



an alumina crucible (I.D. 20 mm, H. 70 mm) and melted at 1823 K in a muffle furnace under the argon atmosphere, followed by continuously cooling from 1773 to 1523 K at a cooling rate of 2 K/min, taking a sample every time when the temperature drops by 50 K and water-quenched, respectively. Afterward, the SEM-EDS and XRD methods were used to analyze the mineral compositions and microstructures of the slags quenched at the different temperatures.

2.4.3.2 Crystallization Behavior of the Carbonized Slag

The variations of XRD patterns, SEM, and EDS images for the carbonized Ti-bearing slag with the decrease of temperature are shown in Figs. 2.63 and 2.64. It is indicated that the TiC powders are the unique solid phase in the molten slag at above 1673 K, which confirms its high melting point. The single ultrafine powders of TiC are distributed throughout the slag in homogeneous dispersion state, which are shown in Fig. 2.64a–c. However, the akermanite phase ($\text{Ca}_2(\text{Mg}_{0.25}\text{Al}_{0.75})(\text{Si}_{1.25}\text{Al}_{0.75}\text{O}_7)$) is crystallized in the molten carbonized Ti-bearing slag at 1623 K, as shown in Fig. 2.64d. When the temperature decreases from 1623 to 1523 K, the akermanite crystallizes and grows further, as shown in Fig. 2.64d–f. The gray akermanite with a large size of 100–200 μm is closely included among the ultrafine TiC powders, which can block the movement of TiC powders in the molten slag. Therefore, the temperature above 1673 K is the solid–liquid coexistence condition for single TiC powders in molten carbonized Ti-bearing slag, which is necessary for the selective separation of TiC powders from the molten carbonized Ti-bearing slag through solid–liquid separation under super gravity field.

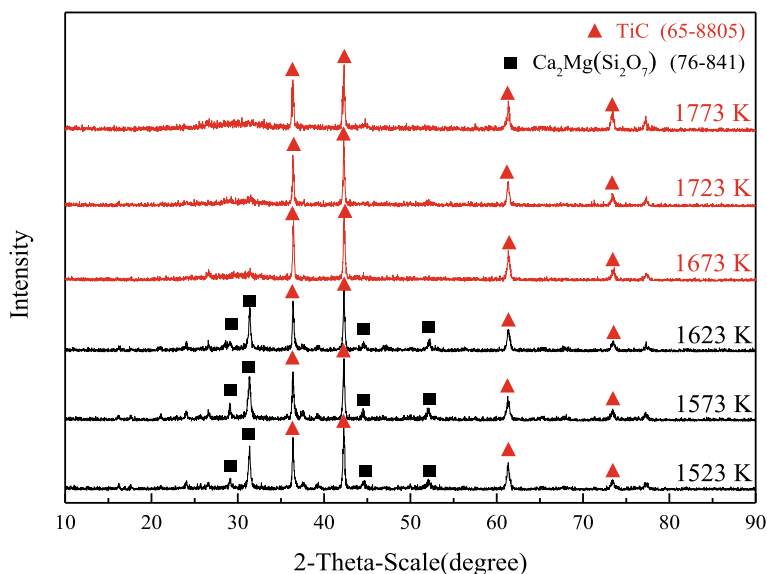


Fig. 2.63 Variation of XRD patterns for carbonized Ti-bearing slags with temperature decreasing

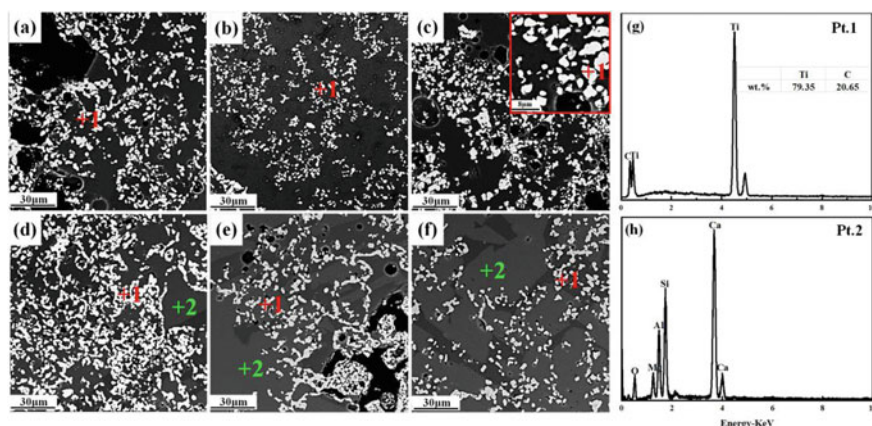


Fig. 2.64 Variations of SEM-EDS images for carbonized Ti-bearing slags with temperature decreasing: **a** 1773 K; **b** 1723 K; **c** 1673 K; **d** 1623 K; **e** 1573 K; **f** 1523 K; **g** and **h** EDS of TiC and akermanite

2.4.4 Motion Behavior of Ultrafine TiC Powders in Carbonized Ti-Bearing Slag Under Super Gravity

Based on the carbothermal reduction of Ti-bearing blast furnace slag and the crystallization behavior of carbonized Ti-bearing slag, the motion and separation behaviors of ultrafine TiC powders from molten carbonized Ti-bearing slag under super gravity are studied.

2.4.4.1 Experimental Procedure

On the basis of the favorable condition for solid-liquid coexistence of single TiC powders in molten carbonized Ti-bearing slag, the motion behavior of TiC powders in the molten slag under the super gravity field was studied. 20 g of carbonized Ti-bearing slag sample was filled into the alumina crucible (I.D. 20 mm, H. 70 mm), followed by heating to 1673 K through the heating furnace in centrifugal device. The centrifugal rotating system was started to drive the slag rotated at the rotational speed of 1645 r/min, for creating a gravity coefficient of $G = 800$.

The samples under the conditions of $G = 800$ and $G = 1$ were both divided into two parts along their longitudinal sections. Five regions (a, b, c, d, and e) in the samples were divided along the super gravity direction, which were measured by the SEM-EDS method for their respective microstructures. After that, the image analyzer (LEICA Qwin 500) was employed to analyze the volume fractions and particle sizes of TiC powders in different regions, and the values were statistically calculated from 20 of the scanning electron micrographs in each region. In addition, the sample obtained under the super gravity field was crossly divided into two parts

along the interface between the TiC layer and slag layer, and the mineral and chemical compositions (wt%) of the two phases were confirmed using XRD and XRF methods. Ti recovery ratio of separated TiC phase was determined through Eq. (2.18).

$$\varepsilon_{\text{Ti-TiC}} = \frac{m_{\text{Ti-TiC}} \times \omega_{\text{Ti-TiC}}}{m_{\text{Ti-TiC}} \times \omega_{\text{Ti-TiC}} + m_{\text{Ti-slag}} \times \omega_{\text{Ti-slag}}} \times 100\%, \quad (2.18)$$

where $\varepsilon_{\text{Ti-TiC}}$ is the Ti recovery ratio in TiC phase; $m_{\text{Ti-TiC}}$ and $\omega_{\text{Ti-TiC}}$ are the mass and mass fraction of Ti in TiC phase; $m_{\text{Ti-slag}}$ and $\omega_{\text{Ti-slag}}$ are the mass and mass fraction of Ti in slag phases, respectively.

2.4.4.2 Motion Behavior of Ultrafine TiC Powders

Longitudinal drawings of samples conducted under super gravity with the conditions of $G = 800$ and $G = 1$ at 1673 K are presented in Fig. 2.65, which are absolutely different in macrostructures. It is observed from Fig. 2.65a that the sample attained under normal gravity shows a homogeneous dark gray structure, in which a certain number of pores are included. By contrast, a significant two-layered structure is appeared under the condition of super gravity, and an apparent interface is formed significantly between the two layers, as shown in Fig. 2.65b. Specifically, the upper layer is presented as a black glass state, while the lower layer shows a different dense dark-brown state.

Combined with the XRD patterns of the two layers in the sample acquired under the condition of $G = 800$ in Fig. 2.66, the single diffraction peak for the typical TiC (PDF#65–8807) is appeared in the lower layer, while that of the upper layer shows a typical diffuse scattering peak. Compared with the XRF results of the two layers, the Ti content in the separated TiC phase reaches 32.35 wt%, while that in the slag phase is only 0.75 wt%. The Ti recovery ratio in the separated TiC phase is up to 96.69% as determined via Eq. (2.16). This indicates that all of the TiC powders are

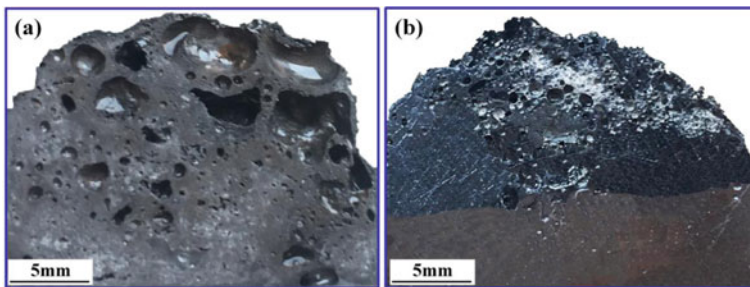


Fig. 2.65 Longitudinal sections of samples obtained under super gravity compared with normal gravity: **a** $G = 1$; **b** $G = 800$

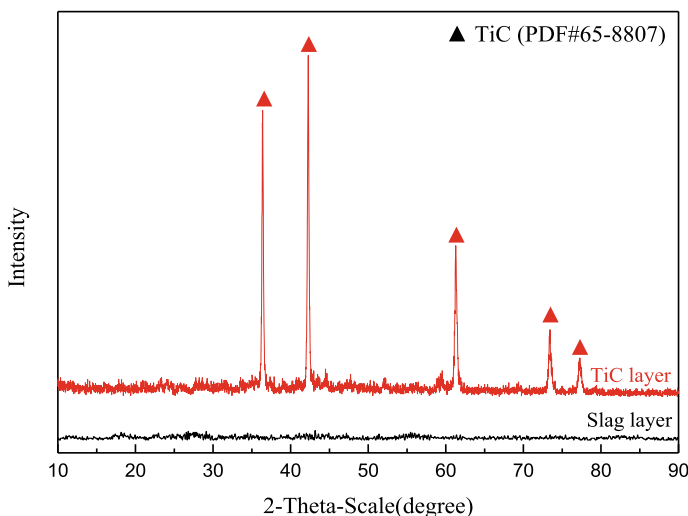


Fig. 2.66 XRD patterns of different layers in the sample attained under super gravity with $G = 800$

efficiently concentrated downward to the TiC layer, whereas the slag melt moves in opposite direction and forms the slag layer, under the force of super gravity.

Figure 2.67a presents the position of different regions in longitudinal section of the layered sample attained under the condition of $G = 800$, and the SEM images of the different regions are shown in Fig. 2.67b–f, to verify the directional motion behavior of the TiC powders under the force of super gravity. It is confirmed that the slag melt is efficiently migrated to the upper layer, in which not any TiC powders are included, as shown in Fig. 2.67b. In contrast, all of the TiC powders are driven to move to the lower layer along the super gravity direction and form a significant interface between the slag melt and TiC powders in the region (c), as shown in Fig. 2.67c. Moreover, the TiC powders are concentrated more and more dense from the region (d)–(f) along the super gravity direction, where only a small amount of slag inclusions are appeared in the interspace of the dense TiC powders, as shown in Fig. 2.67d–f.

Moreover, the variations of volume fractions and particle sizes of TiC powders in different regions of the layered sample are shown in Fig. 2.68. The volume fraction of TiC powders increases significantly from 10.5 to 55.9% with the region approaching from (c) to (e) along the super gravity direction, which confirms the directional motion behavior of the TiC powders in the molten carbonized Ti-bearing slag under the super gravity field. The equivalent diameters of TiC powders are increased from 2.19 to 2.70 μm along the region (b)–(e), which indicates that the larger TiC powders possessed faster sedimentation velocity under the force of super gravity.

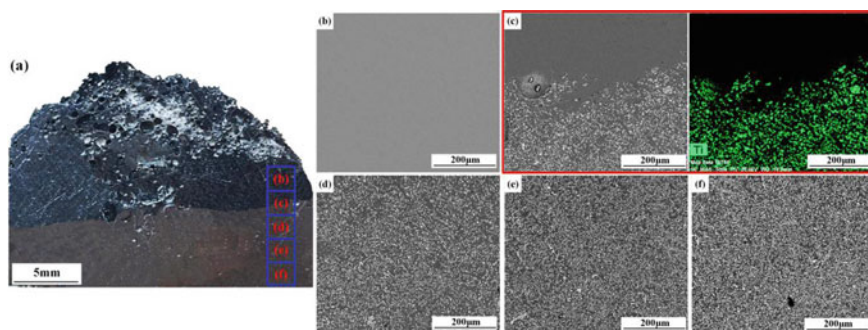


Fig. 2.67 SEM images of different regions in the layered sample attained under super gravity with $G = 800$: **a** positions in longitudinal section of sample; **b–f** SEM images of different regions

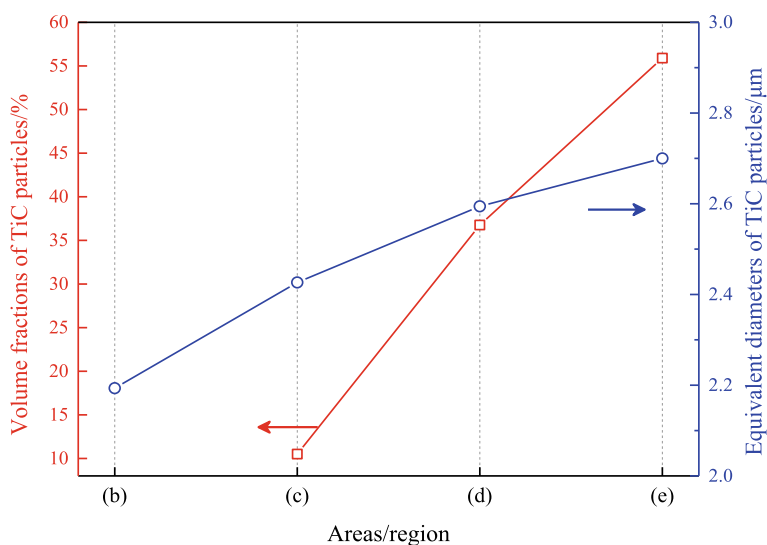


Fig. 2.68 Variations of volume fractions and equivalent diameters for TiC powders in different regions along super gravity direction

2.4.5 Separation of Ultrafine TiC Powders from Carbonized Ti-Bearing Slag by Super Gravity

2.4.5.1 Experimental Procedure

On the basis of the directional motion of ultrafine TiC powders in carbonized Ti-bearing slag under the force of super gravity, separation of the ultrafine TiC powders from molten carbonized Ti-bearing slag enhanced by super gravity was conducted further. 20 g of the carbonized Ti-bearing slag was put onto a graphite fiber felt with

the pore size less than $5\ \mu\text{m}$ in the upper part of a two-layer graphite crucible, which was heated to 1773 K in the heating furnace of centrifugal apparatus. Subsequently, the centrifugal apparatus was started and adjusted to an angular velocity of 1036, 1465, and 1795 r/min to achieve the gravity coefficients of $G = 300$, $G = 600$, and $G = 900$. After centrifugal rotation at a constant temperature for 10 min, the rotation was stopped and the crucible was water-quenched. Simultaneously, the parallel experiments were conducted at 1773 K for 10 min under normal gravity field.

After that, the upper parts (TiC powders) and lower parts (slag phase) were both sectioned longitudinally along their center axis. The microstructures, mineral and chemical compositions, and size distribution of the separated TiC powders were analyzed by SEM-EDS, XRD, Raman, TEM, XRF, ICP-OES, and the particle size analyzer, respectively. The Ti recovery ratio in TiC parts was calculated according to Eq. (2.18).

2.4.5.2 Separation Behavior of Ultrafine TiC Powders

Figure 2.69 shows the vertical profiles of the samples obtained by super gravity as a function of gravity coefficient. Although a mass of ultrafine TiC powders is formed in carbonized Ti-bearing slag, while all of carbonized Ti-bearing slag are blocked by graphite filter in the upper crucible under the condition of $G = 1$, as shown in Fig. 2.68a. In contrast, the molten carbonized Ti-bearing slag is separated into two contrasting parts enhanced by super gravity, as shown in Fig. 2.69b–d.

Combined with the XRD patterns of separated samples as shown in Fig. 2.70, the upper sample is TiC phase with a high diffraction intensity, while the lower sample is the slag phase. It is indicated that the black TiC powders are effectively blocked on the graphite filter, while the slag melt is separated into the lower crucible which

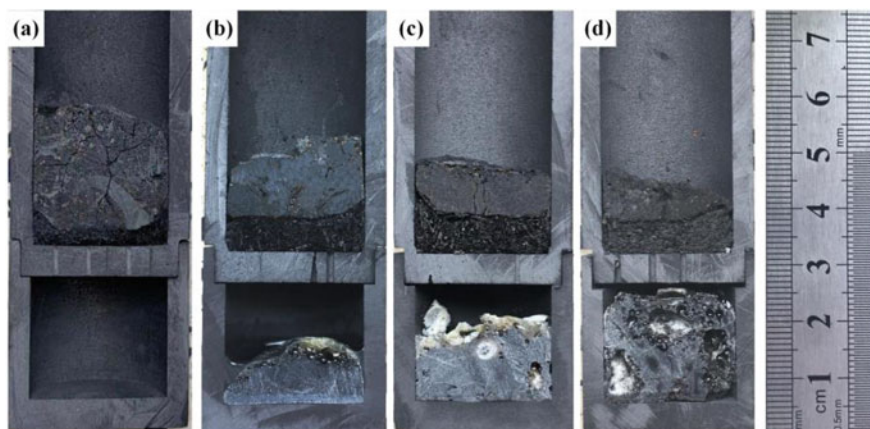


Fig. 2.69 Variation of vertical profiles for samples attained by super gravity as a function of gravity coefficient: **a** $G = 1$; **b** $G = 300$; **c** $G = 600$; **d** $G = 900$

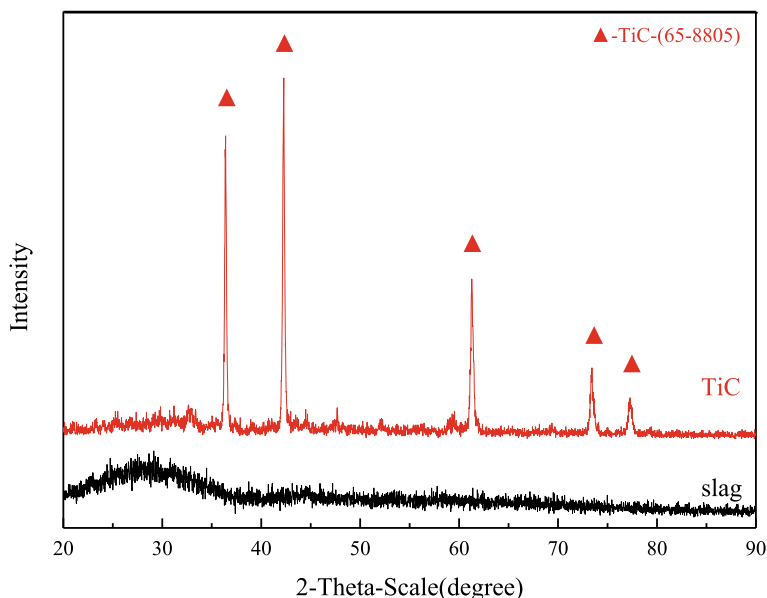


Fig. 2.70 XRD patterns of separated TiC phase and residual slag by super gravity: $G = 600$, $T = 1773$ K and $t = 10$ min

shows a glassy state in the room temperature. With the increase of gravity coefficient, more slag melt is fully separated from the molten carbonized Ti-bearing slag and moved into the lower crucible, and the purity of the separated TiC phase is greatly improved.

Figure 2.71 shows the variations for the content and recovery ratio of Ti in the separated TiC powders as a function of gravity coefficient. The Ti content of separated TiC powders is increased significantly from 13.96 to 77.89 wt% with the increase of gravity coefficient from $G = 1$ to $G = 800$, and the recovery ratio of Ti in the TiC powders reaches 95.58% with the gravity coefficient of $G = 800$. This confirms that the slag melt is fully removed from the TiC powders, and the mass fraction of TiO_2 was only 0.65 wt% in the separated residual slag, as given in Table. 2.19.

Figure 2.72a, b shows the FESEM images of the separated TiC powders from carbonized Ti-bearing slag with the gravity coefficient of $G = 800$. The TiC powders are confirmed to be ultrafine particle with the size of 2–5 μm ; each one is independent without any agglomeration with others. Figure 2.72c shows the TEM image of the cross section of TiC powder, it is clear that the shape of TiC powder is rhombic, and the surfaces are glossy. As indicated from the EDS image presented in Fig. 2.72d, the purity of TiC powders is very high, and only the two elements of Ti and C with an atom ratio of 1:1 are found.

The XRD pattern of the separated TiC powders is shown in Fig. 2.73a. The unique diffraction pattern of the TiC powders with high diffraction intensity is fully matched with the reference card of TiC (PDF Card No. 65-8807), with a cubic

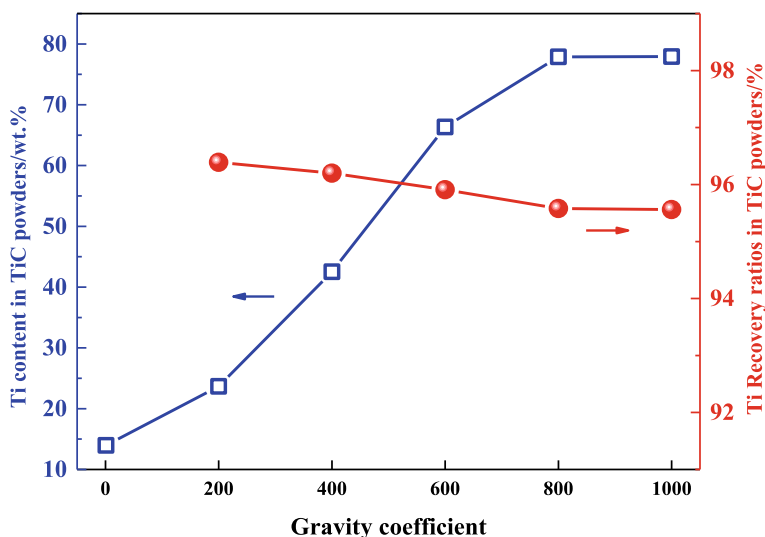


Fig. 2.71 Variations for content and recovery ratio of Ti in separated TiC powders as a function of gravity coefficient

Table 2.19 Chemical composition of slag melt (wt%)

TiO ₂	CaO	SiO ₂	Al ₂ O ₃	MgO	MnO ₂	V ₂ O ₅	Others
0.65	36.62	32.53	15.46	9.03	0.96	0.26	4.49

crystal system and *Fm-3m* (No. 225) space group. The Raman spectra of the TiC powders are presented further in Fig. 2.73b. Three prominent peaks are appeared at the wave number of 260 cm^{-1} , 405 cm^{-1} , and 607 cm^{-1} , which are attributed to the longitudinal acoustic (LA), second-order acoustic (2A), and transverse optical (TO) modes of Ti-C bonding, respectively. The Raman spectra of the TiC powders separated from Ti-bearing blast furnace slag are perfectly accordant with that of the TiC synthesized from the high-purity metallic Ti powders as reported by Lohse [59].

The size distribution of the separated TiC powders is shown further in Fig. 2.74. It is noticeable that the particle size of TiC powders falls into the micron-scale level ($1\text{--}10\text{ }\mu\text{m}$). More than 60% of the TiC powders are in the size of $1\text{--}5\text{ }\mu\text{m}$, and the average particle size of TiC powders is $2.75\text{ }\mu\text{m}$. Furthermore, the TiC powders possess a large surface area of $3016\text{ m}^2/\text{kg}$, which is favorable for the applications of magnetic and electronic materials. Table 2.20 shows the particle sizes of some reported ultrafine TiC powders synthesized by using high-purity ultrafine metallic Ti and TiO₂ powders [60, 61]. It is indicated that the TiC powders separated from Ti-bearing blast furnace slag are ultrafine particles (particle size $2.75\text{ }\mu\text{m}$ on average), which are consistent with the size distribution of the ultrafine TiC powders those prepared by the synthetic methods.

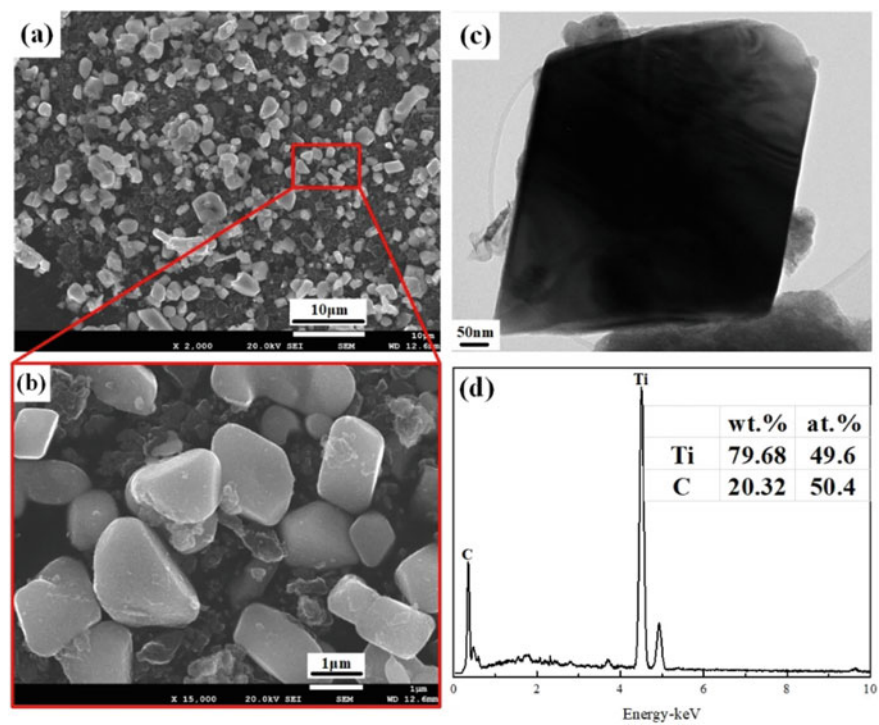


Fig. 2.72 Morphology of the separated TiC powders with $G = 800$: **a** and **b** FE-SEM images; **c** TEM image; **d** EDS image

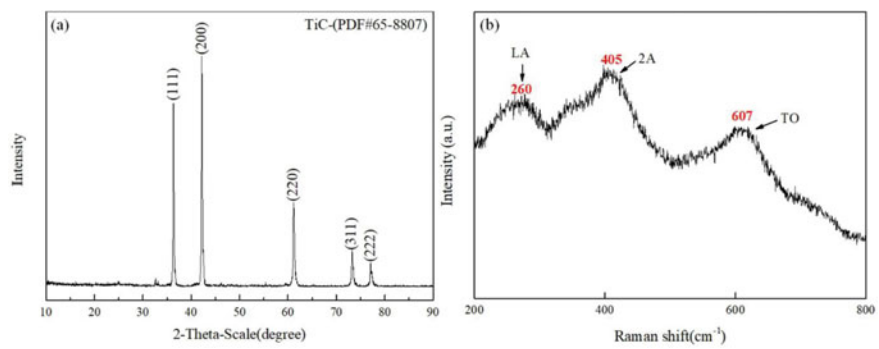


Fig. 2.73 XRD pattern and Raman spectra of the TiC powders: **a** XRD pattern; **b** Raman spectra

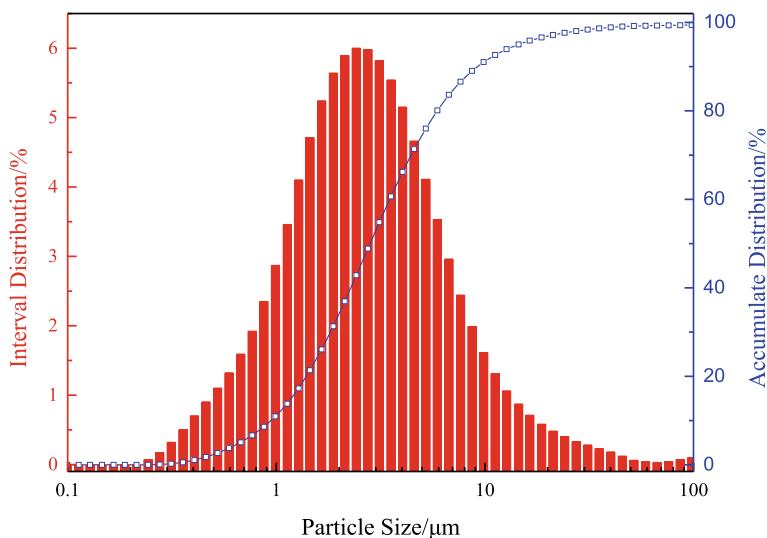


Fig. 2.74 Size distribution of TiC powders separated from Ti-bearing blast furnace slag

Table 2.20 Particle sizes of some reported TiC powders

Preparation method	Particle size	Ref
Separated from Ti-bearing slag	2.75 μm	This work
Synthesis by ultrafine metallic Ti powders	$\sim 5 \mu\text{m}$	Powder technol. 329, 232–240 (2018)
Synthesis by ultrafine TiO_2 powders	0.93–4.34 μm	Int. J. Refract. Met. Hard Mater. 28(5), 628–632 (2010)

2.5 Amplification Study for Selective Separation of Ti in Ti-Bearing Slag by Super Gravity

Based on the studies for selective crystallization and separation of various Ti-rich phases from Ti-bearing slag, an amplification apparatus of super gravity metallurgy is exploited, and the amplification study for continuous crystallization and separation of perovskite from Ti-bearing slag with larger scale is further carried out in this section.

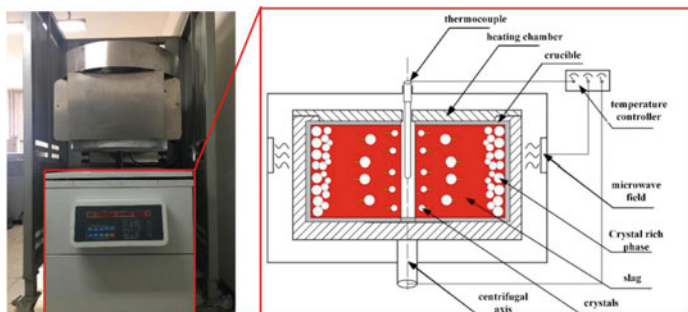


Fig. 2.75 Sketch of the amplification apparatus for super gravity metallurgy: 1 thermocouple, 2 heating chamber, 3 graphite crucible, 4 temperature controller, 5 microwave field, 6 perovskite-rich phase, 7 slag phase, 8 perovskite, and 9 centrifugal axis

2.5.1 *Super Gravity Metallurgy Apparatus for Amplification Study*

To realize the continuous crystallization and separation process and further scale up the experimental scale, an amplification apparatus for super gravity metallurgy is exploited by the authors as illustrated in Fig. 2.75. A vertical heating chamber with an inner diameter of 150 mm and an inside height of 100 mm is fixed horizontally onto the centrifugal rotor, and the distance from the centrifugal axis to the center of sample is to 55 mm. When the centrifugal rotor starts running, the chamber rotates therewith in the horizontal direction, which could impart a maximum angular velocity of 1000 r/min. Furthermore, the centrifugal apparatus used for amplification study is heated by resistance wire, and the temperatures are controlled by a program controller with an R-type thermocouple.

2.5.2 *Amplification Study for Separation of Perovskite from Ti-Bearing Slag by Super Gravity*

2.5.2.1 *Experimental Procedure*

On the basis of the conditions of selective crystallization and separation, the amplification experiment for continuous crystallization and separation of perovskite from Ti-bearing slag with larger scale was further carried out. An amount of 1000 g of the Ti-bearing slag with basicity of 1.30 was put into a graphite crucible with an inner diameter of 125 mm and an inside height of 80 mm and then covered with a graphite lid, which was heated to 1773 K in the heating chamber of centrifugal apparatus (Fig. 2.74). After melting at the constant temperature for 30 min, the molten Ti-bearing slag was cooled slowly at 1593–1563 K with a cooling rate of 0.5 K/

minute for the fully crystallization of perovskite. And then, the temperature was rapidly increased to 1578 K, and the centrifugal apparatus was started and adjusted to the angular velocity of 1000 r/min, namely $G = 62$ at the constant temperature for 25 min. After that, the centrifugal apparatus was shut off, and the graphite crucible was quenched in water.

2.5.2.2 Continuous Crystallization and Separation Behaviors of Perovskite

As the cross and vertical sections of the sample obtained by amplification experiment with the gravity coefficient of $G = 62$ shown in Fig. 2.76, the sample is in a form of annular cylinder close to the inner wall of crucible. The layered structure appears significantly in the sample, with the inner part in a black glassy state and the outer part in a gray-white compact structure. Combined with the XRD analysis shown in Fig. 2.77, the inner part mainly comprises pyrope and diopside and some perovskite, whereas the outer part mainly comprises perovskite and some pyrope and diopside, but the diffraction peak intensity of perovskite in outer part is increased significantly compared with that of the inner part.

Furthermore, the layered sample is divided into eight areas along the super gravity direction and characterized by the metallographic microscopy as shown in Fig. 2.78, and the volume fractions and equivalent diameters of perovskite in different areas of the layered sample are shown in Fig. 2.79. It is obvious that only some fine networks of perovskite are found in the inner areas (a)–(c), whereas majority of fine and larger equiaxed crystals of perovskite concentrate in the interface areas (d)–(e) and the outer areas (f)–(h), respectively. According to the chemical compositions of the different parts in the layered sample, the mass fraction of TiO_2 in the outer part is up to 28.07 wt%, whereas that of the inner part is decreased to 16.11 wt%. The recovery ratio of Ti in the outer part is up to 74.96%.

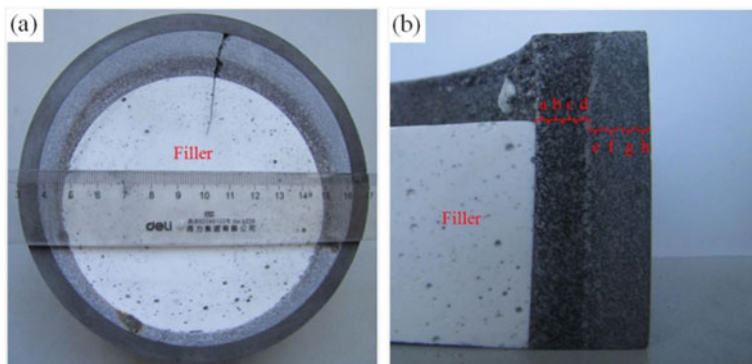


Fig. 2.76 Cross sections and vertical sections of the sample obtained in amplification experiment

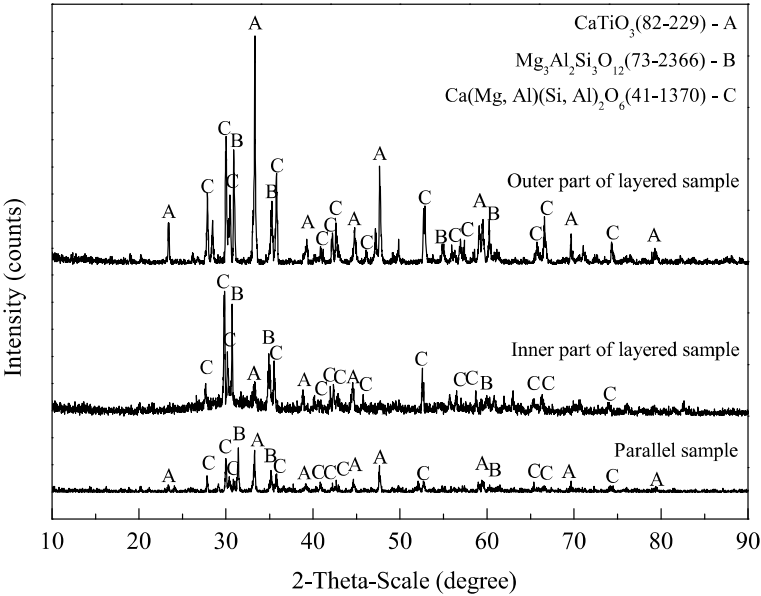


Fig. 2.77 XRD patterns of different areas in the layered sample obtained in amplification experiment

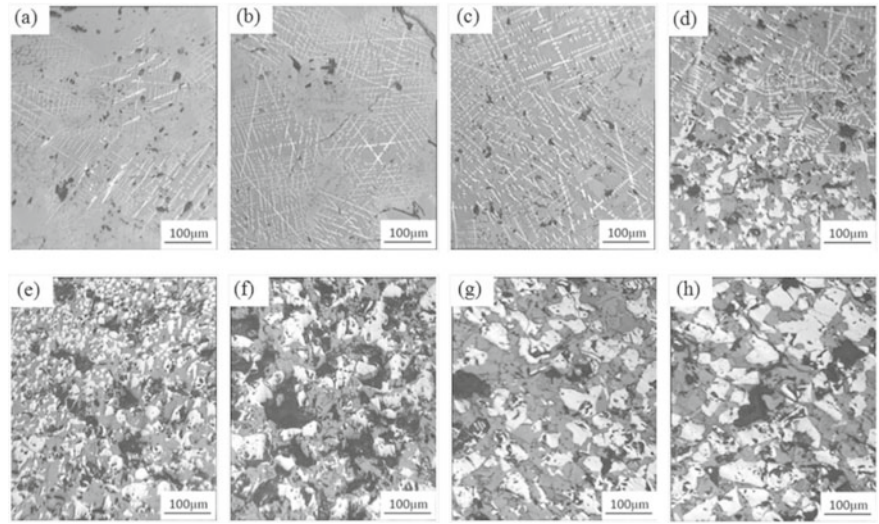


Fig. 2.78 Micrographs of the eight areas in the layered sample obtained in amplification experiment

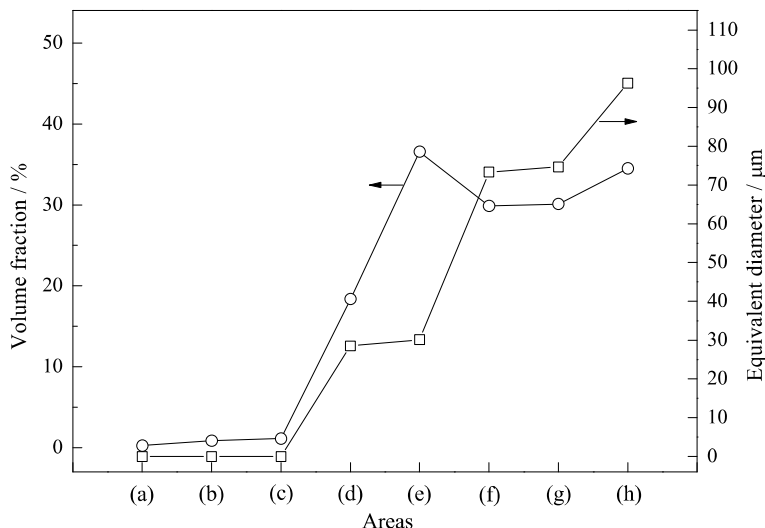


Fig. 2.79 Volume fractions and equivalent diameters of perovskite in different areas of the layered sample obtained in amplification experiment

Consequently, the amplification experiment results confirm that the continuous crystallization and separation of perovskite from the Ti-bearing slag melt by super gravity are a feasible method. Majority of perovskite are separated from the Ti-bearing slag melt and concentrated as perovskite-rich phase along the super gravity direction. Due to the lower gravity coefficient obtained by the amplification experiment, the separation effect of perovskite crystals and slag phase is lower than that with the high gravity coefficient.

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Chapter 3

Selective Crystallization and Separation of B in B-Bearing Slag



Abstract It reports the selective crystallization and separation of B in B-bearing slag. The competitive crystallization behavior of B, Si, and Mg in B-bearing slag is reported in Sect. 3.1. The study on two-stage separation of olivine and suanite, the selective separation of last precipitated suanite, and the crystalline phase transformation and one-step separation of suanite in molten B-bearing slag are included in Sect. 3.2, 3.3, and 3.4, respectively.

Boron (B) is an indispensable microelement in nature [1], and its compounds are applied in various fields, including friction-reducing additives [2], borosilicate glasses [3], microwave dielectric ceramics [4], thermo-luminescent materials [5], and nuclear shielding materials [6]. Boron-containing crystals [e.g., suanite ($\text{Mg}_2\text{B}_2\text{O}_5$)] have received much attention for their wide range of applications for anti-wear substance and friction-reducing additive [7, 8], which have widespread applications for the reinforcements in electronic ceramics, glass, and metal-ceramic composite materials [9]. The suitable chemical compatibility with metallic aluminum and the excellent mechanical behaviors of suanite crystals, such as the high Young's modulus and low thermal expansion coefficient, have encouraged its numerous particular applications in reinforcing materials [10–12]. Moreover, the suanite crystals present appropriate microwave dielectric properties of low dielectric constant and high-quality factor in the dielectric glass–ceramic systems during heat treatment, which are used as an essential ceramics reinforced phase for glass ceramic [13]. Recently, the chemical vapor deposition (CVD), molten salt synthesis (MSS), and solid-state synthesis methods are mainly used for preparing suanite nanowires, nanorods, and whiskers [2, 14, 15]. However, all the starting materials depend on a large amount of pure boron oxide reagents, and the preparation process consists of multi-steps involving liquid phase and gas phase reactions [16].

The rapidly increasing boron consumption has caused the gradual depletion of ascharite, which is the principal raw material for the boron industry in China [17, 18]. In addition to ascharite which has a high B_2O_3 content of 12 wt% [19], the massive ludwigite in Liaoning province of China is another boron-containing mineral resource [20]. However, due to the lower boron content and the complex mineral composition of ludwigite, it is difficult to utilize this mineral in the boron industry directly [21–23].

The utilization of ludwigite has been reported to be performed in the blast furnace in Fengcheng Iron and Steel Group Co. Ltd., in China, which is the main producer of B-bearing slag in the country, to produce the pig iron and the B-bearing slag [24–26].

B-bearing slag is the main by-product produced from the ludwigite ore in the ironmaking process [27, 28], which contains a large amount of valuable chemical elements including boron and magnesium [29]. Generally, the concentration of boron trioxide (B_2O_3) in B-bearing slag is up to 12–22 wt%, which is much higher than that of ludwigite, making it an alternative boron-containing resource for the boron industry [30, 31]. However, all the boron is transformed into the amorphous state during the cooling process, while a large amount of other minerals without boron [e.g., magnesium silicate (Mg_2SiO_4)] is crystallized in the B-bearing slag [32]. The dispersion of amorphous boron mixed with various fine minerals challenges the efficient recovery and utilization of the boron resources in the slag [33]. As a result, the B-bearing slag is mainly discarded in a landfill, which results in a large waste of boron resources and several water pollution problems [34, 35].

B-bearing slag is disposed of in slag dumps, and the boron can migrate into the soil and aquatic environment under natural weathering conditions [36]. If the boron content exceeds the standard level, it can have negative effects on the growth of plants and animal [34]. Therefore, the B-bearing slag is regarded as a typical boron-containing solid waste, and various hydrometallurgical methods are adopted for the recovery of the boron resource to produce boric acid or borax [37]. However, since most of the boron is transformed into the amorphous phase during the cooling process of the molten slag, the extraction rate of boron is lowered and water pollution problems arise [38–40].

In recent years, some research proposed that promoting the crystallization of boron is beneficial for its extraction from B-bearing slag [41, 42]. Sui [30] reported that the $B_2O_5^{4-}$ and SiO_4^{4-} competed for Mg^{2+} in the molten B-bearing slag. Gao [43] found that the Mg^{2+} reacted preferentially with SiO_4^{4-} to form olivine during the crystallization process of the molten slag. These reveal that it is difficult to enrich the boron in its crystalline phase owing to the competitive reactions between $B_2O_5^{4-}$, SiO_4^{4-} , and Mg^{2+} in B-bearing slag. Moreover, Yu [44] found that the crystalline phases of boron exhibited a tight multi-interface interweaved state with others in the cooled B-bearing slag. Thus, the boron-containing crystals cannot be efficiently recovered from the slag through hydrometallurgical or other separation methods at room temperature. On the basis of the significant enhancement of super gravity on mass migration and phase separation of different phases in complex system, selective separation of B-rich phases from B-bearing slag is conducted by super gravity.

In this chapter, competitive crystallization of B, Si, and Mg in B-bearing slag is found, and selective crystallization and separation of B in B-bearing slag are proposed. The study on competitive crystallization and two-stage separation, crystalline phase transformation, and one-step separation for B-rich phases in B-bearing slag is included in the following sections, respectively:

Section 3.1 reports the competitive crystallization of B, Si, and Mg in B-bearing slag [45].

Section 3.2 reports the two-stage separation of olivine and suanite in B-bearing slag [45].

Section 3.3 reports the selective separation of last precipitated suanite in B-bearing slag [46].

Section 3.4 reports the crystalline phase transformation and one-step separation of suanite in B-bearing slag [47].

3.1 Competitive Crystallization of B, Si, and Mg in B-Bearing Slag

3.1.1 Thermodynamic Analysis for B, Si, and Mg in $\text{MgO-SiO}_2\text{-B}_2\text{O}_3\text{-CaO-Al}_2\text{O}_3$ System

The compositions of the B-bearing slag produced from the ludwigite ore in the ironmaking process of Fengcheng Iron and Steel Group Co. Ltd. in China are given in Table 3.1. The B-bearing slag has a relatively high concentration of boron, and the mass fraction of B_2O_3 is up to 19.13 wt% [45–47]. However, the Mg^{2+} reacts preferentially with SiO_4^{4-} instead of $\text{B}_2\text{O}_5^{4-}$ to form olivine during the crystallization process of the molten slag owing to a low MgO content and a high SiO_2 content. Therefore, only the significant diffraction peaks of olivine (Mg_2SiO_4) are appeared in the XRD pattern of the B-bearing slag, while all of the boron is in the form of amorphous state, as indicated in Fig. 3.1.

From the equilibrium phase diagram of $\text{MgO-SiO}_2\text{-B}_2\text{O}_3\text{-3wt\%CaO-2wt\%Al}_2\text{O}_3$ as calculated using FactSage 7.3 and shown in Fig. 3.2, the original composition of the B-bearing slag (Point a in Fig. 3.1) is located within the primary crystallization region of Mg_2SiO_4 . However, boron exists in the amorphous state in this region, which brings great difficulty to efficiently recover boron from the B-bearing slag. Actually, it is difficult to enrich the boron into suanite arising from the competitive reactions between the $\text{B}_2\text{O}_5^{4-}$, SiO_4^{4-} , and Mg^{2+} in B-bearing slag. However, decreasing content of SiO_2 would inhibit the crystallization of olivine, and increasing content of MgO would promote the crystallization of suanite. Therefore, the MgO content of B-bearing slag is adjusted to 50.00 wt%, and the SiO_2 is decreased to 25.00 wt% (Point b in Fig. 3.2) for breaking the network structure of glass phase and promoting the formation of suanite crystals, based on the $\text{MgO-SiO}_2\text{-B}_2\text{O}_3\text{-3wt\%CaO-2wt\%Al}_2\text{O}_3$ phase diagram.

Table 3.1 Chemical compositions of B-bearing slag (wt%)

Composition	B_2O_3	SiO_2	MgO	CaO	Al_2O_3	Other
Point a	19.13	31.12	42.40	3.16	1.98	2.21
Point b	20.00	25.00	50.00	3.00	2.00	—

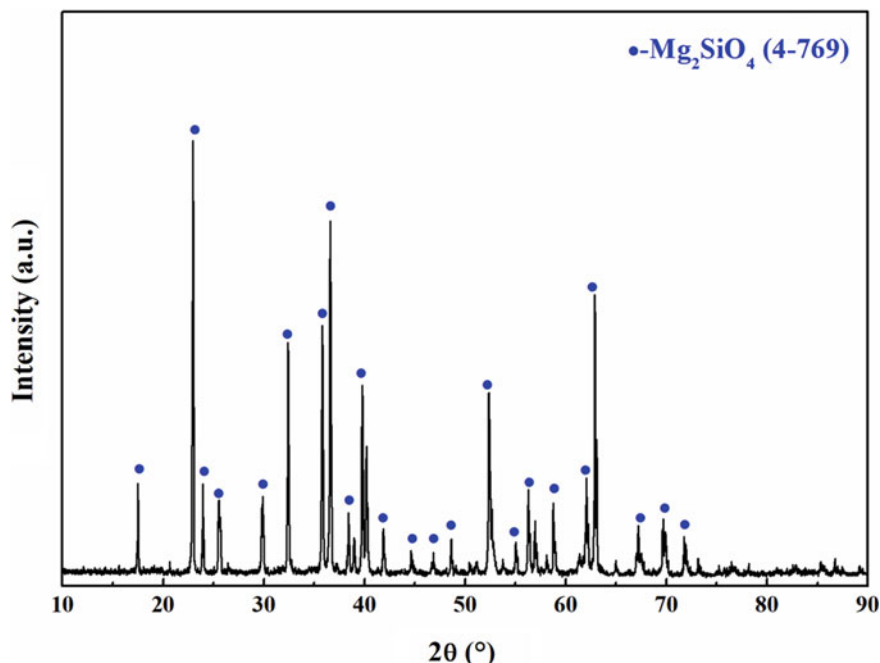


Fig. 3.1 XRD pattern of B-bearing slag (point a)

3.1.2 Competitive Crystallization Behavior of B, Si and Mg in $\text{MgO-SiO}_2\text{-B}_2\text{O}_3\text{-CaO-Al}_2\text{O}_3$ System

3.1.2.1 Experimental Procedure

The competitive crystallization behavior of B, Si, and Mg in B-bearing slag at various temperature ranges was first investigated. A total of 100 g of the B-bearing slag was put evenly into ten graphite crucibles with an inner diameter of 20 mm and a height of 70 mm, which were heated to 1773 K under argon atmosphere in a muffle furnace to ensure complete melting of the slag. Thereafter, the molten B-bearing slags were slowly cooled at 1773–1723 K, 1723–1673 K, 1673–1623 K, 1623–1573 K, 1573–1523 K, 1523–1473 K, 1473–1423 K, 1423–1373 K, or 1373–1323 K with a cooling rate of 1 K/min, respectively. Subsequently, the graphite crucibles were promptly removed from the furnace and water-quenched, and the mineral compositions and microstructures of various crystalline phases attained at different temperatures were analyzed through adopting the XRD and the SEM-EDS.

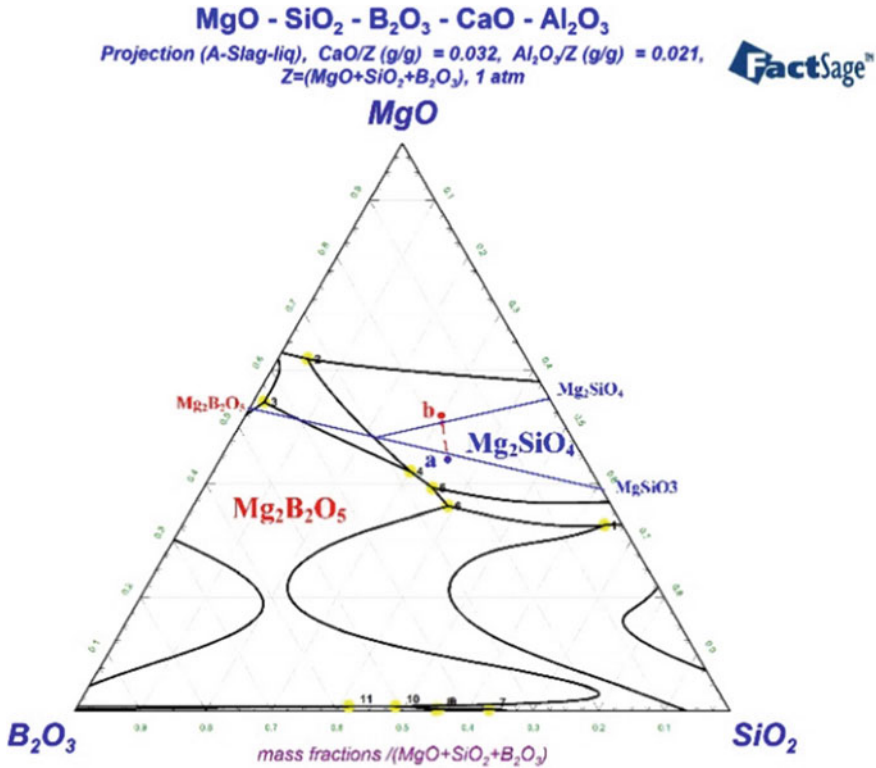


Fig. 3.2 Equilibrium phase diagram of MgO–SiO₂–B₂O₃–3wt%CaO–2wt%Al₂O₃

3.1.2.2 Competitive Crystallization Behavior of B, Si, and Mg

Variations in XRD patterns of the B-bearing slag melt with decreasing temperature are shown in Fig. 3.3. It is indicated that the olivine (Mg₂SiO₄) is the primary crystalline phase in the B-bearing slag, and the olivine crystals are firstly appeared in the slag melt at 1623–1573 K. As the temperature decreases from 1573 to 1473 K, the intensity of single diffraction peaks for olivine increases gradually in this temperature range. Subsequently, the suanite (Mg₂B₂O₅) crystallizes after the olivine in the B-bearing slag melt, and its diffraction peaks appear when the temperature drops below 1473 K. When the temperature decreases further to 1473–1423 K, the suanite (Mg₂B₂O₅) crystals precipitate subsequently from the B-bearing slag melt, and the diffraction peak intensity of suanite increases significantly while that of olivine gradually decreases with decreasing temperature from 1473 to 1323 K.

In addition, variations in SEM images combined with the EDS data of the B-bearing slag melt with decreasing temperature are shown in Fig. 3.4 and Table 3.2, respectively. When the temperature is above 1623 K, the B-bearing slag is in a completely molten state and no crystals are found in the molten slag, as shown in

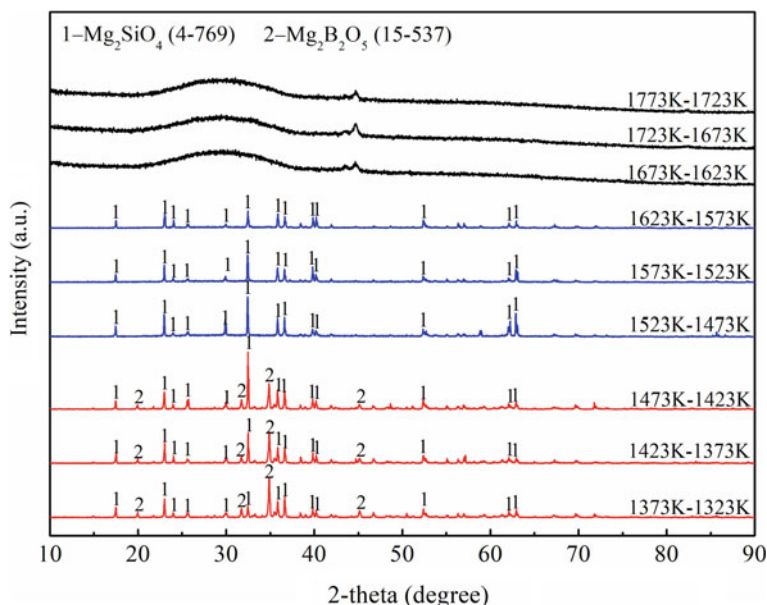


Fig. 3.3 Variation in XRD patterns of B-bearing slag melt with decreasing temperature

Fig. 3.4a–c. As the temperature decreases to 1623–1573 K, the columnar crystal of olivine (Mg_2SiO_4) precipitates firstly from the slag melt. It indicates that the Mg^{2+} preferentially combines with SiO_4^{4-} rather than $\text{B}_2\text{O}_5^{4-}$ at 1623–1573 K, more SiO_4^{4-} crystallize into the olivine with Mg^{2+} , and the growth rate of olivine is greater than the nucleation rate of SiO_4^{4-} and Mg^{2+} . Thus, the olivine is gradually transformed from equiaxed crystals into columnar crystals with a larger size, as presented in Fig. 3.4d–f. When the temperature decreases further to 1473–1423 K, the Mg^{2+} starts to crystallize with $\text{B}_2\text{O}_5^{4-}$ into the suanite, and the suanite ($\text{Mg}_2\text{B}_2\text{O}_5$) crystals precipitate subsequently from the B-bearing slag melt. This is a result of the decrease of SiO_4^{4-} activity leading to the relative enhancement of $\text{B}_2\text{O}_5^{4-}$ activity in the slag melt. Thus, the suanite crystals progressively grow up and aggregate into the larger crystals with a lath shape, whereas the last precipitated suanite crystals are embedded with the first precipitated olivine crystals, which are discretely distributed in the B-bearing slag, as presented in Fig. 3.4g–i.

Above all, the $\text{B}_2\text{O}_5^{4-}$ and SiO_4^{4-} compete for Mg^{2+} in the molten B-bearing slag to form suanite and olivine, and the Mg^{2+} reacts preferentially with SiO_4^{4-} to form olivine during the crystallization process of the molten B-bearing slag. These reveal that competitive crystallization behavior of B, Si, and Mg exists in B-bearing slag, and the suanite as the last precipitated phase is limitedly precipitated.

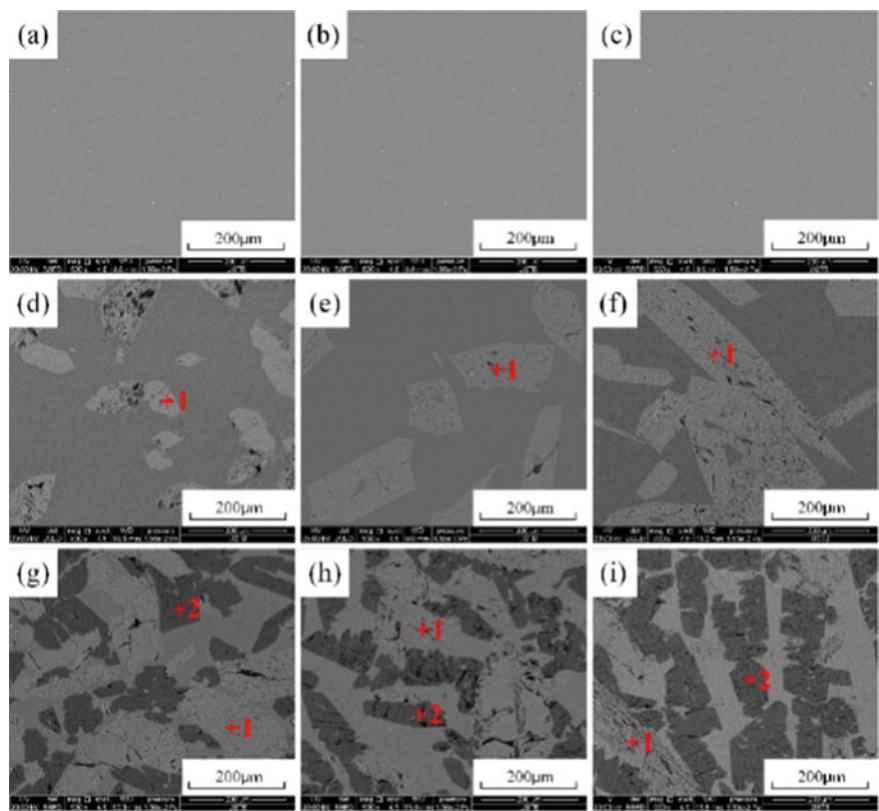


Fig. 3.4 Variation in SEM images of boron-bearing slag melt after cooling at different temperature ranges with a cooling rate of 1 K/min: **a** 1773–1723 K; **b** 1723–1673 K; **c** 1673–1623 K; **d** 1623–1573 K; **e** 1573–1523 K; **f** 1523–1473 K; **g** 1473–1423 K; **h** 1423–1373 K; **i** 1373–1323 K (Pt.1-olivine crystal and Pt.2-suanite crystal, respectively)

Table 3.2 EDS data of different phases attained in B-bearing slag (wt%)

Positions	No	Mg	Si	O	Ca	Al	B	Phases
Figure 3.4d	Pt.1	33.42	20.07	46.51	–	–	–	Olivine
Figure 3.4g	Pt.2	32.16	–	52.47	–	–	15.37	Suanite

3.2 Two-Stage Separation of Olivine and Suanite in B-Bearing Slag

Based on the competitive crystallization behavior of B, Si, and Mg in B-bearing slag, olivine is the first precipitated phase in B-bearing slag, while the suanite as the last precipitated phase is greatly limited. Therefore, the effect of super gravity field on the competitive crystallization behavior of B, Si, and Mg in B-bearing slag

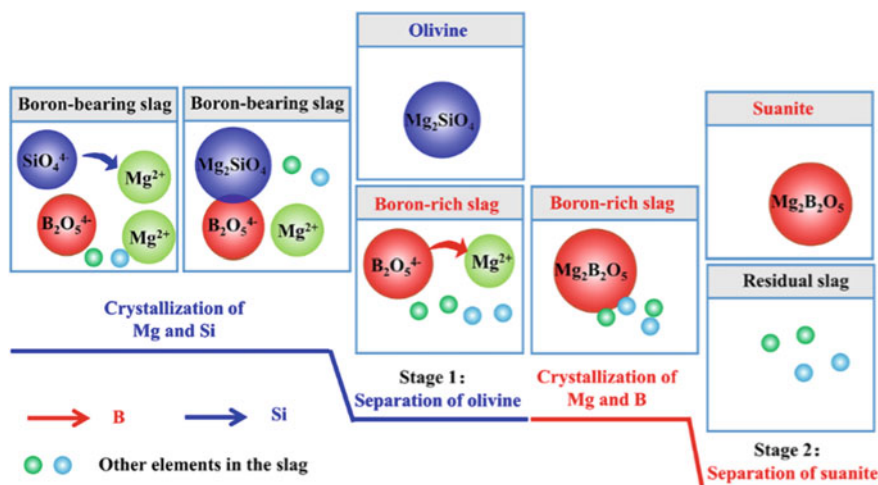


Fig. 3.5 Two-stage separation of olivine and suanite from B-bearing slag by super gravity

is investigated, the appropriate physicochemical conditions for the crystallization of olivine and suanite are created, respectively, and an efficient way for two-stage separation of olivine and suanite crystals from the B-bearing slag melt enhanced by super gravity field is developed as shown in the flowchart in Fig. 3.5 [45]. Moreover, the high purity and high crystallinity of the olivine and suanite separated from the B-bearing slag are verified via XRD, SEM-EDX, XRF, ICP-AES, HR-TEM, and Raman spectroscopy in this section.

3.2.1 Stage 1: Primary Separation of Olivine and B-Rich Slag by Super Gravity

3.2.1.1 Experimental Procedure

Firstly, the primary separation of olivine crystals and B-rich slag from B-bearing slag melt was carried out at the single crystallization temperature range of olivine by super gravity. 10 g of the B-bearing slag was placed into the upper part of a composite graphite crucible, which was melted completely at 1773 K and cooled slowly at 1623–1473 K for the fully crystallization of olivine in the heating furnace of the centrifugal apparatus. The centrifugal apparatus was started at 1513 K with various gravity coefficients of $G = 200, 400, 600, 800$, and 1000 corresponding to the different rotating speeds of 845 r/min, 1196 r/min, 1465 r/min, 1692 r/min, and 1892 r/min, respectively. The rotation was stopped after 10 min, and the crucibles were quenched in water immediately. The samples obtained with various gravity coefficients were first divided into two halves along the longitudinal center line and

then separated into two parts by a filter. Subsequently, the macro and microstructures and the mineral and chemical compositions of the olivine crystals compared with the B-rich slag which separated from the B-bearing slag were investigated using XRD and SEM-EDS.

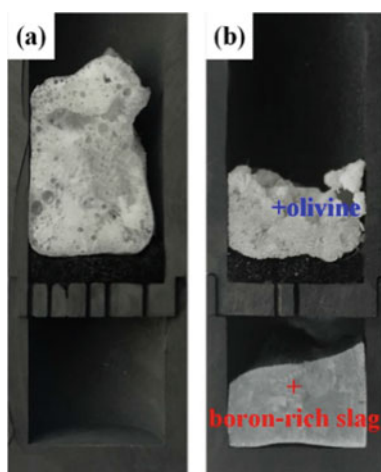
3.2.1.2 Separation Behavior of Olivine and B-Rich Slag in B-Bearing Slag

The vertical profiles for the samples attained from B-bearing slag by super gravity compared to normal gravity are shown in Fig. 3.6. Under the normal gravity of $G = 1$, the slag exhibits a porous state owing to the sufficient crystallization of Mg^{2+} and SiO_4^{4-} , which is completely intercepted by the filter in the upper crucible, as shown in Fig. 3.6a. By contrast, the B-bearing slag melt is separated by the filter into two parts by super gravity at $G = 600$, as presented in Fig. 3.6b.

Compared with the XRD results for the two parts separated from B-bearing slag as shown in Fig. 3.7a, the upper sample is composed only of the diffraction peaks of olivine (PDF card No. 4-769), while the bottom sample shows a typical diffuse scattering peak. Moreover, the SEM images for the separated olivine from B-bearing slag are shown further in Fig. 3.7b. It confirms that the single olivine crystals with a rod shape are separated from the B-bearing slag by super gravity, where no slag inclusions are attached to the surface of olivine crystals.

Actually, the $\Delta\rho g$ ($\Delta\rho$ is density difference and g is acceleration of gravity) is the determinant for phase separation under the gravity. Due to the adequate crystallization of olivine in B-bearing slag melt, the viscosity of the slag melt is high, and the olivine crystals cannot separate from the B-bearing slag met under the normal gravity ($G = 1$). By contrast, the driving force is increased significantly in the super gravity field and so enhances the solid–liquid separation between the olivine crystals and

Fig. 3.6 Vertical profiles for samples attained from B-bearing slag by super gravity compared with normal gravity in stage 1: **a** $G = 1$; **b** $G = 600$



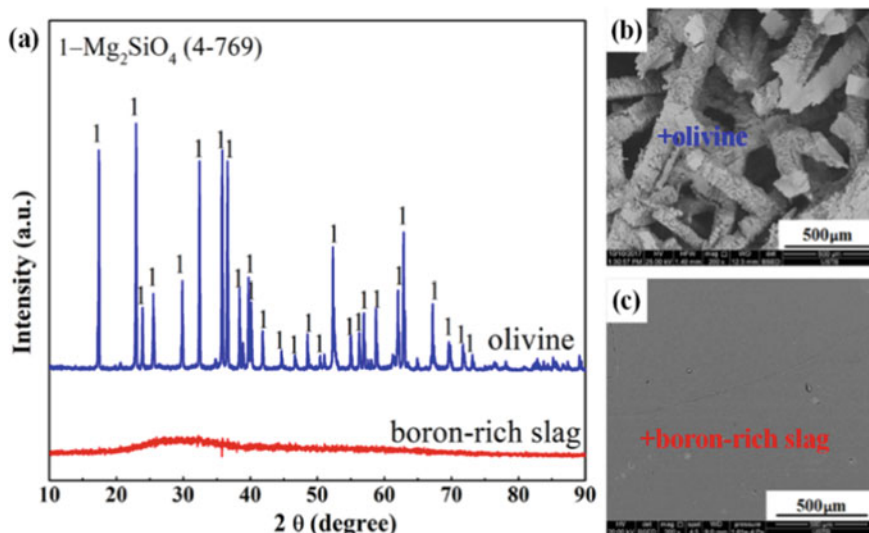


Fig. 3.7 XRD patterns and SEM images for two parts separated from B-bearing slag by super gravity in stage 1

B-rich slag melt. Thus, the B-rich slag melt passes through the filter and flows into the bottom crucible under the force of super gravity, while the olivine crystals are efficiently intercepted on the filter and fully separated from the slag melt.

3.2.2 Crystallization Behavior of B and Mg in Separated B-Rich Slag

In the stage 1, the Si elements are primarily enriched into the olivine crystals and separated from B-bearing slag at its single crystallization temperature by super gravity, whereas all the boron elements are enriched into the slag melt which is referred to the B-rich slag.

3.2.2.1 Experimental Procedure

The crystallization behavior of the separated B-rich slag at various temperature ranges was investigated further. Samples of the B-rich slag (10 g each) were placed into graphite crucibles and fully melted at 1573 K in a muffle furnace, after which they were cooled slowly at a rate of 1 K/min at the temperature ranges of 1573–1523, 1523–1473, 1473–1423, 1423–1373 to 1373–1323 K. Subsequently, the samples were quenched in water immediately and analyzed using XRD and SEM-EDS.

3.2.2.2 Crystallization Behavior of B and Mg in B-Rich Slag

The results of XRD and SEM for the B-rich slag attained at various temperatures are shown in Figs. 3.8 and 3.9. As the XRD patterns are shown in Fig. 3.8, the B-rich slag shows a significant diffuse scattering peak at the temperature range of 1573–1473 K, where no crystal is appeared in the slag melt. When the temperature decreases from 1473 to 1323 K, the diffraction peaks of single suanite firstly appeared in the B-rich slag, and the intensity is increased significantly with the temperature decreasing. Moreover, the single elongated crystals of suanite are presented in the B-rich slag, which gradually grow into larger crystals with decreasing temperature in the temperature range, as shown in Fig. 3.9.

Compared with the crystallization behavior of the original B-bearing slag and the separated B-rich slag in the stage 1, the effects of super gravity on competitive crystallization of B, Si, and Mg in the B-bearing slags are concluded as shown in Fig. 3.10. It is confirmed from the experimental results that the SiO_4^{4-} and Mg^{2+} are preferentially crystallized into the olivine in the B-bearing slag, and the migration of Mg^{2+} is restricted by the existence of olivine crystals in the slag melt, thereby inhibiting the subsequent combination of $\text{B}_2\text{O}_5^{4-}$ and Mg^{2+} to form suanite in the condition of normal gravity, as shown in Fig. 3.10a. In contrast, with the removal of olivine from the B-bearing slag by super gravity in the stage 1, the SiO_4^{4-} ions in the separated B-rich slag are depleted, which results in a significant increase of the

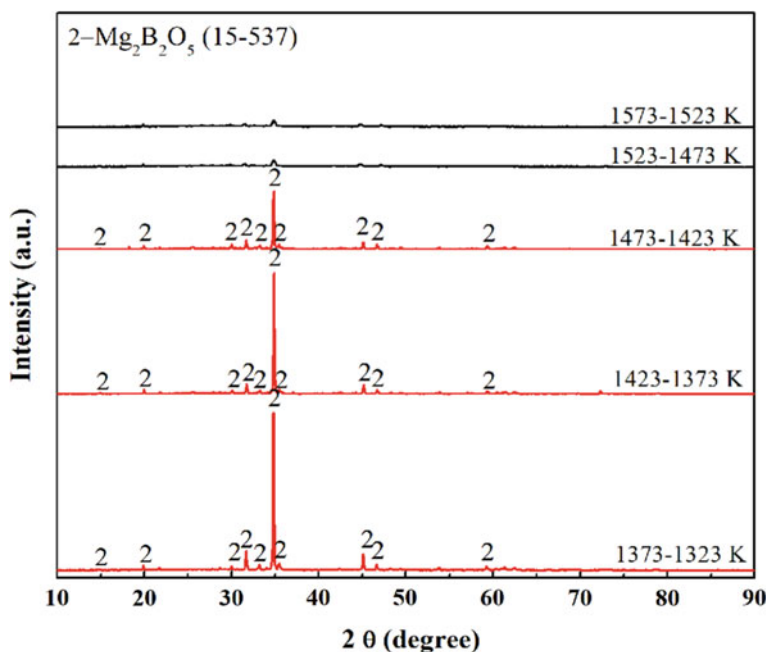


Fig. 3.8 XRD patterns for separated B-rich slag attained at various temperatures

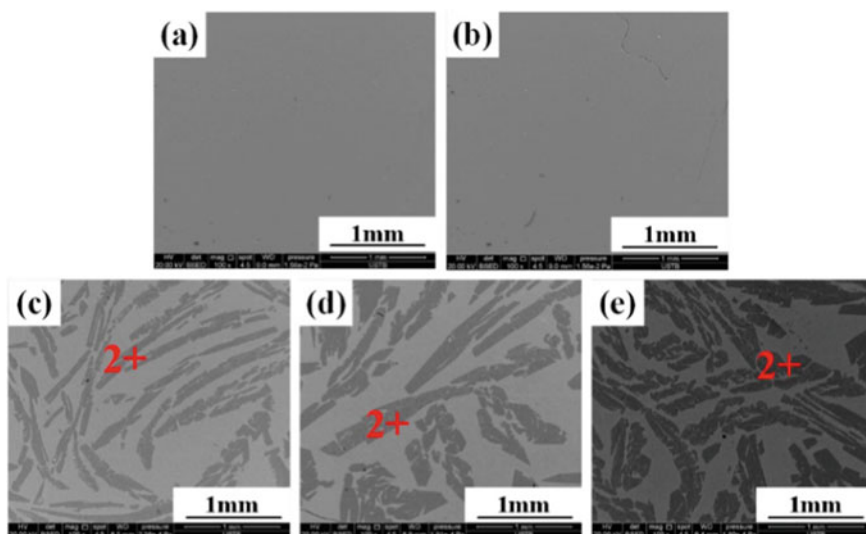


Fig. 3.9 SEM images for separated B-rich slag obtained at various temperatures: **a** 1573–1523 K; **b** 1523–1473 K; **c** 1473–1423 K; **d** 1423–1373 K; **e** 1373–1323 K

$B_2O_5^{4-}$ activity in the B-rich slag. Therefore, the migration of Mg^{2+} is unimpeded and it has greater opportunity to contact with $B_2O_5^{4-}$ in the slag melt, which creates favorable conditions for the single crystallization of suanite in the B-rich slag, as illustrated in Fig. 3.10b.

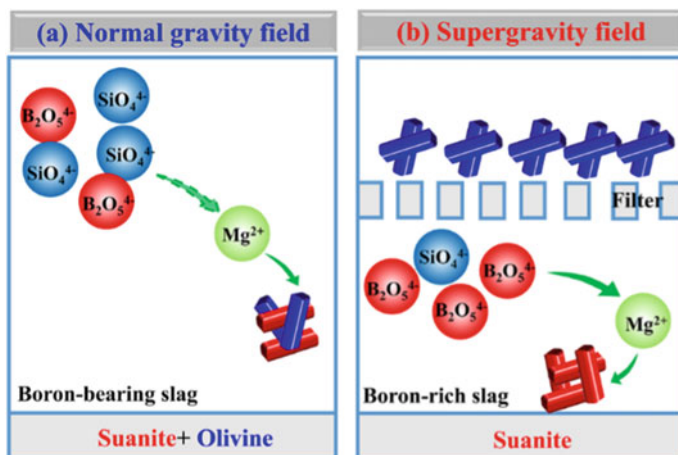


Fig. 3.10 Schematic diagram for the effect of super gravity on competitive crystallization of B, Si, and Mg in B-bearing slag compared to separated B-rich slag

3.2.3 Stage 2: Further Separation of Suanite from B-Rich Slag by Super Gravity

3.2.3.1 Experimental Procedure

The separation of suanite crystals from the separated B-rich slag melt in the stage 1 was carried out further at its single crystallization temperature range by super gravity. 10 g of the separated B-rich slag in the stage 1 was placed into the upper part of a composite graphite crucible, which was melted completely at 1573 K and cooled slowly at 1473–1323 K in the heating furnace of the centrifugal apparatus. After the adequate crystallization of suanite, the slag melt was treated at 1443 K by super gravity with various gravity coefficients of $G = 200, 400, 600, 800$, and 1000 for 10 min. After that, the samples were rapidly quenched in water, and the suanite crystals separated from the B-rich slag were analyzed further using XRD and SEM-EDS.

3.2.3.2 Separation Behavior of Suanite in B-Rich Slag

Figure 3.11 shows the vertical profiles for the samples attained from the separated B-rich slag by super gravity compared to normal gravity. After the separation of olivine from B-bearing slag in the stage 1, the separated B-rich slag is transformed from the glass state into a porous structure due to the adequate crystallization of Mg^{2+} and $\text{B}_2\text{O}_5^{4-}$ into suanite at 1473–1323 K, whereas the suanite crystals cannot be completely separated from the slag melt under the normal gravity, as presented in Fig. 3.11a. However, the B-rich slag melt is separated further into two parts by super gravity in the stage 2, and the suanite crystals are efficiently intercepted by the filter, while the residual slag melt passes through the filter and be separated from the suanite crystals, as shown in Fig. 3.11b.

Moreover, the single diffraction peaks (PDF card No. 15-537) of the separated suanite compared with the diffuse scattering peak of the residual slag are shown in Fig. 3.12a. Compared with the SEM images for the separated suanite and residual slag shown in Fig. 3.12b and c, the suanite crystal is in a shape of elongated crystal with a length of 0.5–2 mm, while no crystal is found in the residual slag.

In summary, the Si and B are enriched into the olivine and suanite, respectively, which are efficiently separated from the B-bearing slag by super gravity in two stages.

In the stage 1, only the Si is crystallized into olivine and separated from the B-bearing slag, while all the B was enriched into the B-rich slag.

In the stage 2, the B was efficiently crystallized into suanite and separated further from the B-rich slag.

Fig. 3.11 Vertical profiles for samples attained from B-rich slag by super gravity compared with normal gravity in stage 2: **a** $G = 1$; **b** $G = 600$

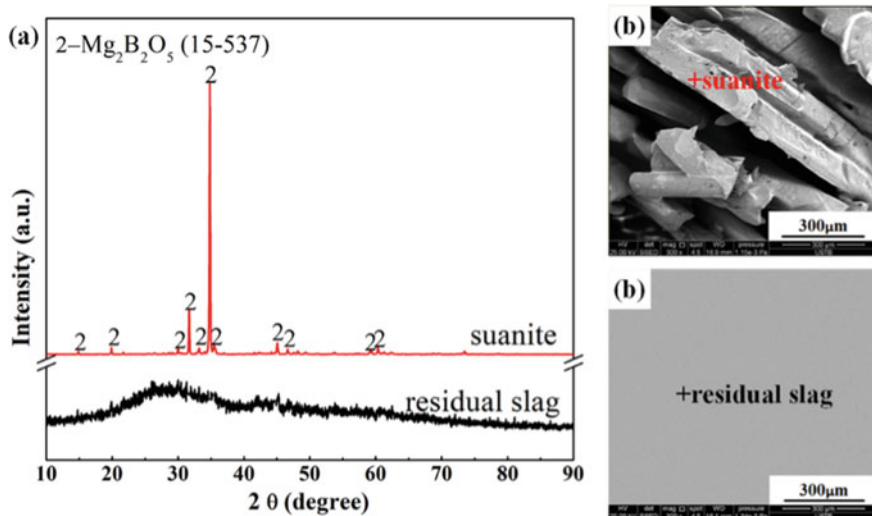
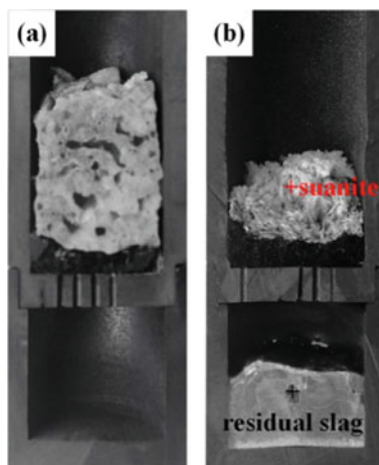


Fig. 3.12 XRD patterns and SEM images for two parts separated from B-rich slag by gravity in stage 2

3.2.4 Characterization for the Separated Olivine and Suanite

On this basis, the ICP-AES, HR-TEM, SAED, and high-resolution Raman spectroscopy are employed further to investigate the B_2O_3 content, crystal structure, and molecule characteristics of the suanite and olivine in the two stages.

Variations of B_2O_3 content in the separated samples from the B-bearing slag through two-stage separation as a function of gravity coefficient are shown in

Fig. 3.13. It is indicated that the super gravity field significantly enhanced the phase separation of olivine and suanite crystals from the B-bearing slag melt in both the two stages. In the stage 1 for primary separation of olivine and B-rich slag, the B_2O_3 content in the olivine is decreased as the gravity coefficient increased. When the gravity coefficient reaches $G = 600$, almost all of the B-rich slag melt is efficiently separated from the olivine, and so the B_2O_3 content in the olivine is decreased significantly to 0.08 wt%, while that of the B-rich slag is increased to 39.14 wt%. In the stage 2 for further separation of suanite from B-rich slag, the B_2O_3 content in the suanite is increased further to 46.67 wt% (namely the theoretical content of B_2O_3 in $Mg_2B_2O_5$) as the gravity coefficient increased to $G = 600$. Evidently, the boron is successively recovered into B-rich slag and then into suanite from the B-bearing slag through two-stage separation enhanced by super gravity.

The TEM method is employed to characterize the crystal structures of the suanite and olivine crystals those separated from B-bearing slag through two-stage separation by super gravity, and the results are shown in Fig. 3.14. The suanite crystals are regarded as triclinic crystals (PDF card No. 15-537, space group: P-1) based on the SAED pattern (Fig. 3.14a, c), which is corresponded to the $[11\bar{2}]$ zone axis. Moreover, its HR-TEM image shows the clear lattice fringes of suanite with d-spacing of 0.565 nm and 0.251 nm corresponding to the $(1\bar{1}0)$ and (111) lattices, respectively. By contrast, the olivine crystal is characterized by a single-crystal feature as the SAED pattern shown in Fig. 3.14b, which is indicated by a focusing electron beam along the (100) zone axis. Its lattice fringes, which has d-spacings of 0.300 and 0.511 nm corresponding to the (002) and (020) lattices, are clearly visible using

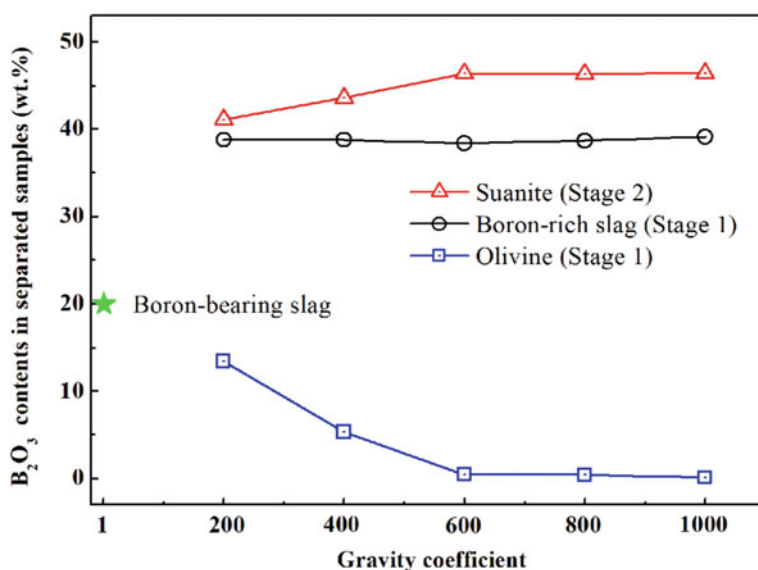


Fig. 3.13 Effect of gravity coefficient on variations of B_2O_3 content in the separated samples from B-bearing slag through two-stage separation

HR-TEM. Moreover, the olivine crystals are verified as orthorhombic crystals (PDF card No. 4-769, space group: Pbnm) (Fig. 3.14d).

Raman spectroscopy is employed further to characterize the molecular characteristics of the suanite and olivine crystals. Based on the vibrational features of $\text{Mg}_2\text{B}_2\text{O}_5$ (Fig. 3.15a), the peaks of suanite at 232.59, 279.06, 302.19, 339.02, and 409.06 cm^{-1} are assigned to the external lattice vibration of suanite crystal, which corresponding to the translational motion of metal ions. Moreover, the peak at 844.03 cm^{-1} is attributed to the symmetric stretching vibration of $\text{B}_{(4)}\text{-O}$ in B_2O_5 unit (ν_1), and the peak at 1282.03 cm^{-1} is ascribed to the asymmetric stretching vibration of the

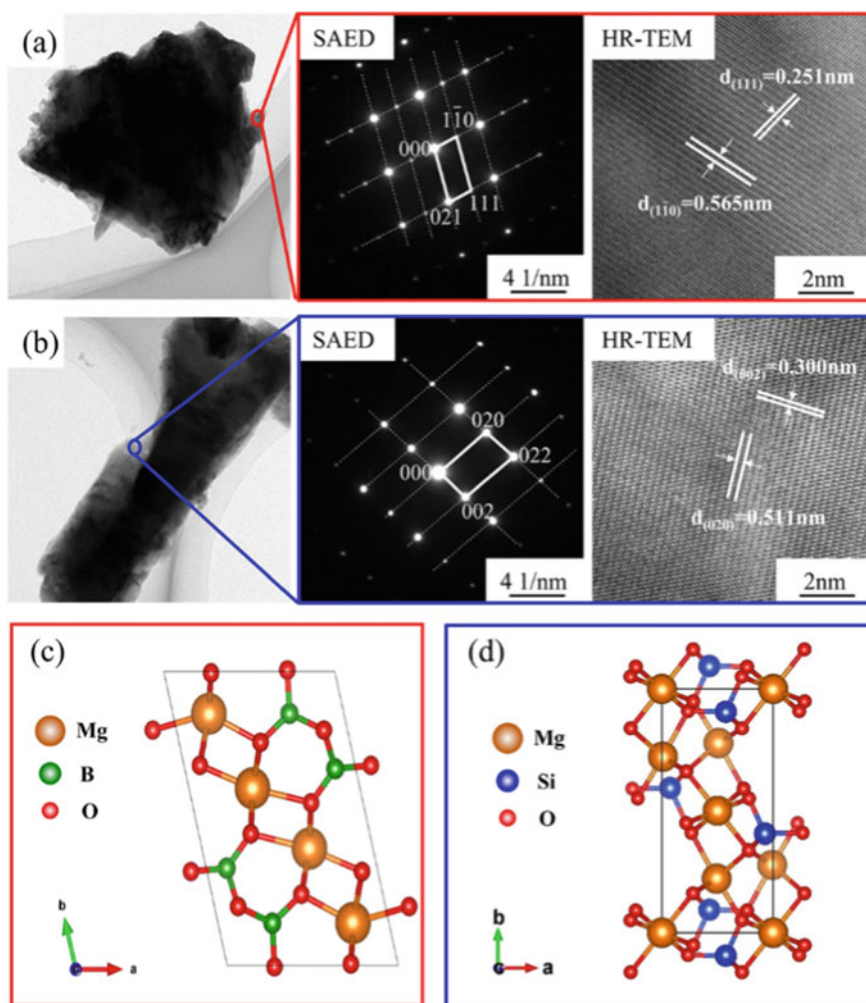


Fig. 3.14 TEM results of the suanite and olivine crystals separated from B-bearing slag: **a** and **b** TEM results; **c** and **d** crystal structures

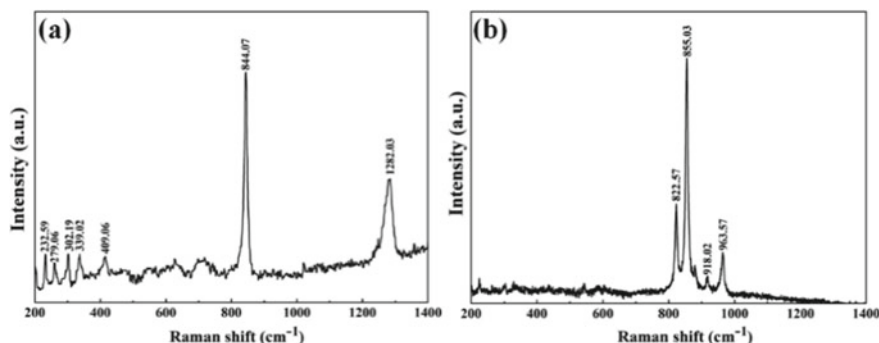


Fig. 3.15 Raman spectroscopy results of the suanite and olivine crystals separated from B-bearing slag: **a** suanite; **b** olivine

$B_{(3)}-O$ bond in the B_2O_5 unit (ν_3). By contrast, the peak at 822.57 cm^{-1} is assigned to the symmetric stretching vibration of the silicon tetrahedron (ν_1), and the peaks at 855.03 , 918.02 , and 963.57 cm^{-1} are regarded as the asymmetric stretching vibration for the silicon tetrahedron (ν_3), based on the vibrational features of the olivine crystal shown in Fig. 3.15b.

3.3 Selective Separation of Last Precipitated Suanite in B-Bearing Slag

Through investigating crystallization behavior of B-bearing slag melt, olivine and suanite crystals are precipitated successively at various temperature ranges. Hence, selective crystallization conditions for the last precipitated suanite crystals are investigated, and another way for selective separation of the last precipitated suanite crystals in B-bearing slag is conducted further in a super gravity field [46], as shown in Fig. 3.16. Firstly, the mixture of suanite and olivine crystals is separated from slag melt at crystallization temperature of suanite. Subsequently, the molten suanite phase is separated further from olivine crystals at melting temperature of suanite, which precipitated further into suanite crystals after cooling process. Furthermore, the microstructure, mineralogical constitution, chemical composition, and crystal structure of the suanite crystals separated from the slag are investigated in this section.

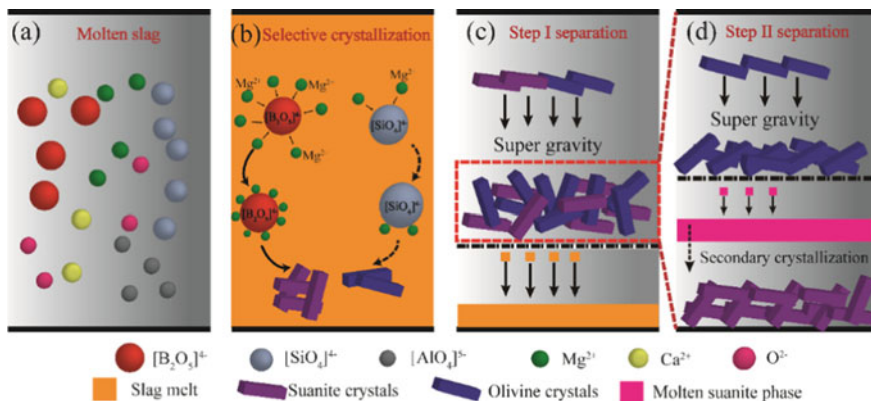


Fig. 3.16 Systematic diagram for selective crystallization and separation of last precipitated suanite from B-bearing slag by super gravity

3.3.1 Thermodynamic Analysis for Crystallization of B in $\text{MgO-SiO}_2\text{-B}_2\text{O}_3\text{-CaO-Al}_2\text{O}_3$ System

Based on the thermodynamic analysis for competitive crystallization of B, Si, and Mg in $\text{B}_2\text{O}_3\text{-SiO}_2\text{-MgO-CaO-Al}_2\text{O}_3$ system in the section of 3.1.1, the MgO content is adjusted to 25.00 wt% and the SiO_2 content is adjusted to 25.00 wt% (Point b in Fig. 3.2) for promoting the formation of suanite crystals based on the $\text{MgO-SiO}_2\text{-B}_2\text{O}_3\text{-3wt\%CaO-2wt\%Al}_2\text{O}_3$ phase diagram. According to the phase diagram, the content of B-bearing slag (point b) falls in the primary crystalline region of olivine, and the suanite will be gradually precipitated in B-bearing slag with the decrease of temperature. Thus, for the lasted precipitated phase of suanite, the rapid cooling at the high temperature is helpful to inhibit the first precipitation of olivine in B-bearing slag and provide more Mg^{2+} for the crystallization of suanite at the low temperature. Subsequently, slow cooling at the low temperature is conducive to promote the combination of Mg^{2+} and $\text{B}_2\text{O}_5^{4-}$ to form suanite in B-bearing slag.

3.3.2 Selective Crystallization of Last Precipitated Suanite in B-Bearing Slag

3.3.2.1 Experimental Procedure

To further determine the selective crystallization conditions for the last precipitated suanite crystals, each 10 g of the B-bearing slag was filled into the graphite crucible and heat to 1773 K for 30 min. Subsequently, the molten B-bearing slags were rapidly cooled to 1623 K or 1473 K with a cooling rate of 10 K/min and then cooled

at the crystallization temperature range of olivine (1623–1473 K) or that of suanite (1473–1323 K) with various cooling rates of 0.5 K/min, 1 K/min, 5 K/min, or 10 K/min, respectively. After that, the crucibles were immediately water-quenched, and the samples were analyzed by using SEM–EDS method.

3.3.2.2 Selective Crystallization Behavior of Suanite

Through comparing the SEM images of olivine crystals precipitated at the temperature range of 1623–1473 K with various cooling rates, its crystal size decreases obviously with increasing the cooling rate from 1 to 10 K/min, as shown in Fig. 3.17a–c. As accordingly verified, the viscosity of B-bearing slag melt increases rapidly with the increase of cooling rate at the crystallization temperature range of olivine, which limits the migration of Mg^{2+} and SiO_4^{4-} in the melt, and inhibits the nucleation and growth of olivine crystals.

Compared further with the SEM images of suanite crystals precipitated at the temperature range of 1473–1323 K with different cooling rates, its crystal size increases significantly with decreasing the cooling rate from 5 to 0.5 K/min, as presented in Fig. 3.18a–c. The EDS data of different phases precipitated in B-bearing slag is given in Table 3.3. As further verified, decreasing cooling rate at the crystallization temperature range of last precipitated suanite with insufficient crystallization of olivine, more Mg^{2+} and sufficient contact condition between Mg^{2+} and $\text{B}_2\text{O}_5^{4-}$ are provided for the nucleation and crystallization of suanite crystals. Hence, an approach for selective crystallization of the last precipitated suanite crystals through rapid cooling from 1623 to 1473 K and subsequent slow cooling from 1473 to 1323 K is conducted to selective separation of suanite crystals from B-bearing slag melt.

Based on the selective crystallization process for suanite crystals determined above, the molten B-bearing slag is rapidly cooled at 1623–1473 K with a cooling rate of 10 K/min, slowly cooled at 1473–1323 K with a cooling rate of 0.5 K/min, and then water-quenched. After that, two-step selective separation of suanite crystals from B-bearing slag is conducted in a super gravity field, including the step I: primary

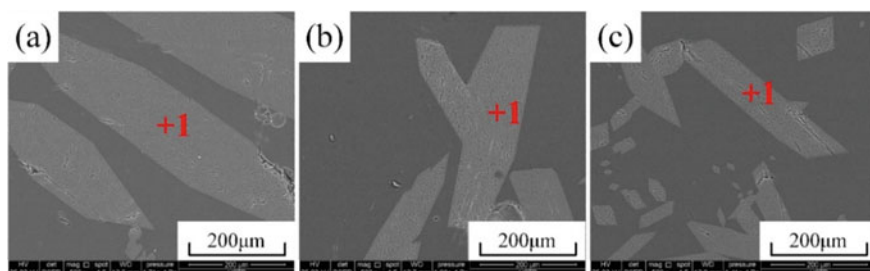


Fig. 3.17 Variation in SEM images of B-bearing slag melt after cooling at 1623–1473 K with various cooling rates: **a** 1 K/min; **b** 5 K/min; **c** 10 K/min

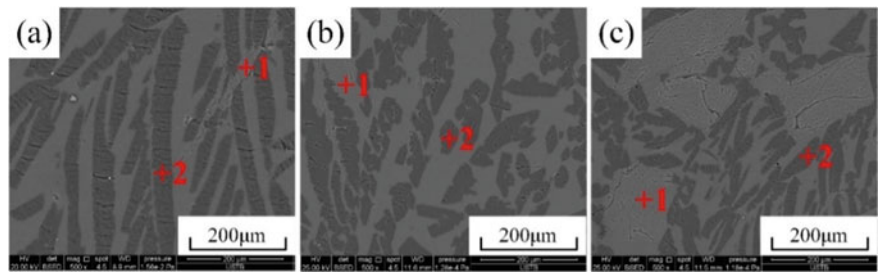


Fig. 3.18 Variation in SEM images of B-bearing slag melt after cooling at 1473–1323 K with various cooling rates: **a** 0.5 K/min; **b** 1 K/min; **c** 5 K/min

Table 3.3 EDS data of different phases precipitated in B-bearing slag (wt%)

Positions	No	Mg	Si	O	Ca	Al	B	Phases
Figure 3.18a	Pt.1	33.42	20.07	46.51	–	–	–	Olivine
Figure 3.19a	Pt.1	32.72	18.91	48.37	–	–	–	Olivine
Figure 3.19b	Pt.2	32.16	–	52.47	–	–	15.37	Suanite

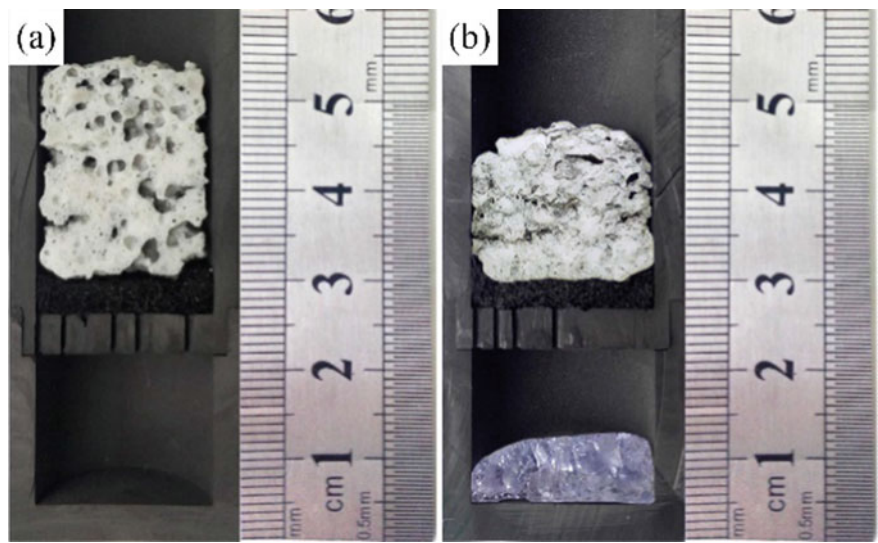


Fig. 3.19 Vertical sections of samples attained by super gravity compared with normal gravity (Step I): **a** $T = 1443\text{ K}$, $G = 1$; **b** $T = 1443\text{ K}$, $G = 1000$

separation of the mixture of suanite and olivine from B-bearing slag in Sect. 3.3.3, and the step II: further separation of molten suanite and olivine crystal in Sect. 3.3.4.

3.3.3 *Sept I: Primary Separation of the Mixture of Suanite and Olivine from B-Bearing Slag by Super Gravity*

3.3.3.1 Experimental Procedure

Firstly, 10 g of the quenched B-bearing slag in which the suanite was fully crystallized based on the selective crystallization condition of suanite was placed on a graphite felt with 0.01 mm pore size and embedded in a graphite crucible, which were heated to the crystallization temperature of suanite (1443 K) in the heating furnace of centrifugal apparatus. Subsequently, the centrifugal apparatus was initiated and adjusted to a rotating speed of 1895 r/min to achieve the gravity coefficient of $G = 1000$. After centrifugation at the constant temperature for 10 min, the rotor was stopped and the crucible was water-quenched. Simultaneously, the parallel experiments were conducted without super gravity treatment. After that, the samples were sectioned longitudinally following the center axis to form a macrograph, and then the samples retained (mixture of suanite and olivine crystals) and passed through (slag phase) the filter were analyzed through adopting the XRD and SEM-EDS methods, respectively.

3.3.3.2 Separation Behavior of Mixture of Suanite and Olivine in B-Bearing Slag

Vertical sections of the samples attained from B-bearing slag under super gravity with $G = 1000$ compared with the parallel sample with $G = 1$ at 1443 K (Step I) are shown in Fig. 3.19. Apparently, the entire sample is blocked by the filter, and a uniform porous structure is observed for the sample attained in a normal gravity field ($G = 1$), as presented in Fig. 3.19a. In comparison, the B-bearing slag is separated into two parts by the filter by super gravity ($G = 1000$). The evident diverse macroscopic structures are clearly observed in the separated samples as shown in Fig. 3.19b, where the sample above the filter shows a white crystal structure, whereas the sample below the filter shows a transparent glassy state.

Compared with the XRD patterns of the separated samples attained by super gravity with $G = 1000$ and $T = 1443$ K as shown in Fig. 3.20, the significant diffraction peaks of suanite included some of olivine appear in the upper sample, whereas the diffraction peak of the lower sample presents as a typical dispersive peak. Considering the SEM and EDS data of the separated samples as shown in Fig. 3.21 and Table 3.4, respectively, we conclude that the boron-containing crystalline phase consisting of suanite and olivine crystals exist as the solid phase, whereas CaO, Al_2O_3 , MgO, and SiO_2 form into the slag melt at the precipitation temperature range of suanite (1323–1473 K). However, the driving force generated by the difference in density between the crystals and slag melt is insufficient to drive the crystals move and separate from the slag melt via free sedimentation arising from the high viscosity of solid–liquid mixture at the low temperature, resulting in a dispersing distribution of suanite and olivine crystals among the entire slag melt at the normal gravity (G

= 1). In contrast, the slag melt evidently migrates and goes through the filter as driven by super gravity, whereas the boron-containing crystalline phases are overall intercepted by the filter and effectively separated from the slag melt.

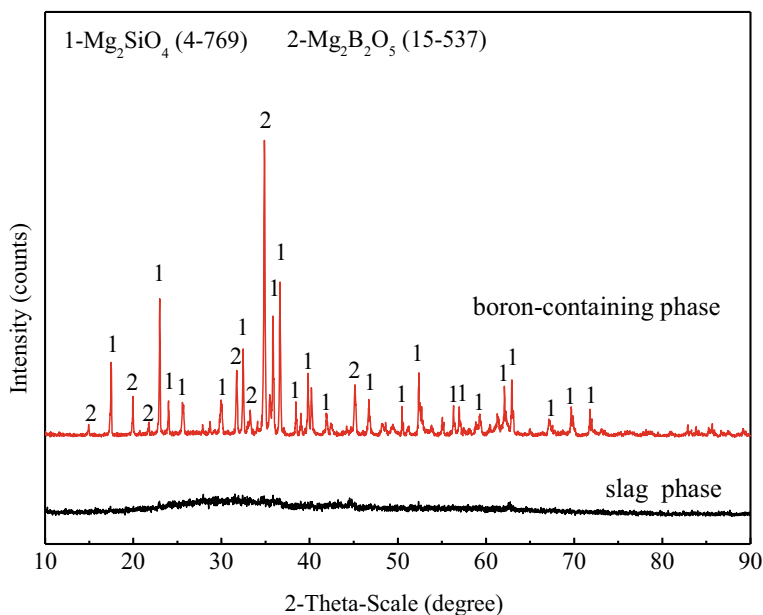


Fig. 3.20 XRD patterns of the separated samples attained by super gravity (Step I: $T = 1443$ K, $G = 1000$)

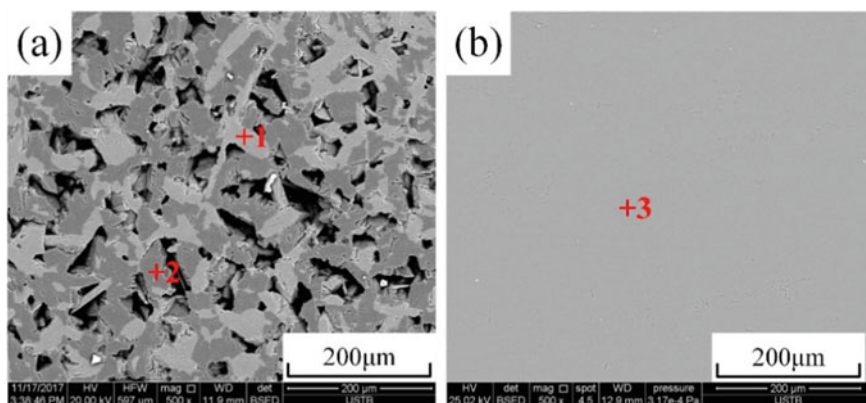


Fig. 3.21 SEM images of the separated samples attained by super gravity (Step I: $T = 1443$ K, $G = 1000$): **a** boron-containing crystalline phase; **b** slag phase

Table 3.4 EDS data of the separated samples attained by super gravity (Step I: $T = 1443$ K, $G = 1000$) (wt%)

Positions	No	Mg	Si	O	Ca	Al	B	Samples
Figure 3.21a	Pt.1	32.53	21.37	46.10	–	–	–	Olivine
Figure 3.21a	Pt.2	32.58	–	52.50	–	–	14.92	Suanite
Figure 3.21b	Pt.3	23.33	10.99	47.99	7.08	3.51	7.10	Slag

3.3.4 Mineral Evolution of Suanite and Olivine with Temperature

3.3.4.1 Experimental Procedure

To remove further the included olivine crystals from the separated boron-containing crystalline phase attained in Step I, separation of molten suanite phase and olivine crystals was carried out by super gravity. Firstly, the mineral evolution and the migration behaviors of B and Si in suanite and olivine were investigated with hot-quenching and ex situ characterization. The separated boron-containing crystalline phases were heated to different temperatures (1473, 1523, 1573, 1623, 1673 K) for 30 min in the muffle furnace, after which the slags were taken out from the furnace and rapidly quenched in water. Subsequently, the samples were then prepared for EPMA to obtain the mapping results of B and Si elements.

3.3.4.2 Mineral Evolution Behavior of Suanite and Olivine

The B and Si contents in various phases of boron-containing crystalline phase after melting at different temperature are shown in Fig. 3.22. It confirms that only the two phases of suanite and olivine exist in the boron-containing crystalline phase that separated from B-bearing slag in step I, and the B and Si are distributed, respectively, in the suanite and olivine crystals, as shown in Fig. 3.22a. With increasing temperature to 1473–1523 K, the suanite crystals are gradually melted into liquid, and the B transfer from suanite crystals into the molten suanite phase, while most olivine crystals remain in a solid state, as presented in Fig. 3.22b. As temperature rises further to 1543–1623 K, the suanite crystals are overall melted down, whereas some olivine crystals are also melted along with suanite crystals, and some Si also appear in the molten suanite phase resulting from the formation of low melting point phase based on the B_2O_3 –MgO– SiO_2 phase diagram, as indicated in Fig. 3.22c. Hence, separation of molten suanite phase and olivine crystals is conducted further at the melting temperature range of suanite (1473–1523 K) by super gravity.

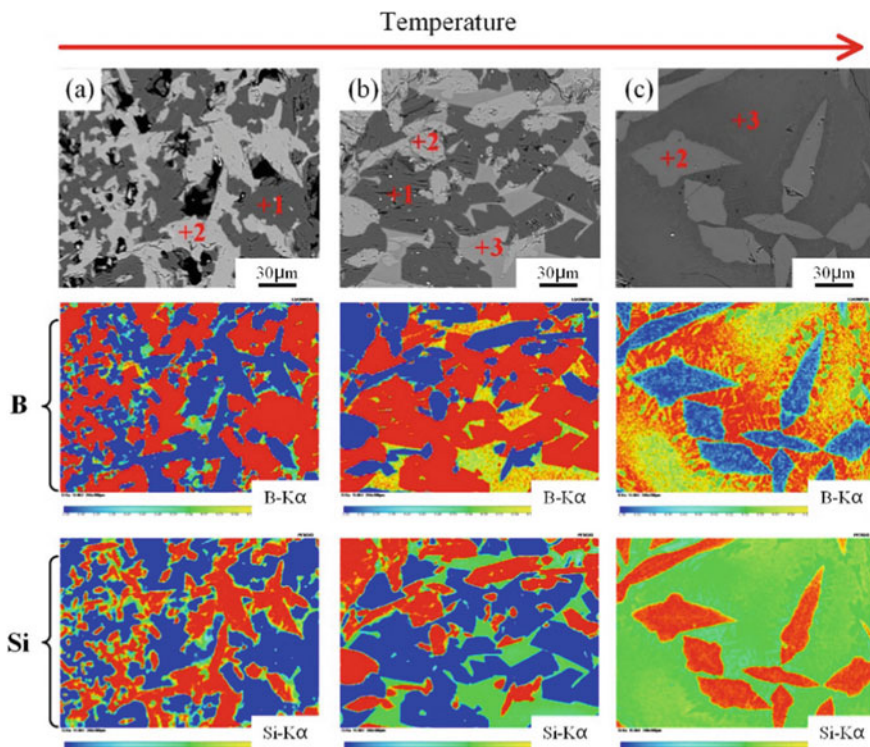


Fig. 3.22 EPMA results of B and Si content in various phases of boron-containing crystalline phase after melting at different temperature: **a** room temperature; **b** 1473–1523 K; **c** 1543–1623 K (Pt.1-suanite crystal, Pt.2-olivine crystal, Pt.3-molten suanite phase)

3.3.5 *Sept II: Further Separation of Molten Suanite and Olivine Crystal*

3.3.5.1 Experimental Procedure

Based on the mineral evolution behavior of suanite and olivine with temperature, the separated crystals mixture of suanite and olivine in step I was put in the composite crucibles and heated at the melting temperatures of suanite (1483, 1503, 1523, 1543, or 1563 K) in the heating furnace of centrifugal apparatus. The samples were treated at each constant temperature in a super gravity field with $G = 1000$ for 10 min and then quenched in water or cooled inside the furnace to room temperature, respectively. After that, the separated samples (olivine and suanite phases) attained in Step II were analyzed using XRD and SEM-EDS methods to investigate their mineral compositions and microstructures.

3.3.5.2 Separation Behavior of Molten Suanite and Olivine Crystal

Figure 3.23 shows the vertical sections of samples attained through the separation of boron-containing crystalline phase by super gravity with $G = 1000$ at 1523 K (Step II). Apparently, the boron-containing crystalline phase is separated further into two parts by the filter under super gravity, and the separated samples present the evidently diverse macroscopic structures, as presented in Fig. 3.23b. From a macroscopic perspective, the sample above the filter appears as a white rod-shaped structure, whereas the sample below the filter presents in a glassy state.

Through drawing the comparison of XRD patterns of the separated samples attained by super gravity with $G = 1000$ and $T = 1523$ K as shown in Fig. 3.24, the only diffraction peak of olivine or suanite with a high intensity appears in the upper or lower sample, respectively. As further verified, the suanite crystals are melted into the molten phase, which evidently go through the filter along super gravity direction, and subsequently precipitate further into the high-purity suanite crystals in the bottom crucible after furnace cooling, as presented in Fig. 3.23c, d. Conversely, the olivine crystals remain in a solid state, which are effectively intercepted by the filter and separate from the molten suanite phase. Moreover, the separated olivine crystals present as a large columnar crystal with a size of 300–1000 μm , and each crystal is structurally independent, as shown in Fig. 3.25a. The separated suanite crystals appear as a large columnar crystal with a size of 300–500 μm , and its secondary dendrite is very developed, as presented in Fig. 3.25b. The EDS data of the separated samples attained by super gravity is given in Table 3.5.

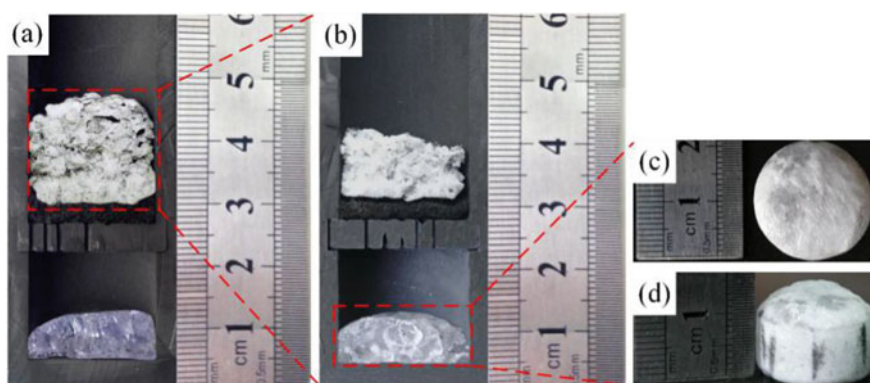


Fig. 3.23 Vertical sections of samples attained by super gravity in Step II: **a** $T = 1443$ K, $G = 1000$ (Step I); **b** $T = 1523$ K, $G = 1000$ (Step II); **c** and **d** bottom sample (Step II) after furnace cooling

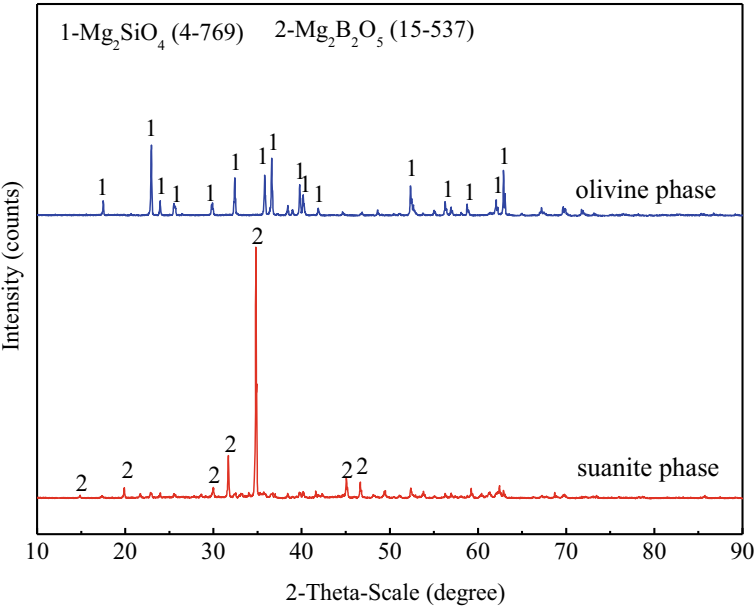


Fig. 3.24 XRD patterns of the separated samples attained by super gravity (Step II: $T = 1523\text{ K}$, $G = 1000$)

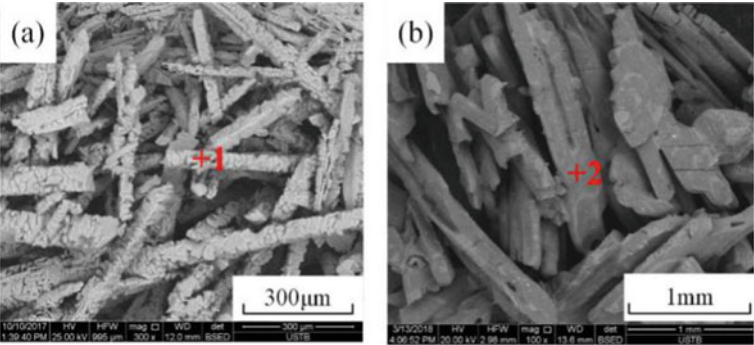


Fig. 3.25 SEM images of the separated samples attained by super gravity (Step II: $T = 1523\text{ K}$, $G = 1000$): **a** olivine phase; **b** suanite phase

Table 3.5 EDS data of the separated samples attained by super gravity (Step II: $T = 1523\text{ K}$, $G = 1000$) (wt %)

Positions	No	Mg	Si	O	Ca	Al	B	Samples
Figure 3.25a	Pt.1	33.31	22.27	44.42	–	–	–	Olivine
Figure 3.25b	Pt.2	32.00	–	53.33	–	–	14.67	Suanite

3.3.6 Characterization for Separated Suanite

3.3.6.1 Experimental Procedure

Each sample attained from the two steps for selective separation of the last precipitated suanite in B-bearing slag was ground into powders and dissolved in HNO_3 and HF , which were analyzed by the ICP-AES to attain the B_2O_3 content of the separated suanite and olivine phase. In addition, the crystal structure of the separated suanite crystals was analyzed further through using the TEM. The suanite crystals were ground into powders, which were ultrasonically dispersed in alcohol for 5 min in a low-power ultrasonic bath at room temperature, then the suanite dispersions were pipetted and dripped onto a copper grid and air drying, and the dried sample was used for TEM observation by bright field imaging (BF) at an accelerating voltage of 200 kV.

3.3.6.2 Characterization for the Separated Suanite

Figure 3.26 presents further the variations of B_2O_3 content in the separated suanite and olivine phases as a function of separating temperature. As the temperature increases from 1483 to 1523 K, the mass fraction of B_2O_3 in the separated suanite phase increases evidently from 27.32 to 42.36 wt%, whereas that of the separated olivine phase decreases significantly from 15.23 to 0.001 wt%. However, the mass fraction of B_2O_3 in the suanite phase gradually reduces with the increasing temperature further from 1523 to 1563 K, resulting from the melting of some olivine crystals along with suanite crystals at the higher temperatures. As further verified, almost all of the suanite crystals are fully melted down and efficiently separated from the olivine crystals with the rising of temperature from 1483 to 1523 K, which precipitate further into high-purity suanite crystals with a high B_2O_3 content that approaching the theoretical content of B_2O_3 in suanite (46.67 wt%).

Moreover, on the basis of TEM image and SAED pattern of the suanite crystal as shown in Fig. 3.27, the suanite crystal is confirmed to be a high crystallinity and high purity. The crystal structure of suanite is indexed for the triclinic (JCPDF number: 15-537, space group: P-1, $a = 6.155$, $b = 9.220$, $c = 3.122$, $\alpha = 90.47^\circ$, $\beta = 92.15^\circ$, $\gamma = 104.4^\circ$). The single-crystal structure of suanite is confirmed by the SAED pattern which is focused by $[11\bar{2}]$ zone axis, and its diffraction spots are calibrated in crystal faces of $(1\bar{1}0)$, (021) and (131) , as indicated in Fig. 3.27b.

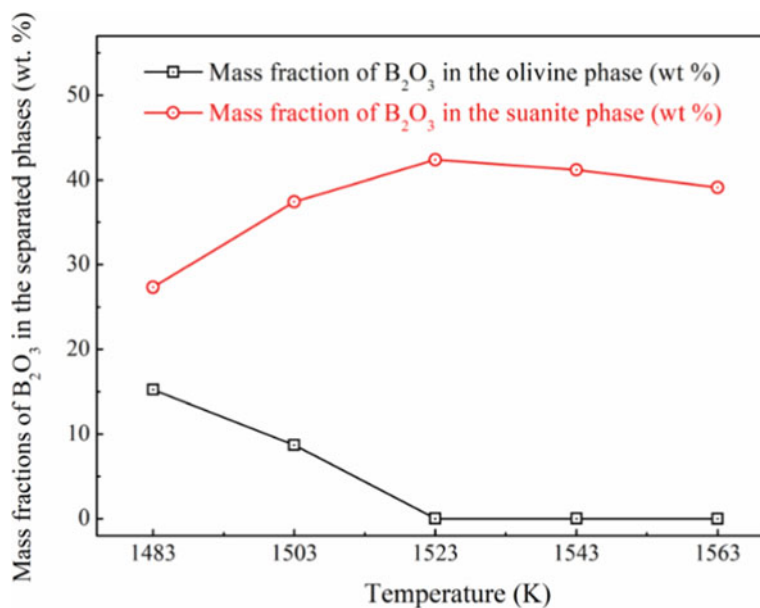


Fig. 3.26 Variations in mass fractions of B_2O_3 in the separated suanite and olivine phases as a function of temperature (Step II)

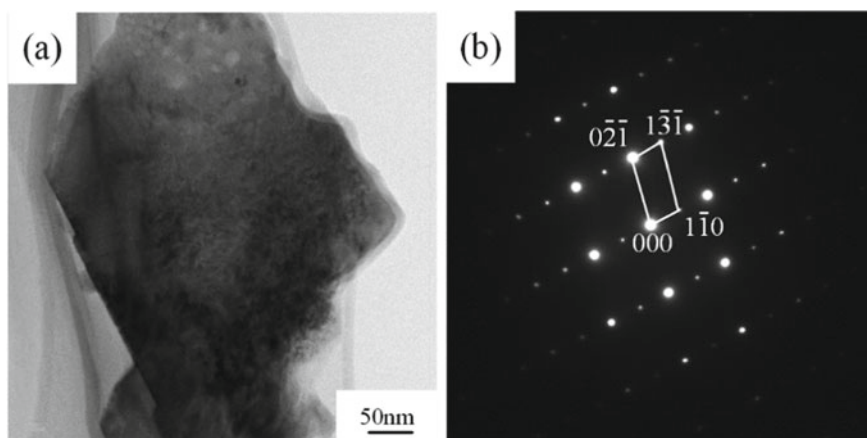


Fig. 3.27 TEM results of the separated suanite crystal: **a** TEM image; **b** SAED pattern

3.4 Crystalline Phase Transformation and One-Step Separation of Suanite in B-Bearing Slag

Due to the competitive crystallization behavior of B, Si, and Mg in B-bearing slag, crystallization of suanite ($\text{Mg}_2\text{B}_2\text{O}_5$) is greatly limited by the first precipitated olivine. Therefore, the transformation of the primary crystalline phase in B-bearing slag for directly enriching boron from the amorphous state into $\text{Mg}_2\text{B}_2\text{O}_5$ is studied further. On this basis, one-step separation of $\text{Mg}_2\text{B}_2\text{O}_5$ crystals from molten B-bearing slag via super gravity separation is conducted, and the properties of the separated $\text{Mg}_2\text{B}_2\text{O}_5$ crystals are investigated in this section [47].

3.4.1 Thermodynamic Analysis for Crystalline Phase Transformation in B_2O_3 – SiO_2 – MgO – CaO – Al_2O_3 System

There are two primary crystalline regions consisting of suanite and olivine in the equilibrium phase diagram of MgO – SiO_2 – B_2O_3 –3wt% CaO –2wt% Al_2O_3 as calculated using FactSage 7.3, as shown in Fig. 3.28. The original composition of the B-bearing slag (Point a in Fig. 3.28) is located within the primary crystallization region of Mg_2SiO_4 , where the boron exists in the amorphous state in this region, which brings great difficulty to efficiently separate boron from the B-bearing slag [47]. Therefore, the primary crystalline phase in B-bearing slag is conducted to transform from Mg_2SiO_4 to $\text{Mg}_2\text{B}_2\text{O}_5$ for enriching boron from the amorphous state into suanite to directly recovery of boron from the B-bearing slag.

3.4.2 Primary Crystalline Phase Transformation for Enriching Amorphous B into Suanite

3.4.2.1 Experimental Procedure

Based on the phase equilibria of MgO – SiO_2 – B_2O_3 –3wt% CaO –2wt% Al_2O_3 , the crystallization behavior of B-bearing slag was experimented by varying the $\text{B}_2\text{O}_3/\text{SiO}_2$ (B/S) ratio from 0.60, 0.80, 1.00, and 1.20 and the MgO content from 42.00, 40.00, 38.00, and 36.00 wt%, as given in Table 3.6 (Points a–g). A mass of 10 g of each slag with a different B/S ratio and MgO content was fully mixed and filled into a graphite crucible and heated at 1773 K for 30 min in a muffle furnace to ensure a complete melting and homogenization. Subsequently, the slags were cooled down slowly from molten to the solid state (1773–1373 K) with a cooling rate of 2 K/min and then quenched in water rapidly. Subsequently, XRD, SEM–EDS, and EPMA were utilized

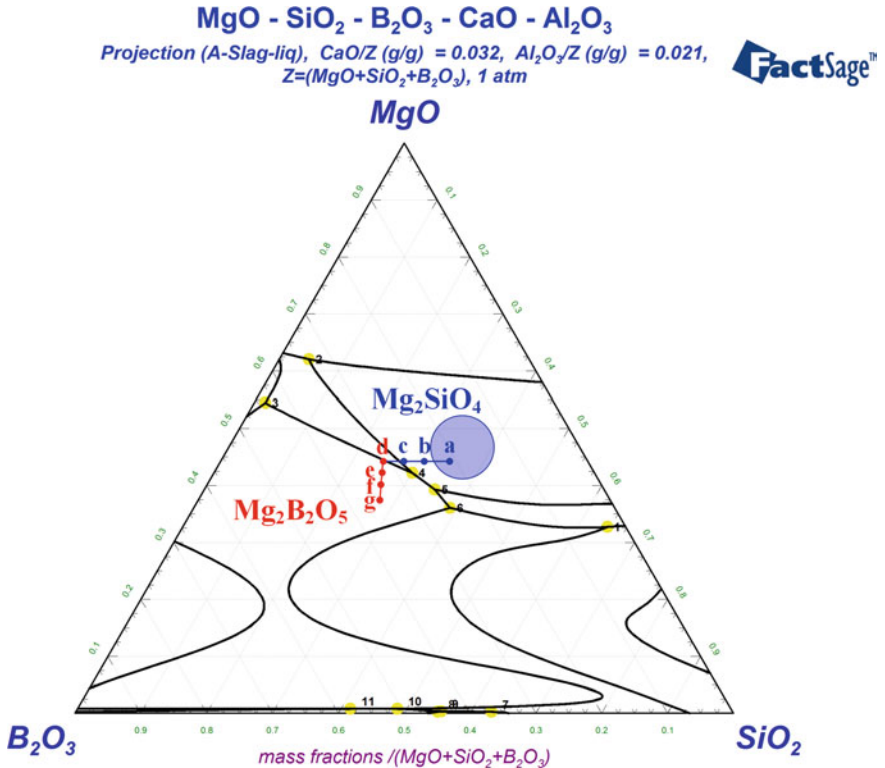


Fig. 3.28 Equilibrium phase diagram of MgO–SiO₂–B₂O₃–3wt%CaO–2wt%Al₂O₃

to analyze the variations in crystallization and element migration behavior of the primary crystalline phases in the B-bearing slag.

Table 3.6 Chemical compositions of B-bearing slags (wt%)

Composition	MgO	SiO ₂	B ₂ O ₃	CaO	Al ₂ O ₃	Others	(B/S)
Boron-bearing slag (Point a)	42.40	31.12	19.13	3.16	1.98	2.21	0.61
Point b	42.40	28.29	22.63	2.87	1.80	2.01	0.80
Point c	42.40	25.76	25.76	2.62	1.64	1.83	1.00
Point d	42.40	23.64	28.37	2.40	1.50	1.68	1.20
Point e	40.00	24.87	29.85	2.26	1.42	1.58	1.20
Point f	38.00	25.90	31.09	2.15	1.34	1.51	1.20
Point g	36.00	26.93	32.32	2.04	1.27	1.43	1.20

3.4.2.2 Primary Crystalline Phase Transformation Behavior of B-Bearing Slag

The XRD patterns and SEM–EDS images for the crystalline phases in B-bearing slag with various B/S ratios are shown in Fig. 3.29a and Fig. 3.30a. It is found that the single olivine appears in the original B-bearing slag with the condition of $B/S = 0.60$, while all the B elements are dispersed in the slag phase, indicating that Mg^{2+} primarily reacts with SiO_4^{4-} and crystallized into olivine. As the B/S ratio increases from 0.60 to 0.80, the slag viscosity decreases, and the nucleation and growth conditions for olivine in the molten B-bearing slag are improved; thus, the diffraction peak intensity of olivine increase and the olivine crystals become larger.

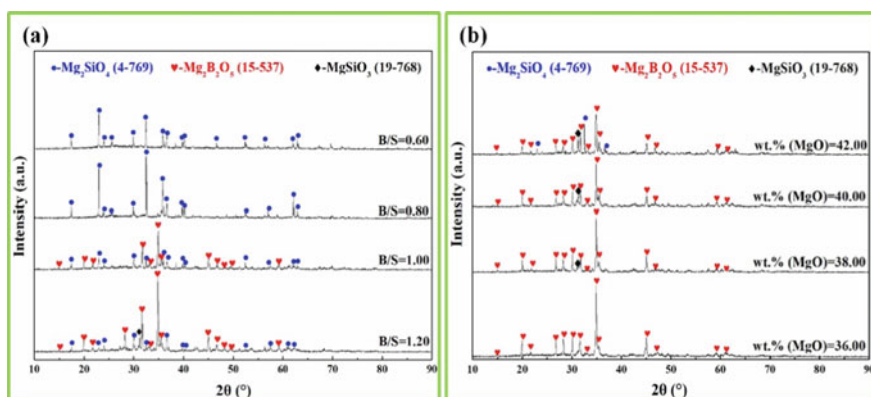


Fig. 3.29 XRD patterns of B-bearing slag with B/S ratio and MgO content: **a** variations of XRD with B/S ratio (wt% (MgO) = 42.00); **b** variations of XRD with MgO content ($B/S = 1.20$)

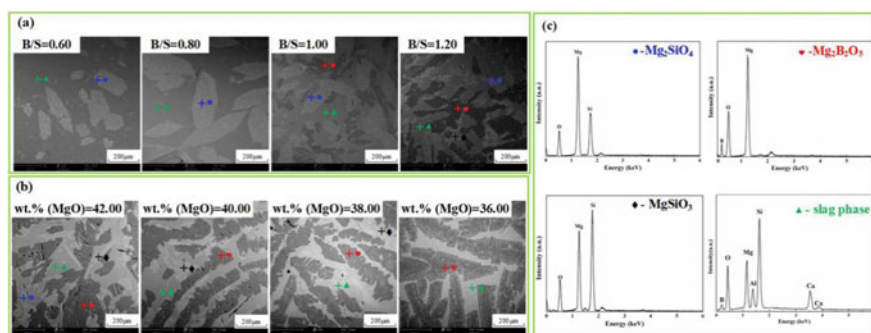


Fig. 3.30 SEM–EDS images of B-bearing slag with B/S ratio and MgO content: **a** variations of SEM images with B/S ratio (wt% (MgO) = 42.00); **b** variations of SEM images with MgO content ($B/S = 1.20$); **c** EDS images of Mg_2SiO_4 , $Mg_2B_2O_5$, $MgSiO_3$ and slag phase

When the B/S ratio increases to 1.00, the diffraction peaks of suanite appear while that of the olivine is decreased. In addition, fine crystals of suanite with sizes of 50–100 μm are evenly distributed among the olivine crystals in the B-bearing slag. In fact, based on the equilibria phase diagram of $\text{MgO-SiO}_2\text{-B}_2\text{O}_3\text{-3wt\%CaO-2wt\%Al}_2\text{O}_3$, the combination of $B/S = 1.00$ and $\text{wt\% (MgO)} = 36.00$ is in the primary crystallization region of olivine. With the formation of olivine in the molten B-bearing slag, the composition of the remaining melt gradually moves to the crystallization region of suanite, and $\text{B}_2\text{O}_5^{4-}$ starts to crystallize with the Mg^{2+} to form suanite in the melt.

With the further increase of B/S ratio from 1.00 to 1.20, the primary crystallization region is transferred from olivine into suanite. Thus, more Mg^{2+} primarily react with $\text{B}_2\text{O}_5^{4-}$ in the molten B-bearing slag, which causes the significant increase of the diffraction peak intensity of suanite instead of the olivine for $B/S = 1.20$. The crystal size of suanite shows an obvious increase to 150–200 μm with the decrease of olivine. In addition, the weak diffraction peaks of enstatite (MgSiO_3) are detected and some fine crystals are included among the suanite and olivine in the B-bearing slag.

Figure 3.29b and Fig. 3.30b show further variations of the XRD patterns and SEM-EDS images for the crystalline phases in the B-bearing slag with the MgO content. The diffraction peak intensity of suanite is significantly increased with the decrease of MgO content from 42.00 to 36.00 wt%. By constant, the diffraction peaks of olivine and enstatite both decrease significantly with the decrease of MgO content, the diffraction peaks of olivine are completely disappeared for $\text{wt\% (MgO)} = 40.00$, and those of the enstatite are fully disappeared for $\text{wt\% (MgO)} = 36.00$. Hence, the single diffraction peaks of suanite are appeared for $\text{wt\% (MgO)} = 36.00$, as indicated by Fig. 3.29b. Moreover, both the amount and size of suanite crystals increase obviously with the decrease of MgO content from 42.00 to 36.00 wt%, while the olivine and enstatite successively disappear from the B-bearing slag, as confirmed by Fig. 3.30b. This observation indicates that the Mg^{2+} primarily reacts with $\text{B}_2\text{O}_5^{4-}$ rather than SiO_4^{4-} or SiO_3^{2-} with the decrease of MgO content, and less Mg^{2+} is provided for further crystallization of olivine or enstatite in the B-bearing slag. The primary crystalline phase is completely transformed from olivine to the suanite, and the single columnar crystals of suanite with a size of 300–500 μm are presented in the B-bearing slag for $B/S = 1.20$ and $\text{wt\% (MgO)} = 36.00$.

The migration behavior of B and Si elements in B-bearing slag with the variations of B/S ratio and MgO content is verified by EPMA as presented in Fig. 3.31. The figure shows that all of the B elements are distributed in the slag phase, while the Si elements are mainly enriched in the olivine in the original B-bearing slag for $B/S = 0.60$ and $\text{wt\% (MgO)} = 42.00$, as detailed in Fig. 3.31a. By contrast, the B elements are gradually transferred from the slag phase into the suanite, while the Si elements are increasingly shifted from the olivine into the slag phase as the B/S ratio increased from 0.60 to 1.20, as indicated in Fig. 3.31b. Additional B is fully enriched into the suanite, while all of the Si elements are transferred into the slag phase with the decrease of the MgO content from 42.00 to 36.00 wt%, as confirmed by Fig. 3.31c. Therefore, it is confirmed that the B is efficiently enriched from the amorphous state into suanite through changing the primary crystalline phase in B-bearing slag.

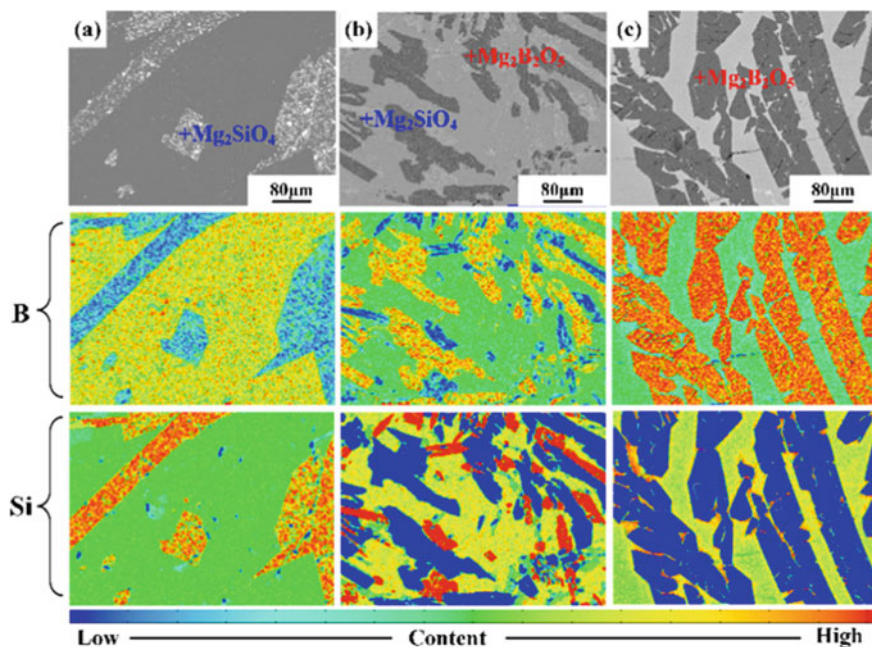


Fig. 3.31 EPMA results for migration of B and Si elements in B-bearing slag with B/S ratio and MgO content: **a** $B/S = 0.60$, wt% (MgO) = 42.00; **b** $B/S = 1.20$, wt% (MgO) = 42.00; **c** $B/S = 1.20$, wt% (MgO) = 36.00

3.4.3 Separation of Suanite from B-Bearing Slag by Super Gravity

3.4.3.1 Experimental Procedure

Based on the favorable conditions for the transformation of the primary crystalline phase into suanite, one-step separation of suanite crystals from the molten B-bearing slag was conducted via super gravity separation. The B-bearing slag with $B/S = 1.20$ and wt% (MgO) = 42.00 was put into the upper part of the composite graphite crucible, in which graphite felt with a pore size of 10 μm was embedded for intercepting the suanite crystals in the molten slag. The slag was completely melted at 1773 K and then cooled down slowly from 1773 to 1403 K with a cooling rate of 1 K/min to allow the sufficient crystallization of suanite. Subsequently, the centrifuge was started to drive the rotation of the heating furnace at a constant temperature, and the rotating speed was varied from 597, 1036, 1336, 1581, and 1793 rpm for gravity coefficients of 100, 300, 500, 700, and 900. After centrifugal separation for 10, 60, 120, 180, 240, and 300 s at a constant rotating speed, the crucible was rapidly taken out and quenched in water. Then, the samples were analyzed by the XRD, SEM-EDX, and ICP-AES for evaluating the microstructure, and the mineral and chemical

compositions of the separated suanite compared to those of the residual slag. The recovery ratio of B_2O_3 in the separated suanite was calculated using Eq. (3.1).

$$R_B = \frac{m_B \times \omega_B}{m_B \times \omega_B + m_S \times \omega_S} \times 100\%, \quad (3.1)$$

where R_B is the recovery ratio of B_2O_3 in suanite; m_B and m_S are the mass of suanite and residual slag, respectively; ω_B and ω_S are the mass fractions of B_2O_3 in suanite and residual slag, respectively.

3.4.3.2 Separation Behavior of Suanite in B-Bearing Slag

The cross section drawings of the sample obtained with $G = 1$ are presented in Fig. 3.32a, showing all the suanite crystals are homogeneously included in the B-bearing slag owing to its high viscosity, none of which could be separated from the molten slag under the normal gravity. Conversely, the molten B-bearing slag is separated into two contrasting parts by the graphite filter for $G = 500$, which is attributed to the larger driving force for phase separation generated in the super gravity field. As described in the schematic diagram of Fig. 3.32b, the slag melt is driven to flow through the filter and move into the bottom crucible along the direction of super gravity, while the suanite crystals are wholly intercepted by the filter on the upper crucible and completely separated from the slag melt.

The XRD patterns of suanite and residual slag separated from the molten B-bearing slag are shown in Fig. 3.33. It is confirmed that the only significant diffraction

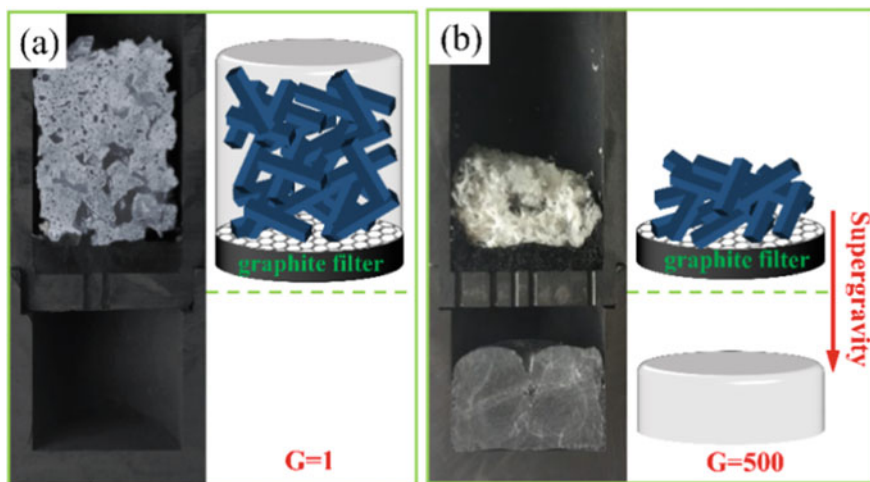


Fig. 3.32 Cross section drawings for separation of suanite crystals from molten B-bearing slag by super gravity compared with normal gravity: **a** $G = 1$, $T = 1403$ K and $t = 240$ s; **b** $G = 500$, $T = 1403$ K and $t = 240$ s

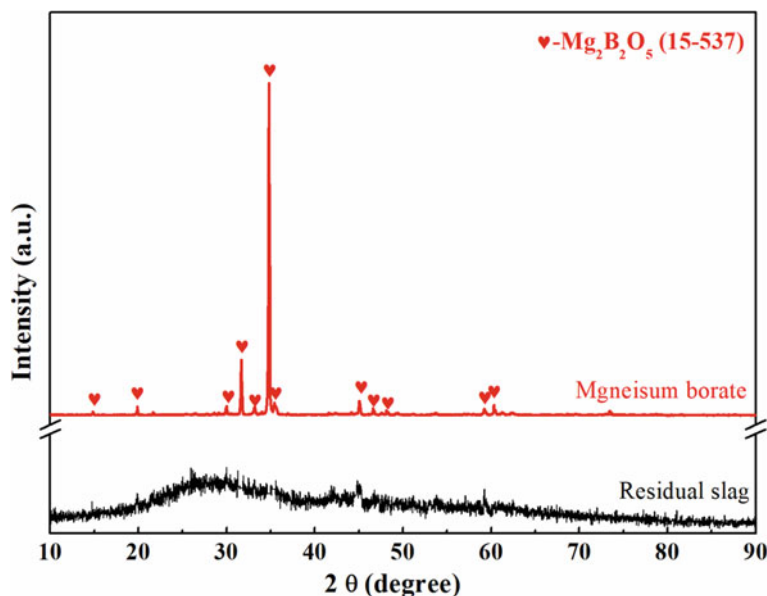


Fig. 3.33 XRD patterns of suanite compared with residual slag separated from B-bearing slag by super gravity ($G = 500$, $T = 1403$ K and $t = 240$ s)

peaks of suanite (PDF Card No. 15-537) appear in the suanite spectra compared to the broad peak in the residual slag. The SEM image of the suanite presented in Fig. 3.34a shows that the single columnar crystals of suanite without any inclusions are efficiently separated from the molten B-bearing slag, and its crystal size is up to 300–500 μm , which confirms the high crystallinity and high purity of the suanite crystals from the microscopic point of view. In contrast, no suanite crystals are included in the residual slag, as shown in Fig. 3.34b, which confirms that the suanite crystals are completely separated from the molten slag by super gravity.

Figure 3.35 presents further the variations in the mass fraction of B_2O_3 in the suanite separated from the B-bearing slag with gravity coefficient and separation time. When the gravity coefficient is lower than 500, the mass fractions of B_2O_3 in the suanite increase continuously with the separation time within 300 s. By contrast, the mass fractions of B_2O_3 in the suanite increase more significantly with the gravity coefficient to $G = 500$ –900, which rapidly reach the maximum value within 240 s and then remained stable. This indicates that the solid–liquid separation of the suanite crystals from molten B-bearing slag is significantly enhanced by super gravity. Furthermore, the separation efficiency of the two phases is increased evidently with the increase of gravity coefficient. The mass fractions of B_2O_3 in the suanite are up to 46.61–46.66 wt% in the condition of $G \geq 500$ and $t \geq 240$ s, where the values approach the theoretical content of B_2O_3 in $\text{Mg}_2\text{B}_2\text{O}_5$ (46.67 wt%). The recovery ratios of B_2O_3 in the suanite are 60.18–62.01%. It is confirmed that the boron is adequately enriched from the amorphous state into the suanite, and the

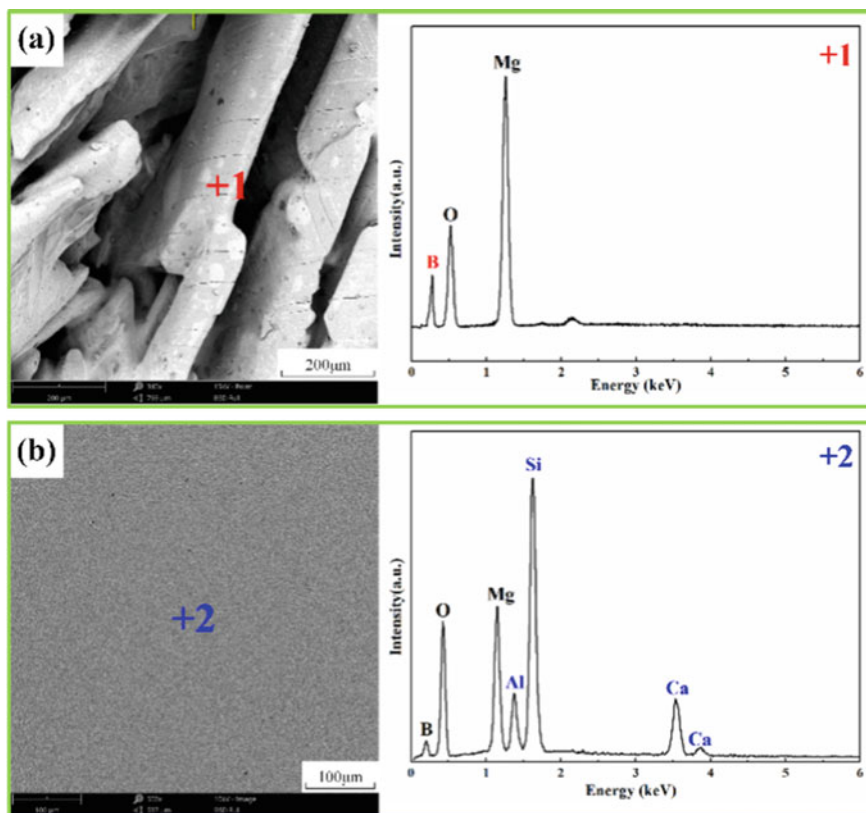


Fig. 3.34 SEM–EDX images of suanite compared with residual slag separated from B-bearing slag by super gravity ($G = 500$, $T = 1403$ K and $t = 240$ s): **a** suanite; **b** residual slag

high-purity suanite crystals are efficiently separated from the molten B-bearing slag by super gravity.

3.4.4 Characterization for the Properties of Separated Suanite

3.4.4.1 Experimental Procedure

Firstly, the microwave dielectric properties of the separated suanite ($\text{Mg}_2\text{B}_2\text{O}_5$) crystals from the B-bearing slag were studied. The suanite crystals were fully ground for 4 h in a ball mill with a small amount of ethanol as a medium. The suanite powder after dried at 373 K for 10 h was calcined at 773 K for 4 h in air. The dried suanite powders were mixed with 10 wt% PVA organic binder and pressed into cylindrical pellets

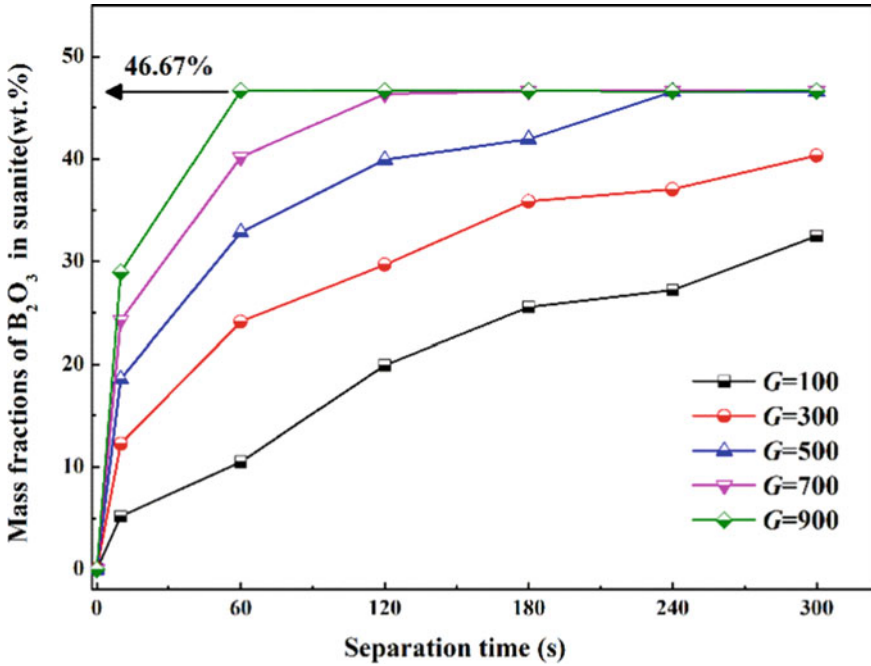


Fig. 3.35 Variations in the mass fraction of B_2O_3 in suanite separated from B-bearing slag with gravity coefficient and separation time

(10.00 mm in diameter and 5.00–6.00 mm in thickness) under uniaxial pressure of 200 MPa and then sintered at 1273, 1323, 1373, 1423, and 1473 K for 4 h in air. The densities of the $Mg_2B_2O_5$ samples were measured through the Archimedes method. The surface morphology of the $Mg_2B_2O_5$ samples with sintering temperature was analyzed by the SEM method. The molecular vibration of the $Mg_2B_2O_5$ sample was measured by FT-IR and Raman spectroscopy. After painting the pellets with silver paint to form the electrodes, the microwave dielectric properties of the $Mg_2B_2O_5$ crystals, including dielectric constant (ϵ_r), quality factor ($Q \times f$), and temperature coefficient of resonant frequency (TCF), were measured using a network analyzer equipped with a heating system operating in the fundamental TE_{018} dielectric resonator mode. The TCF was calculated from Eq. (3.2).

$$TCF = \frac{f_{358} - f_{298}}{f_{298} \times (358 - 298)} \times 10^6, \quad (3.2)$$

where f_{358} and f_{298} are the resonant frequencies at 358 K and 298 K, respectively.

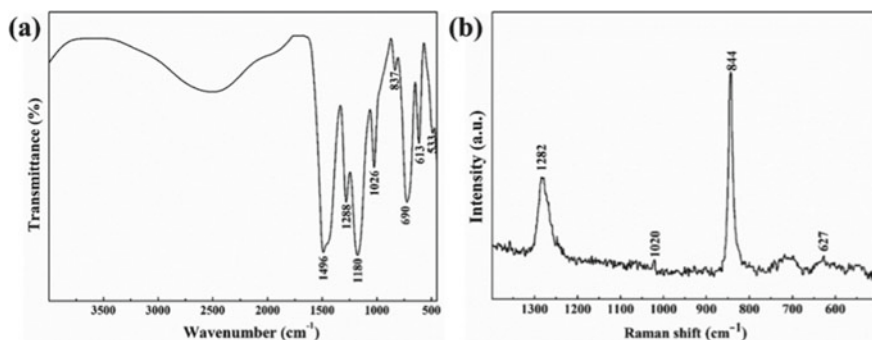


Fig. 3.36 FT-IR and Raman spectra of the $\text{Mg}_2\text{B}_2\text{O}_5$ crystals: **a** FT-IR spectrum; **b** Raman spectrum

3.4.4.2 Properties of the Separated Suanite

The factors affecting the dielectric properties of $\text{Mg}_2\text{B}_2\text{O}_5$ include the intrinsic and the extrinsic factors, the intrinsic factors primarily related to the lattice vibration, and the extrinsic factors mainly including the density, grain boundary, pores, and secondary phase [48, 49]. Therefore, the molecule vibration information, density, microstructure, and the detailed dielectric properties of the $\text{Mg}_2\text{B}_2\text{O}_5$ crystals are investigated. The detailed molecule vibration information of the $\text{Mg}_2\text{B}_2\text{O}_5$ crystals is confirmed by the FT-IR and Raman spectroscopy as presented in Fig. 3.36. The FT-IR spectrum in Fig. 3.36a, shows obvious transmission bands of $\text{Mg}_2\text{B}_2\text{O}_5$ crystals on account of high crystallinity. According to the vibrational features of $\text{Mg}_2\text{B}_2\text{O}_5$ crystals, the bands at 1496 and 1288 cm^{-1} are ascribed to the asymmetric stretching of trigonal units ($\text{B}_{(3)}\text{-O}$), and the bands at 1180 , 1026 , and 837 cm^{-1} corresponded to the asymmetric stretching of tetrahedral units ($\text{B}_{(4)}\text{-O}$). The band at 690 cm^{-1} is ascribed to the out-plane bending of B-O-B trigonal units, and the band at 613 cm^{-1} is attributed to the in-plane bending of B-O-B trigonal units. The band at 533 cm^{-1} is due to the bending of trigonal units and tetrahedral units.

Furthermore, the Raman spectrum of $\text{Mg}_2\text{B}_2\text{O}_5$ crystals in the frequency range from 1400 to 500 cm^{-1} shown in Fig. 3.36b displays two of the characteristic absorption bands at 844 and 1282 cm^{-1} . The peak at 844 cm^{-1} is attributed to the symmetric stretching vibration tetrahedral units, and the peak at 1282 cm^{-1} is ascribed to the asymmetric stretching vibration of trigonal units. Moreover, the peak at 1020 cm^{-1} is attributed to the stretching vibration of B-O bond in trigonal units and B_2O_5 units, and peak at the 627 cm^{-1} is ascribed to the scissor bending of O-B-O bond in B_2O_5 units and in-plane torsion vibration of trigonal units. Compared with the results of Zhu [50] and Li [51], the FT-IR and Raman spectra of the $\text{Mg}_2\text{B}_2\text{O}_5$ crystals prepared from the B-bearing slag are perfectly accordant with that of the $\text{Mg}_2\text{B}_2\text{O}_5$ prepared by the synthetic methods use high-purity oxides.

The SEM images of thermally etched surface of $\text{Mg}_2\text{B}_2\text{O}_5$ samples sintered at various temperatures for 4 h are shown in Fig. 3.37. It is found from Fig. 3.37a that

only some micropores appeared in the $\text{Mg}_2\text{B}_2\text{O}_5$ samples sintered at a low temperature of 1273 K. With the increase of sintering temperature from 1273 to 1373 K, the pores are significantly eliminated and a dense microstructure is formed with the rod-shaped crystals of $\text{Mg}_2\text{B}_2\text{O}_5$, as shown in Fig. 3.37b. With the sintering temperature increase further to 1473 K, some partial melting of $\text{Mg}_2\text{B}_2\text{O}_5$ crystals is appeared in the sample, as shown in Fig. 3.37c. Moreover, the variation of relative density of $\text{Mg}_2\text{B}_2\text{O}_5$ with the sintering temperature is shown in Fig. 3.38. It is indicated that the relative density of the $\text{Mg}_2\text{B}_2\text{O}_5$ samples sintered at 1273 K is 88.79%, which is increased significantly to 95.14% with the sintering temperature increased to 1373 K. With the sintering temperature increase further to 1473 K, the relative density of $\text{Mg}_2\text{B}_2\text{O}_5$ stabilizes at about 95.14%. This confirms that the pores are significantly eliminated and the densification of the $\text{Mg}_2\text{B}_2\text{O}_5$ sample is improved greatly with the increase of sintering temperature.

Figure 3.39a–c shows the variations of dielectric properties including the dielectric constant (ϵ_r), quality factor ($Q \times f$), and the temperature coefficient of resonant frequency (TCF) of $\text{Mg}_2\text{B}_2\text{O}_5$ with the sintering temperature. It is indicated from Fig. 3.39a that the dielectric constant of $\text{Mg}_2\text{B}_2\text{O}_5$ is increased significantly from 5.54 to 6.05 with the increase of sintering temperature from 1273 to 1373 K. Based on the measurements results of Fang [52] and Duan [53], the dielectric constant of pore is 1 which is much smaller than that of oxide material, and the extrinsic factor of pore can cause a detrimental deviation from the intrinsic dielectric properties of the $\text{Mg}_2\text{B}_2\text{O}_5$ material. Hence, the increase of dielectric constant with sintering temperature is mainly attributed to the efficient elimination of the pores from the $\text{Mg}_2\text{B}_2\text{O}_5$, and the appropriate sintering temperature for $\text{Mg}_2\text{B}_2\text{O}_5$ is confirmed to be 1373 K. With the further increase of sintering temperature to 1473 K, the dielectric constant of $\text{Mg}_2\text{B}_2\text{O}_5$ sample is almost stabilized at 6.04–6.05.

As the variation of $Q \times f$ value of $\text{Mg}_2\text{B}_2\text{O}_5$ shown in Fig. 3.39b, it exhibits the similar variation trend to the relative density with the increase of sintering temperature. The $Q \times f$ value of $\text{Mg}_2\text{B}_2\text{O}_5$ is increased significantly with the sintering temperature increased from 1273 to 1373 K, which confirm further greatly the improvement of densification to eliminate the defects pores in the $\text{Mg}_2\text{B}_2\text{O}_5$. The $Q \times f$ value of the

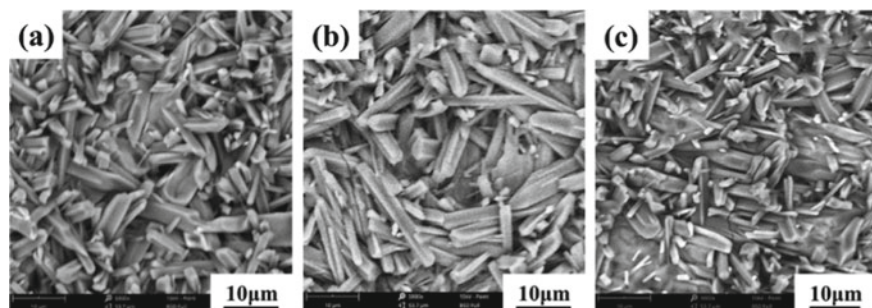


Fig. 3.37 SEM images of thermally etched surface of $\text{Mg}_2\text{B}_2\text{O}_5$ sample sintered at various temperatures for 4 h: **a** 1273 K; **b** 1373 K; **c** 1473 K

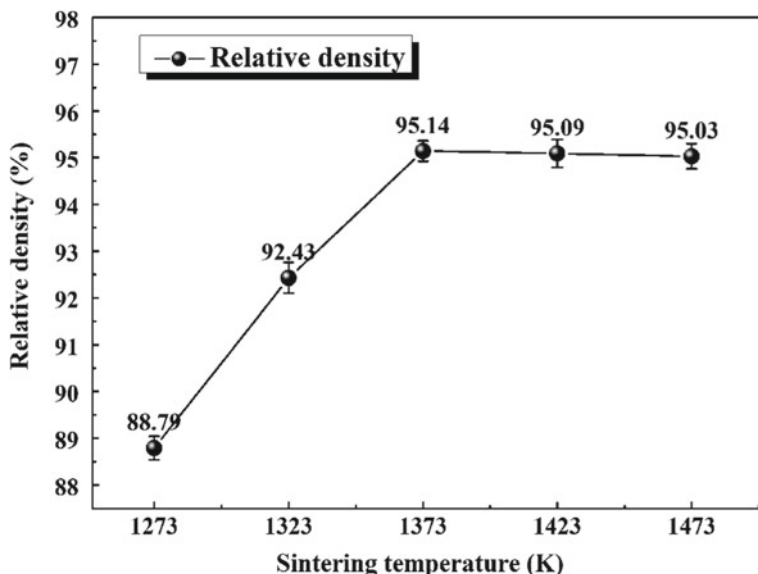


Fig. 3.38 Variation of relative density of $\text{Mg}_2\text{B}_2\text{O}_5$ with sintering temperature

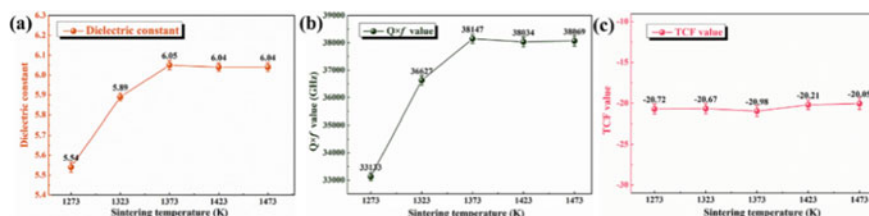


Fig. 3.39 Variations of dielectric properties of $\text{Mg}_2\text{B}_2\text{O}_5$ sample with sintering temperature: **a** dielectric constant; **b** $Q \times f$ value; **c** TCF value

$\text{Mg}_2\text{B}_2\text{O}_5$ sample sintered at 1373 K is up to 38,147 GHz, which almost stabilizes at 38,034–38,147 GHz with the sintering temperature increase further from 1373 to 1473 K. A slightly decrease of the $Q \times f$ value appeared at 1423 K is mainly attributed to some partial melting of $\text{Mg}_2\text{B}_2\text{O}_5$ crystals.

Figure 3.39c shows further the variation of TCF value of $\text{Mg}_2\text{B}_2\text{O}_5$ with sintering temperature. The TCF value of the $\text{Mg}_2\text{B}_2\text{O}_5$ exhibits the relatively negative value of -20.98 ppm/K and almost stable with the increase of sintering temperature. As reported by Butee [54] and Feng [55], the second phase and additives are easily brought in during the synthesis of $\text{Mg}_2\text{B}_2\text{O}_5$ materials through oxides, which are the main factors that limited the TCF value of $\text{Mg}_2\text{B}_2\text{O}_5$ materials. The stability of TCF value with temperature is attributed to the high purity and high crystallinity of the separated $\text{Mg}_2\text{B}_2\text{O}_5$ crystals from B-bearing slag through sufficient removal of inclusions.

Table 3.7 Dielectric properties of some reported Mg₂B₂O₅

Composition	ϵ_r	$Q \times f$ (GHz)	τ_f (ppm/K)	Preparation method	Ref.
Mg ₂ B ₂ O ₅	6.05	38,147	– 20.98	Separation from B-bearing slag	This work
Mg ₂ B ₂ O ₅	6.20	32,100	– 18.00	Synthesis by oxides	[4]
Mg ₂ B ₂ O ₅	7.50	52,000	– 27.00	Synthesis by oxides	[56]

Table 3.7 shows the microwave dielectric properties including the dielectric constant, the $Q \times f$ value, and the TCF value of some reported Mg₂B₂O₅ prepared by synthetic methods use high-purity oxides [56]. Compared with the reported results, the Mg₂B₂O₅ crystals separated from the B-bearing slag shows a favorable dielectric property including the dielectric constant of 6.05, the $Q \times f$ value of 38,147 GHz, and the TCF value of – 20.98 ppm/K, which are consistent with the reported dielectric constant of 6.20–7.50, and $Q \times f$ value of 32,100–52,000 GHz and TCF value of – 18.00 to – 27.00 ppm/K for the Mg₂B₂O₅ prepared by synthetic methods use high-purity boron and magnesium oxides.

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Chapter 4

Selective Crystallization and Separation of REEs in RE-Bearing Slag



Abstract It reports the selective crystallization and separation of REEs in RE-bearing slag. The selective crystallization behaviors of RE in RE-bearing slag, including the isothermal phase diagram of $\text{CaO-SiO}_2\text{-CaF}_2\text{-Ce}_2\text{O}_3$ system, the phase equilibria of RE-phase, and the isothermal crystallization and growth kinetics of RE-phase are reported, respectively, in Sect. 4.1. The study on selective separation of RE in RE-bearing slag, including the motion and separation behaviors of cefluosil in molten RE-bearing slag, is included in Sect. 4.2.

Rare earth elements (REEs) are a group of chemical elements with unique properties and include yttrium, scandium, and all the lanthanides (chemical elements with atomic numbers from 57 to 71) [1]. REEs play an important role in numerous fields of advanced materials due to their high chemical activity. Therefore, the industrial demand for REEs has increased dramatically in recent years [2].

It is well known that the Bayan Obo mine located in the Inner Mongolia region of North China is the largest REE ore deposit in the world, which accounts for 35% rare earth resource of world's proven reserves and approximately 80% in China [3, 4]. Currently, it is mined mainly as an iron ore. After grinding to smaller than $76\text{ }\mu\text{m}$, a feeble magnetic powerful magnetic-flotation process is used for recovering about 70 pct of iron and less than 10 wt% of the rare earth, while most of the rare metal minerals remain in the tailings [5]. In order to efficiently utilize the Bayan Obo ore, several high-temperature metallurgical processes have been employed to separate the rare earth and iron, such as blast furnace process [6, 7], direct reduction, [8] and smelting reduction process [9, 10]. Generally, the niobium-bearing hot metal and RE-bearing slag are produced from the reduction and smelting process, where almost all of rare earth transform into the RE-bearing slag which contains 13–15 wt% of RE_2O_3 .

In recent years, several mineral and hydrometallurgy processes such as gravity separation, magnetic separation combined with gravity separation, and hydrometallurgical methods have been proposed for separation and recovery of rare earth in the RE-bearing slag [11–13]. However, the traditional separating technique cannot effectively separate the rare earth phases from the RE-bearing slag, due to the content and complex mineral compositions formed in the high-temperature process.

In view of the following advantages of pyrometallurgical technology, such as large processing capacity, high efficiency, no hazardous wastes production, and less secondary pollution [14], much attention has been paid to the application of pyrometallurgy to the recovery of valuable resources in industrial slags. However, there are many divergences in mineralogical and chemical compositions of the RE-phases in RE-bearing slags, as reported in various research, which is resulted from the lack of thermodynamic data of REEs. Therefore, the phase equilibria of RE-bearing slag system, the phase equilibria of RE-phase in the system, and the isothermal crystallization and growth kinetics for the RE-phase are studied in this chapter, to provide the necessary thermodynamic data and kinetic information for separation and recovery of REEs in RE-bearing slag. On this basis, selective crystallization and separation of RE-phases from RE-bearing slag are conducted further by super gravity.

In this chapter, selective crystallization and separation of REEs in RE-bearing slag are proposed, and the isothermal phase equilibria of RE-bearing slag system ($\text{CaO-SiO}_2\text{-CaF}_2\text{-Ce}_2\text{O}_3$ system), the phase equilibria, isothermal crystallization and growth kinetics of RE-phase (cefluosil) in RE-bearing slag [15], and the selective separation for RE-phase [16, 17] are included in the following sections, respectively.

Section 4.1 reports the selective crystallization of RE in RE-bearing slag and includes the isothermal phase diagram of $\text{CaO-SiO}_2\text{-CaF}_2\text{-Ce}_2\text{O}_3$ system, phase equilibria of RE-phase, and the isothermal crystallization and growth kinetics of RE-phase.

Section 4.2 reports the selective separation of RE in RE-bearing slag and includes the motion and separation behaviors of cefluosil in RE-bearing slag enhanced by super gravity.

4.1 Selective Crystallization of REEs in RE-Bearing Slag

4.1.1 Isothermal Phase Diagram of $\text{CaO-SiO}_2\text{-CaF}_2\text{-Ce}_2\text{O}_3$ System

The phase structures, phase compositions, and transformation information of RE-bearing slag are important to the separation and recovery of REEs in RE-bearing slag. However, the basic data on REEs in RE-bearing slag are scarce, and few studies are available on the thermodynamic and kinetic data for REE-bearing slag systems, which greatly limits the separation and recovery of rare earth in RE-bearing slag [18, 19]. Wang [20] reported the binary system of CaO-SiO_2 , and the solid compounds of SiO_2 , CaO , $\text{CaO} \cdot \text{SiO}_2$ (CS), $2\text{CaO} \cdot \text{SiO}_2$ (C_2S), and $3\text{CaO} \cdot \text{SiO}_2$ (C_3S) were reported in the CaO-SiO_2 system. Tas and Akinc [21] found that three congruently melting binary compounds of Ce_2SiO_5 , $\text{Ce}_{4.67}(\text{SiO}_4)_3\text{O}$, and $\text{Ce}_2\text{Si}_2\text{O}_7$ were presented in the $\text{Ce}_2\text{O}_3\text{-SiO}_2$ system. Zhao et al. [22] studied that two solid solution phases of $\text{Ce}_{9.33-x}\text{Ca}_x(\text{SiO}_4)_6\text{O}_{2-\delta}$ and $\text{Ca}_{2-x}\text{Ce}_x\text{SiO}_{4+\delta}$ were presented in $\text{CaO-SiO}_2\text{-Ce}_2\text{O}_3$ system at 1873 K. The authors [23] previously

reported the ternary phase diagram for $\text{CaO-SiO}_2\text{-Ce}_2\text{O}_3$ system at 1773–1573 K and found that the equilibrium solid phases mainly included SiO_2 , $\text{Ca}_2\text{SiO}_4(\text{Ce}_2\text{O}_3)$, $\text{Ce}_{9.33-x}\text{Ca}_x(\text{SiO}_4)_6\text{O}_{2-0.5x}$, $\text{Ce}_2\text{Si}_2\text{O}_7$, and Ce_2O_3 .

Based on the mineral compositions of rare earth ore [24], the bastnaesite (CeCO_3F) and fluorite (CaF_2) account for a high proportion, and almost all of F will be transformed into REE-bearing slag during the iron-making process. Therefore, the authors study the phase equilibria of the quaternary $\text{CaO-SiO}_2\text{-CaF}_2\text{-Ce}_2\text{O}_3$ system, which is more consistent with the REE-bearing slag produced from the rare earth ore [25]. Generally, the investigation of the phase equilibria of multi-component systems can be simplified by constructing isothermal pseudo-ternary diagrams by fixing one of the typical components.

4.1.1.1 Materials and Apparatus

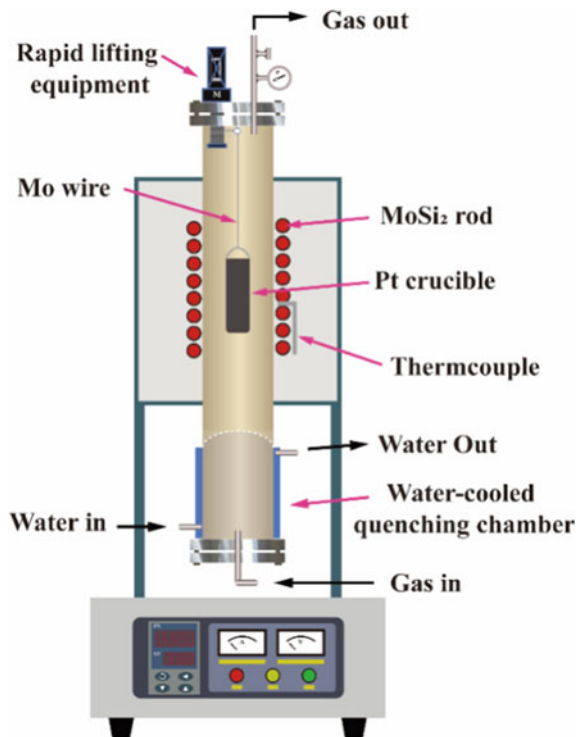
Oxide powders with a purity of 99.99 wt% were used as the starting materials, including CaO (CAS No. 1305-78-8), SiO_2 (CAS No. 7631-86-9), CaF_2 (CAS No. 7789-75-5), and CeO_2 (CAS No. 1306-38-3) powders.

The core of phase equilibria research is to accumulate information on high-temperature phase equilibria, and the rapid quenching technique can maintain the equilibrium properties of the multi-component system at high temperatures. In this work, a vertical water-quenching furnace was employed in the phase equilibria experiments of the $\text{CaO-SiO}_2\text{-CaF}_2\text{-Ce}_2\text{O}_3$ system, which can provide the necessary experimental conditions for obtaining accurate temperatures and rapid quenching cooling rates, as shown in Fig. 4.1. The experimental device mainly consisted of an alumina tube used for high-temperature reaction and a water-cooled chamber closed by the alumina tube. A graphite crucible containing the sample was positioned in the constant temperature zone of the vertical tube furnace with MoSi_2 heating elements, and a hanging rod was installed that could move up and down to adjust the position of the sample. The temperature measurement error was controlled within 1 °C by a type B (Pt 6% Rh) thermocouple. When the holding time in the isothermal experiments reached the target time, or the experimental temperature in non-isothermal experiments reached the target temperature, the crucible flushed by CO gas was quenched quickly by dropping from the constant temperature zone into the water-cooled chamber, and the molten slag was immediately cooled down to room temperature in seconds to maintain the mineral compositions at high temperatures.

4.1.1.2 Experimental Procedure

To investigate the phase equilibria of the quaternary $\text{CaO-SiO}_2\text{-CaF}_2\text{-Ce}_2\text{O}_3$ system, an isothermal pseudo-ternary phase diagram was constructed using numerous equilibrium points. Based on the industrial conditions and common composition of REE-bearing slag, the content of CaF_2 was fixed at 30 wt%, the temperature was selected to be 1373 K which is a key temperature for formation of RE-phases in REE-bearing

Fig. 4.1 Schematic illustration of the vertical water-quenching furnace



slag [22, 25], and the phase equilibria experiments were conducted under a CO atmosphere for creating a reducing atmosphere. Twenty primary and decentralized component points in the $\text{CaO-SiO}_2\text{-CaF}_2\text{-Ce}_2\text{O}_3$ system were selected in the phase equilibria experiments, as given in Table 4.1. The four components with the desired contents were mixed homogeneously with ethanol and then dried. A total of 20 g samples was separately placed in a platinum crucible, the crucible was positioned adjacent to the thermocouple in the constant temperature zone of the vertical water-quenching furnace, and the temperature was controlled within ± 1 K. After equilibrating at 1373 K for 24 h under a CO atmosphere, the crucible was quenched in the water-cooled chamber.

The quenched samples were separated into two parts from the crucibles. One part was ground into powder and analyzed by XRD to determine the mineral compositions in the phase equilibrium state. The other part was mounted and polished, and SEM and EPMA were employed to quantitatively analyze the microscale compositions of the different phases in the quenched samples. An accelerating voltage of 20 kV and a probe current of 20 nA were used for the EPMA measurements, and the average accuracy on the main elements was ± 1 wt%. CaSiO_3 (K2(z), GSB A70015) was used as the standard to quantitatively analyze CaO and SiO_2 , $\text{CeP}_5\text{O}_{14}$ (X21, GSB 01-1794-2004) was used as the standard for Ce_2O_3 , and CeF_3 (SZ3) was used as the standard for F. The compositions of these standard samples are as follows:

Table 4.1 Initial compositions for the CaO–SiO₂–CaF₂–Ce₂O₃ system (wt%)

Sample	CaO	CeO ₂	SiO ₂	CaF ₂
1	10.5	17.5	42.0	30.0
2	40.6	2.8	26.6	30.0
3	14.0	35.0	21.0	30.0
4	7.0	28.0	35.0	30.0
5	28.0	27.3	14.7	30.0
6	17.5	7.0	45.5	30.0
7	32.2	1.4	36.4	30.0
8	2.1	50.4	17.5	30.0
9	37.8	2.1	34.3	30.0
10	1.4	58.1	10.5	30.0
11	17.5	31.5	21.0	30.0
12	19.6	30.8	19.6	30.0
13	39.9	8.4	21.7	30.0
14	3.5	52.5	14.0	30.0
15	4.2	33.6	32.2	30.0
16	12.6	47.6	9.8	30.0
17	7.0	37.1	25.9	30.0
18	46.9	2.8	20.3	30.0
19	21.0	35.0	14.0	30.0
20	7.0	49.0	14.0	30.0

CaSiO₃: CaO[48.000%], SiO₂[50.940%], FeO[0.110%], MnO[0.280%]. CeP₅O₁₄: Ce₂O₃[31.640%], P₂O₅[68.310%]. CeF₃: F[28.920%], and Ce[71.080%]. For each phase, more than three different points were analyzed, and the average value was calculated.

4.1.1.3 Construction of Isothermal Phase Diagram for CaO–SiO₂–CaF₂–Ce₂O₃ System

The XRD patterns and SEM images showing the typical microstructures of the samples in the phase equilibrium state are shown in Figs. 4.2 and 4.3, respectively, which are the basis for constructing the isothermal section of the pseudo-ternary phase diagram of CaO–SiO₂–CaF₂–Ce₂O₃ system. The mineral compositions of the equilibrium phases in CaO–SiO₂–CaF₂–Ce₂O₃ system are determined as follows: Ca₄Si₂O₇F₂ (JCPDS Card No. 13-410), CaF₂ (JCPDS Card No. 77-2093), Ce_{9.33}(SiO₄)₆O₂ (JCPDS Card No. 54-618), Ce₂O₃ (JCPDS Card No. 74-1145), Ca₂SiO₄ (JCPDS Card No. 86-401), and SiO₂ (JCPDS Card No. 71-261). However, these results are the basic structures of the equilibrium phases indicated by the XRD

patterns and SEM–EDS images, which are not the exact chemical formulas of the equilibrium phases.

There is an incomplete occupancy relationship between Ca^{2+} and Ce^{3+} , as reported by Elwert et al. [26]. This exchange can be attributed to the similarity of ionic radii and oxygen coordination between Ca^{2+} and Re^{3+} . Therefore, the microscale chemical compositions of the equilibrium phases are quantitatively analyzed by EPMA measurement, and the EPMA results for each sample in the equilibrium state are given in Table 4.2. By comparing these results with those from XRD and SEM–EDS, two new solid solution phases of $\text{Ce}_{9.33-x}\text{Ca}_x(\text{SiO}_4)_4\text{O}_{5-0.5x}\text{F}_2$ and $\text{Ca}_2\text{SiO}_4(\text{Ce}_2\text{O}_3)$ are found in the phase equilibrium state of $\text{CaO-SiO}_2\text{-CaF}_2\text{-Ce}_2\text{O}_3$

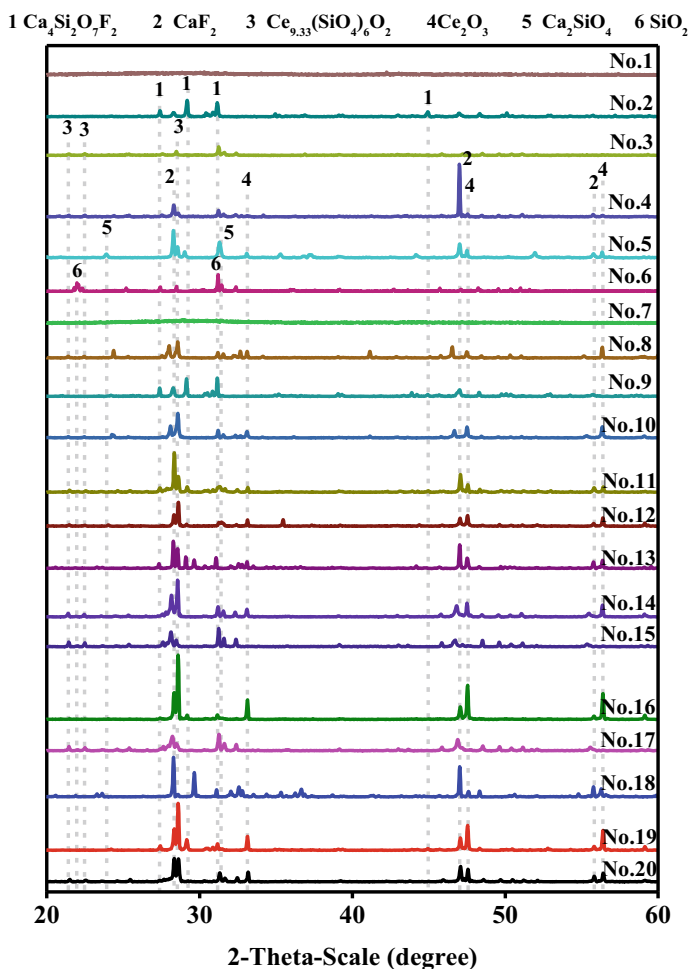


Fig. 4.2 XRD patterns of the 20 samples in the equilibrium state of $\text{CaO-SiO}_2\text{-CaF}_2\text{-Ce}_2\text{O}_3$ system at 1373 K

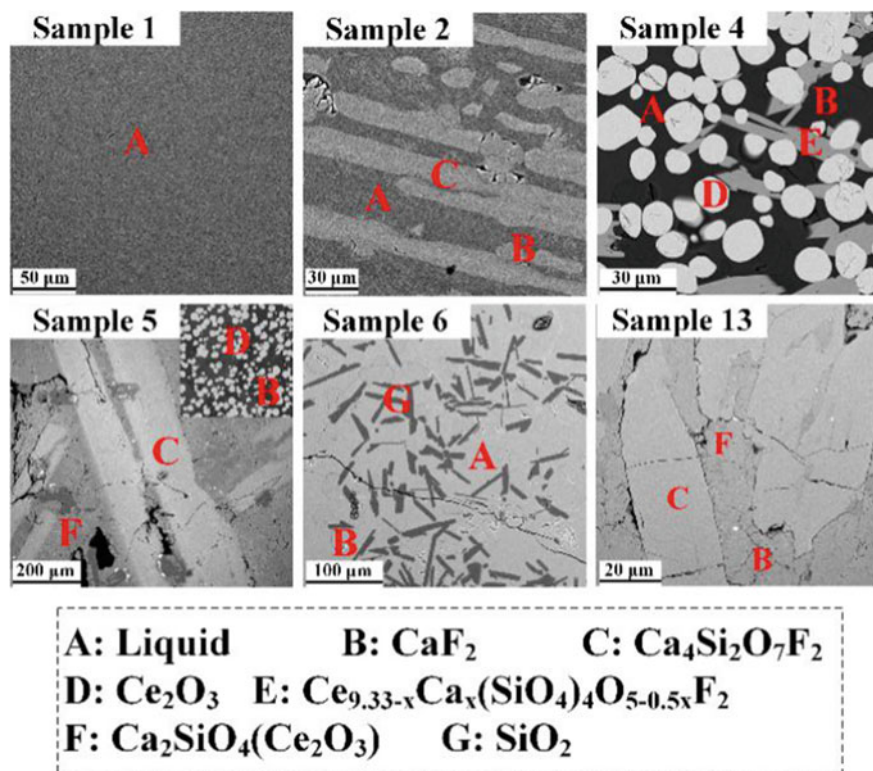


Fig. 4.3 Typical SEM images for the equilibrium phases in CaO–SiO₂–CaF₂–Ce₂O₃ system at 1373 K

system. Ce_{9.33-x}Ca_x(SiO₄)₄O_{5-0.5x}F₂ (cefluosil) evolved from Ce_{9.33}(SiO₄)₆O₂, where Ce³⁺ is partially replaced by Ca²⁺, while F⁻ occupies the position of some O²⁻, and oxygen vacancies balance the valence state. Ca₂SiO₄(Ce₂O₃) originates from Ca₂SiO₄ by partially substituting Ce³⁺ for Ca²⁺. Among these phases, the Ce₂O₃ content in the cefluosil phase is much higher than that in the Ca₂SiO₄(Ce₂O₃) phase; therefore, the cefluosil phase is preferred as the only RE-phase in this system.

On this basis, the phase equilibria of the CaO–SiO₂–CaF₂–Ce₂O₃ system are determined experimentally according to the zero-phase-fraction lines [27, 28] and Schreinemaker's rule [29, 30]. The ZPF line for each phase divides a two-dimensional phase diagram into two regions: on one side of the line, the phase occurs, while on the other side it does not. For drawing the isothermal sections of multi-component systems, the overlapping zero-phase-fraction (ZPF) lines are drawn firstly according to the phase equilibrium relationships of the experimental samples. As shown in Fig. 4.4a, ZPF lines of each phase are the approximate position of the phase boundaries, and the intersection of two ZPF lines is the intersection of four-phase boundaries. Subsequently, the trend of the phase boundaries is determined by using the

Table 4.2 Compositions of the equilibrium phases in CaO–SiO₂–CaF₂–Ce₂O₃ system at 1373 K (wt%)

Sample	Initial composition				Final composition			
	CaO	Ce ₂ O ₃	SiO ₂	CaF ₂	Phase	CaO	Ce ₂ O ₃	SiO ₂
L								
1	10.5	17.5	42	30	L	30.18 ± 0.3	18.23 ± 0.8	40.04 ± 0.7
7	32.2	1.4	36.4	30	L	51.29 ± 0.2	1.39 ± 0.5	31.8 ± 0.6
L + SiO ₂								
6	17.5	7	45.5	30	L	37.17 ± 0.1	8.46 ± 0.6	42.14 ± 0.9
					SiO ₂	0.88 ± 0.4	0.49 ± 0.5	97.4 ± 0.4
L + Ca ₄ Si ₂ O ₇ F ₂								
2	40.6	2.8	26.6	30	L	51.66 ± 0.1	2.7 ± 0.2	27.42 ± 0.7
					Ca ₄ Si ₂ O ₇ F ₂	57.56 ± 0.5	2.35 ± 0.3	29.81 ± 0.7
9	37.8	2.1	34.3	30	L	48.66 ± 0.9	4.85 ± 0.8	31.12 ± 0.6
					Ca ₄ Si ₂ O ₇ F ₂	58.59 ± 0.5	0.59 ± 0.3	30.19 ± 0.9
L + Ca ₂ SiO ₄ (Ce ₂ O ₃) + Ce ₂ O ₃ + CaF ₂								
5	28	27.3	14.7	30	Ce ₂ O ₃	0.56 ± 0.8	97.94 ± 0.2	0
					CaF ₂	60.7 ± 0.7	1.02 ± 0.1	0.04 ± 0.5
					Ca ₂ SiO ₄ (Ce ₂ O ₃)	53.63 ± 0.3	16.78 ± 0.4	27.83 ± 0.9
					L	65.16 ± 0.9	7.97 ± 0.8	26.32 ± 0.7
Ca ₄ Si ₂ O ₇ F ₂ + Ca ₂ SiO ₄ (Ce ₂ O ₃) + CaF ₂								
13	39.9	8.4	21.7	30	Ca ₄ Si ₂ O ₇ F ₂	56.28 ± 0.6	5.86 ± 0.3	27.51 ± 0.2
					Ca ₂ SiO ₄ (Ce ₂ O ₃)	56.7 ± 0.5	10.24 ± 0.7	29.62 ± 0.3
					CaF ₂	59.42 ± 0.7	1.39 ± 0.2	0.99 ± 0.8
18	46.9	2.8	20.3	30	Ca ₂ SiO ₄ (Ce ₂ O ₃)	60.72 ± 0.7	7.28 ± 0.7	31.88 ± 0.4

(continued)

Table 4.2 (continued)

Sample	Initial composition				Phase	Final composition			
	CaO	Ce ₂ O ₃	SiO ₂	CaF ₂		CaO	Ce ₂ O ₃	SiO ₂	F
					Ca ₄ Si ₂ O ₇ F ₂	56.68 ± 0.9	7.2 ± 0.8	26.48 ± 0.7	9.64 ± 0.2
					CaF ₂	59.23 ± 0.5	2.96 ± 0.2	0.93 ± 0.3	36.88 ± 0.4
L + Ce ₂ O ₃ + CaF ₂									
19	21	35	14	30	L	47.74 ± 0.3	3.63 ± 0.1	38.94 ± 0.7	9.69 ± 0.6
					Ce ₂ O ₃	1.31 ± 0.6	97.95 ± 0.4	0.22 ± 0.9	0.52 ± 0.8
					CaF ₂	58.31 ± 0.7	4.17 ± 0.2	0.06 ± 0.5	37.46 ± 0.4
						0.34 ± 0.3	98.16 ± 0.7	0.03 ± 0.1	1.47 ± 0.6
L + Ce _{0.33-<i>x</i>} Ca _{<i>x</i>} (SiO ₄) ₄ O _{5-0.5<i>x</i>} F ₂ + Ce ₂ O ₃ + CaF ₂									
3	14	35	21	30	Ce _{0.33-<i>x</i>} Ca _{<i>x</i>} (SiO ₄) ₄ O _{5-0.5<i>x</i>} F ₂	11.07 ± 0.5	66.48 ± 0.7	19.46 ± 0.2	2.99 ± 0.3
					L	31.16 ± 0.6	16.26 ± 0.2	34.79 ± 0.1	17.79 ± 0.9
					CaF ₂	57.56 ± 0.7	3.24 ± 0.3	0.14 ± 0.1	39.06 ± 0.8
					Ce ₂ O ₃				
4	7	28	35	30	L	39.86 ± 0.3	13.11 ± 0.8	31.77 ± 0.2	15.26 ± 0.4
					Ce ₂ O ₃	0.34 ± 0.4	98.16 ± 0.3	0.03 ± 0.1	1.47 ± 0.2
					Ce _{0.33-<i>x</i>} Ca _{<i>x</i>} (SiO ₄) ₄ O _{5-0.5<i>x</i>} F ₂	13.00 ± 0.2	63.98 ± 0.7	19.72 ± 0.3	3.3 ± 0.6
					CaF ₂	58.57 ± 0.7	2.49 ± 0.5	0.05 ± 0.3	38.89 ± 0.8
8	2.1	50.4	17.5	30	Ce _{0.33-<i>x</i>} Ca _{<i>x</i>} (SiO ₄) ₄ O _{5-0.5<i>x</i>} F ₂	10.33 ± 0.3	67.85 ± 0.9	18.68 ± 0.7	3.14 ± 0.2
					L	34.81 ± 0.4	14.58 ± 0.7	36.02 ± 0.1	14.59 ± 0.2
					CaF ₂	46.14 ± 0.2	18.46 ± 0.3	0.03 ± 0.4	35.37 ± 0.7
					Ce ₂ O ₃	0.13 ± 0.7	98.16 ± 0.8	0.05 ± 0.6	1.66 ± 0.4

(continued)

Table 4.2 (continued)

Sample	Initial composition				Phase	Final composition			
	CaO	Ce ₂ O ₃	SiO ₂	CaF ₂		CaO	Ce ₂ O ₃	SiO ₂	F
10	1.4	58.1	10.5	30	L	35.94 ± 0.9	15.65 ± 0.4	32.78 ± 0.3	15.63 ± 0.7
					CaF ₂	49.27 ± 0.3	14.73 ± 0.6	0.03 ± 0.5	35.97 ± 0.8
					Ce _{0.33-x} Ca _x (SiO ₄) ₄ O _{5-0.5x} F ₂	10.63 ± 0.7	67.04 ± 0.1	18.36 ± 0.7	3.97 ± 0.9
					Ce ₂ O ₃	0.21 ± 0.4	98.39 ± 0.2	0.02 ± 0.3	1.38 ± 0.4
11	17.5	31.5	21	30	Ce _{0.33-x} Ca _x (SiO ₄) ₄ O _{5-0.5x} F ₂	15.2 ± 0.1	61.93 ± 0.2	20.1 ± 0.6	2.77 ± 0.4
					Ce ₂ O ₃	0.82 ± 0.3	98.36 ± 0.3	0.02 ± 0.6	0.8 ± 0.7
					CaF ₂	62.25 ± 0.8	0.49 ± 0.9	0.04 ± 0.2	37.22 ± 0.3
					L	37.86 ± 0.4	2.23 ± 0.7	59.41 ± 0.5	0.5 ± 0.8
12	19.6	30.8	19.6	30	L	37.18 ± 0.2	12.97 ± 0.2	49.3 ± 0.8	0.55 ± 0.6
					Ce _{0.33-x} Ca _x (SiO ₄) ₄ O _{5-0.5x} F ₂	13.32 ± 0.8	64.47 ± 0.3	18.96 ± 0.3	3.25 ± 0.8
					CaF ₂	59.97 ± 0.1	1.87 ± 0.6	0.02 ± 0.7	38.14 ± 0.9
					Ce ₂ O ₃	0.42 ± 0.3	98.05 ± 0.8	0.03 ± 0.4	1.5 ± 0.2
14	3.5	52.5	14	30	Ce ₂ O ₃	0.33 ± 0.6	98.29 ± 0.5	0.01 ± 0.3	1.37 ± 0.2
					Ce _{0.33-x} Ca _x (SiO ₄) ₄ O _{5-0.5x} F ₂	12.08 ± 0.2	66.75 ± 0.2	17.91 ± 0.4	3.26 ± 0.8
					CaF ₂	52.88 ± 0.6	9.13 ± 0.6	0.05 ± 0.1	37.94 ± 0.6
					L	25.83 ± 0.8	13.64 ± 0.2	50.49 ± 0.3	10.04 ± 0.8
15	4.2	33.6	32.2	30	L	22.77 ± 0.7	15.38 ± 0.8	52.57 ± 0.2	9.28 ± 0.5
					Ce _{0.33-x} Ca _x (SiO ₄) ₄ O _{5-0.5x} F ₂	11.94 ± 0.3	66.72 ± 0.6	17.81 ± 0.1	3.53 ± 0.2
					CaF ₂	50.69 ± 0.9	12.26 ± 0.4	0.1 ± 0.8	36.95 ± 0.8
					Ce ₂ O ₃	0.46 ± 0.2	98.12 ± 0.6	0.07 ± 0.2	1.35 ± 0.3

(continued)

Table 4.2 (continued)

Sample	Initial composition				Phase	Final composition			
	CaO	Ce ₂ O ₃	SiO ₂	CaF ₂		CaO	Ce ₂ O ₃	SiO ₂	F
16	12.6	47.6	9.8	30	L	51.37 ± 0.5	1.05 ± 0.8	40.01 ± 0.2	7.57 ± 0.9
					Ce _{0.33-x} Ca _x (SiO ₄) ₄ O _{5-0.5x} F ₂	13.32 ± 0.7	67.21 ± 0.6	16.7 ± 0.3	2.77 ± 0.7
					Ce ₂ O ₃	2.93 ± 0.2	94.76 ± 0.2	0.37 ± 0.4	1.94 ± 0.6
					CaF ₂	56.13 ± 0.1	10.57 ± 0.6	0.15 ± 0.8	33.15 ± 0.7
17	7	37.1	25.9	30	Ce _{0.33-x} Ca _x (SiO ₄) ₄ O _{5-0.5x} F ₂	13.66 ± 0.3	64.86 ± 0.6	17.33 ± 0.8	4.15 ± 0.2
					L	36.94 ± 0.7	1.51 ± 0.9	60.37 ± 0.5	1.18 ± 0.4
					CaF ₂	53.33 ± 0.6	8.43 ± 0.3	0.07 ± 0.1	38.17 ± 0.9
					Ce ₂ O ₃	1.44 ± 0.4	96.23 ± 0.3	0.73 ± 0.3	1.6 ± 0.6
20	7	49	14	30	Ce _{0.33-x} Ca _x (SiO ₄) ₄ O _{5-0.5x} F ₂	12.66 ± 0.9	65.75 ± 0.8	18.84 ± 0.2	2.75 ± 0.2
					CaF ₂	58.31 ± 0.3	4.17 ± 0.2	0.06 ± 0.3	37.46 ± 0.7
					L	34.89 ± 0.1	3.77 ± 0.4	60.96 ± 0.9	0.38 ± 0.6
					Ce ₂ O ₃	0.31 ± 0.7	98.13 ± 0.5	0.19 ± 0.6	1.37 ± 0.8

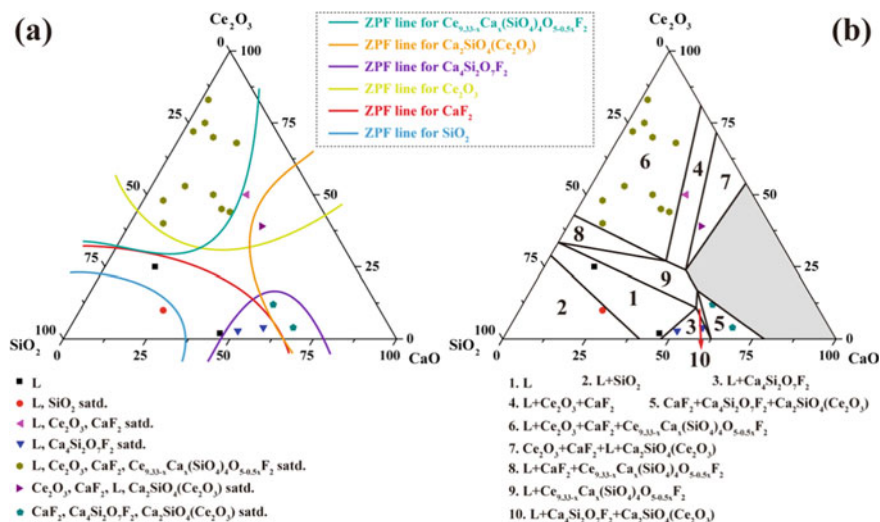


Fig. 4.4 **a** ZPF lines of each phase; **b** isothermal phase equilibria diagram of CaO–SiO₂–CaF₂–Ce₂O₃ system at 1373 K with fixed CaF₂ component

Schreinemaker's rule, where the extended lines of the boundary of a single-phase region enter a three-phase region or two different two-phase regions, respectively.

Accordingly, the isothermal pseudo-ternary phase equilibria diagram of CaO–SiO₂–CaF₂–Ce₂O₃ system at 1373 K is constructed in Fig. 4.4b. All the boundaries in Fig. 4.4b are drawn as the straight lines because there is no information on their curvature. The boundaries should be strictly straight for invariant equilibria only for four-phase fields in the present case of four components and constant temperature (T) and pressure (P). The phase relations in the area indicated by light gray are not covered in this study. The isothermal sections in the isothermal phase equilibria diagram not only provide the basic thermodynamic data for phase equilibria of REEs in REE-bearing slag, but also provide the necessary information for sustainable utilization of REEs in the REE-bearing slag. Based on the phase equilibria of REEs in the system, cefluosil is found to be a favorable stable phase of REEs, and fully enriching REEs into cefluosil in its equilibrium region can be beneficial for the efficient separation and recovery of REEs in REE-bearing slag.

4.1.2 Phase Equilibria of RE-Phase in CaO–SiO₂–CaF₂–Ce₂O₃ System

Phase compositions and concentration of REEs are the main factors affecting the efficient and economical utilization of REEs in REE-bearing slag. However, the phase compositions of REEs in REE-bearing slag are divergent, and the formation

and transformation information of RE-phases are unclearly [31, 32]. Based on the phase equilibria of $\text{CaO-SiO}_2\text{-CaF}_2\text{-Ce}_2\text{O}_3$ system, the typical components (CaO : 21 wt%, SiO_2 : 35 wt% CaF_2 : 30 wt%, Ce_2O_3 : 14 wt%) according to the composition of industrial REE-bearing slag are selected, and the phase equilibria of RE-phase in $\text{CaO-SiO}_2\text{-CaF}_2\text{-Ce}_2\text{O}_3$ system are further investigated, to provide the basic thermodynamic data for crystallization and separation of REEs in REE-bearing slag.

4.1.2.1 Experimental Procedure

According to the isothermal pseudo-ternary phase diagram of $\text{CaO-SiO}_2\text{-CaF}_2\text{-Ce}_2\text{O}_3$ system, a typical component for REE-bearing slag (CaO : 21 wt%, SiO_2 : 35 wt% CaF_2 : 30 wt%, Ce_2O_3 : 14 wt%) was selected to investigate the phase equilibria of the RE-phase in $\text{CaO-SiO}_2\text{-CaF}_2\text{-Ce}_2\text{O}_3$ system at various temperatures. First, the formation behavior of the RE-phase in the system was observed in situ via high-temperature confocal laser scanning microscope (CLSM). A 1.5 g sample was placed in a dense alumina crucible with an inner diameter (ID) of 7.9 mm and a height (H) of 3.5 mm, which was placed in the heating furnace under CLSM. A vacuum was firstly generated before the CO into the CLSM, and the sample was rapidly heated from 298 to 1673 K at a rate of 50 K/min under a CO atmosphere and then cooled slowly at a rate of 1 K/min to 1373 K.

The phase equilibria experiment of the RE-phase in $\text{CaO-SiO}_2\text{-CaF}_2\text{-Ce}_2\text{O}_3$ system was verified by the quenching method in a vertical water-quenching furnace. A total of 20 g of the sample was heated to 1673 K under CO atmosphere in the constant temperature zone of the vertical water-quenching furnace and then cooled with a slow cooling rate of 1 K/min to 1573, 1473, or 1373 K. After holding the sample at each target temperature for 120 min, the crucible was immediately quenched in water. Subsequently, the microstructures and elemental compositions of the samples were acquired using SEM-EDS to confirm the phase equilibria of the RE-phase in $\text{CaO-SiO}_2\text{-CaF}_2\text{-Ce}_2\text{O}_3$ system at each target temperature.

4.1.2.2 Phase Equilibria of RE-Phase

According to the phase equilibria of $\text{CaO-SiO}_2\text{-CaF}_2\text{-Ce}_2\text{O}_3$ system, the composition range of the REE-bearing slags is commonly located in the two-phase equilibrium area of the liquid and ceffluosil. Thus, the typical component (CaO : 21 wt%, SiO_2 : 35 wt% CaF_2 : 30 wt%, Ce_2O_3 : 14 wt%) was selected based on the industrial conditions and composition of REE-bearing slag. In addition, the phase equilibria of RE-phase in $\text{CaO-SiO}_2\text{-CaF}_2\text{-Ce}_2\text{O}_3$ system at various temperatures are studied using dynamic techniques, including the in situ observation and the quenching method combined with offline analysis.

The observation of $\text{CaO-SiO}_2\text{-CaF}_2\text{-Ce}_2\text{O}_3$ system (CaO : 21 wt%, SiO_2 : 35 wt% CaF_2 : 30 wt%, Ce_2O_3 : 14 wt%) with decreasing temperature observed by high-temperature CLSM is shown in Fig. 4.5. Figure 4.5 reveals that when the temperature

is above 1450 K, the system is in a fully molten state. When the temperature is reduced to 1450 K, fine needle-like crystals of cefluosil begin to appear in the molten slag. The results suggest that the exact initial crystallization temperature of cefluosil in the system is 1450 K. Moreover, the variations in the mineral compositions and microstructures of the cefluosil in the REE-bearing slag at different temperatures are confirmed by the SEM–EDS results as shown in Fig. 4.6. The in situ and offline results verify the conclusions that the REE-bearing slags with compositions of $\text{CaO} = 21 \text{ wt\%}$, $\text{SiO}_2 = 35 \text{ wt\%}$, $\text{CeO}_2 = 14 \text{ wt\%}$, and $\text{CaF}_2 = 30 \text{ wt\%}$ are in a molten state at the temperature above 1473 K, and the RE-phase (cefluosil) starts to crystallize from the molten slag between 1450 and 1373 K. In addition, Fig. 4.6 reveals that the cefluosil crystals have a hollow hexagonal prism shape. Based on the phase equilibria results of RE-phase, the formation and transformation conditions of cefluosil were acquired and provide the necessary thermodynamic data for the crystallization and separation of REEs in REE-bearing slag.

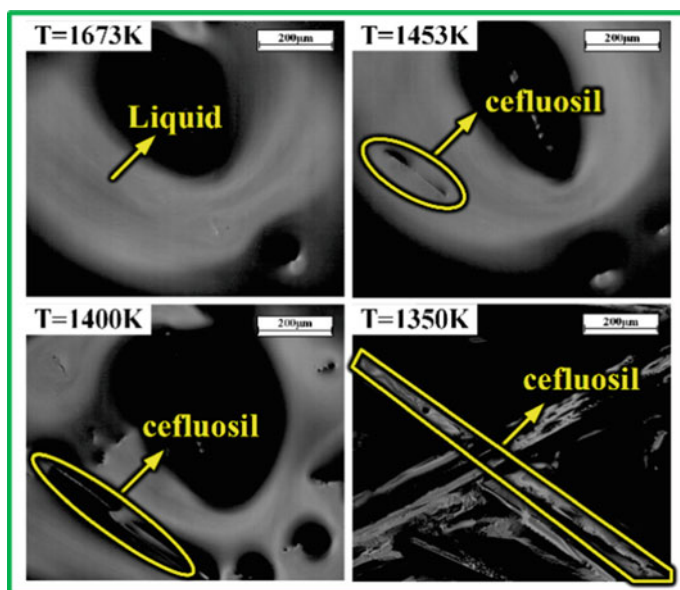


Fig. 4.5 In situ observation of CaO – SiO_2 – CaF_2 – Ce_2O_3 system (CaO : 21 wt%, SiO_2 : 35 wt% CaF_2 : 30 wt%, Ce_2O_3 : 14 wt%) with decreasing temperature by high-temperature CSLM

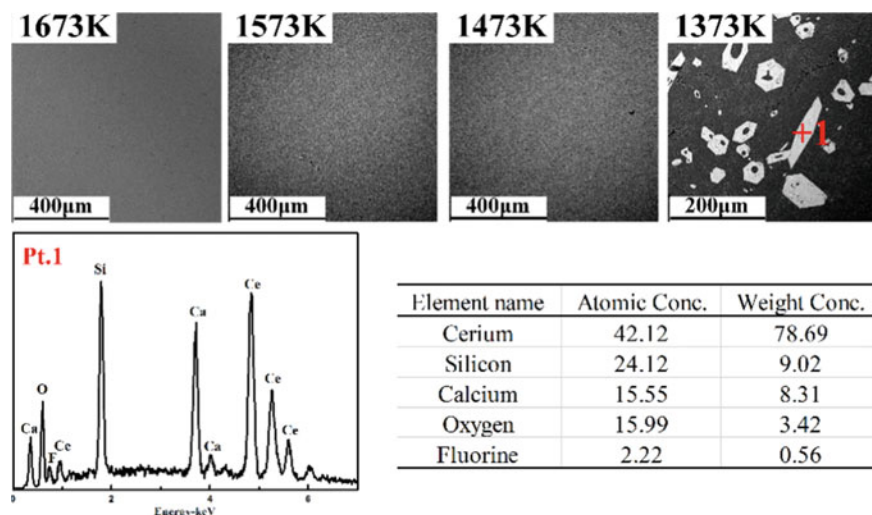


Fig. 4.6 Variations in SEM-EDS images of CaO–SiO₂–CaF₂–Ce₂O₃ system (CaO: 21 wt%, SiO₂: 35 wt% CaF₂: 30 wt%, Ce₂O₃: 14 wt%) at various temperatures: **a** 1673 K; **b** 1573 K; **c** 1473 K; **d** 1373 K

4.1.3 Isothermal Crystallization and Growth Kinetics of RE-Phase in CaO–SiO₂–CaF₂–Ce₂O₃ System

The separation and recovery of REEs in REE-bearing slag are determined to a large extent by the amount and grain size of RE-phase. To be specific, research on the crystallization and growth kinetics of RE-crystals can provide the information and guidance for the crystallization and separation of REEs in REE-bearing slag, while few studies are reported. Thus, the isothermal crystallization and growth kinetics of the RE-phase (cefluosil) are further studied, to provide the necessary kinetic information for crystallization and separation of REEs in REE-bearing slag.

4.1.3.1 Experimental Procedure

Based on the phase equilibria of the RE-phase in CaO–SiO₂–CaF₂–Ce₂O₃ system, the isothermal kinetics for the crystallization and growth of the RE-phase (cefluosil) were studied in a vertical water-quenching furnace. The slag with a typical component (CaO: 21 wt%, SiO₂: 35 wt% CaF₂: 30 wt%, Ce₂O₃: 14 wt%) was fully melted at 1673 K for 30 min, then rapidly cooled to various temperatures of 1420, 1390, and 1360 K with a cooling rate of 30 K/min, and kept at the target temperatures for different time of 1, 10, 20, 30, ..., 180 min, and one sample was taken out for water quenching every 10 min. The samples with different temperatures were quenched in the water-cooled chamber for different amounts of time, and then the

quenched samples were ground and polished. The morphology was observed by SEM-EDS, and the average grain sizes defined as the equivalent spherical diameters and the volume fractions of the RE-phase in different samples were analyzed using a Quantum 520 image analyzer. The values were statistically calculated from the average of ten fields in each sample.

4.1.3.2 Isothermal Crystallization and Growth Kinetics of RE-Phase

Based on the phase equilibria of ceffuosil in $\text{CaO-SiO}_2\text{-CaF}_2\text{-Ce}_2\text{O}_3$ system, the isothermal crystallization and growth kinetics of ceffuosil are studied. The typical micrographs of the ceffuosil crystals obtained isothermally at different temperatures for various time are illustrated in Fig. 4.7. A large number of dispersed and fine ceffuosil crystals with a hollow hexagonal shape rapidly crystallized at the beginning of the isothermal process at 1420, 1390, and 1360 K, as shown in Fig. 4.7a, d, g, respectively. The rapid crystallization of ceffuosil in the molten slag at the beginning of the isothermal process is mainly caused by the supersaturated concentration of ceffuosil in a non-equilibrium state. As the time increased from 1 to 90 min, the number of ceffuosil crystals decreases, but their size and volume fraction increase significantly. The growth of ceffuosil with increased time is mainly caused by the supersaturation and grain coarsening attributed to Ostwald coarsening [33].

Figure 4.8a shows the relationship between the volume fraction of ceffuosil crystals and the isothermal hold time. The volume fraction of ceffuosil crystals is revealed to increase rapidly at the beginning of the isothermal process, reaching a maximum value at 60 min, and remaining constant with a further increase in time. The results show that the crystallization of ceffuosil caused by supersaturated concentration is completed in a period at the beginning of constant temperature. In addition, the higher the hold temperature, the lower the volume fraction of ceffuosil. Because the higher the hold temperature is, the higher the solubility of ceffuosil is, and the less crystals precipitate. The transformed fraction (χ) is defined as the ratio of the volume fraction of ceffuosil at a certain time to the volume fraction at equilibrium, and its variations with aging time are shown in Fig. 4.8b. When $\chi < 1$, the crystallization of ceffuosil is in the dynamic region, and when $\chi = 1$, the crystallization is in the quasi-equilibrium state region. In general, the transformation fraction $\chi(t)$ for crystallization of ceffuosil in the dynamic region can be described by the JMAK [34] equation:

$$\chi(t) = 1 - \exp(-kt^n), \quad (4.1)$$

where k is the dynamics constant and n is the time factor.

In addition, Eq. (4.2) can be derived from Eq. (4.1):

$$\ln[-\ln(1 - \chi(t))] = n \ln t + \ln k. \quad (4.2)$$

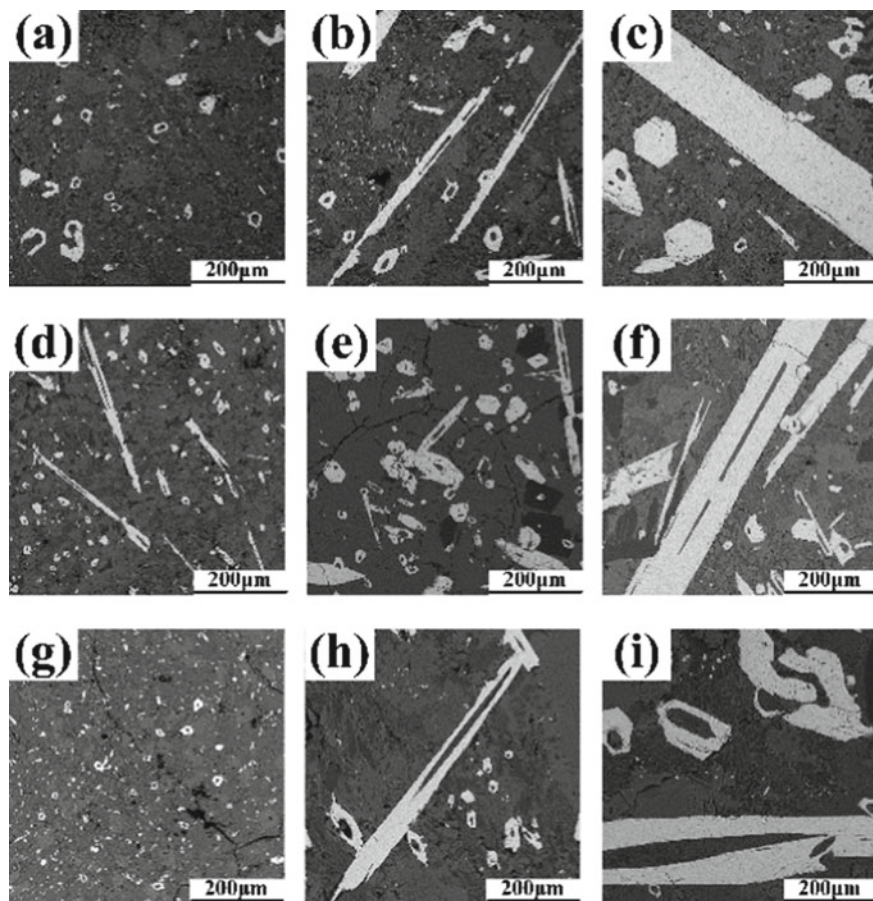


Fig. 4.7 Typical micrographs of the cefluosil crystals obtained isothermally at different temperatures with various time: **a** 1420 K–1 min; **b** 1420 K–10 min; **c** 1420 K–90 min; **d** 1390 K–1 min; **e** 1390 K–10 min; **f** 1390 K–90 min; **g** 1360 K–1 min; **h** 1360 K–10 min; **i** 1360 K–90 min

Figure 4.8c further illustrates the curves of $\ln[-\ln(1 - \chi(t))]$ changing with $\ln t$, which are basically straight lines, demonstrating that the JMAK equation is suitable for describing the crystallization kinetics of cefluosil in the $\text{CaO-SiO}_2\text{-CaF}_2\text{-Ce}_2\text{O}_3$ system.

The relationship between the grain radius of cefluosil crystals and aging time is shown in Fig. 4.9a, which reveals that with the increasing aging time, the grain radius of cefluosil crystals increases rapidly at the beginning stage and more slowly at the later stage. At the beginning stage, the growth of cefluosil is caused by supersaturated concentration; at the same time, the difference of particle size will lead to the coarsening and growth of cefluosil. Therefore, the growth of cefluosil is simultaneously controlled by the crystallization and coarsening. At the later stage, the grain

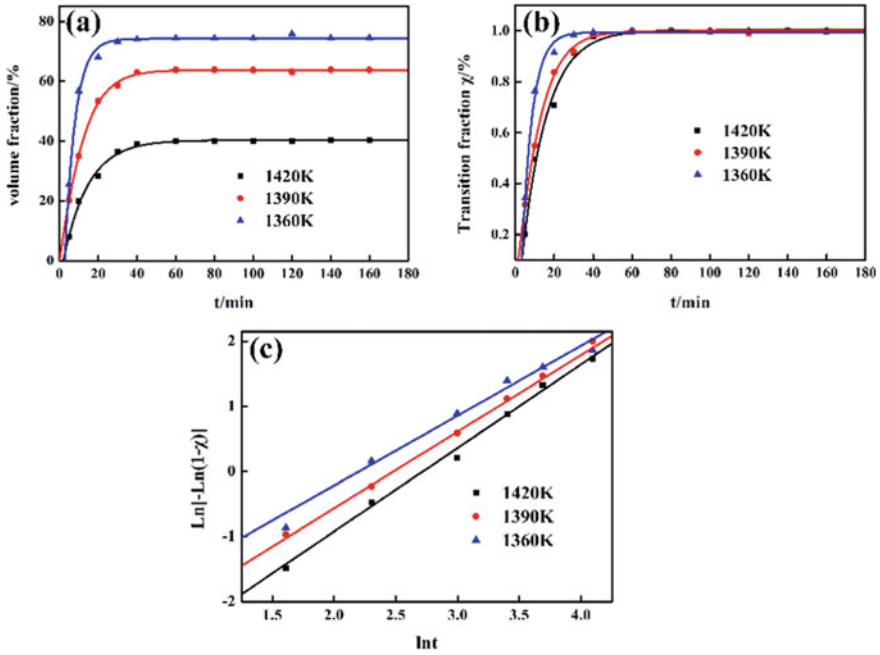


Fig. 4.8 **a** Variation in volume fraction of cefluosil crystals with aging time; **b** variation in the transformed fraction (χ) of cefluosil with aging time; **c** $\text{Ln}[-\text{Ln}(1-\chi(t))]$ against $\text{ln } t$ ($\chi < 1$)

radius of cefluosil continues to grow when the transformed fraction χ is close to 1, and the difference in the grain size of cefluosil leads to growth being controlled by coarsening energy. The growth of cefluosil in the non-equilibrium stage can be described by the following equation [35]:

$$\frac{d}{dt} \left(\frac{r^3}{x} \right) = \frac{k_1}{x} - k_2, \quad (4.3)$$

where k_1 and k_2 are constant; r is the average radius of cefluosil crystals; and χ is the transformed fraction.

The relationship between r^3 (i.e., the cubed radius of cefluosil) and time ($t \geq 60$ min) shown in Fig. 4.9b is approximately linear, which confirms that the growth of cefluosil in the non-equilibrium stage can be described by Eq. (4.3), as reported by Erukhimovitch [36]. In addition, the higher the hold temperature is, the smaller the viscosity of slag is, which is conducive to the diffusion, coarsening, and growth of cefluosil. Therefore, the grain size of cefluosil increases with the increasing of the constant temperature. Based on the crystallization and growth kinetic results of cefluosil, the amount and grain size of RE-phase can be selectively controlled in the REE-bearing slag and provide the necessary kinetic information for crystallization and separation in REE-bearing slag.

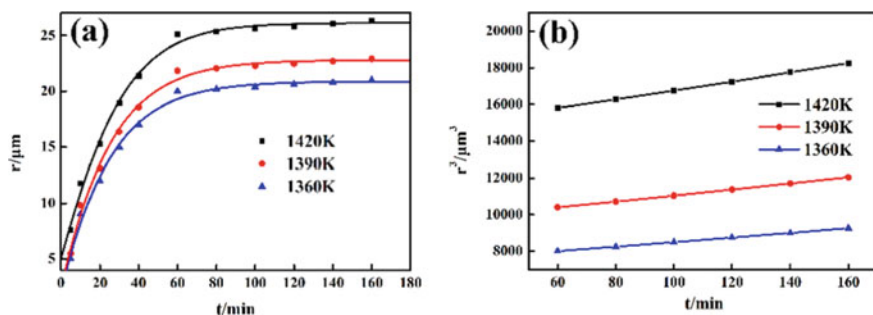


Fig. 4.9 **a** Variation in the grain radius of cefluosil crystals with aging time; **b** relationship between r^3 and time ($t \geq 60$ min)

4.2 Selective Separation of REEs in RE-Bearing Slag

4.2.1 Motion Behavior of Cefluosil in RE-Bearing Slag Under Super Gravity

Based on the necessary thermodynamic data and kinetic information for formation and transformation of REEs in RE-bearing slag, the selective separation of RE-phase (cefluosil) in RE-bearing slag enhanced by super gravity is conducted, and the motion and separation behavior of cefluosil in RE-bearing slag under super gravity are studied [16, 17].

4.2.1.1 Experimental Procedure

An amount of 30 g of the RE-bearing slag was put into a graphite crucible with the inner diameter of 19 mm and heated to target temperature (1373 K) based on the phase equilibria of the RE-phase (cefluosil) in $\text{CaO-SiO}_2\text{-CaF}_2\text{-Ce}_2\text{O}_3$ system, at which the REEs were fully enriched into RE-rich phase (cefluosil), while the slag was at a molten state. And then the centrifugal apparatus was started and adjusted to the specified angular velocity. The centrifugal apparatus was not shut off until the target time, then took out of the graphite crucible, and finally water-quenched the slag. The sample obtained under super gravity was sectioned longitudinally along the center axis. One part was crossly divided into two parts, which were characterized by XRD and XRF in order to obtain the respective mineral composition and chemical component. The other part was measured on the SEM and image analyzer by the line intercept method (average of ten fields) in order to gain the volume fraction and equivalent diameter of cefluosil phase. Simultaneously, the parallel experiment was carried out at 1373 K for 15 min under the normal gravity.

4.2.1.2 Motion Behavior of Cefluosil

Figure 4.10 shows cross section of the samples obtained by super gravity with the gravity coefficient $G = 500$, $t = 15$ min and $T = 1373$ K compared with the parallel sample with the gravity coefficient $G = 1$, $t = 15$ min, and $T = 1373$ K. As illustrated in Fig. 4.10b, a layered structure appears significantly in the sample obtained by the gravity coefficient of $G = 500$, with the upper area black and the bottom area gray, respectively. In contrast, the uniform structure presents in the parallel sample under the normal gravity, as shown in Fig. 4.10a.

Eight areas are divided into the layered sample obtained by super gravity as shown in Fig. 4.11, which are characterized by SEM for their microstructures, and the corresponding results are given in Fig. 4.12. Generally, the size of cefluosil crystals increases with the area approaching to the bottom of the sample; that is, the gradient size distribution of cefluosil crystals presents in the sample along the direction of super gravity. Moreover, an obvious interface appears between the slag and cefluosil in the layered sample, as shown in Fig. 4.12 (e). As shown in Fig. 4.12 (a) in (c), it is practically impossible to find any cefluosil crystals in the upper areas ranged from area (a) to area (c). Some cefluosil crystals with the characteristic of fine dispersing spicule appear in the upper side of the interface area (d), as shown in Fig. 4.12 (d). Under the force of super gravity, almost all of cefluosil crystals are concentrated to the lower areas ranged from (f) to (h), the size of equiaxed crystals increases with the area approaching to the bottom of the sample along the super gravity direction, and the peak value lies in the bottom area (h) of the layered sample.

Tables 4.3 and 4.4 present the variations of volume fraction of cefluosil crystals in different areas of the samples with different gravity coefficient at $t = 15$ min and $T = 1373$ K, and with different time at $G = 500$ and $T = 1373$ K, respectively, and the corresponding equivalent diameter of cefluosil crystals in different areas of the samples is shown in Figs. 4.13 and 4.14. It is in evidence that the volume fraction

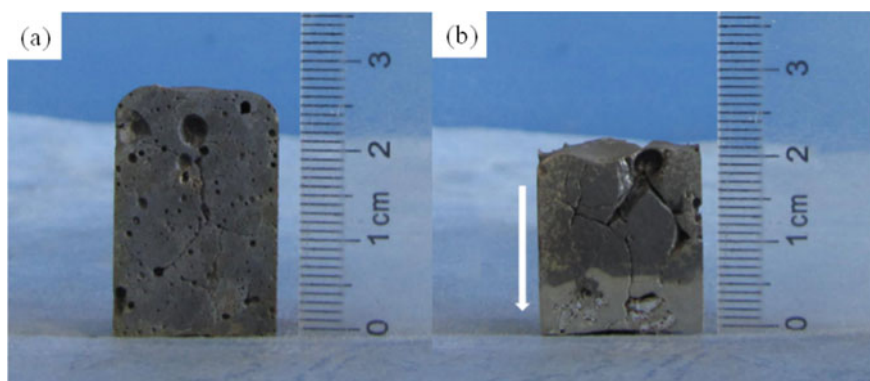


Fig. 4.10 Cross section of the samples obtained by super gravity compared with normal gravity: **a** $G = 1$, $t = 15$ min and $T = 1373$ K; **b** $G = 500$, $t = 15$ min and $T = 1373$ K

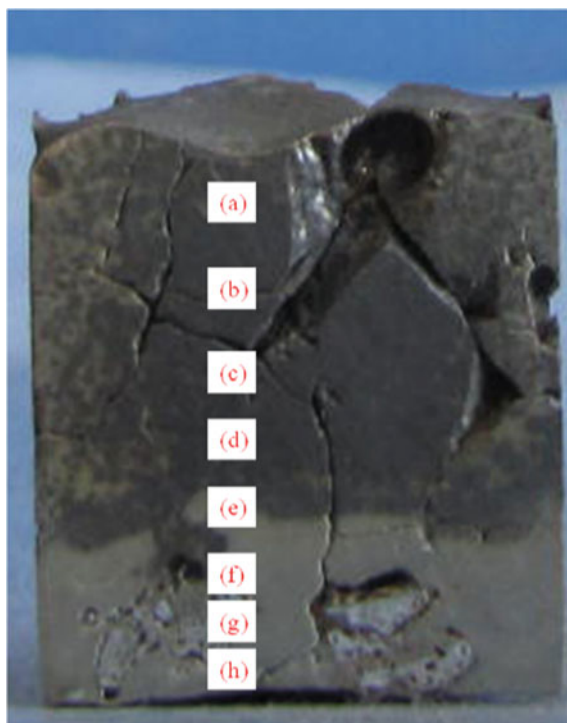


Fig. 4.11 Positions of eight areas of the layered sample obtained by super gravity at $G = 500$, $t = 15$ min, and $T = 1373$ K

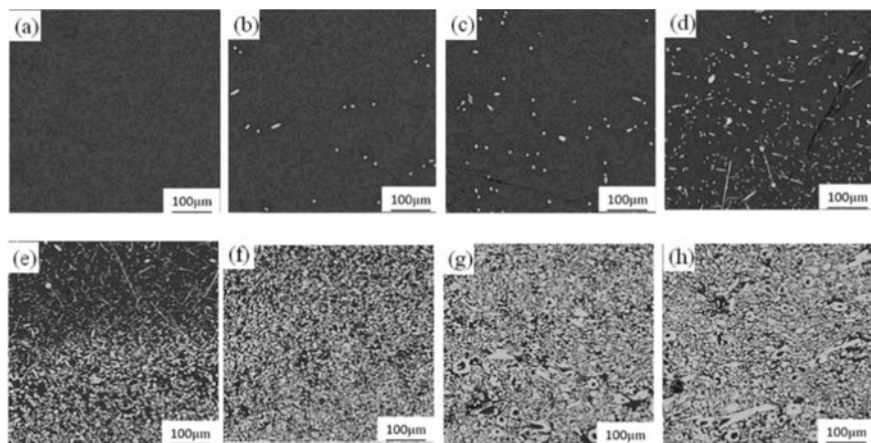


Fig. 4.12 Micrographs of eight areas of the layered sample obtained by super gravity at $G = 500$, $t = 15$ min and $T = 1373$ K

of ceffuosil crystals is approaching to zero in the upper area (a) to area (c), with the conditions of $G \geq 500$ and $t \geq 15$ min as given in Tables 4.3 and 4.4, while the volume fraction of ceffuosil crystals increases slightly in the bottom area (f) to area (h) along the direction of super gravity. Moreover, the particle distribution of ceffuosil crystals varies in different areas of the layered sample along the super gravity direction, as shown in Figs. 4.13 and 4.14. Generally, the equivalent diameter of ceffuosil crystals increases with the area approaching to the bottom of the sample, and the peak value appears in the bottom area (h).

In the conditions of $G = 500$, $t = 15$ min, and $T = 1373$ K, an overwhelming majority of ceffuosil crystals accumulates in the bottom as derived by super gravity, while the slag melt including CaF_2 and FeS phases moves to the upper along the opposite direction of super gravity. With the gravity coefficient of $G = 500$, $t = 15$ min and $T = 1373$ K, the mass fraction of RE_2O_3 in the ceffuosil phase is up to 23.29 wt%, while that of the slag phase is just 5.57%, as listed in Table 4.5. The recovery ratio of RE in the ceffuosil phase is up to 71.19%, as given in Table 4.6.

Table 4.3 Variations of volume fraction of ceffuosil crystals in different areas of the layered samples with different gravity coefficient at $t = 15$ min and $T = 1373$ K

Gravity coefficient	Areas (%)						
	(a)	(b)	(c)	(d)	(f)	(g)	(h)
200	0	3.13	7.58	12.24	54.29	63.32	64.46
350	0	0	4.36	7.69	57.49	65.21	67.84
500	0	0	0	4.86	60.62	68.88	69.35
650	0	0	0	3.11	61.83	70.21	70.83
800	0	0	0	1.97	63.35	71.69	71.33

Table 4.4 Variations of volume fraction of ceffuosil crystals in different areas of the layered samples with different time at $G = 500$ and $T = 1373$ K

Time (min)	Areas (%)						
	(a)	(b)	(c)	(d)	(f)	(g)	(h)
5	0	0	6.02	8.35	56.35	64.84	65.62
10	0	0	2.84	6.23	58.02	66.56	67.04
15	0	0	0	4.86	60.62	68.88	69.35
20	0	0	0	3.01	61.99	69.20	69.54
25	0	0	0	2.27	62.48	69.49	70.08

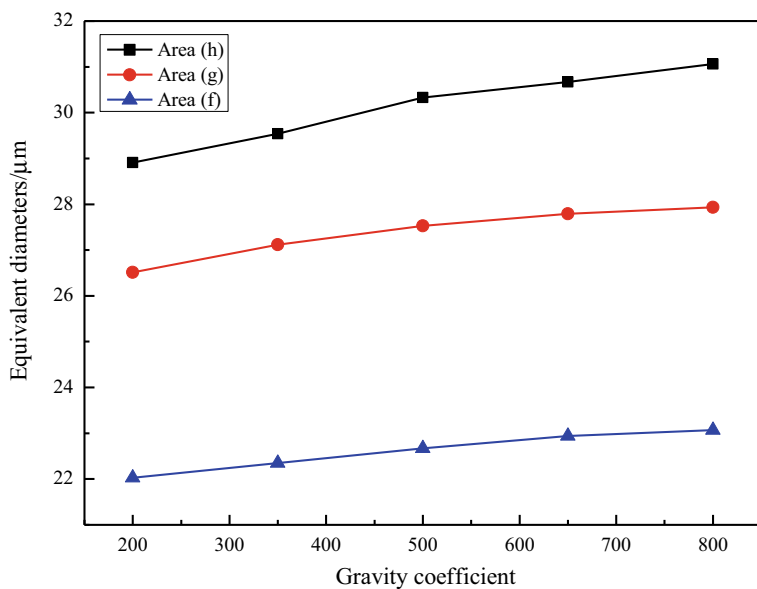


Fig. 4.13 Variations of equivalent diameters of cefluosil crystals in different areas of the layered samples with different gravity coefficient at $t = 15$ min and $T = 1373$ K

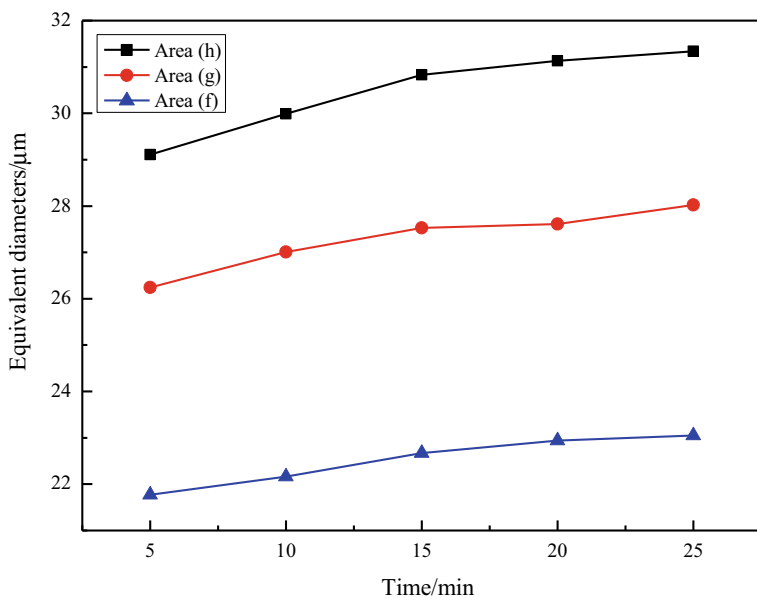


Fig. 4.14 Variations of equivalent diameters of cefluosil crystals in different areas of the layered samples with different time at $G = 500$ and $T = 1373$ K

Table 4.5 Chemical compositions of cefluosil and slag phases obtained by super gravity (wt%)

Phases	CaF ₂	SiO ₂	CaO	RE ₂ O ₃	FeO	BaO	MnO
Cefluosil	34.84	16.79	17.83	23.29	4.59	1.57	1.09
Slag	47.18	23.34	18.08	5.57	1.22	2.44	2.17
Parallel sample	42.94	20.98	17.89	12.01	2.58	2.04	1.56

Table 4.6 Recovery ratio of RE in the cefluosil phase obtained by super gravity (wt%)

Phases	Mass fraction	Mass fraction of RE ₂ O ₃	Recovery ratio of RE
Cefluosil phase	37.14	23.29	71.19
Slag phase	62.86	5.57	28.81

4.2.2 Separation of Cefluosil from RE-Bearing Slag by Super Gravity

Based on the selective crystallization and motion behaviors of RE-phase (cefluosil) in RE-bearing slag under the force of super gravity, selective separation of cefluosil from RE-bearing slag by super gravity is conducted further.

4.2.2.1 Experimental Procedure

An amount of 15 g of the RE-bearing slag was heated to 1373 K, and then the centrifugal apparatus was started and adjusted to the specified angular velocity at the constant 1373 K for 5 min. After that, the centrifugal apparatus was shut off, and the sample was quenched into water. The samples obtained by super gravity were sectioned longitudinally along the center axis. One was characterized by XRD and XRF in order to obtain the respective mineral composition and chemical component, while the other was measured by the SEM-EDS to gain the microstructure and elementary composition. Simultaneously, the parallel experiment was carried out at 1373 K for 5 min under normal gravity.

4.2.2.2 Separation Behavior of Cefluosil

Figure 4.15 shows cross section of the sample obtained by super gravity separation with the parameter of $G = 500$, $t = 5$ min, $T = 1373$ K compared with the parallel sample with the gravity coefficient of $G = 1$, $t = 5$ min, and $T = 1373$ K. Obviously, a uniform structure present in the parallel sample under the normal gravity is shown in Fig. 4.15a, while the RE-bearing slag is separated into two parts by the filter under the super gravity as shown in Fig. 4.15b, where the sample held back on the filter

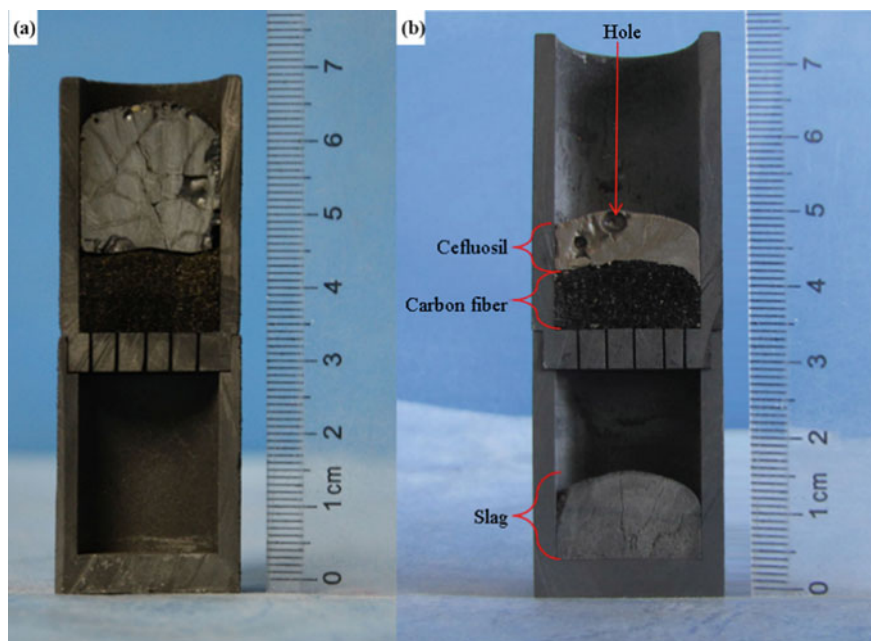


Fig. 4.15 Cross section of the samples obtained by super gravity compared with normal gravity: **a** $G = 1$, $t = 5$ min, $T = 1373$ K; **b** $G = 500$, $t = 5$ min, $T = 1373$ K

appears porosity, and the sample went through the filter presents gray, with a glassy state.

Combined with the X-ray diffraction analysis as shown in Fig. 4.16, almost all cefluosil crystals are held back on the filter, while the slag melt made up of CaF_2 goes through the filter and separates from the cefluosil. With the help of SEM and random EDXA analysis, the microstructure of the separated cefluosil and slag phases are displayed in Fig. 4.17 and Table 4.7. It is clear that three different phases with dark gray, light gray, and white are included in the parallel sample obtained under normal gravity, as shown in Fig. 4.17a. By constant, the white cefluosil crystals are fully blocked on the filter, while the dark gray slag melt is efficiently separated from the cefluosil and concentrates in the lower crucible, as compared in Fig. 4.17b, c.

As listed in Table 4.8, it is indicated that the mass fraction of RE_2O_3 in the separated cefluosil phase is up to 24.67 wt%, which are fully separated from RE-bearing slag under the force of super gravity, while the mass fraction of RE_2O_3 in the slag phase is only 4.51 wt%, but including 50.01 wt% of CaF_2 . The recovery ratio of RE in the separated cefluosil phase from RE-bearing slag is up to 76.47%, as listed in Table 4.9.

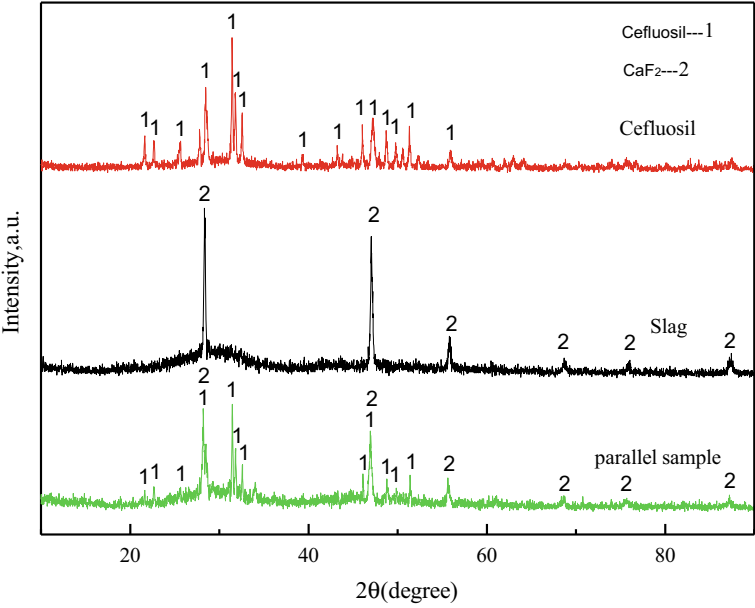


Fig. 4.16 X-ray diffraction of the samples obtained by super gravity

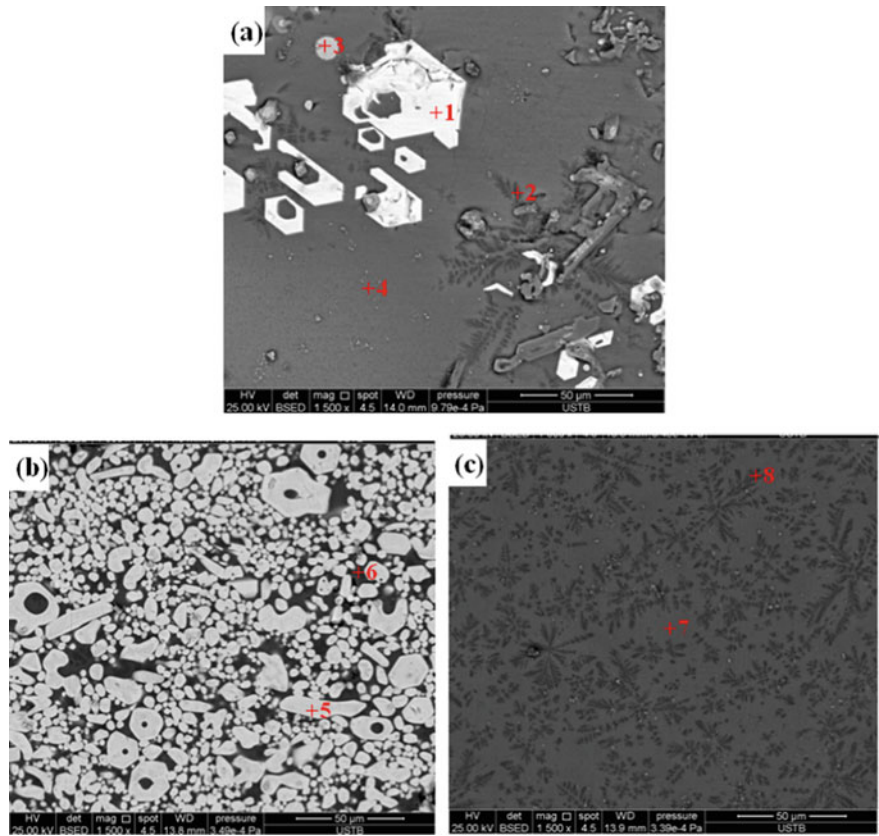


Fig. 4.17 Microstructure of separated samples compared with normal gravity: **a** normal gravity; **b** cefluosil; **c** slag

Table 4.7 EDS data of the various phases in different separated samples

No	Ce	La	O	Ca	Si	F	Mn	Mg	Fe	Al	S
Pt 1	44.73	20.73	10.67	14.16	9.72	3.97	0	0	0	0	0
Pt 2	0	0	0	55.56	3.80	38.16	1.21	0	0	0	0
Pt 3	0	0	0	7.90	1.92	0	8.13	0	51.36	0	29.06
Pt 4	0	0	35.78	25.79	15.04	10.69	7.12	2.35	1.74	0.79	0
Pt 5	45.43	18.10	14.59	11.62	10.26	0	0	0	0	0	0
Pt 6	0	0	30.21	40.04	9.24	18.32	0	1.39	0	0.80	0
Pt 7	0	0	27.44	39.29	8.54	22.04	0	1.59	0	0.96	0
Pt 8	0	0	0	56.07	2.30	41.63	0	0	0	0	0

Table 4.8 Chemical compositions of the separated ceffluosil and slag phases

Phases	CaF ₂	SiO ₂	CaO	RE ₂ O ₃	FeO	BaO	MnO
Ceffluosil phase	30.82	22.53	13.58	24.67	4.87	2.23	1.30
Slag phase	50.01	20.07	20.46	4.51	1.07	2.03	1.85
Parallel sample	42.94	20.98	17.89	12.01	2.58	2.04	1.56

Table 4.9 Recovery ratio of RE in the separated ceffluosil and slag phases

Phases	Mass fraction (%)	Mass fraction of RE ₂ O ₃ (%)	Recovery ratio of RE (%)
Ceffluosil phase	37.27	24.67	76.47
Slag phase	62.73	4.51	23.53

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Chapter 5

Selective Crystallization and Separation of REEs in RE-Concentrate



Abstract Reports the selective crystallization and separation of REEs in RE-concentrate. The mineral evolution and mineral reconstruction behaviors of RE-concentrate are reported, and the study on selective concentration and selective separation of cerium oxyfluoride in RE-concentrate is included in Sects. 5.1 and 5.2, respectively. The study on stepwise crystallization, stepwise concentration, and stepwise separation of REEs (Ce, La, Pr, Nd) in RE-concentrate is included in Sect. 5.3.

Rare earth elements (abbreviated as REEs), a group of chemically similar and physically similar metallic elements, are used as essential constituents in a wide range of applications, such as catalysts, metallurgical additives, and alloys, as well as in glass polishing and ceramics, and their low substitutability implies the need to secure a stable REEs supply [1, 2]. Therefore, the rare earths are proved to have progressively crucial significance in the transition to a green and low-carbon economy [3, 4].

The Bayan Obo RE-Nb-Fe deposit in China, the largest REEs resource over the world, has been primarily adopted by mineral process to extract iron resource currently [5]. As a result, massive REEs are transformed into RE-concentrate [6], which has a high rare earth content and complex mineral composition. It is another main by-product produced from rare earth ore except the RE-bearing slag reported in Chap. 4. Yet the REEs are difficult to be extracted through adopting conventional beneficiation methods [7], arising from the ultrafine dissemination of various primary rare earth minerals in the RE-concentrate [8].

Several hydrometallurgy methods incorporating various acids [9, 10], alkalis [11, 12], and chlorine [13, 14] have been proposed to extract rare earths from RE-concentrate. However, the hydrometallurgy methods are limited by a number of disadvantages, which include the large amounts of leachate consumed and leaching waste produced, slow leaching rate, and long production process [15]. At present, the low utilization rate of RE-concentrate causes itself to be massively disposed at the tailing dams. It leads directly to a huge waste of rare earth resources and contributes to serious environmental pollution.

Due to the complex mineral compositions and the ultrafine dissemination of rare-earth minerals, it is difficult to effectively separate the rare-earth minerals from other

minerals by the conventional beneficiation methods [16]. In view of the similar ionic radii of various rare-earth elements and the diversity between the rare earth and other elements [17], it will be beneficial to effectively separate rare earth from the RE-concentrate if the rare-earth elements could be enriched into a single mineral phase. As for the precipitation and crystallization behaviors of rare-earth minerals, most investigations are focused on the rare-earth-bearing blast furnace slag and the direct reduced rare-earth ore. Li [18] proposed that rare-earth elements precipitated as the calcium cerite phase from the rare-earth-bearing blast furnace slag with a lower CaF_2 content during slow cooling process. Ding proposed that rare-earth elements precipitated as the strip-shape cefluosil phase from the carbon-reduced rare-earth ore during furnace cooling process, while Li reported that the britholite-Ce phase precipitated from which during slow cooling process, respectively. Wang et al. [19] finds the britholite phase with a theoretical hexagonal structure precipitated from the gaseous reduced rare-earth ore. However, few investigations on RE-concentrate, which is characterized by a higher rare-earth content and various rare-earth minerals, are proposed due to the lack of thermodynamic data of rare earth.

If the RE-rich phases can be separated directly from other minerals at a specific high temperature, at which the rare-earth elements enriched into a solid phase while other minerals form into molten slag, it will be beneficial for effectively separating the two different phases, whereas it is infeasible to accomplish this task under the conventional conditions. Ramshaw and Mallinson [20] found that the mass transfer and mass migration of heterogeneous phases are improved immensely in a super gravity field, and thus the super gravity technology has been successfully applied to the preparation of functionally graded materials and removing impurities from alloy melts. Rajan et al. [21] prepared the functionally graded Al matrix composite components with the centrifugal casting method, and he found that the primary Si particles are dispersed toward inner periphery of the casting. Zhao et al. [22] reported that the refined grains of pure aluminum could be effectively removed in a super gravity field, and the grain size of aluminum decreased rapidly with gravity coefficient increasing. The super gravity field is confirmed to significantly enhance the directional migration and concentration of heterogeneous phases in the complex system. Consequently, the selective crystallization and separation of various RE-rich phases in RE-concentrate enhanced by a super gravity field are conducted in this chapter.

In this chapter, selective crystallization and separation of REEs in RE-concentrate is proposed, the mineral evolution and mineral reconstruction for selective separation of RE-phases in RE-concentrate and the stepwise crystallization, concentration, and separation of REEs (Ce, La, Pr, Nd) from the RE-concentrate are included in the following sections, respectively [8, 23–25].

Section 5.1 reports the mineral evolution and selective concentration of cerium oxyfluoride in RE-concentrate [8].

Section 5.2 reports the mineral reconstruction and selective separation of cerium oxyfluoride from RE-concentrate in reductive atmosphere [23].

Section 5.3 reports the stepwise crystallization and separation of REEs (Ce, La, Pr, Nd) in RE-concentrate [24, 25].

5.1 Mineral Evolution and Selective Concentration of Cerium Oxyfluoride in RE-Concentrate

5.1.1 Mineral Evolution and Enriching of REEs in RE-Concentrate

5.1.1.1 Experimental Procedure

Firstly, the mineral evolutions of rare-earth phases and the migrations of rare earth in various phases of Bayan Obo RE-concentrate with temperature rising were investigated by hot-quenching method at different temperature ranges combined with various offline analysis methods. About 200 g RE-concentrate powder was filled in 10 magnesia crucibles with an inner diameter of 18 mm and a high of 60 mm evenly, which were sequentially heated to 1323, 1373, 1423, 1473, 1523, 1573, 1623, 1673, 1723, and 1773 K under argon atmosphere in a muffle furnace at a heating rate of 1 K/min, respectively. After heating at each targeted temperature for 30 min, the magnesia crucibles were taken out and water-quenched immediately. Thereafter, the samples were measured by the X-ray diffraction method from a macroscopic view, combined with the SEM-EDS and EPMA methods from a microscopic view, to determine the variations in mineral compositions and microstructures of various rare-earth phases at different temperature ranges. Moreover, average of 10 fields of scanning electron micrograph in each sample was characterized further on image analyzer, and average of 10 sets of energy-dispersive spectrum data of each rare-earth phase was measured to conduct the statistical analysis on variations in the volume fractions of rare-earth phases and the RE contents in various rare-earth phases with temperature rising, respectively.

5.1.1.2 Mineral Evolution and Enriching Behaviors of REEs with Temperature

The variations in the mineral compositions and microstructures of various rare-earth phases in Bayan Obo RE-concentrate with temperature rising are shown in Figs. 5.1 and 5.2, respectively. Combined with the EDS data of various rare-earth phases obtained at different temperatures given in Table 5.1, it is obvious that the primary rare-earth mineral of bastnaesite ($[\text{Ce, La, Nb, Pr}]\text{CO}_3\text{F}$) is decomposed with temperature increasing, and the rare-earth phases transform from the original dispersed bastnaesite and monazite ($[\text{Ce, La, Nd, Pr}]\text{PO}_4$) minerals into the acicular britholite ($\text{Ca}_3[\text{Ce, La, Nd, Pr}]_2[(\text{Si, P})\text{O}_4]_3\text{F}$), the fine granular cerium oxyfluoride ($[\text{Ce, La, Pr, Nd}]_3\text{O}_4\text{F}_3$), the rare-earth ferrate ($[\text{Ce, La, Pr, Nd}]\text{FeO}_3$), and the monazite particles at a low-temperature range of 1423–1523 K as shown in Fig. 5.2a–c.

With temperature increasing further to a higher temperature range of 1573–1773 K as shown in Fig. 5.2d–h, the monazite is disappeared completely, and the britholite

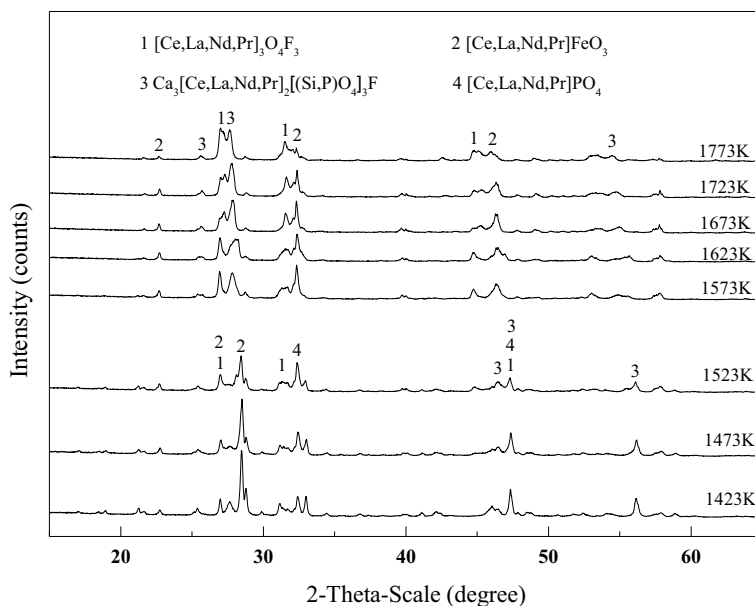


Fig. 5.1 Variation in XRD patterns of the RE-concentrate with temperature

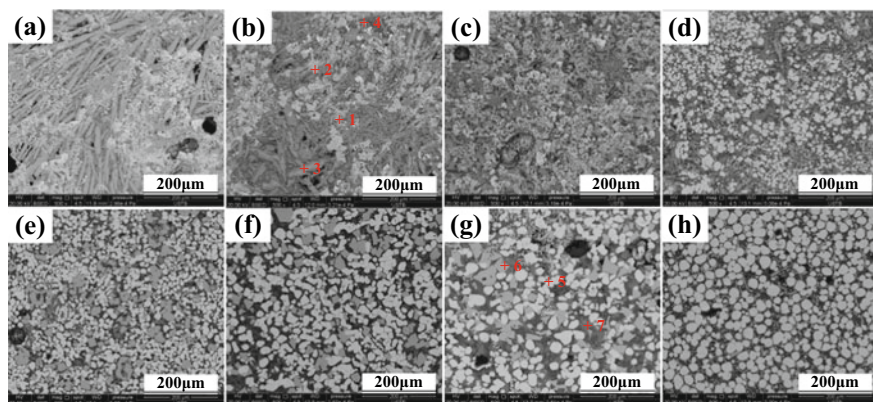


Fig. 5.2 Variation in SEM photographs of the RE-concentrate with temperature: **a** 1423 K; **b** 1473 K; **c** 1523 K; **d** 1573 K; **e** 1623 K; **f** 1673 K; **g** 1723 K; **h** 1773 K

and rare-earth ferrate decrease significantly instead of forming the slag melt, whereas the fine cerium oxyfluoride particles gradually aggregate and grow into the larger equiaxed crystals. As the variation in volume fractions of various rare-earth phases is shown in Fig. 5.3a, with temperature increasing from 1423–1523 K to 1573–1773 K, the volume fraction of monazite decreases from 6.20% to zero, the volume fraction of britholite decreases from 58.10 to 25.86%, and the volume fraction of

Table 5.1 Energy-dispersive spectrum data of various rare-earth phases at different temperature ranges (wt%)

No	Positions	O	P	C	F	Ca	Si	Fe	Ce	La	Pr	Nd
Pt.1	Figure 5.2b	26.64	—	—	4.27	—	—	—	34.13	23.49	4.41	7.06
Pt.2	Figure 5.2b	10.17	—	—	—	—	—	28.64	22.80	24.06	3.16	11.17
Pt.3	Figure 5.2b	16.34	8.48	—	11.23	16.40	1.55	—	12.25	20.33	3.30	10.12
Pt.4	Figure 5.2b	17.56	16.34	—	—	—	—	—	25.15	24.65	4.21	12.09
Pt.5	Figure 5.2g	10.29	—	—	2.15	—	—	—	80.16	7.4	0	0
Pt.6	Figure 5.2g	10.09	—	—	—	—	—	24.93	28.16	21.61	3.60	11.61
Pt.7	Figure 5.2g	28.67	12.74	—	4.92	33.94	1.50	—	7.19	8.99	0	2.05

rare-earth ferrate decreases from 15.80 to 8.26%. In contrast, the volume fraction of cerium oxyfluoride increases significantly from 20.23 to 65.88%. These indicate that the rare-earth phases transform further into the larger equiaxed cerium oxyfluoride crystals at the high-temperature range.

Moreover, Fig. 5.3b presents further the variation of RE contents in various rare-earth phases with temperature rising. Obviously, with temperature increasing from 1423–1523 K to 1573–1773 K, the mass fraction of RE in cerium oxyfluoride phase increases from 69.09 to 87.56 wt%, in which the mass fraction of cerium (Ce) increases significantly from 34.13 to 80.16 wt%, whereas the mass fraction of RE in britholite phase decreases from 46.00 to 18.23 wt%. It is evidenced that most rare-earth elements, especially the cerium, are enriched into the cerium oxyfluoride phase at the high-temperature range, which is further verified by the EPMA results of the cerium content in various rare-earth phases obtained at different temperature ranges as shown in Fig. 5.4.

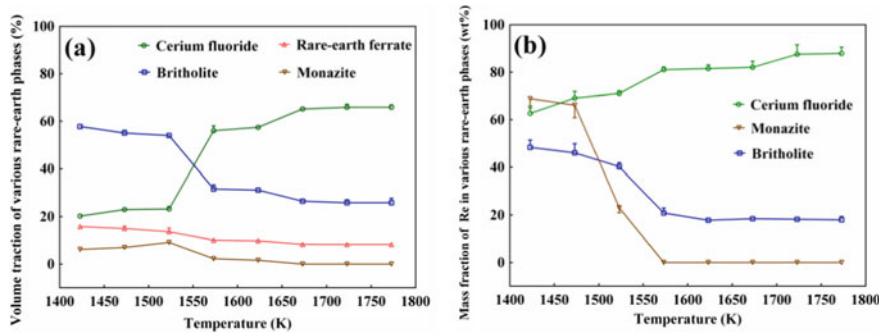


Fig. 5.3 Variations in volume fractions of rare-earth phases and the RE contents in various rare-earth phases with temperature: **a** volume fractions of rare-earth phases; **b** mass fractions of RE in rare-earth phases

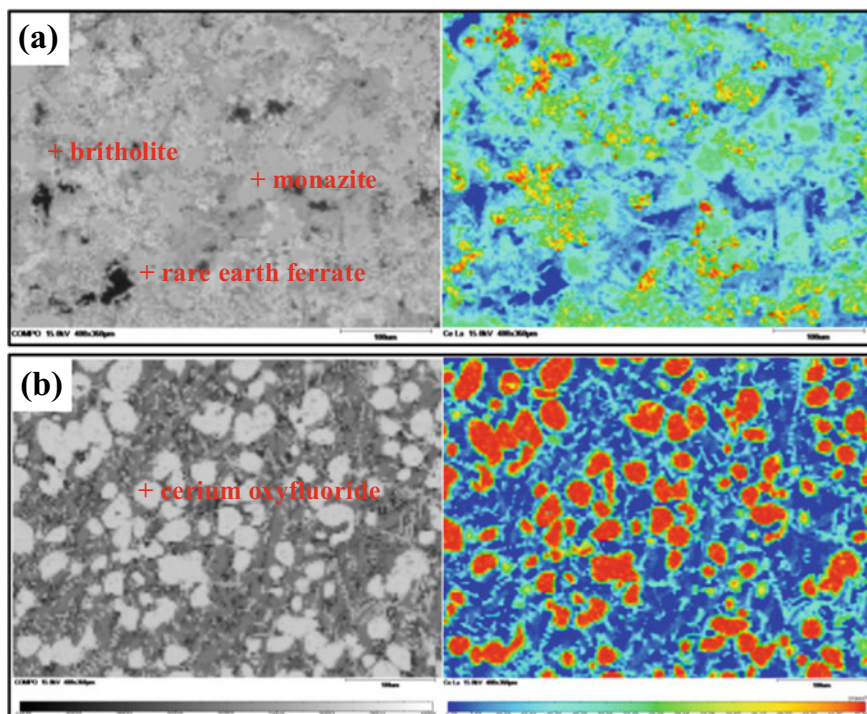


Fig. 5.4 EPMA results of the cerium content in various rare-earth phases at different temperature ranges: **a** 1423–1523 K; **b** 1573–1773 K

5.1.2 *Selective Concentration of Cerium Oxyfluoride in RE-Concentrate Under Super Gravity*

Based on the mineral evolutions of rare-earth phases and the migrations of rare earth in various rare-earth phases, it is indicated that the REEs are transformed to the cerium oxyfluoride phase with temperature increasing. Therefore, selective concentration of the cerium oxyfluoride phase from RE-concentrate is conducted under super gravity.

5.1.2.1 Experimental Procedure

To further separate the cerium oxyfluoride phase from RE-concentrate, selective concentration experiments were carried out at the high-temperature range of 1573–1773 K in a super gravity field. About 20 g RE-concentrate was placed into a same magnesia crucible and heated to 1623 K in the heating furnace of centrifugal apparatus for 10 min to make other minerals forming molten slag while keeping RE-rich phases in a solid state, and then the centrifugal apparatus was started and adjusted to an angular velocity of 1625 r/min to achieve gravity coefficient of $G = 600$. After

centrifugal rotating at the constant temperature for 5 min, the apparatus was shut off and the crucible was water-quenched, then the sample was sectioned longitudinally along the center axis to gain a macrograph, and the layered samples were analyzed further by SEM-EDS, XRD, and XRF methods for accurately characterizing the mineralogical constitutions and the chemical compositions of the separated samples obtained by super gravity.

5.1.2.2 Concentration Behavior of Cerium Oxyfluoride Phase

As the macrograph and micrograph of the samples obtained by super gravity with gravity coefficient of $G = 600$ at 1623 K are shown in Fig. 5.5a, b, two different layers with an explicit interface appear significantly in the sample. Combined with the SEM-EDS analysis of different areas in the layered sample, it is obvious that all the equiaxed cerium oxyfluoride crystals migrate along the super gravity direction due to its density that is greater than that of the slag, and thus the cerium oxyfluoride crystals concentrate at the bottom area, as shown in Fig. 5.6b, d. Conversely, the slag melt containing britholite crystals with a hollow hexagonal prism structure migrates to the upper area against the super gravity direction and is separated from the cerium oxyfluoride phase, as shown in Fig. 5.6a, c.

Furthermore, the chemical compositions of the separated samples obtained by super gravity are given in Table 5.2. After separating in a super gravity field with the gravity coefficient of $G = 600$ at 1623 K for 5 min, the mass fraction of $\sum \text{REO}$ in the cerium oxyfluoride phase is up to 57.37 wt%, and that of CeO_2 is up to 32.76 wt%. In contrast, the mass fractions of $\sum \text{REO}$ and CeO_2 in the britholite containing slag phase are decreased to 34.44 wt% and 17.07 wt%, respectively.

As described in Fig. 5.7, most rare-earth elements are enriched and transformed into the cerium oxyfluoride crystals, while other minerals are formed to the slag melt

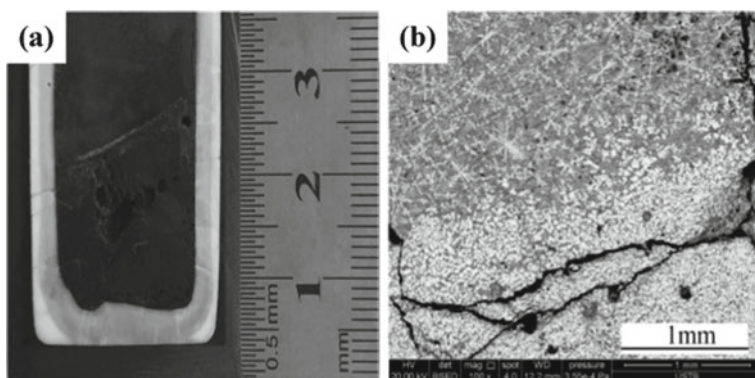


Fig. 5.5 Macrograph and micrograph of the layered samples obtained by super gravity: **a** vertical profile; **b** SEM image of layered interface

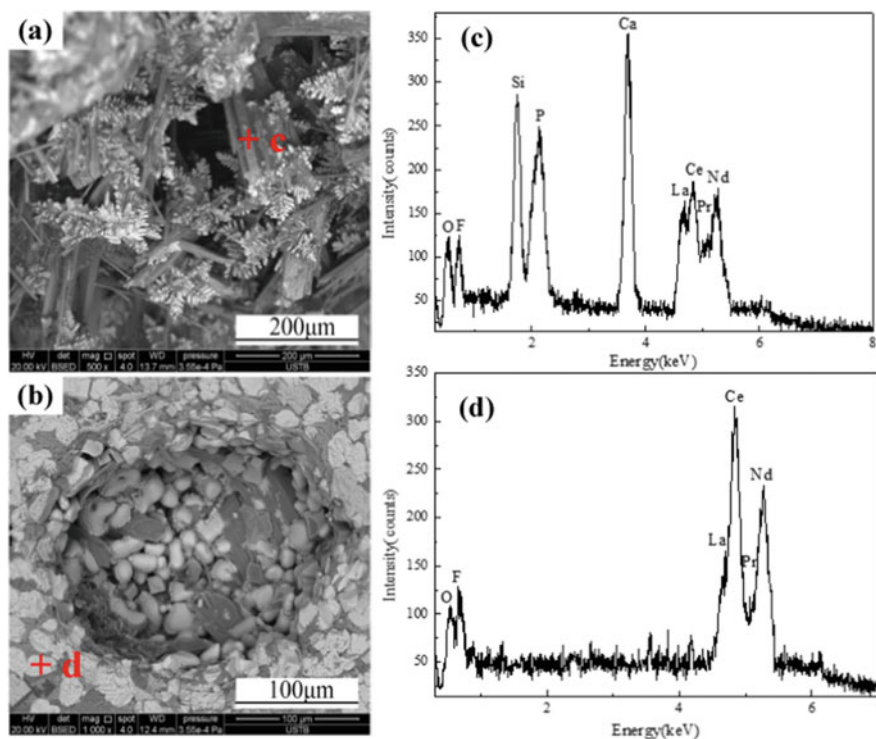


Fig. 5.6 SEM-EDS images of the separated samples obtained by super gravity: **a** and **c** SEM-EDS images of britholite phase; **b** and **d** SEM-EDS images of cerium oxyfluoride phase

at the high-temperature range of 1573–1773 K. However, the viscosity of slag melt increases with the existence of cerium oxyfluoride crystals, and so the crystals are difficult to move or aggregate thereby dispersing among the slag melt in the normal gravity field. In case of a super gravity field, the diffusion rate of cerium oxyfluoride crystals is enhanced significantly, all of which migrate along the super gravity direction as a result of the density difference with slag melt, which concentrates at the bottom area and is effectively separated from the slag melt. Moreover, the interfacial free energy between the crystals and slag melt increased in a super gravity field, and thus the super gravity forces the fine cerium oxyfluoride crystals aggregated and grown further into the larger crystals.

Table 5.2 Chemical compositions of the separated samples obtained by super gravity (wt%)

Phases	CaO	P ₂ O ₅	Fe ₂ O ₃	SO ₃	F	SiO ₂	MgO	BaO	MnO	Ce ₂ O ₃	La ₂ O ₃	Nd ₂ O ₃	Pr ₆ O ₁₁
Cerium oxyfluoride phase	9.66	9.05	7.84	0.25	11.38	0.96	2.23	1.01	0.25	32.76	13.54	9.94	1.13
Britholite containing slag	15.34	14.98	8.38	0.38	18.05	1.22	4.91	1.81	0.49	17.07	10.36	6.32	0.69

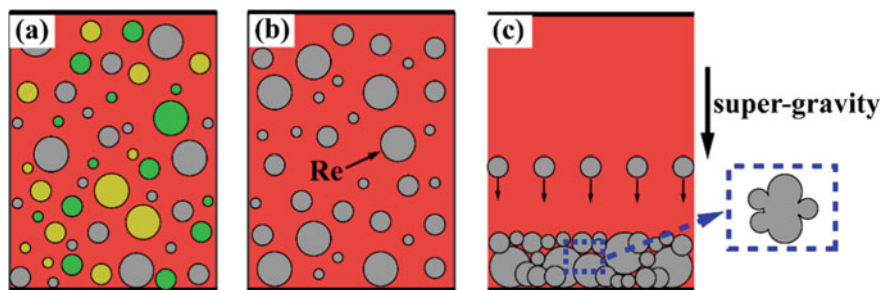


Fig. 5.7 Systematic diagram of concentration and growth process of cerium oxyfluoride crystals in a super gravity field

5.2 Mineral Reconstruction and Selective Separation of Cerium Oxyfluoride in Reductive Atmosphere

5.2.1 Mineral Reconstruction and REEs Enrichment in RE-Concentrate Under Reductive Atmosphere

Based on the mineral evolutions of rare-earth phases and the migrations of rare earth in RE-concentrate with temperature, the mineral reconstruction for selectively enriching REEs from the RE-concentrate is conducted under reductive atmosphere [8, 23].

5.2.1.1 Experimental Procedure

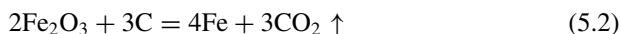
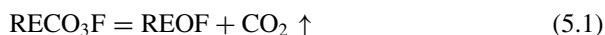
The mineral reconstruction of RE-concentrate was investigated further through conducting the TGA and the hot-quenching method, while the whole process would be incorporated with various ex-situ characterization techniques. Firstly, a certain amount of activated carbon powder (6N), which was calculated from the oxygen contents in the iron oxide and monazite, was added into the RE-concentrate. Subsequently, 280 mg of the mixed powder was put into an alumina crucible (I.D. 8 mm and H. 4 mm), which was measured in a TGA ranging from 323 to 1773 K with a heating rate of 10 K/min under a pressure of 1 bar to attain the mass losses of various reactions due to the rising temperature. Furthermore, a total of 250 g of the mixed powder was filled evenly into 5 graphite crucibles (I.D. 19 mm and H. 80 mm). Afterward, the five samples were heated to 1373 K, 1473 K, 1573 K, 1673 K, and 1773 K, respectively, under an argon atmosphere in a muffle furnace with a heating rate of 1 K/min. After holding the samples for 30 min at each target temperature, the crucibles were promptly removed from the furnace and water-quenched. Subsequently, the mineral compositions and microstructures of various rare earth phases

attained at different temperatures were analyzed by using the XRD and SEM–EDS methods.

5.2.1.2 Mineral Reconstruction and Enriching Behaviors of REEs

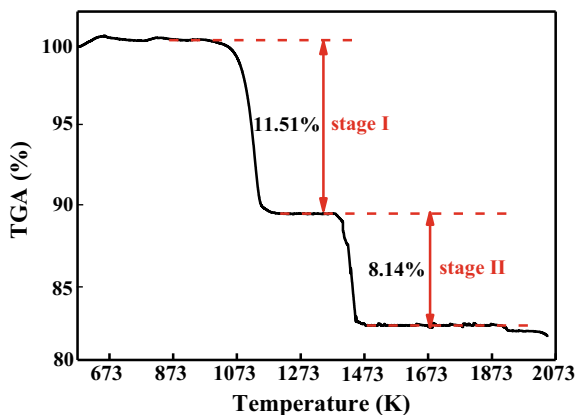
The TGA curve of the mixed powder of RE-concentrate and activated carbon with rising temperature is shown in Fig. 5.8. Two mass losses occur at the temperature ranges of 1023–1123 K (stage I) and 1373–1473 K (stage II), respectively.

The first mass loss (stage I) from 1023 to 1123 K is primarily stemmed from the decomposition of bastnaesite ($[\text{Ce}, \text{La}, \text{Pr}, \text{Nd}]\text{CO}_3\text{F}$) and the reduction of iron oxide (Fe_2O_3) in the RE-concentrate, in line with thermodynamic data of the bastnaesite [26] and iron oxides [27]. The mass fraction of bastnaesite in the Bayan Obo RE-concentrate is 44.87 wt%, and its decomposition reaction is 8.56% in the theoretical mass loss, as calculated according to Eq. (5.1). Meanwhile, the mass fraction of Fe_2O_3 in the Bayan Obo RE-concentrate is 8.09 wt%, and its reduction reaction is 3.17% in the theoretical mass loss, as calculated according to Eq. (5.2). With respect to the TGA curve as shown in Fig. 5.8, the first mass loss is corresponded to nearly 11.51%, which agrees well with the total theoretical loss of 11.73%.



For the second mass loss (stage II) from 1373 to 1473 K, which is potentially triggered by the mineral reconstruction reactions of various rare earth minerals, it is detected further through the hot-quenching and ex-situ analysis. The SEM–EDS images and the XRD patterns of the mixed powder as the temperature rose from 1373 to 1773 K are presented in Figs. 5.9 and 5.10, respectively. As the temperature rises to 1373 K,

Fig. 5.8 TGA curve of the mixed powder of RE-concentrate and carbon with temperature rising



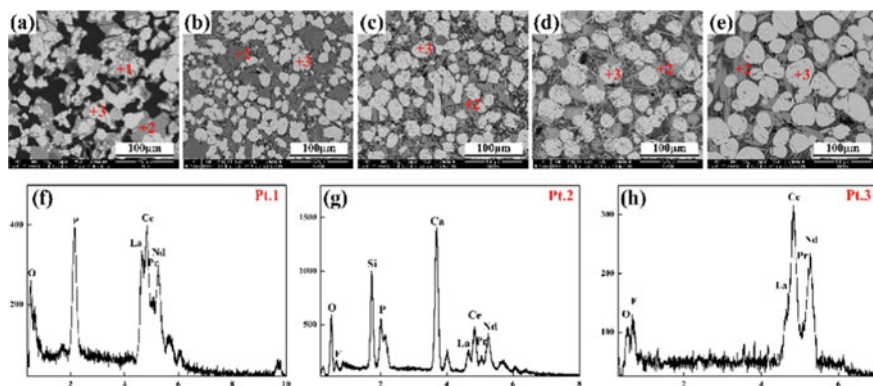


Fig. 5.9 Variations in SEM-EDS images of the mixed powder of RE-concentrate and carbon with temperature rising: **a** SEM-1373 K; **b** SEM-1473 K; **c** SEM-1573 K; **d** SEM-1673 K; **e** SEM-1773 K; **f** EDS-[Ce, La, Pr, Nd]PO₄; **g** EDS-Ca₃[Ce, La, Pr, Nd]₂[(Si, P)O₄]₃F; **h** EDS-[Ce, La, Pr, Nd]OF

the REEs are evidently converted into the acicular britholite (Ca₃[Ce, La, Pr, Nd]₂[(Si, P)O₄]₃F) and the equiaxed cerium oxyfluoride ([Ce, La, Pr, Nd]OF), which are discretely distributed among the primary monazite ([Ce, La, Pr, Nd]PO₄) particles, as shown in Fig. 5.9a. As the temperature rises to 1473 K, the primary monazite is reduced further and disappeared as shown in Fig. 5.9b. The mass fraction of monazite in the RE-concentrate is 20.32 wt%, and its reduction reaction is 8.30% in the theoretical mass loss as calculated according to Eq. (5.3), which agrees well with the second mass loss in the TGA curve corresponding to approximately 8.14% as shown in Fig. 5.8.



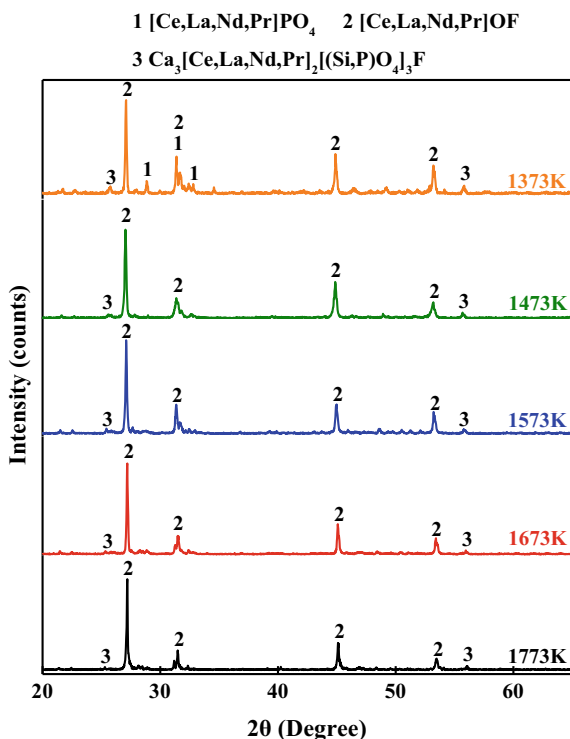
As the temperature increases further from 1473 to 1773 K, the REEs are enriched selectively into the single cerium oxyfluoride phase, which progressively grows and aggregates into the larger equiaxed crystals, whereas other minerals disappear completely instead of forming into the slag melt, as illustrated in Fig. 5.9b–e.

5.2.2 Selective Separation of Cerium Oxyfluoride from RE-Concentrate by Super Gravity

5.2.2.1 Experimental Procedure

According to the selective enriching conditions for REEs as cerium oxyfluoride phase ascertained above, separation of the cerium oxyfluoride phase from RE-concentrate was conducted at the enriching temperature range in a field of super gravity. About

Fig. 5.10 Variation in XRD patterns of the mixed powder of RE-concentrate and carbon with temperature rising



20 g of the mixed powder was placed on a graphite felt with 0.01 mm pore size embedded in a graphite filter. The crucibles were heated in the heating furnace of the centrifugal apparatus at various enriching temperatures for cerium oxyfluoride phase, respectively (1473, 1573, 1673, and 1773 K), under an argon atmosphere. Subsequently, the centrifugal apparatus commenced operation, as then it was adjusted to 1892 rpm angular velocity, $G = 1000$. After 10 min of centrifugation at each specific temperature, the rotation was stopped and the crucible was water-quenched. Simultaneously, parallel experiments were conducted at 1473, 1573, 1673, and 1773 K for 10 min without the super gravity treatment.

After the selective separation of cerium oxyfluoride phase from the RE-concentrate by super gravity, the samples were split longitudinally along with the center axis to form a macrograph view. Subsequently, the samples which were retained in the filter (cerium oxyfluoride phase) and passed through the filter (slag phase) were analyzed via the XRD and SEM-EDS methods, respectively, for the purpose of ascertaining the variations in mineral compositions and microstructures of the separated samples attained at various temperatures. Moreover, 10 fields on the average of each scanning electron micrograph were characterized by the image analyzer (LEICA Qwin 500) to statically analyze the variations in volume fractions and equivalent diameters of the separated cerium oxyfluoride as a function of separating temperature. In addition, each sample was measured by the XRF

method incorporating with the ICP method to attain the $\sum \text{REO}$ contents of the separated cerium oxyfluoride phases at various temperatures. The XPS and TEM were employed further to accurately characterize the chemical formula and crystal structure of the separated cerium oxyfluoride.

5.2.2.2 Separation Behavior of Cerium Oxyfluoride

Vertical sections of the samples attained under super gravity with gravity coefficient of $G = 1000$ in contrast to the parallel samples with $G = 1$ at 1473 to 1773 K for 10 min are shown in Fig. 5.11. Apparently, the entire sample is blocked by the filter, and a uniform structure is taken on by the sample attained under a normal gravity field ($G = 1$), as presented in Fig. 5.11a. In contrast, the sample is separated into two parts by the filter in a super gravity field ($G = 1000$), and the separated samples present the evidently diverse macroscopic structures, as shown in Fig. 5.11b–e. From a macroscopic perspective, the sample above the filter shows a black color and porous structure, whereas the sample below the filter shows a grayish-green color and compact structure.

Through drawing the comparison of XRD patterns of the separated samples attained by super gravity with $G = 1000$ at 1773 K, as shown in Fig. 5.12, the only significant diffraction peak of cerium oxyfluoride appears in the upper sample, whereas the only diffraction peak of britholite is presented in the lower sample. Considering the SEM–EDS images of the separated samples as shown in Fig. 5.13, we conclude that the REEs are enriched selectively into the cerium oxyfluoride, which exists as the only solid phase at 1473–1773 K, while other minerals form the slag melt, respectively. The slag melts evidently move and pass through the filter as they are driven by the super gravity. Conversely, the cerium oxyfluoride is overall intercepted by the filter and effectively separated from the slag melt. Moreover, the separated cerium oxyfluoride presents ad a large equiaxed crystal, and each crystal is structurally independent as shown in Fig. 5.13a. Some britholite with a hexagonal prism structure (100–200 μm) are precipitated further from the separated slag melt after the cooling process, as shown in Fig. 5.13c.

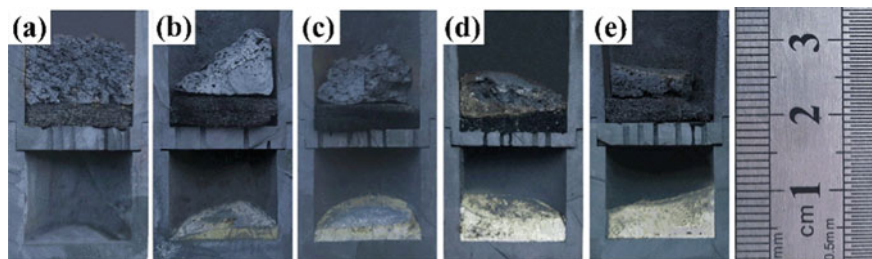
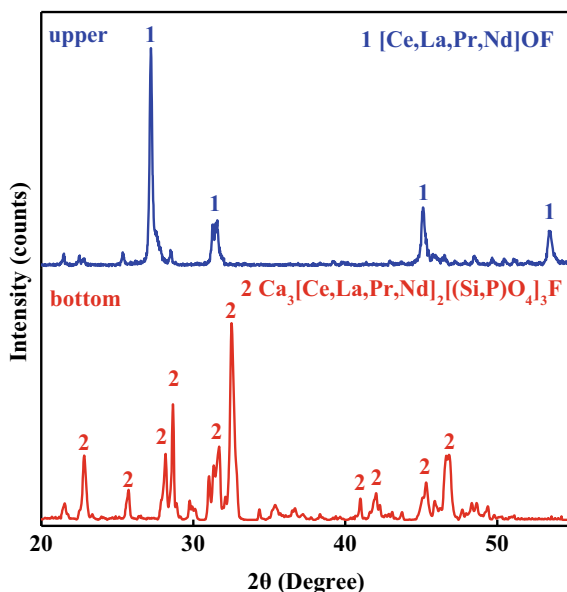


Fig. 5.11 Vertical sections of samples attained by super gravity compared with normal gravity: **a** 1773 K, $G = 1$; **b** 1473 K, $G = 1000$; **c** 1573 K, $G = 1000$; **d** 1673 K, $G = 1000$; **e** 1773 K, $G = 1000$

Fig. 5.12 XRD patterns of the separated samples attained by super gravity ($G = 1000$, $T = 1773$ K)



Variations in equivalent diameters and volume fractions of the separated cerium oxyfluoride attained by super gravity as a function of separating temperature are shown in Fig. 5.14. As the temperature increases from 1473 to 1773 K, the equivalent diameter of cerium oxyfluoride increases from 16.92 μm to 66.97 μm , and the volume fractions increases significantly from 53.57% to 88.22%, respectively. As further verified, the cerium oxyfluoride is effectively separated from the RE-concentrate in a super gravity field and then grows into the larger equiaxed crystals as the temperature increases from 1473 to 1773 K.

Figure 5.15 presents further the variations of $\sum\text{REO}$ contents in the separated cerium oxyfluoride and slag phases attained under super gravity with the rising temperature. The mass fraction of $\sum\text{REO}$ in the separated cerium oxyfluoride phase is up-regulated evidently from 70.02 to 90.35 wt% with temperature increasing from 1473 to 1773 K. By contrast, the mass fraction of $\sum\text{REO}$ in the separated slag phase drops from 8.69 to 2.70 wt%. As accordingly verified, the REEs are efficiently enriched into the cerium oxyfluoride, and the slag melt is effectively removed from the cerium oxyfluoride phase with the temperature increasing from 1473 to 1773 K. Obviously, high-purity cerium oxyfluoride crystals are efficiently separated from the RE-concentrate at 1773 K with $G = 1000$, while there are no slag inclusions included in the separated cerium oxyfluoride phase, as shown in Fig. 5.14a.

Due to the lacking of relevant data for cerium oxyfluoride, the detailed characterizations of the separated high-purity cerium oxyfluoride phase are given further. Firstly, the chemical formula of the cerium oxyfluoride is analyzed by using XPS method. For the REEs (Ce, La, Pr, Nd), there is only one stable valence of trivalent for lanthanum (La), praseodymium (Pr), and neodymium (Nd), whereas cerium (Ce)

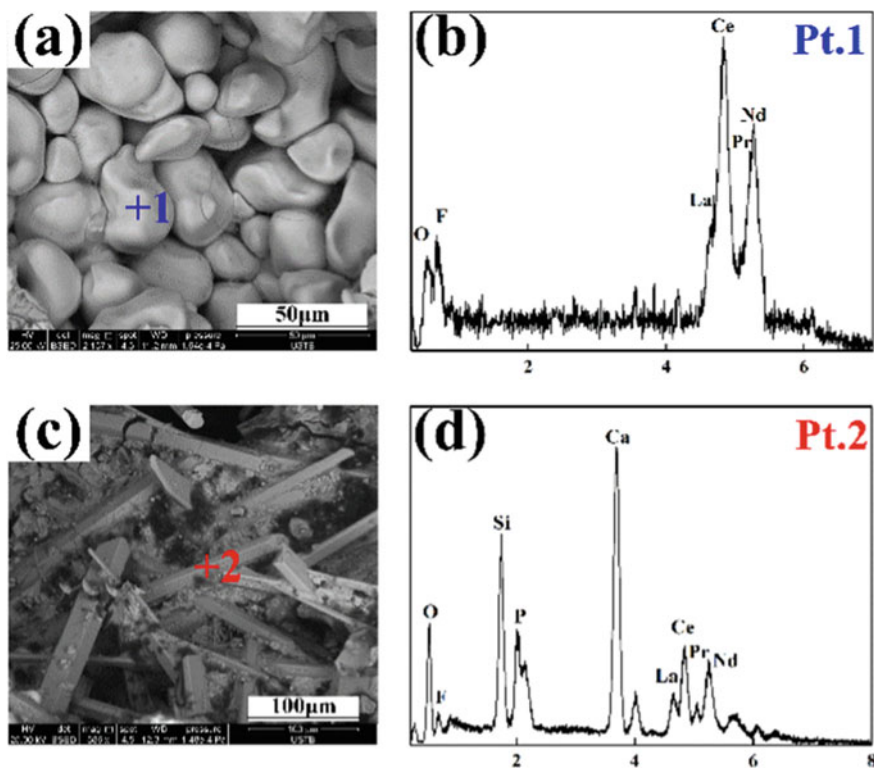


Fig. 5.13 SEM–EDS images of the separated samples attained by super gravity ($G = 1000$, $T = 1773$ K): **a** and **b** upper—cerium oxyfluoride phase; **c** and **d** bottom—slag phase

takes on two types of valences. Therefore, it is confirmed firstly for the valence of Ce to determine the chemical formula of cerium oxyfluoride. Given the XPS Ce 3d spectra of the cerium oxyfluoride is illustrated in Fig. 5.16 (the black-solid lines denote the experimental spectra after background subtraction, and the red-solid lines are provided for the results with peak fitting), five peak assignments in the spectra are labeled, abiding by the convention established by Burroughs [28]. Specifically, the peaks U' and V' at 903.9 eV and 884.9 eV refer to the 3d3/2 and 3d5/2 presented for CeIII 3d state, respectively. Due to the peak of 3d3/2 being partially overlapped by the Mn element, the 3d5/2 peak areas in the XPS spectra are adopted to estimate the contributions of CeIII and CeIV. The calculated proportion of CeIII for the cerium oxyfluoride reaches 88.95%. CeIII is confirmed to be dominant in the separated cerium oxyfluoride phase. Further, the peak U corresponding to the CeIV, typically locates at 916.9 eV, does not appear in the XPS Ce 3d spectra. Hence, Ce is trivalent in the cerium oxyfluoride, and its chemical formula is defined as [Ce, La, Pr, Nd]OF.

Moreover, the separated high-purity cerium oxyfluoride phase is analyzed further through using the TEM to accurately characterize the crystal structure. On the basis

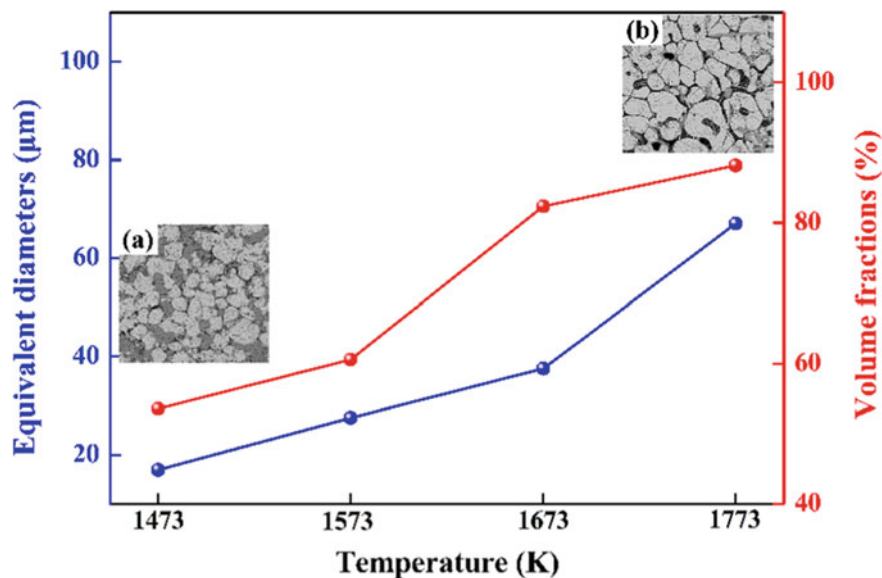
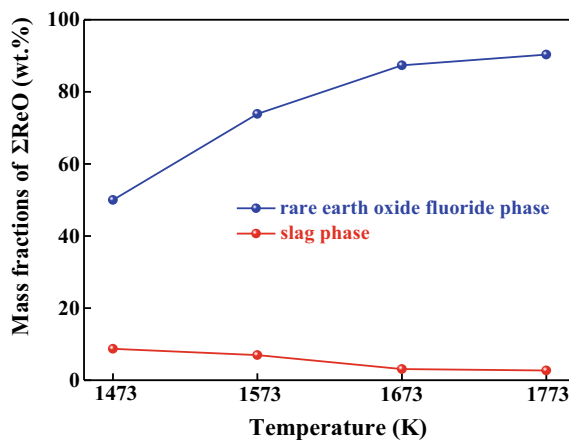


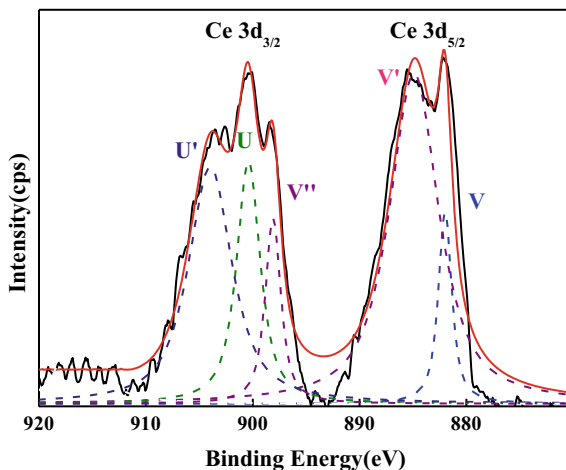
Fig. 5.14 Variations in equivalent diameters and volume fractions of the separated cerium oxyfluoride with temperature rising: **a** SEM-1473 K; **b** SEM-1773 K

Fig. 5.15 Variation in mass fractions of ΣREO in the separated cerium oxyfluoride and slag phases with temperature rising



of the TEM image of the grated cerium oxyfluoride as shown in Fig. 5.17a and the corresponding selected-area electron diffraction (SAED) pattern as presented in Fig. 5.17b, the separated cerium oxyfluoride is confirmed to be characterized by a high crystallinity and the single-crystal feature. Additionally, its crystal structure can be indexed for the [110] zone axis of a single crystal of $[\text{Ce}, \text{La}, \text{Pr}, \text{Nd}]\text{OF}$ (FCC). The single-crystal structure of the cerium oxyfluoride is confirmed by the HRTEM images, and the single-crystal structure of the nanowire and the [110] lattice fringes

Fig. 5.16 Ce 3d spectra for the cerium oxyfluoride attained at $T = 1773$ K with $G = 1000$



with interplanar spacings of around 0.3422 nm are clearly observed in the HRTEM image, as presented in Fig. 5.17c.

Based on the results obtained in this section, the process of selectively enriching and separating REEs from RE-concentrate under reductive atmosphere by super gravity can be intuitively described by Fig. 5.18. Firstly, the REEs are selectively enriched from the dispersed and intimate intermixing of various original bastnaesite, monazite, and gangue minerals into the single cerium oxyfluoride phase, while other minerals form molten slag as reconstructed under a reductive atmosphere between the range from 1473 to 1773 K, and a solid–liquid coexisting zone is formed. However, as the existence of a large amount of cerium oxyfluoride increases the viscosity of the slag melt, the driving force generated by the difference in density between them is insufficient to effectively overcome the large interfacial tension for driving their movement and coalescence via free sedimentation in the normal gravity field, which results in the dispersed distribution of cerium oxyfluoride among the entire slag melt, as presented in Fig. 5.18b. In contrast, the buoyancy factor ($\Delta\rho g$) between

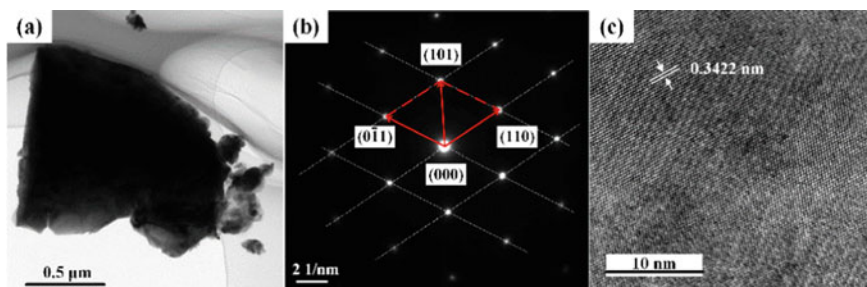


Fig. 5.17 TEM analysis results of the cerium oxyfluoride attained at $T = 1773$ K with $G = 1000$: **a** TEM image; **b** SAED pattern; **c** HRTEM image

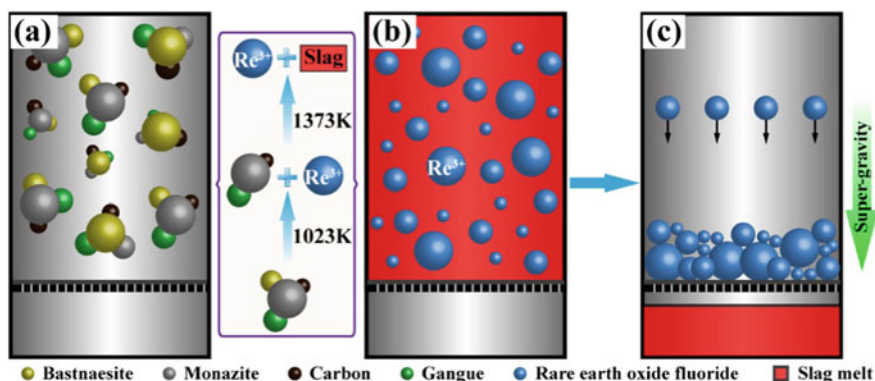


Fig. 5.18 Systematic diagram of selectively enriching and separating REEs from RE-concentrate under reductive atmosphere by super gravity

them increases and significantly enhances the migration of these two different phases in a super gravity field. Therefore, the slag melt surpasses the barriers of the cerium oxyfluoride and follows by going through the filter along with the super gravity direction. The high-purity cerium oxyfluoride phase with a high REEs content is intercepted by the filter and effectively separated from the slag melt, as shown in Fig. 5.18c.

5.3 Stepwise Crystallization and Separation of REEs (Ce, La, Pr, Nd) in Concentrate

The RE-concentrate consists of more than 13 species elements including various REEs of Ce, La, Pr, and Nd; thus, the stepwise crystallization, concentration, and separation of the various REEs (Ce, La, Pr, Nd) in RE-concentrate are conducted further [24, 25].

5.3.1 Stepwise Crystallization Behavior of REEs (Ce, La, Pr, Nd) in RE-Concentrate

5.3.1.1 Experimental

The crystallization behaviors of REEs (Ce, La, Pr, Nd) in RE-concentrate with decreasing temperature were investigated further through conducting the hot-quenching method in normal gravity. About 250 g of the RE-concentrate was put evenly into 5 magnesia crucibles with an inner diameter of 20 mm and a height

of 80 mm. Then they were heated to 1773 K to ensure the sample was completely melted and subsequently cooled slowly at the continuous temperature ranges of 1773–1673 K, 167–1573 K, 1573–1473 K, or 1473–1373 K and with a cooling rate of 1 K/min under argon atmosphere in a muffle furnace, respectively. After holding the sample at each temperature ranges for 100 min, the magnesia crucible was taken out from the furnace and was water-quenched immediately to attain the high-temperature in-situ crystallization behaviors of the various RE-rich phases. Thereafter, the microstructures and elemental compositions of various RE-phases precipitated at different temperature ranges were acquired by using SEM–EDS. In addition, EPMA method was employed to characterize the migration of REEs (Ce, La, Pr, Nd) in various RE-rich phases.

5.3.1.2 Stepwise Crystallization Behavior of REEs (Ce, La, Pr, Nd)

Variations in SEM–EDS images of the RE-concentrate with decreasing temperature are shown in Fig. 5.19. Apparently, the single RE-rich phase of cerium oxyfluoride ($[\text{Ce, La, Pr, Nd}]_3\text{O}_4\text{F}_3$) is firstly precipitated from the molten RE-concentrate at 1773 K, as shown in Fig. 5.19a. The cerium oxyfluoride precipitates further and grows up as larger equiaxed crystals as the temperature decreased from 1773 to 1673 K, as presented in Fig. 5.19b. The second RE-rich phase of lanthanum ferrate ($[\text{Ce, La, Pr, Nd}]\text{FeO}_3$) is precipitated subsequently from the slag melt at the temperature range of 1673–1573 K, as shown in Fig. 5.19c. The crystal size of lanthanum ferrate increases significantly as the temperature decreased from 1573 to 1473 K, as presented in Fig. 5.19d. When the temperature dropped to 1473–1373 K, the third RE-rich phase of britholite ($\text{Ca}_3[\text{Ce, La, Nd, Pr}]_2[(\text{Si, P})\text{O}_4]_3\text{F}$) is precipitated further from the slag melt, as shown in Fig. 5.19e.

In addition, Fig. 5.20 presents the variations of REEs (Ce, La, Pr, Nd) contents in various RE-rich phases which were precipitated at different temperature ranges. It

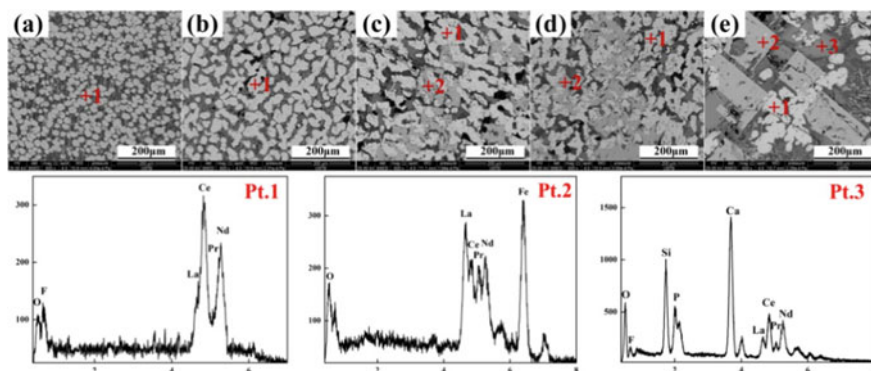


Fig. 5.19 Variations in SEM–EDS images of the RE-concentrate with decreasing temperature: **a** 1773 K; **b** 1773–1673 K; **c** 1673–1573 K; **d** 1573–1473 K; **e** 1473–1373 K

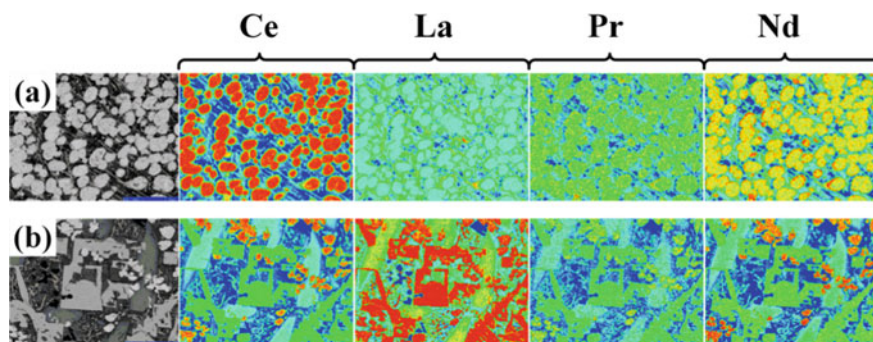


Fig. 5.20 EPMA results of REEs (Ce, La, Pr, Nd) contents in various RE-rich phases precipitated in the RE-concentrate: **a** cerium oxyfluoride; **b** lanthanum ferrate and britholite

is evident that most (Ce) elements are precipitated to the cerium oxyfluoride phase as shown in Fig. 5.20a, while most (La) elements are precipitated subsequently to the lanthanum ferrate phase as shown in Fig. 5.20b, and the (Pr) and (Nd) elements are slightly inclined to enter the cerium oxyfluoride phase when comparing with the lanthanum ferrate phase. Moreover, the residual REEs are precipitated further into britholite phase. However, the subsequent precipitated lanthanum ferrate and britholite phases are discretely intertwined with the first precipitated cerium oxyfluoride phase, as presented in Figs. 5.19 and 5.20. Hence, it is difficult to separate the various intertwined RE-rich phases from RE-concentrate under the force of gravity.

5.3.2 Successive Concentration of REEs (Ce, La, Pr, Nd) in RE-Concentrate Under Super Gravity

5.3.2.1 Experimental Procedure

Based on the stepwise crystallization behavior of various REEs (Ce, La, Pr, Nd) in RE-concentrate, successive concentration of the various REEs under super gravity was carried out. Each 20 g of the RE-concentrate was filled into a magnesia crucible, which was melted completely at 1773 K for 30 min in the constant temperature zone of the heating furnace of centrifugal device under an argon atmosphere. Subsequently, the centrifugal device was started at a gravity coefficient of $G = 800$ corresponding to the angular velocity of 1691 r/min, and the crucible was continuously cooled from 1773 to 1373 K where the RE-concentrate fully solidified, with various cooling rates of 2 K/min, 5 K/min or 10 K/min, respectively. After the temperature decreasing to 1373 K, the rotation function of the centrifuge was turned off, and the water-quenching was performed immediately when the crucibles were taken out. Simultaneously, the parallel experiment was carried out under the condition of normal gravity through continuous cooling from 1773 to 1373 K with 2 K/min.

All of the samples with various cooling rates were divided into two halves on average along the longitudinal center line and observed using a Leica optical microscope to characterize the multi-layer structure in the entire sample. Subsequently, the multi-layer samples were crossly divided into three parts along the two interfaces and analyzed further by SEM-EDS, XRD, and Raman spectrometer, to investigate the microstructures, mineral structures, and mineral compositions of the various layers, respectively. Furthermore, the distribution of REEs in different layers was characterized by EPMA. The mass fractions of Ce_2O_3 , La_2O_3 , Pr_6O_{11} , and Nd_2O_3 in the different layers were detected with the XRF and ICP methods, and the recovery percentages of REEs in the different layers were acquired.

5.3.2.2 Successive Concentration Behavior of REEs (Ce, La, Pr, Nd)

The Leica optical microscope is used to characterize accurately the multi-layer structure in the samples attained under super gravity and that of normal gravity. The overall optical micrographs montaged by over 20 images (magnification 5×10) of the samples attained at the various cooling rates of 10, 5, and 2 K/min are shown in Fig. 5.21. Apparently, various mineral phases are discretely distributed in the entire sample, and it is difficult to confirm the crystallization behaviors of various REEs with decreasing temperature under the normal gravity, as shown in Fig. 5.21a. By contrast, a multi-layer structure consisting of three layers with two explicit interfaces appears significantly in the samples that attained under super gravity, as presented in Fig. 5.21b–d. Moreover, the three layers (bottom, middle, and top) are presented as the obvious diverse macroscopic structures along the direction of super gravity.

The mineral structures in different layers attained under super gravity and that of normal gravity are characterized by XRD. As the XRD pattern of the sample with $G = 1$ shown in Fig. 5.22a, the different RE-phases that precipitated from the molten RE-concentrate are mixed together in the entire sample attained under normal gravity. On the contrary, each layer attained under super gravity is only composed of a single RE-phase, the top layer only consists of britholite phase, the middle layer is the only lanthanum ferrate phase, while the bottom layer is the single cerium oxyfluoride phase, respectively, as presented in Fig. 5.22b.

The microstructures and element composition of RE-phases in different layers attained under super gravity and that of normal gravity are determined further by SEM-EDS. From the SEM-EDS images of the sample with $G = 1$ as shown in Fig. 5.23, the various RE-phases are discretely distributed among the entire slag, it is indicated that the difference in density between them produces the insufficient driving force to drive any precipitated RE-phase moved and separates from each other in the molten RE-concentrate via free sedimentation.

By contrast, the RE-phases are successively precipitated and separated into different layers under the force of super gravity, as presented in Fig. 5.24. As accordingly verified, the RE^{3+} is firstly precipitated into the cerium oxyfluoride with OF^{3-} from the molten RE-concentrate. The driving force generated through super gravity is

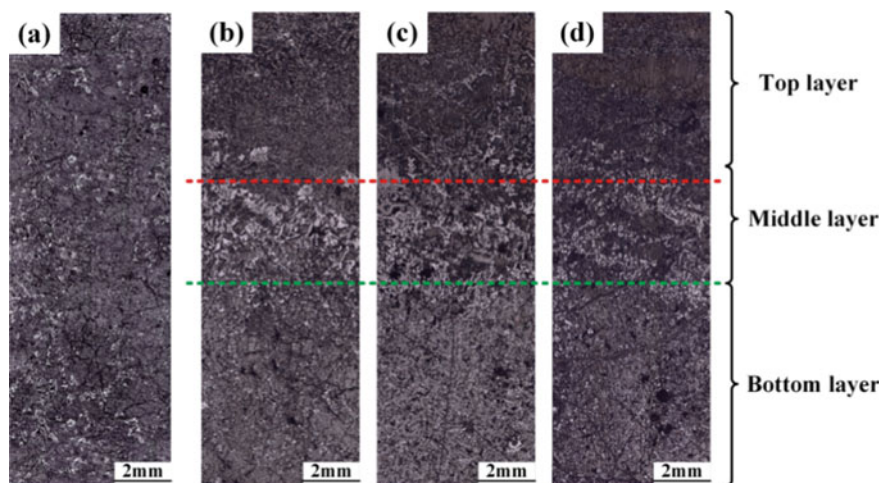


Fig. 5.21 Overall optical micrographs of the samples obtained under super gravity compared with normal gravity with various cooling rates: **a** $G = 1$, 2 K/min; **b–d** $G = 800$, 2 K/min, 5 K/min, and 10 K/min, respectively

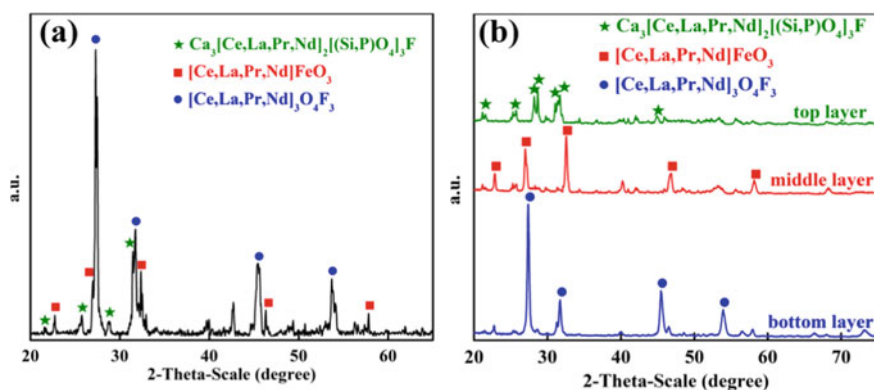


Fig. 5.22 Comparison of XRD patterns for the samples obtained under super gravity and normal gravity with the cooling rate of 2 K/min: **a** $G = 1$; **b** $G = 800$

sufficient to overcome the solid–liquid interface tension and drive the cerium oxyfluoride evidently migrated and separated to bottom layer along the direction of super gravity. Moreover, the cerium oxyfluoride appears as the obvious equiaxed crystals, which are agglomerated into the dense structure under the action of super gravity. Subsequently, the RE^{3+} is precipitated further with FeO_3^{3-} into the lanthanum ferrate with continuous decreasing of temperature, which are presented as the cube crystals and separated to the middle layer under the action of super gravity. Finally, the RE^{3+}

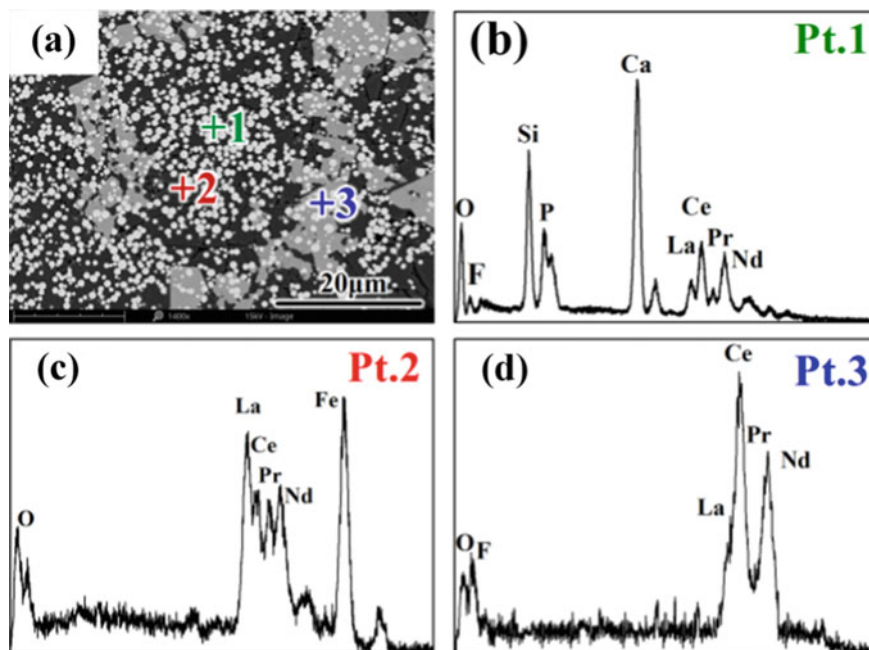


Fig. 5.23 SEM–EDS images of the sample obtained under normal gravity with the cooling rate of 2 K/min: **a** SEM; **b–d** EDS of $\text{Ca}_3[\text{Ce, La, Nd, Pr}]_2[(\text{Si, P})\text{O}_4]_3\text{F}$, EDS— $[\text{Ce, La, Pr, Nd}]\text{FeO}_3$, and $[\text{Ce, La, Pr, Nd}]_3\text{O}_4\text{F}_3$, respectively

is precipitated into the britholite with SiO_4^{4-} and PO_4^{3-} , which shows a dendritic structure and stayed in the top layer.

Comparing the sizes of RE-phases attained under super gravity and normal gravity, it is evident that the RE-phases are significantly grown into the larger crystals under the action of super gravity, as shown in Figs. 5.23 and 5.24. Moreover, compared with the crystal sizes of the different RE-phases attained under super gravity with various cooling rates as revealed in Fig. 5.24, the sizes of cerium oxyfluoride, lanthanum ferrate, and britholite are increased from 2 μm , 100 μm , and 200 μm to 5 μm , 400 μm , and 1000 μm , respectively. It is indicated that the effect of super gravity on nucleation and growth of the three RE-crystals is improved significantly with the decreasing of cooling rates.

The mineral compositions in the different layers obtained under super gravity are collected further using Raman spectrometer. Through comparing the exhibit several vibrational features in the different layers of the sample as shown in Fig. 5.25, the bands of britholite (440 cm^{-1} , 856 cm^{-1} , 959 cm^{-1}), the lanthanum ferrate (674 cm^{-1} , 1359 cm^{-1}), and the cerium oxyfluoride (445 cm^{-1} , 562 cm^{-1}) are appeared on the upper, middle, and bottom layers, respectively, which confirm further the significant distinct in the mineral compositions of the separated RE-phases under the action of super gravity.

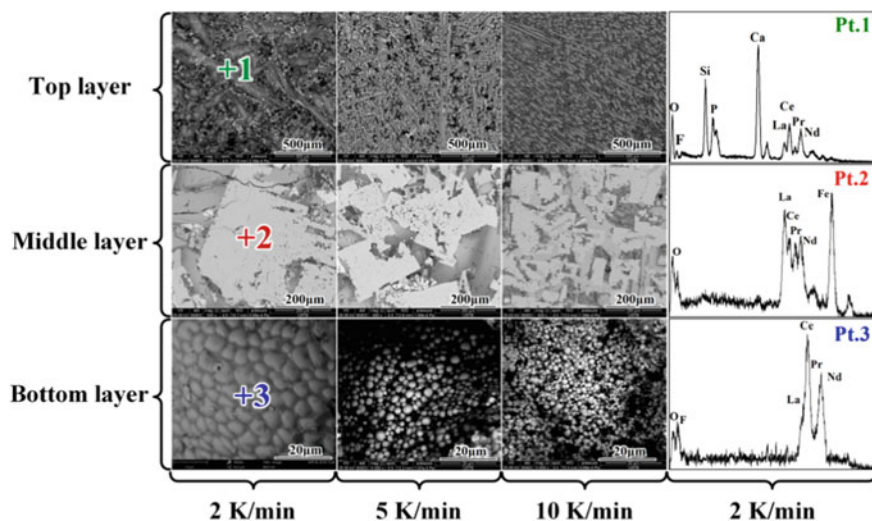


Fig. 5.24 SEM-EDS images of different layers in the samples obtained under super gravity with various cooling rates: Pt.1- $\text{Ca}_3[\text{Ce, La, Nd, Pr}]_2[(\text{Si, P})\text{O}_4]_3\text{F}$, Pt.2- $[\text{Ce, La, Pr, Nd}]\text{FeO}_3$, Pt.3- $[\text{Ce, La, Pr, Nd}]\text{O}_4\text{F}_3$

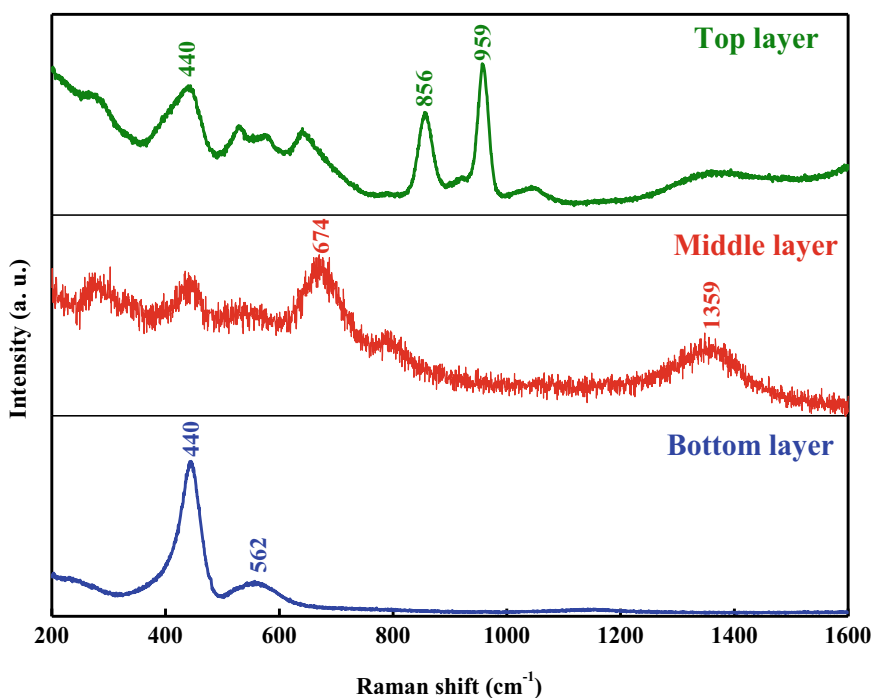


Fig. 5.25 Raman spectra of different layers in the sample obtained under super gravity with $G = 800$ and 2 K/min

Accordingly, the successive crystallization and concentration behaviors of various REEs in the condition of super gravity are described as Fig. 5.26. In a normal gravity field, the various RE-phases that precipitated from the RE-concentrate melt are difficult to move and aggregate via the free sedimentation, which are dispersed among the whole slag melt, as presented in Fig. 5.26a. Instead, the driving force $\Delta\rho g$ is enhanced significantly in the case of a super gravity field. As a result, the various RE-phases that precipitated successively from the RE-concentrate melt with continuous decreasing temperature are separated successively into the different layers under the action of super gravity, as shown in Fig. 5.26b–d. In addition, the super gravity significantly enhances the sizes and amounts of RE-crystals, that is, because the interfacial tension between the RE-crystals and the slag melt is easily broken under the action of super gravity, so the agglomeration and growth are more likely to occur for the RE-crystals, and the directional migration of the RE-crystals creates a better dynamic condition for the crystallization of the remaining REEs in the slag melt.

The EPMA results of different REEs (Ce, La, Pr, and Nd) in the various RE-phases in the multi-layer sample attained under super gravity are shown in Fig. 5.27. Considering the mass fractions and the recovery ratios of REEs in each RE-phase as listed in Table 5.3, it is indicated that the different REEs are recovered into the various RE-phases from the RE-concentrate as driven by super gravity, respectively. The cerium element is precipitated and recovered efficiently into the cerium oxyfluoride phase with a high recovery ratio of 96.21% and the mass fraction of Ce_2O_3 in which is up to 71.87 wt%. The lanthanum element is recovered further into the lanthanum ferrate phase with a high recovery ratio of 94.68% and a mass fraction of 39.76 wt% for La_2O_3 . In addition, the remaining REEs are recovered further as the britholite phase with a $\sum\text{REO}$ content of 2.92 wt%.

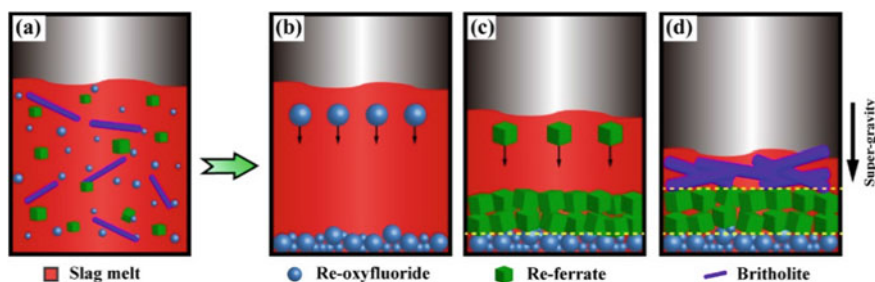


Fig. 5.26 Diagram of successive crystallization and concentration process of different RE-phases in RE-concentrate melt under super gravity: **a** normal gravity; **b–d** super gravity

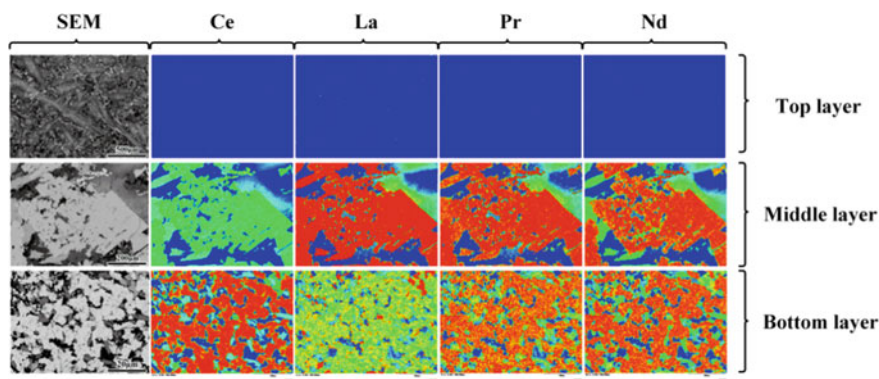


Fig. 5.27 EPMA results of different REEs (Ce, La, Pr, and Nd) in the various RE-phases attained under super gravity with $G = 800$ and 2 K/min

Table 5.3 Mass fractions and recovery ratio of different REEs (Ce, La, Pr, and Nd) in the various RE-phases attained under super gravity with $G = 800$ and 2 K/min

Layers	Mass fractions (wt%)					Recovery ratios (%)			
	$\sum \text{REO}$	Ce_2O_3	La_2O_3	Pr_6O_{11}	Nd_2O_3	R_{Ce}	R_{La}	R_{Pr}	R_{Nd}
Top	2.92	1.07	0.66	0.50	0.69	0.95	0.16	8.10	4.39
Middle	52.41	3.18	39.76	4.80	4.67	2.83	94.68	48.38	60.31
Bottom	80.14	71.87	1.05	3.87	3.34	96.21	3.75	36.52	45.30

5.3.3 Respective Separation of REEs (Ce, La, Pr, Nd) from RE-Concentrate by Super Gravity

Respective separation REEs (Ce, La, Pr, Nd) from Bayan Obo RE-concentrate are conducted further on the basis of stepwise crystallization of the various REEs. The behaviors of each crystallization from REEs (Ce, La, Pr, Nd) as various RE-rich phases in the RE-concentrate are investigated for the first time. On this basis, respective separation of REEs (Ce, La, Pr, Nd) from RE-concentrate at their corresponding crystallization temperatures is implemented under super gravity for achieving the respective separation of REEs (Ce, La, Pr, and Nd) from the RE-concentrate.

5.3.3.1 Experimental Procedure

Firstly, 20 g of the RE-concentrate was put into the upper part of a composite magnesia crucible, the filter plate and the felt of which were with the pore size of 0.5 mm and 0.01 mm, respectively, and then heated the composite crucible to 1773 K under argon atmosphere in the heating furnace of centrifugal apparatus. The crucible was

slowly cooled at the crystallization temperature range of cerium oxyfluoride (1773–1673 K) with a cooling rate of 1 K/min. As the temperature decreased to 1673 K, the centrifugal apparatus was initiated and adjusted to an angular velocity of 1465 r/min to achieve gravity coefficient of $G = 600$. After centrifugation for 10 min, the rotation stopped, and the upper crucible was taken out and be water-quenched immediately. Subsequently, the separated slag melt in the lower crucible was refilled into another composite magnesia crucible, which then was continued to be cooled at the crystallization temperature range of lanthanum ferrate (1673–1473 K) with 1 K/min in the centrifugal apparatus. As the temperature decreased to 1473 K, the slag melt was treated further at the constant temperature with $G = 600$ for 10 min, and then the upper crucible was water-quenched, while the lower crucible was cooled inside the furnace to promote further the crystallization of britholite. Simultaneously, the parallel experiment was conducted by cooling from 1773 to 1373 K with the rate of 1 K/min under normal gravity.

The separated RE-rich phases under super gravity were sectioned longitudinally along the center axis to characterize their macrographs. Subsequently, each one was analyzed by SEM–EDS and XRD methods to determine the variations in microstructures and mineral compositions of the separated RE-rich phases and was analyzed further by EPMA method to characterize the enriching behaviors of REEs (Ce, La, Pr, Nd) in various RE-rich phases. In addition, the mass fractions of Ce_2O_3 , La_2O_3 , Pr_6O_{11} , and Nd_2O_3 in the separated RE-rich phases were measured by ICP method and the recovery ratios of Ce, La, Pr, and Nd in various RE-rich phases, respectively.

5.3.3.2 Respective Separation Behavior of REEs (Ce, La, Pr, Nd)

The vertical sections of the samples attained from various temperatures under the super gravity with $G = 600$ are compared with the parallel sample with $G = 1$, as the results are shown in Fig. 5.28. Comparing with the entire sample which is blocked by the filter in the normal gravity as shown in Fig. 5.28a, the RE-concentrate is separated into two parts by the filter at 1673 K under the super gravity as shown in Fig. 5.28b. Moreover, the lower sample is separated into two more parts and with an evident diverse macroscopic structure at 1473 K under the super gravity, as presented in Fig. 5.28c.

The SEM–EDS images, EDS data, and XRD patterns of the separated RE-rich phases are shown in Figs. 5.29, 5.30 and Table 5.4, respectively, and it is obvious that the three RE-rich phases (cerium oxyfluoride, lanthanum ferrate, and britholite) are separated completely from each other under the super gravity from a microcosmic view.

Firstly, the cerium oxyfluoride crystals are fully precipitated from molten RE-concentrate at the temperature from 1773 to 1673 K, and thus the slag melts evidently move and flow through the filter driven by the super gravity. Conversely, the cerium oxyfluoride crystals are overall intercepted by the filter and effectively separated from the slag melt under the super gravity, and the separated cerium oxyfluoride

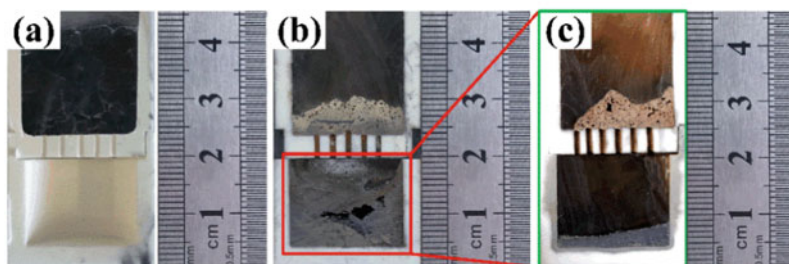


Fig. 5.28 Vertical sections of samples attained by super gravity compared with normal gravity: **a** $T = 1673$ K, $G = 1$; **b** $T = 1673$ K, $G = 600$; **c** $T = 1473$ K, $G = 600$

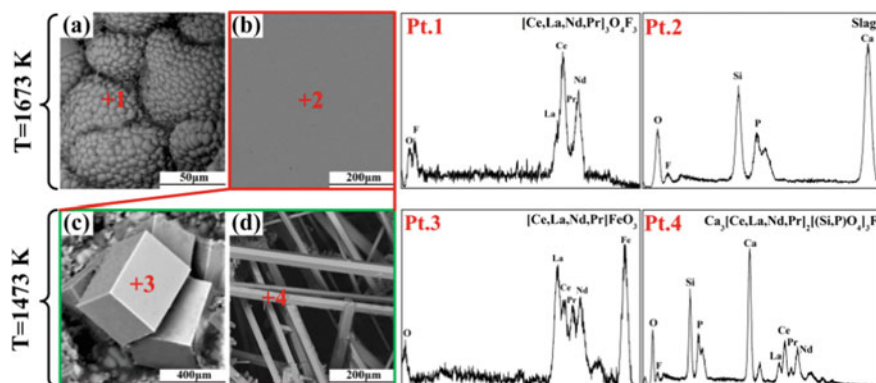


Fig. 5.29 SEM-EDS images of the separated RE-rich phases under super gravity: **a** cerium oxyfluoride; **b** slag; **c** lanthanum ferrate; **d** britholite

shows a large equiaxed crystal structure which is formed by agglomeration of the small particles as shown in Fig. 5.29a.

Subsequently, the lanthanum ferrate crystals are precipitated further at the temperature from 1673 to 1473 K from the separated slag melt as shown in Fig. 5.29b. Besides, the lanthanum ferrate crystals, which are with a large cube structure, are effectively intercepted by the filter and separated further from the slag melt under the super gravity, as presented in Fig. 5.29c.

Finally, the britholite crystals with a hexagonal prism structure, as presented in Fig. 5.29d, are precipitated further from the remainder slag melt during the furnace cooling process.

Consequently, high-purity cerium oxyfluoride, lanthanum ferrate, and britholite crystals are separated respectively from the RE-concentrate under the super gravity, while almost no inclusions are included in the separated RE-rich phases, as shown in Fig. 5.29.

Figure 5.31 presents the distributions of different REEs (Ce, La, Pr, Nd) in various separated RE-rich phases under the super gravity, and the mass fractions of Ce_2O_3 ,

Fig. 5.30 XRD patterns of the separated RE-rich phases under super gravity

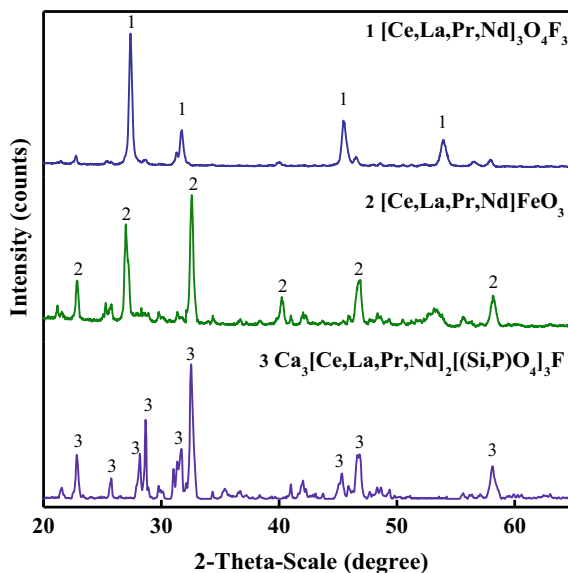


Table 5.4 Energy-dispersive spectrum data of various RE-rich phases (wt%)

No	O	P	F	Ca	Si	Fe	Ce	La	Pr	Nd
Pt.1	24.14	—	5.23	—	—	—	45.77	10.03	4.82	10.01
Pt.2	15.67	8.50	3.78	51.22	20.89					
Pt.3	12.46	—	—	—	—	30.56	17.18	28.71	3.64	7.45
Pt.4	23.07	10.02	13.36	15.56	17.67	—	10.88	5.90	1.52	2.02

La_2O_3 , Pr_6O_{11} , Nd_2O_3 and the recovery ratios of Ce, La, Pr, and Nd in the separated RE-rich phases are shown in Fig. 5.32. As further verified, cerium oxyfluoride is the optimal enriching phase for cerium (Ce) elements, and almost all of the (Ce) elements are enriched into cerium oxyfluoride phase from the RE-concentrate. The mass fractions of REO and Ce_2O_3 in the separated cerium oxyfluoride phase are up to 90.14 wt% and 87.88 wt%, respectively, and the recovery ratio of (Ce) in which is high up to 98.38%. In contrast, lanthanum ferrate is the optimal enriching phase for lanthanum (La) elements, whereas 97.70% of the (La) elements are enriched into lanthanum ferrate phase. The mass fractions of REO and La_2O_3 in the separated lanthanum ferrate phase are 77.41 wt% and 72.76 wt%, respectively. Moreover, the residual Ce, La, Pr, and Nd elements are enriched further into britholite phase from the slag melt, while the mass fraction of REO in the separated britholite is 0.92 wt%.

The respective recovery of REEs (Ce, La, Pr, Nd) from RE-concentrate under the super gravity can be intuitively described as Fig. 5.33 based on the results in this section. Firstly, almost all of the (Ce) are enriched into the single cerium oxyfluoride crystals, while others transform into slag melt at the temperature from 1773

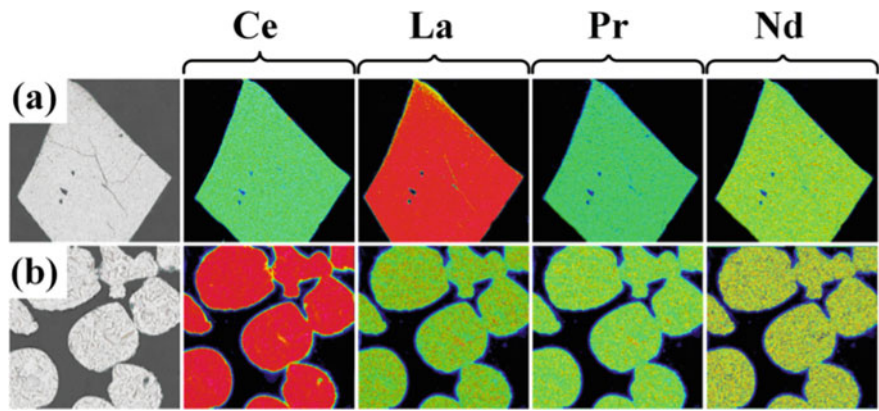


Fig. 5.31 EPMA results of different REEs (Ce, La, Pr, Nd) in various separated RE-rich phases under super gravity: **a** cerium oxyfluoride; **b** lanthanum ferrate

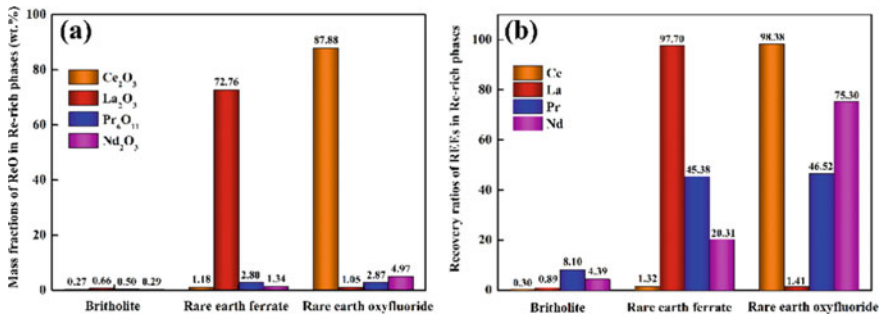


Fig. 5.32 Mass fractions (wt%) of Ce₂O₃, La₂O₃, Pr₆O₁₁, and Nd₂O₃ and recovery ratios (%) of Ce, La, Pr, and Nd in various separated RE-rich phases under super gravity

to 1673 K, as presented in Fig. 5.33a, which are overall separated from the molten RE-concentrate under the super gravity at its crystallization temperature, as shown in Fig. 5.33b. Subsequently, almost all of (La) are enriched further into the lanthanum ferrate crystals at the temperature from 1673 to 1473 K from the separated slag melt as presented in Fig. 5.33c, and they are separated further from the slag melt under the super gravity, as shown in Fig. 5.33d. Finally, the residual REEs are precipitated further into the britholite crystals from the remainder slag melt during the furnace cooling process, as presented in Fig. 5.33e. Accordingly, high-purity cerium oxyfluoride, lanthanum ferrate, and britholite phases are attained, respectively, under the super gravity, for achieving the respective separation of REEs (Ce, La, Pr, Nd) from RE-concentrate with no additives and no wastes.

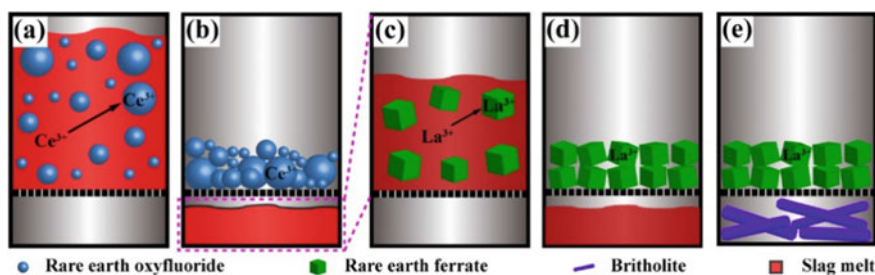


Fig. 5.33 Systematic diagram of respective separation of REEs (Ce, La, Pr, Nd) from RE-concentrate under super gravity: **a** 1773–1673 K; **b** $T = 1673$ K, $G = 600$; **c** 1673–1473 K; **d** $T = 1473$ K, $G = 600$; **e** 1473–1373 K

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Chapter 6

Selective Crystallization and Separation of P in P-Bearing Slag



Abstract Reports the selective crystallization and separation of P in P-bearing slag. The solid solution behavior of P and selective crystallization behavior of C_2S-C_3P in $CaO-SiO_2-FeO-MgO-P_2O_5$ system are reported in Sect. 6.1. The study on motion and separation of C_2S-C_3P in $CaO-SiO_2-FeO-MgO-P_2O_5$ system and steelmaking slag is included in Sects. 6.2 and 6.3, respectively.

It is known that steelmaking slag is one of the major by-products in the steelmaking process, whose productivity equals to 10–20% crude steel productivity [1], which includes many useful components such as FeO , Fe_2O_3 , MgO , MnO , and CaO for ironmaking and steelmaking process. If the steelmaking slag can be reused in ironmaking and steelmaking process, which is beneficial for the reduction of steelmaking slag production and sustainable utilization of valuable resources in steelmaking slag [2].

However, the existence of phosphorus (P) in steelmaking slag is inevitable resulting from the high-temperature process of ironmaking and steelmaking especially by using high phosphorus hematite as raw material, which greatly limits the reuse of steelmaking slag in the ironmaking and steelmaking process. Therefore, separation of phosphorus from steelmaking slag is key to the sustainable utilization of the massive steelmaking slag [3].

Solid solution of phosphorus from molten slag into solid phase is beneficial for dephosphorization of the P-bearing slag [4]. The mechanism for solid solution of phosphorus in P-bearing slag has been widely studied [5–8], which indicates that phosphorus mainly distributes in the dicalcium silicate (Ca_2SiO_4) phase in a form of solid solution. Many researches on the phosphorus solubility in steelmaking slag have been reported, also including some studies about different additives of Al_2O_3 [9, 10], SiO_2 [11], CaF_2 [12], and TiO_2 [13] in the slag. Ono et al. [14] and Sasaki et al. [15] studied the solid solution mechanism of phosphorus and found that the phosphorus mainly transferred into the dicalcium silicate (C_2S) phase during the cooling process of molten steelmaking slag. Yokoyama et al. [16] and Hamano et al. [17] reported that the Ca_2SiO_4 and tricalcium phosphate $Ca_3(PO_4)_2(C_3P)$ could form the solid solutions of $nCa_2SiO_4-Ca_3(PO_4)_2$ solid solution in the steelmaking slag. Inoue and Suito [18] investigated the migration behavior of phosphorus between Ca_2SiO_4 particle and

$\text{FeO}_x\text{--CaO--SiO}_2$ melt at 1573 K and 1833 K and found that the mass transfer of phosphorus was fast and a uniform $\text{CaO--SiO}_2\text{--P}_2\text{O}_5$ solid phase was formed in the melt within 5 s. Kitamura et al. [19] and Shimauchi et al. [20] confirmed that the solid solution method was an efficient way to the dephosphorization of steelmaking slag.

The significance of the removal of phosphorus for sustainable utilization of steel-making slag has been recognized, and several methods have been proposed for the enrichment and separation of phosphorus from steelmaking slag. Kubo et al. [21] and Yokoyama et al. [22, 23] reported the magnetic separation method for the separation of P-rich phase and Fe-rich phase in steelmaking slag based on the significant difference of magnetic properties between the two phases. However, due to the micron-level size and embedded distribution of phosphorus in the matrix, the P-rich phase could not be efficiently separated from steelmaking slag via a strong magnetic field. Ono et al. [24] took the advantage of the density difference between P-rich phase (dicalcium silicate) and other phases in steelmaking slag and proposed a floating separation method to remove the P-rich phase from molten steelmaking slag during the slowly solidification process, while the high viscosity of the molten slag greatly limited the movement and separation of P-rich phase from the slag melt under the force of gravity.

Based on previous studies of super gravity technology on removing of impurities from alloy melt [25, 26] and preparation of functionally gradient materials [27–31], the significant enhancement of super gravity field on phase separation and mass transfer in high-temperature process are confirmed. Consequently, the selective crystallization and separation of P-rich phase in P-bearing slag enhanced by a super gravity field are conducted in this chapter.

In this chapter, selective crystallization and separation of P in P-bearing slag are proposed, the solid solution behavior of P in $\text{C}_2\text{S--C}_3\text{P}$, the motion and separation behaviors of $\text{C}_2\text{S--C}_3\text{P}$ in the $\text{CaO--SiO}_2\text{--FeO--MgO--P}_2\text{O}_5$ system, and the steelmaking slag are included in the following sections, respectively:

Section 6.1 reports the selective crystallization of $\text{C}_2\text{S--C}_3\text{P}$ in $\text{CaO--SiO}_2\text{--FeO--MgO--P}_2\text{O}_5$ system.

Section 6.2 reports the motion and separation of $\text{C}_2\text{S--C}_3\text{P}$ in $\text{CaO--SiO}_2\text{--FeO--MgO--P}_2\text{O}_5$ system.

Section 6.3 reports the motion and separation of $\text{C}_2\text{S--C}_3\text{P}$ in steelmaking slag.

6.1 Selective Crystallization of C_2S-C_3P in $CaO-SiO_2-FeO-MgO-P_2O_5$ System

6.1.1 Thermodynamic Analysis for P in $CaO-SiO_2-FeO-MgO-P_2O_5$ System

According to equilibrium phase diagram of $CaO-SiO_2-FeO-MgO-P_2O_5$ system calculated through FactSage 7.2 as shown in Fig. 6.1, the composition of the original steelmaking slag is located in the primary phase field of $2CaO \cdot SiO_2$ (C_2S). Based on the study on the equilibrium distribution ratio (L_p) of phosphorus between the solid $2CaO \cdot SiO_2$ and molten $CaO-SiO_2-FeO$ and $CaO-SiO_2-Fe_2O_3$ slags in the temperature ranging from 1623 to 1723 K as reported by Kimihisa et al. [32], about 80% of phosphorus precipitates into $2CaO \cdot SiO_2$ in the solidification process of molten steelmaking slag. Inoue and Suito [18, 33] confirms that the phosphorous transfer from P_2O_5 -containing $CaO-SiO_2-FeO$ molten slag to solid $2CaO \cdot SiO_2$ which homogeneously dispersed in the slag. The maximum phosphorus distribution ratio between $2CaO \cdot SiO_2$ and molten slag is appeared at the composition of $2CaO \cdot SiO_2$ primary phase region in the phase diagram, and the temperature dependence of this distribution ratio is small.

6.1.2 Solid Solution Behavior of P in $CaO-SiO_2-FeO-MgO-P_2O_5$ System

6.1.2.1 Experimental Procedure

Slag basicity (CaO/SiO_2) is a crucial factor to affect the properties of steelmaking slag, including melting temperature [34], viscosity [9], and dephosphorization. In this section, the effect of basicity on solid solution behavior of phosphorus in $CaO-SiO_2-FeO-MgO-P_2O_5$ system was firstly studied, based on the chemical composition and smelting conditions of the steelmaking slag produced in the Laiwu Iron and Steel Corporation of China. The P-bearing slag was prepared use the oxide powders of CaO , SiO_2 , FeO , MgO , and P_2O_5 with a purity of 99.99 wt%, to eliminate the influence of microelement from the steelmaking slag. The chemical composition for the P-bearing slag is presented in Table 6.1, and the solid solution behavior of phosphorus in the slag with basicity was experimented by varying the CaO/SiO_2 ratio from 2.5, 2.7, 2.9, 3.1, 3.3, and 3.5.

The effect of basicity on solid solution behavior of phosphorus in the P-bearing slag was firstly studied by adopting the rapid quenching combined with the offline measurements of solid solutions formed in molten P-bearing slag at high temperature. A mass of 20 g P-bearing slag with a different basicity of 2.5, 2.7, 2.9, 3.1, 3.3, and 3.5 was fully mixed and filled into the magnesia crucible and then heated at 1823 K

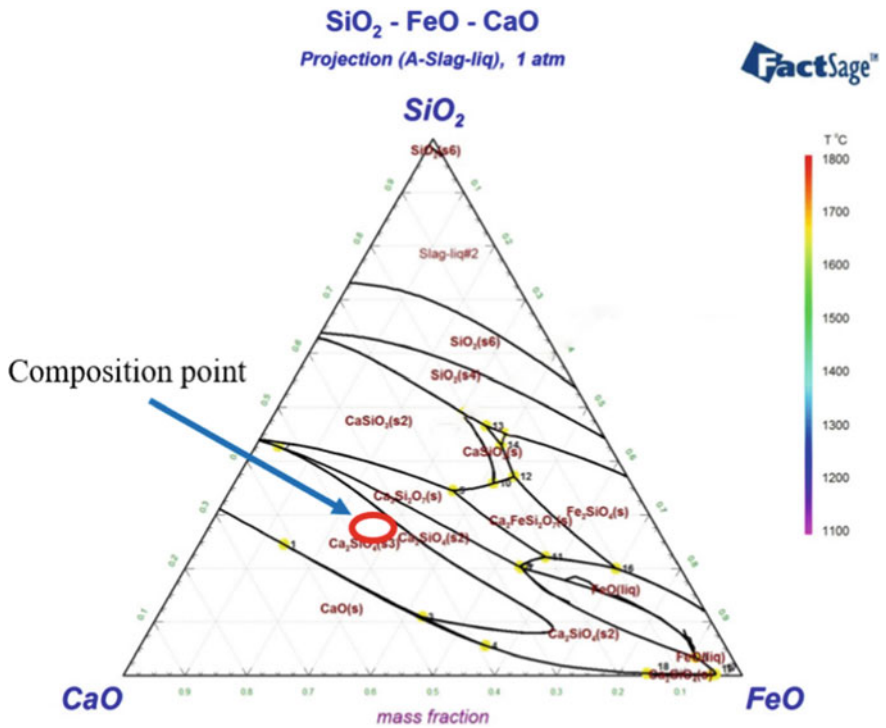


Fig. 6.1 Equilibrium phase diagram of CaO–SiO₂–FeO–MgO–P₂O₅ system

Table 6.1 Chemical compositions of P-bearing slag (wt%)

Composition	CaO	SiO ₂	FeO	MgO	P ₂ O ₅	Basicity
Slag-1	47.9	19.1	27.0	3.0	3.0	2.5
Slag-2	48.9	18.1	27.0	3.0	3.0	2.7
Slag-3	49.8	17.2	27.0	3.0	3.0	2.9
Slag-4	50.7	16.3	27.0	3.0	3.0	3.1
Slag-5	51.4	15.6	27.0	3.0	3.0	3.3
Slag-6	52.1	14.9	27.0	3.0	3.0	3.5

for 60 min in the muffle furnace under the argon atmosphere, to ensure a complete melting and homogenisation. Subsequently, the molten P-bearing slag was cooled slowly from 1823 to 1623 K and kept at 1623 K for 60 min for the fully solid solution of phosphorus in molten slag. Then, the magnesia crucible with the P-bearing slag was quenched in water immediately, to maintain the mineral compositions of solid solutions formed at high temperature.

After that, the XRD and SEM–EDS were utilized to analyze the variations of microstructures and mineral compositions of solid solutions included in the P-bearing

slag with different basicity. Moreover, a Quantum 520 image analyzer was employed to analyze the variations in volume fractions and particle sizes of n .

C_2S-C_3P solid solution with different basicity and the values were statistically calculated from 20 fields in the scanning electron micrographs of each slag.

6.1.2.2 Effect of Basicity on Solid Solution Behavior of Phosphorus

The variation of XRD patterns for the P-bearing slag with basicity is shown in Fig. 6.2. It is indicated that the single diffraction peaks of nC_2S-C_3P (49–1674) solid solutions are appeared dramatically in the P-bearing slag with the basicity of 2.5–3.5. The diffraction peak intensity of nC_2S-C_3P solid solution is increased significantly with the increase of basicity from 2.5 to 3.5. The variation of SEM-EDS images for the nC_2S-C_3P solid solutions in P-bearing slag with various basicity is presented in Fig. 6.3. It is found that the gray equiaxed crystals of nC_2S-C_3P solid solution with a large size of 30–100 μm are formed in the molten P-bearing slag. The nC_2S-C_3P solid solutions are dispersed in the P-bearing slag, and the crystal size of nC_2S-C_3P is decreased obviously with the increase of basicity from 2.5 to 3.5. The variations of mean diameter and volume fraction for nC_2S-C_3P solid solution with basicity are shown further in Fig. 6.4. It is confirmed that the mean diameter of nC_2S-C_3P solid solution is decreased significantly from 72.51 to 30.20 μm with the basicity increase from 2.5 to 3.5. While the volume fraction of nC_2S-C_3P solid solution is increased from 47.54 to 62.09% with the increase of basicity from 2.5 to 3.5.

The P_2O_5 content in nC_2S-C_3P solid solutions with the various basicity is shown in Table 6.2. It is indicated that the content of P_2O_5 in the nC_2S-C_3P solid solution is decreased from 6.55 to 4.08% with the basicity decreased from 2.5 to 3.5. Figure 6.5 presents the EPMA results for the distributions of phosphorus between nC_2S-C_3P solid solution and slag phase with the various basicity. It is clear that the concentration of P_2O_5 in nC_2S-C_3P solid solution is significantly higher than that in the slag phase and confirms that the phosphorus is efficiently enriched into the nC_2S-C_3P solid solution from the molten P-bearing slag with the basicity of 2.5–3.5. By contrast, more phosphorus is enriched into the nC_2S-C_3P solid solution with the decrease of basicity from 3.5 to 2.5, as indicated from the map analyses in Fig. 6.5. Based on the results of thermodynamic calculations [11], the C_2S is firstly precipitated in molten P-bearing slag. With the increase of basicity, the activity of Ca^{2+} increases, more fine-grained C_2S are precipitated and dispersed in the molten P-bearing slag, and the viscosity of the solid–liquid mixture is increased. Thus, the migration of phosphorus from molten P-bearing slag into nC_2S-C_3P solid solution is limited, and the P content in nC_2S-C_3P solid solutions is decreased with the increase of basicity.

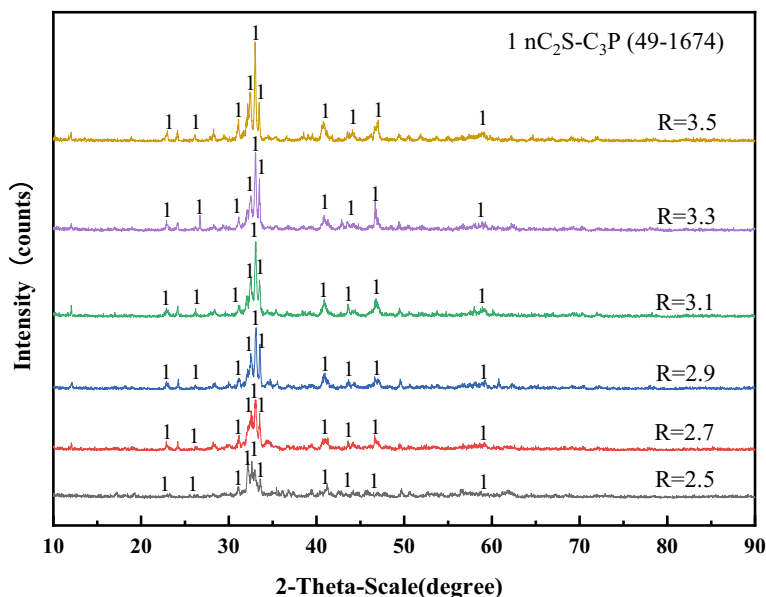


Fig. 6.2 Variation of XRD patterns for P-bearing slag with basicity

6.2 Motion and Separation of C_2S-C_3P in $CaO-SiO_2-FeO-MgO-P_2O_5$ System

Based on the solid solution behavior of P and the crystallization condition for C_2S-C_3P in $CaO-SiO_2-FeO-MgO-P_2O_5$ system, selective separation of the P-rich phase (C_2S-C_3P) in P-bearing slag enhanced by super gravity is proposed, and the motion and separation behaviors of C_2S-C_3P in P-bearing slag under the super gravity are studied in this section.

6.2.1 Motion Behavior of C_2S-C_3P in $CaO-SiO_2-FeO-MgO-P_2O_5$ System Under Super Gravity

6.2.1.1 Experimental Procedure

The $CaO-SiO_2-FeO-MgO-P_2O_5$ system based on the main compositions of steel-making slag produced in the Laiwu Iron and Steel Corporation of China was prepared by mixing the reagent-grade CaO , SiO_2 , MgO , $3CaO \cdot P_2O_5$, and FeO powders [35]. As the chemical composition of the P-bearing slag is listed in Table 6.3, the mass fraction of P_2O_5 and FeO is 2.5 and 30 wt%, and the slag basicity (CaO/SiO_2) is 2.0.

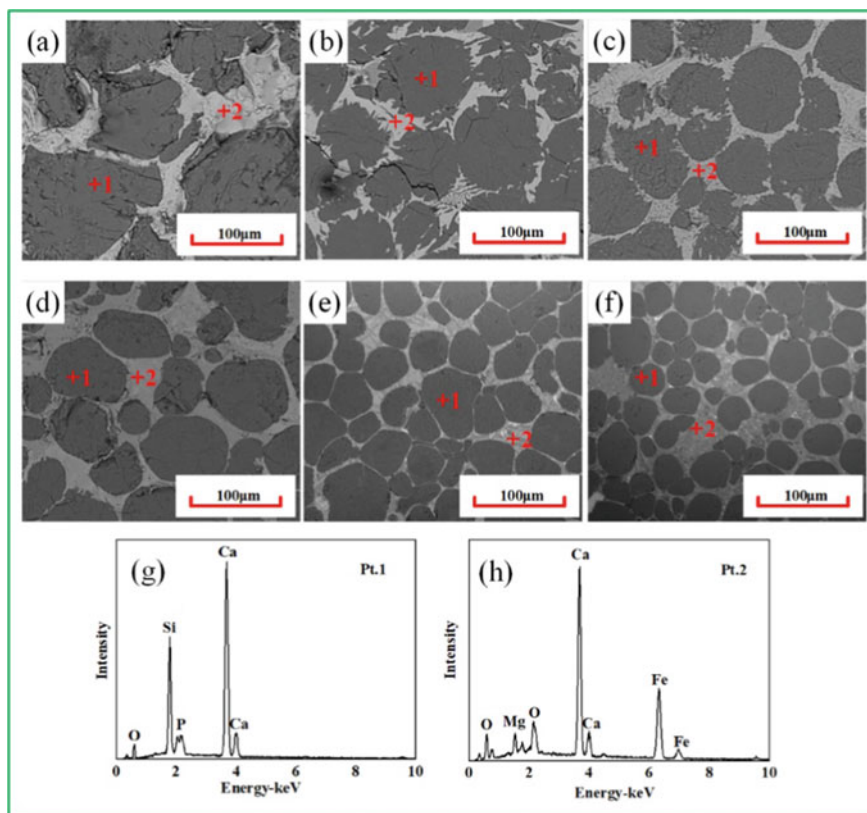


Fig. 6.3 Variation of SEM-EDS images for nC_2S-C_3P solid solutions in P-bearing slag with basicity: **a-f** SEM of slag with $R = 2.5$, $R = 2.7$, $R = 2.9$, $R = 3.1$, $R = 3.3$, and $R = 3.5$; **g** EDS of nC_2S-C_3P solid solution; **h** EDS of slag phase

The chemical powders were fully mixed and then placed into a magnesia crucible, which was heated in the muffle furnace to 1773 K in Ar atmosphere. After keeping at the constant temperature for 30 min, the melted P-bearing slag was cooled to 1623 K with a rate of 3 K/min and kept at this temperature for 30 min to ensure the fully crystallization of P-rich phase (C_2S-C_3P), and then the melted P-bearing slag was quenched in water.

About 30 g of the P-bearing slag in which the C_2S-C_3P was fully crystallized was put into a magnesia crucible and heated to various temperatures of 1583, 1593, 1603, 1613, and 1623 K. After keeping at the specified temperature for 10 min to ensure the C_2S-C_3P in a solid state while the slag in a molten state, the super gravity apparatus was started and adjusted to different rotational speed of 732 r/min, 1036 r/min, 1268 r/min, 1465 r/min, and 1637 r/min for the gravity coefficient of $G = 150$, $G = 300$, $G = 450$, $G = 600$, and $G = 750$, respectively. The super gravity apparatus was turned off after different time of 5, 10, 20, 30, and 40 min, and then the sample was taken out

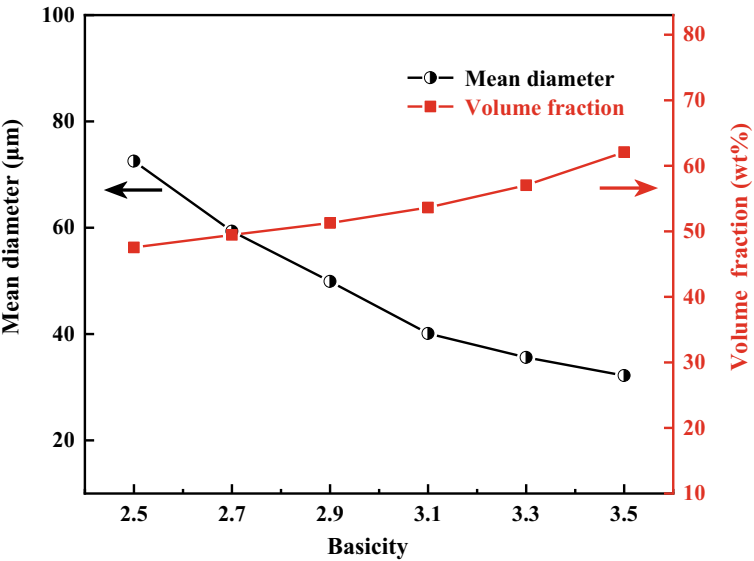


Fig. 6.4 Variations of mean diameter and volume fraction for $n\text{C}_2\text{S}\text{--}\text{C}_3\text{P}$ solid solution with basicity

Table 6.2 P_2O_5 content in $n\text{C}_2\text{S}\text{--}\text{C}_3\text{P}$ solid solutions with various basicity

Basicity (R)	2.5	2.7	2.9	3.1	3.3	3.5
P_2O_5 (wt%)	6.55	6.12	5.76	5.31	5.00	4.08

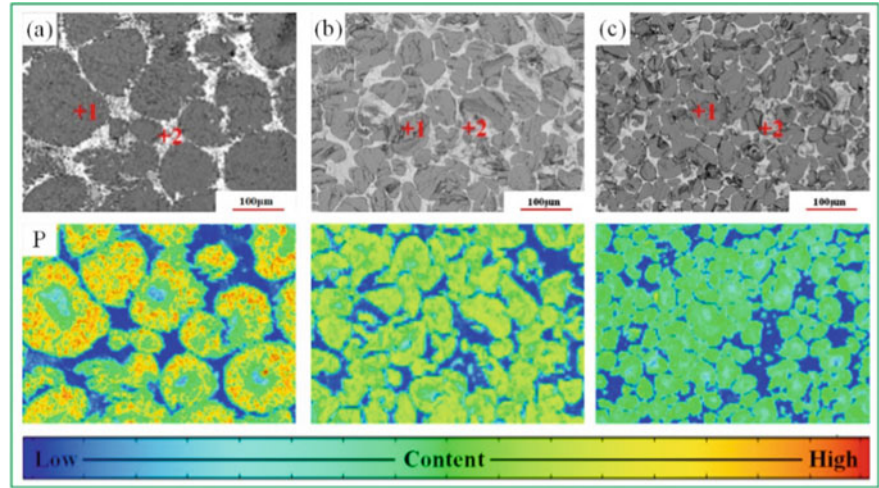


Fig. 6.5 EPMA results for distribution of phosphorus between $n\text{C}_2\text{S}\text{--}\text{C}_3\text{P}$ solid solution and slag phase with various basicity: **a** $R = 2.5$; **b** $R = 3.1$; **c** $R = 3.5$

Table 6.3 Chemical composition of the P-bearing slag (wt%)

Composition	CaO	SiO ₂	FeO	MgO	P ₂ O ₅	Sum	Basicity
P-bearing slag	43	21.5	30	3	2.5	100	2.0

to cool in air. The samples obtained by super gravity were divided into two halves along the center axis. One part was polished and taken optical micrographs randomly along the specific location (average 20 fields) by metallographic microscope (9XB-PC type). The image analyzer software (Image-Pro plus 6.0) was used to gain the volume fraction of C_2S-C_3P by calculating the average value of areal fraction of 20 fields. The equivalent diameter, namely the diameter of a circle which has the equivalent area of C_2S-C_3P , was measured by the line intercept method. The other one was cut along the interface of the layered sample into two parts, and both of them were characterized by XRF and XRD method to determine the chemical and mineral compositions. At the same time, the parallel experiment was conducted at 1623 K for 20 min in normal gravity.

6.2.1.2 Motion Behavior of C_2S-C_3P

Figure 6.6 shows the macrostructures of the sample obtained by super gravity with the gravity coefficient of $G = 600$, temperature of $T = 1623$ K, and time of $t = 20$ min, compared with the parallel sample under the conditions of $G = 1$, $T = 1623$ K, and $t = 20$ min. As shown in Fig. 6.6b, the sample obtained by super gravity appears an obvious layered structure, while the uniform structure presents in the parallel sample as shown in Fig. 6.6a. The SEM images of the two layers (A) and (B) in the layered sample obtained by super gravity are compared in Fig. 6.7, where the upper part is loose and porous, while the lower part is smooth and compact.

The layered sample is divided into six areas in equal interval (5 mm) in sequence from the upper as shown in Fig. 6.6b, which are characterized by the metallographic microscopy, and the corresponding microstructures for each area are shown in Fig. 6.8. It is clear that the upper part from area (a) to (d) is mainly composed of C_2S-C_3P which appears to be dark gray and oval particles. The particle size of C_2S-C_3P is increased with the area approaching to the top area of (a), namely the gradient size distribution along the direction of super gravity as well as the volume fraction. By contrast, it is scarcely possible to find any C_2S-C_3P in the lower part from area (e) to (f). The interface between the C_2S-C_3P and slag phases locates in the middle area (d).

It is confirmed from the macro- and microstructures of the samples obtained by super gravity compared with normal gravity that the dicalcium silicate (C_2S) is primarily precipitated where most of phosphorus are fully enriched into C_2S and transformed into the C_2S-C_3P . However, the driving force generated by the gravity is not enough for the movement and separation of the C_2S-C_3P in the molten P-bearing slag due to the high viscosity, and the uniform structure presents in the Fig. 6.6a. In

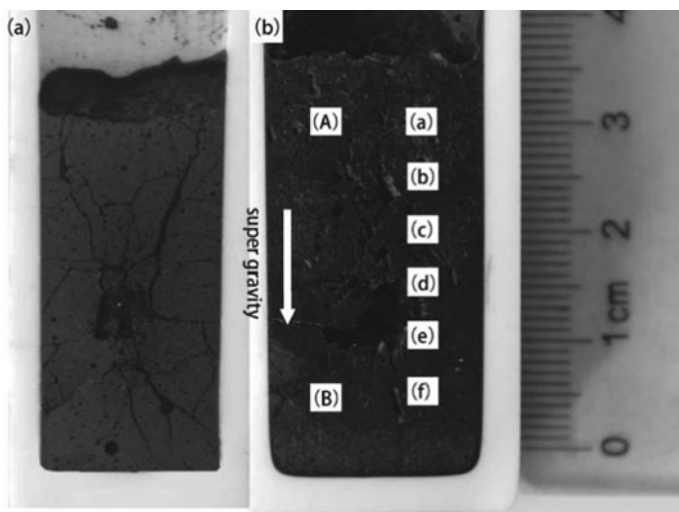


Fig. 6.6 Macrostructures of samples obtained by super gravity compared with normal gravity: **a** $G = 1$, $t = 20$ min, and $T = 1623$ K; **b** $G = 600$, $t = 20$ min, and $T = 1623$ K

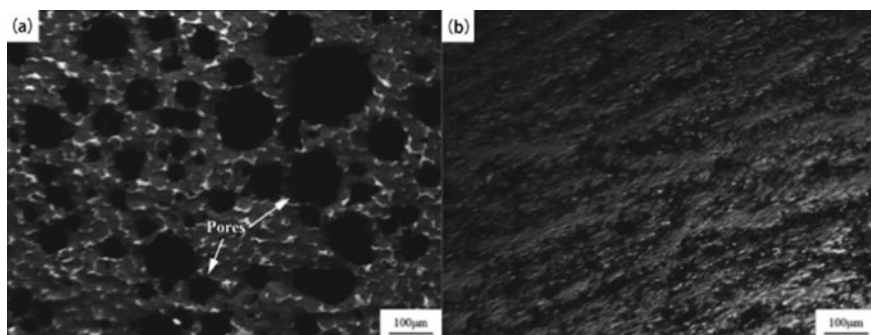


Fig. 6.7 SEM images for the different layers in the layered sample obtained by super gravity: **a** and **b** refer to areas A and B in the layered sample

contrast, the driving force between the C_2S – C_3P and slag melt is increased greatly under the super gravity, the slag melt moves along the super gravity direction, while the C_2S – C_3P moves along the opposite direction and separate from the slag melt. Thus, a layered structure and an obvious interface between the C_2S – C_3P and slag phases are appeared significantly in Fig. 6.6b.

Tables 6.4, 6.5, and 6.6 present the variations of volume fraction of C_2S – C_3P in different areas of the layered samples with different gravity coefficients at $t = 20$ min and $T = 1623$ K, with different time at $G = 600$ and $T = 1623$ K and with different temperature at $G = 600$ and $t = 20$ min, respectively. The corresponding equivalent diameters of C_2S – C_3P in different areas of the layered samples are shown

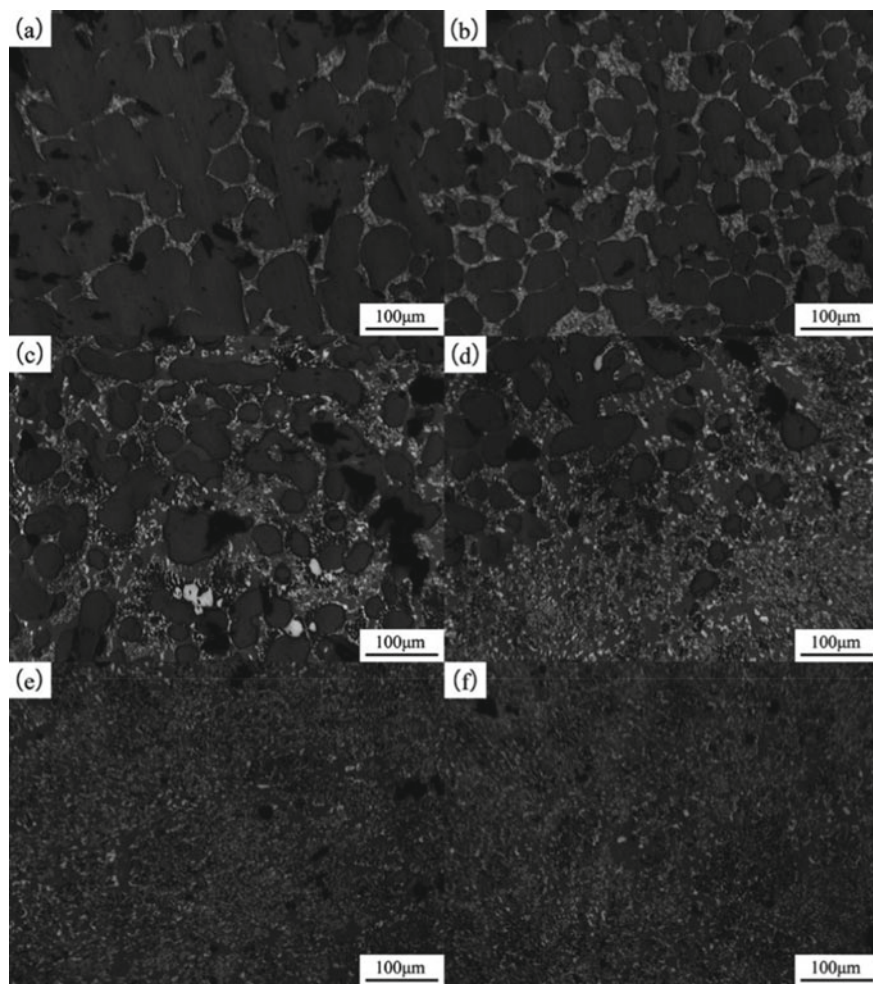


Fig. 6.8 Micrographs of the six areas in the layered sample obtained by super gravity at $G = 600$, $t = 20$ min, and $T = 1623$ K

in Figs. 6.9, 6.10, and 6.11. It is indicated that the volume fraction of C_2S-C_3P gradually increases from the bottom area (f) to the top area (a) in the layered sample along the opposite direction of super gravity, and the peak value appears in the top area (a), as confirmed from Tables 6.4, 6.5 and 6.6. Moreover, the equivalent diameter of C_2S-C_3P also increases gradually from the lower area (d) to the top area (a) of the C_2S-C_3P rich phase in the layered sample obtained by super gravity, as shown in Figs. 6.9, 6.10 and 6.11.

Because the C_2S-C_3P precipitated in the molten P-bearing slag is in the form of equiaxed crystal, which are nearly circular particles. Thus, the directional movement of C_2S-C_3P in the molten P-bearing slag which can be considered as viscous liquid

Table 6.4 Effect of gravity coefficient on volume fraction of C_2S-C_3P in different areas of the samples at $t = 20$ min and $T = 1623$ K

Gravity coefficient	Areas					
	(a)	(b)	(c)	(d)	(e)	(f)
150	69.52	66.24	64.03	62.34	51.72	20.47
300	71.25	69.62	67.23	50.66	28.21	0
450	81.96	70.02	51.79	30.25	0	0
600	82.79	70.75	58.52	18.45	0	0
750	83.51	71.26	68.72	0	0	0

Table 6.5 Effect of time on volume fraction of C_2S-C_3P in different areas of the samples at $G = 600$ and $T = 1623$ K

Time (min)	Areas					
	(a)	(b)	(c)	(d)	(e)	(f)
5	75.02	68.54	55.21	32.59	15.37	0
10	79.17	68.84	54.39	30.58	0	0
20	82.79	70.75	58.52	18.45	0	0
30	83.16	73.34	65.48	0	0	0
40	84.59	75.97	69.12	0	0	0

Table 6.6 Effect of temperature on volume fraction of C_2S-C_3P in different areas of the samples at $G = 600$ and $t = 20$ min

Temperature (K)	Areas					
	(a)	(b)	(c)	(d)	(e)	(f)
1583	79.62	68.64	62.63	31.64	18.91	0
1593	80.57	68.91	64.17	30.58	17.24	0
1603	81.32	69.19	62.24	22.53	0	0
1613	82.26	69.61	62.57	19.76	0	0
1623	82.79	70.75	58.52	18.45	0	0

under the super gravity can be explained by Stokes' law [35]. The motion velocity of C_2S-C_3P in the molten P-bearing slag obeys the following equation:

$$\frac{dx}{dt} = \frac{|\rho_p - \rho_m| G g D_p^2}{18\eta} \quad (6.1)$$

where $\frac{dx}{dt}$, ρ , G , g , D , and η are velocity, density, gravity coefficient, normal gravitational acceleration, particle diameter, and slag viscosity, respectively. The subscripts p and m denote the particle and matrix, respectively.

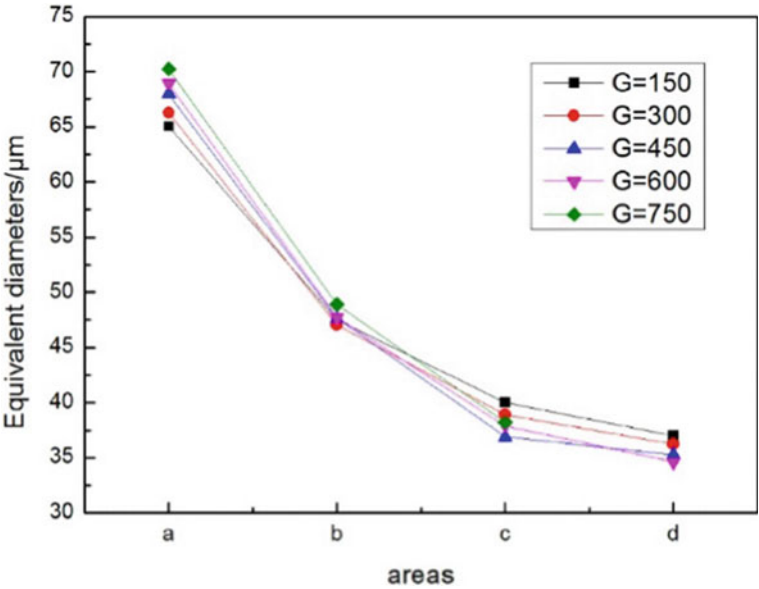


Fig. 6.9 Effect of gravity coefficient on equivalent diameter of C_2S-C_3P in different areas of the samples at $t = 20$ min and $T = 1623$ K

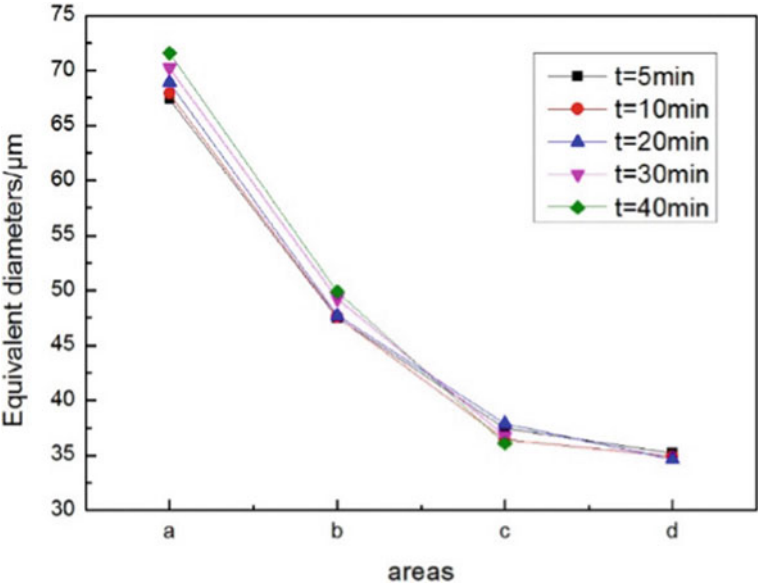


Fig. 6.10 Effect of time on equivalent diameter of C_2S-C_3P in different areas of the samples at $G = 600$ and $T = 1623$ K

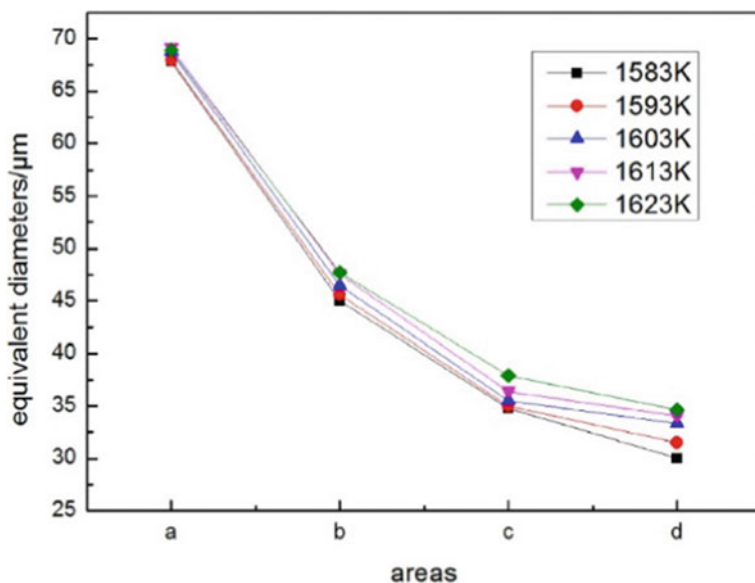


Fig. 6.11 Effect of temperature on equivalent diameters of C_2S-C_3P in different areas of the samples at $G = 600$ and $t = 20$ min

It is indicated from Eq. (6.1) that the motion velocity of C_2S-C_3P in molten P-bearing slag is proportional to the gravity coefficient, the square of particle diameter, and the reciprocal of slag viscosity. Thus, the movement velocity of C_2S-C_3P is improved with the increase of gravity coefficient, and the C_2S-C_3P of large size moves faster than the small ones. Based on the difference of density between C_2S-C_3P and slag melt, the C_2S-C_3P moves directionally along the opposite direction of super gravity, all of which concentrate in the upper part and separate from the slag melt, and the larger C_2S-C_3P accumulates in the top areas.

The XRD patterns of the separated samples obtained under super gravity compared with normal gravity are shown in Fig. 6.12. Compared to the mixed diffraction peaks of dicalcium silicate and magnesium iron oxide included in the parallel sample under the normal gravity, the significant diffraction peak of dicalcium silicate appeared in the C_2S-C_3P while that of magnesium iron oxide presented in the slag phase obtained by super gravity with the conditions of $G = 600$, $t = 20$ min, and $T = 1623$ K. It confirms that most of phosphorus are precipitated into the C_2S-C_3P and separate from the slag melt, and the magnesium iron oxide and dicalcium silicate are formed further in the separated slag melt during cooling process.

Table 6.7 shows the chemical compositions of the separated C_2S-C_3P and slag phases from molten P-bearing slag by super gravity with the conditions of $G = 600$, $t = 20$ min, and $T = 1623$ K. The mass fraction of P_2O_5 in the C_2S-C_3P phase is up to 4.92 wt%, while that in the slag phase is just 1.08 wt%. The recovery ratio of P in the separated C_2S-C_3P phase is up to 72.62%, as calculated via Eq. (6.2). The

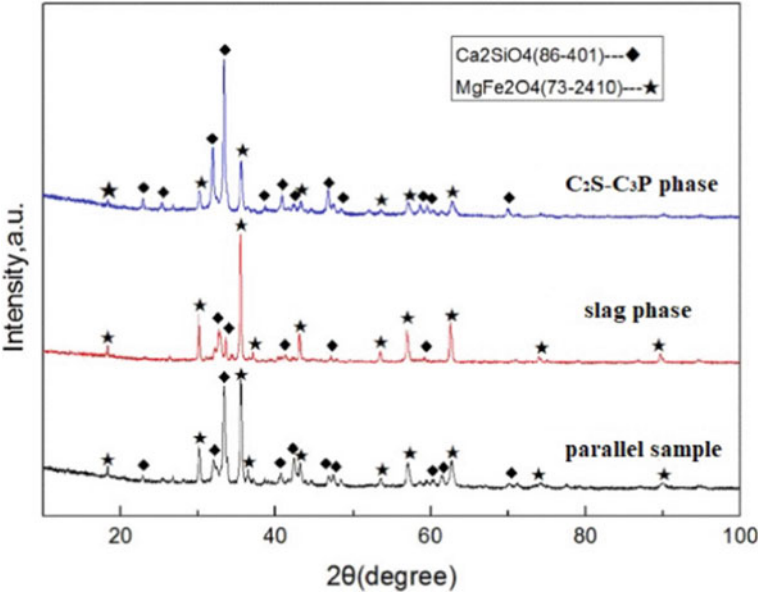


Fig. 6.12 XRD patterns of the sample obtained by super gravity

chemical compositions of separated C₂S–C₃P and slag phases by super gravity are shown in Table 6.8.

$$R_c = \frac{m_c \omega_c}{m_c \omega_c + m_t \omega_t} \times 100\% \tag{6.2}$$

where R_c is recovery ratio of P in the C₂S–C₃P; m_c and m_t are mass of the C₂S–C₃P and slag phases; and ω_c and ω_t are mass fraction of P₂O₅ in the C₂S–C₃P and slag phases, respectively.

Table 6.7 Chemical compositions of separated C₂S–C₃P and slag phases by super gravity (wt%)

Phases	CaO	SiO ₂	FeO	MgO	P ₂ O ₅
C ₂ S–C ₃ P phase	53.71	23.65	13.65	4.06	4.92
Slag phase	33.89	18.52	42.52	3.91	1.08
Parallel sample	44.42	20.92	29.04	3.07	2.52

Table 6.8 Recovery ratio of P₂O₅ in the C₂S–C₃P and slag phases

Phases	Mass (g)	Mass fraction of P ₂ O ₅ (wt%)	Recovery ratio of P (%)
C ₂ S–C ₃ P phase	11.04	4.92	72.62
Slag phase	18.96	1.08	27.38

6.2.2 Separation Behavior of C_2S-C_3P in $CaO-SiO_2-FeO-MgO-P_2O_5$ System by Super Gravity

On the basis of the crystallization and motion behaviors of the P-rich phase (C_2S-C_3P) in $CaO-SiO_2-FeO-MgO-P_2O_5$ system under the super gravity, selective separation of C_2S-C_3P and slag phases from P-bearing slag by super gravity are conducted further [35, 36].

6.2.2.1 Experimental Procedure

Based on the main chemical compositions of the steelmaking slag produced in the Laiwu Iron and Steel Corporation of China, the $CaO-SiO_2-FeO-MgO-P_2O_5$ system was prepared by mixing the reagent-grade CaO , SiO_2 , MgO , P_2O_5 , and FeO powders, as the chemical compositions shown in Table 6.9. The chemical powders were fully mixed and then placed into a magnesia crucible and heated in the muffle furnace at 1773 K for 30 min in Ar atmosphere, to prepare the molten P-bearing slag with the slag basicity (CaO/SiO_2) of 2.0. After that, the molten P-bearing slag was cooled to 1623 K at a rate of 3 K/min and kept at this temperature for 30 min to ensure the fully crystallization of C_2S-C_3P and then quenched into water.

About 30 g of the P-bearing slag in which the C_2S-C_3P was fully precipitated was put into the magnesia crucible with several pores of 0.5 mm at the bottom. The carbon fiber felt with the thickness of 4 mm was put into the bottom of the crucible, which was used as the filter to intercept the C_2S-C_3P in molten P-bearing slag. Below, another magnesia crucible was used for holding the slag melt passing through the filter. The P-bearing slag was heated to the 1623 K in the heating furnace of the centrifugal apparatus, which was kept for 10 min to ensure the C_2S-C_3P and slag in a state of solid-liquid mixture. The centrifugal apparatus was started, and the specified rotational speed was adjusted to an appropriate value of 1637 r/min, namely the gravity coefficient of $G = 750$, and then kept at the constant 1623 K for 20 min. After that, the centrifugal apparatus was turned off, and the sample was taken out and cooled in air. The samples stopped on the filter and went through the filter were both cut into two halves along the center axis. One part was polished and measured on the metallographic microscope, and the other one was characterized by X-ray fluorescence and X-ray diffraction to determine the chemical component and mineral composition. The parallel experiment was carried out further at 1623 K for 20 min under normal gravity of $G = 1$.

Table 6.9 Chemical compositions of the P-bearing slag (wt%)

CaO	SiO ₂	FeO	P ₂ O ₅	MgO	Sum	Basicity
42.3	21.2	30	2.5	4	100	2.0

6.2.2.2 Separation Behavior of C_2S-C_3P

The vertical profiles of the sample obtained by super gravity compared with normal gravity are shown in Fig. 6.13. A uniform structure is presented in the parallel sample under the normal gravity, as shown in Fig. 6.13a. By contrast, the P-bearing slag is separated into two parts by super gravity under the conditions of $G = 750$, $T = 1623$ K, and $t = 20$ min. The sample that held on the filter presents rough and porous morphology, while the sample that went through the filter presents smooth and compact morphology, as shown in Fig. 6.13b. The microstructures of the separated sample by super gravity are displayed in Fig. 6.14. It is clear that a large quantity of equiaxed crystals of C_2S-C_3P is gathered on the filter, while the slag melt that went through the filter form some coarse columnar crystal of Fe magnesium solid solutions.

With the help of XRD analysis shown in Fig. 6.15, it is confirmed that most of phosphorus are precipitated into dicalcium silicate and formed the C_2S-C_3P , and the equiaxed crystals of C_2S-C_3P are efficiently stopped on the filter and separated from the slag melt. In contrast, the slag melt passes through the filter which transforms further into the Fe magnesium solid solution during cooling process.

Table 6.10 shows the chemical compositions of the separated C_2S-C_3P and slag phases by super gravity with the conditions of $G = 750$, $T = 1623$ K, and $t = 20$ min.

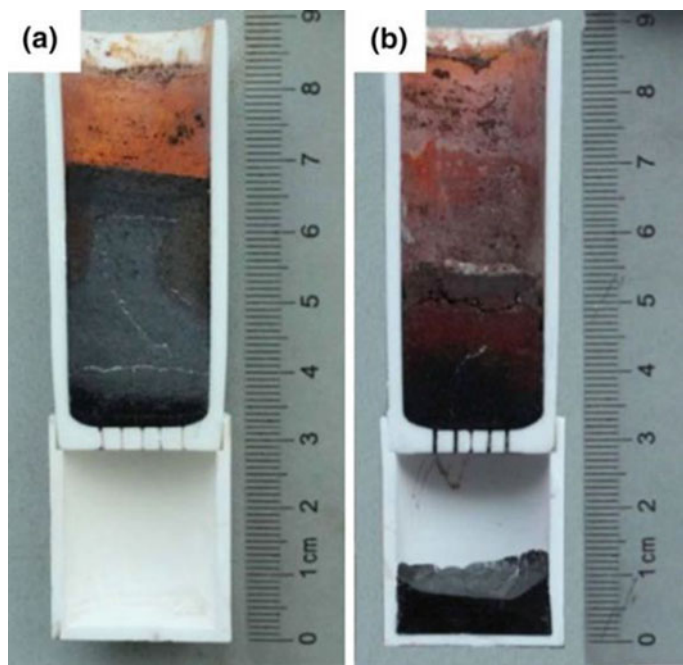


Fig. 6.13 Vertical profiles of the sample obtained by super gravity compared with normal gravity: **a** $G = 1$, $T = 1623$ K, $t = 20$ min; **b** $G = 750$, $T = 1623$ K, $t = 20$ min

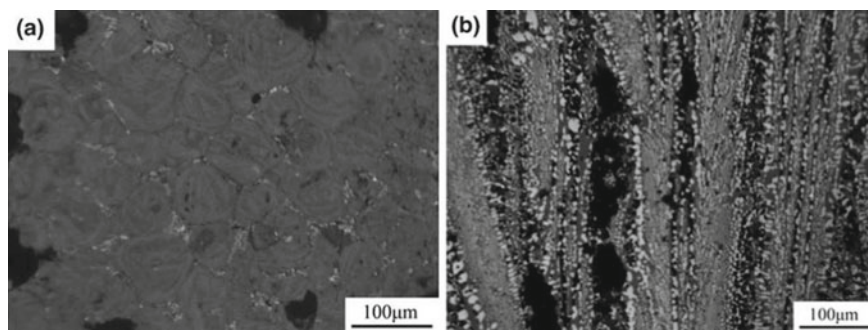


Fig. 6.14 Microstructures of the separated C_2S-C_3P and slag phases: **a** C_2S-C_3P ; **b** slag phase

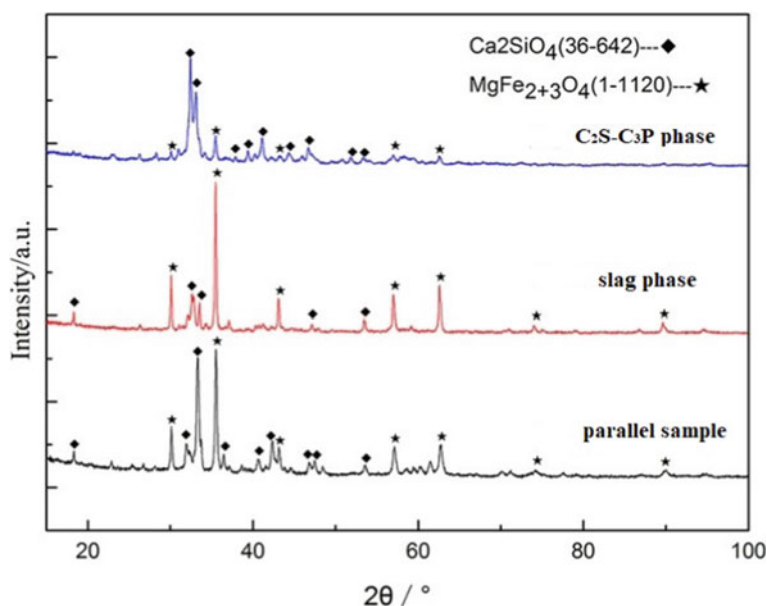


Fig. 6.15 XRD patterns of the sample samples obtained by super gravity

The mass fraction of P_2O_5 in the C_2S-C_3P phase is up to 4.05 wt%, while that in the slag phase is just 1.13 wt%. On the contrary, the mass fraction of FeO in the C_2S-C_3P phase is just 10.02 wt%, while that in the slag phase is up to 52.06 pct. Table 6.11 shows further the mass fractions and recovery ratios of P_2O_5 and FeO in the separated C_2S-C_3P and slag phases. The recovery ratio of P_2O_5 in the C_2S-C_3P phase is up to 76.67% compared to 23.33% of the slag phase, while the recovery ratio of FeO in the slag phase is up to 85.02% compared to 23.33% of the C_2S-C_3P phase, as calculated via Eqs. (6.3) and (6.4). It confirms that the phosphorus is fully enriched into C_2S-C_3P , while most of iron is enriched into the slag phase, both of

Table 6.10 Chemical compositions of the separated samples obtained by super gravity (wt%)

Phases	CaO	SiO ₂	FeO	P ₂ O ₅	MgO
C ₂ S–C ₃ P phase	56.80	27.66	10.04	4.05	0.73
Slag phase	27.89	16.14	52.16	1.13	1.68
Parallel sample	43.23	21.62	28.82	2.41	3.92

Table 6.11 Recovery ratios of P₂O₅ and FeO in the separated C₂S–C₃P and slag phases by super gravity (%)

Samples	Mass fraction (%)	Recovery ratio of P ₂ O ₅ (%)	Recovery ratio of FeO (%)
C ₂ S–C ₃ P phase	47.8	76.67	14.98
Slag phase	52.2	23.33	85.02

which are efficiently separated from the molten P-bearing slag enhanced by the super gravity.

$$R_p = \frac{m_p \times \omega_{p1}}{m_p \times \omega_{p1} + m_{Fe} \times \omega_{p2}} \times 100\% \tag{6.3}$$

$$R_{Fe} = \frac{m_{Fe} \times \omega_{Fe2}}{m_p \times \omega_{Fe1} + m_{Fe} \times \omega_{Fe2}} \times 100\% \tag{6.4}$$

where R_p and R_{Fe} are recovery ratio of P₂O₅ and FeO in the C₂S–C₃P and slag phases, wt%; m_p and m_{Fe} are mass of the C₂S–C₃P and slag phases, wt%; ω_{p1} and ω_{p2} are mass fractions of P₂O₅ in the C₂S–C₃P and slag phases, wt%; and ω_{Fe1} and ω_{Fe2} are mass fractions of FeO in the C₂S–C₃P and slag phases, wt%, respectively.

6.3 Motion and Separation of C₂S–C₃P in Steelmaking Slag

Based on the crystallization, motion, and separation behaviors of C₂S–C₃P in CaO–SiO₂–FeO–MgO–P₂O₅ system, phosphorus can be selectively enriched and separated as the C₂S–C₃P from molten P-bearing slag enhanced by super gravity. In this section, selective crystallization and separation of phosphorus from steelmaking slag by super gravity are conducted further, and the motion and separation behaviors of C₂S–C₃P in the steelmaking slag produced from the Laiwu Iron and Steel Corporation of China are studied [37–39].

Table 6.12 Chemical composition of the steelmaking slag (wt%)

CaO	FeO	SiO ₂	MgO	P ₂ O ₅	MnO	Al ₂ O ₃	TiO ₂	CaF ₂
47.37	24.38	13.56	4.10	3.10	2.16	1.80	1.21	2.32

6.3.1 Motion Behavior of C₂S–C₃P in Steelmaking Slag Under Super Gravity

6.3.1.1 Experimental Procedure

The steelmaking slag produced from LaiWu Iron and Steel Corporation in China is employed as the raw material. The chemical composition of the steelmaking slag is listed in Table 6.12, and 2 wt% of CaF₂ is added to decrease the viscosity of steelmaking slag and improve the solid solution of phosphorus into C₂S–C₃P [11].

The steelmaking slag was ground and fully mixed with 2 wt% of CaF₂ powders, and the steelmaking slag was fully melted in muffle furnace at 1873 K for 20 min. The melted steelmaking slag was cooled to 1663 K at a cooling rate of 20 K/min and kept for 20 min at this temperature to make the fully crystallization of C₂S–C₃P, and then water-quenched. About 25 g steelmaking slag in which the C₂S–C₃P was fully precipitated was put into a magnesia crucible and heated to 1663 K in the heating furnace of centrifugal apparatus for 10 min. Subsequently, the centrifugal apparatus was started and adjusted to different rotational speed, and the melted steelmaking slag was treated under various gravity coefficients for different time, including the conditions of the gravity coefficient of $G = 800$ for different time of 10 min, 20 min, 30 min, and 40 min, and with the different gravity coefficients of $G = 200$, $G = 400$, $G = 600$, and $G = 800$ for 40 min, respectively. At the same time, the parallel experiment was carried out at 1663 K for 40 min under the normal gravity of $G = 1$.

After that, the samples were taken out and cooled in air. The samples obtained by super gravity and normal gravity were both halved along the center axis. One part was polished and measured by SEM–EDS to analyze the phase morphology, distribution of elements, and the volume fraction of C₂S–C₃P. The other one was cut along the interface into two parts, and both of them were characterized by XRF and XRD to determine the chemical component and the mineral composition of the C₂S–C₃P and slag phases, respectively.

6.3.1.2 Motion Behavior of C₂S–C₃P in Steelmaking Slag

Figure 6.16 shows the cross sections of the sample obtained by super gravity of $G = 800$, $T = 1663$ K, and $t = 40$ min, compared with the parallel sample under the conditions of $G = 1$, $T = 1663$ K, and $t = 40$ min. It can be seen that the uniform structure presents in the parallel sample under the normal gravity, while there is an obvious interface as depicted in the white line appears in the layered sample under the super gravity.

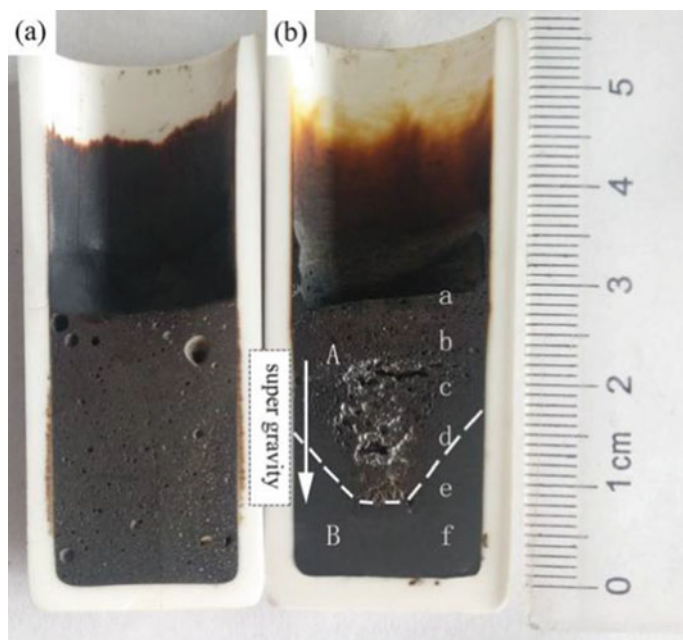


Fig. 6.16 Cross sections of the sample by super gravity compared with normal gravity: **a** $G = 1$, $T = 1663$ K, and $t = 40$ min; **b** $G = 800$, $T = 1663$ K, and $t = 40$ min

As the SEM images for the layered sample shown in Fig. 6.17, the sample above the white line is loose and porous, while the lower sample is compact and tight. Six areas are divided further in the layered sample as shown in Fig. 6.16b, each area is characterized by the SEM for their respective microstructures, and the corresponding results are shown in the Fig. 6.18. It confirms that the upper part of the layered sample was mainly composed of circular crystals of C_2S-C_3P , which is gradually distributed from upper area (a)–(d) with respect to volume fraction. By contrast, it can hardly find any C_2S-C_3P particles in area (e)–(f) of the lower part.

Figures 6.19 and 6.20 show the effects of time and gravity coefficient on the volume fraction of C_2S-C_3P in different areas of the layered samples obtained by super gravity, respectively. It indicates that the volume fraction of C_2S-C_3P is gradually increased from the lower area (e) to upper area (a) along the opposite direction of super gravity, and the gradient distribution of C_2S-C_3P in the layered samples is increased significantly with the increase of gravity coefficient and the time.

The motion law for C_2S-C_3P which is nearly circular particles in the molten steelmaking slag which can be considered as viscous liquid under the super gravity can be also explained by Stokes' law, as given in Eq. (6.1). Based on the Stokes' law [30, 35], the moving distance of C_2S-C_3P in the viscous melt is proportional to the gravity coefficient and time, and thus the gradient distribution of C_2S-C_3P along the opposite direction of super gravity becomes more significant with the increase

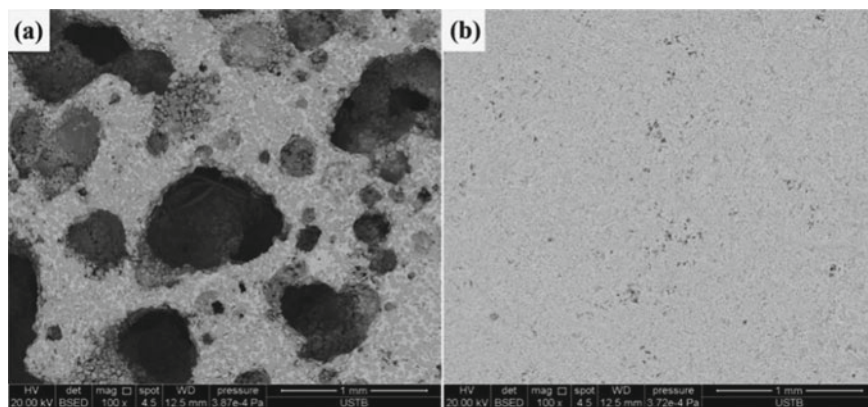


Fig. 6.17 SEM images for the different layers in the layered sample obtained by super gravity: **a** and **b** refer to A and B marked in the layered sample

gravity coefficient and time. Through comparing the variations in volume fraction of C_2S-C_3P in different areas of the layered sample with time and gravity coefficient shown in Figs. 6.19 and 6.20, the sudden drop for the volume fraction of C_2S-C_3P from the lower area (d) to the bottom area (e) can be clearly found in the conditions of $G = 800$ for ≤ 10 min, or with the gravity coefficient of $G \leq 400$ for 40 min, respectively. It can conclude that a time of ≥ 20 min under the condition of gravity coefficient of $G = 800$ or a gravity coefficient of $G \geq 600$ under the condition of $t = 40$ min are necessary conditions for the fully movement of C_2S-C_3P from the bottom areas to the upper areas under the force of super gravity, respectively.

Figure 6.21 shows the XRD patterns of the samples obtained by super gravity with the conditions of $G = 800$, $T = 1663$ K, and $t = 15$ min compared with normal gravity. It confirms that most of phosphorus is fully enriched into the C_2S-C_3P , and the C_2S-C_3P is efficiently concentrated in the upper part as driven by super gravity. On the contrary, the slag melt gathers at the lower part and separates from the C_2S-C_3P along the opposite direction of super gravity, and the slag melt is transformed further into the $MgO \cdot Fe_2O_3 \cdot MnO$ solid solution (RO phase) during the cooling process.

The chemical compositions of the separated C_2S-C_3P and slag phases are shown in Table 6.13. Under the conditions of $G = 600$, $T = 1663$ K, and $t = 15$ min, the mass fraction of P_2O_5 in the separated C_2S-C_3P phase is up to 4.12 wt%, while that in the slag phase is just 1.67 wt%. On the contrary, the mass fraction of FeO in the slag phase is increased to 38.67 wt%, and that in the C_2S-C_3P is decreased to 13.18 wt%. Accordingly, the recovery ratio of P_2O_5 in the C_2S-C_3P phase is 77.56%, and the recovery ratio of FeO in the slag phase is 60.18%, as calculated via Eqs. (6.3) and (6.4). The recovery ratio of P_2O_5 and FeO in the C_2S-C_3P and slag phases is shown in Table 6.14.

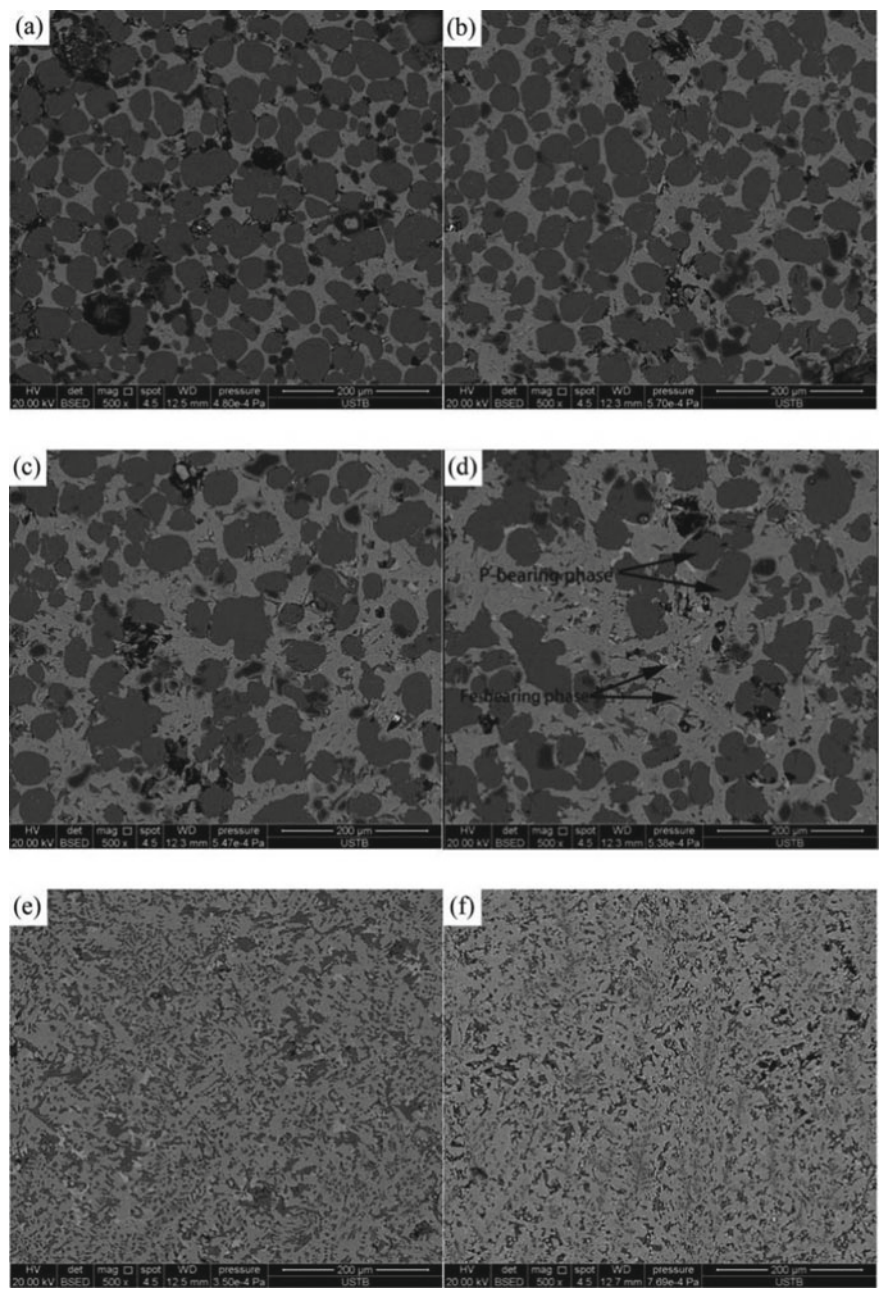


Fig. 6.18 Micrographs of the six areas in the layered sample obtained by super gravity at $G = 800$, $t = 40$ min and $T = 1663$ K

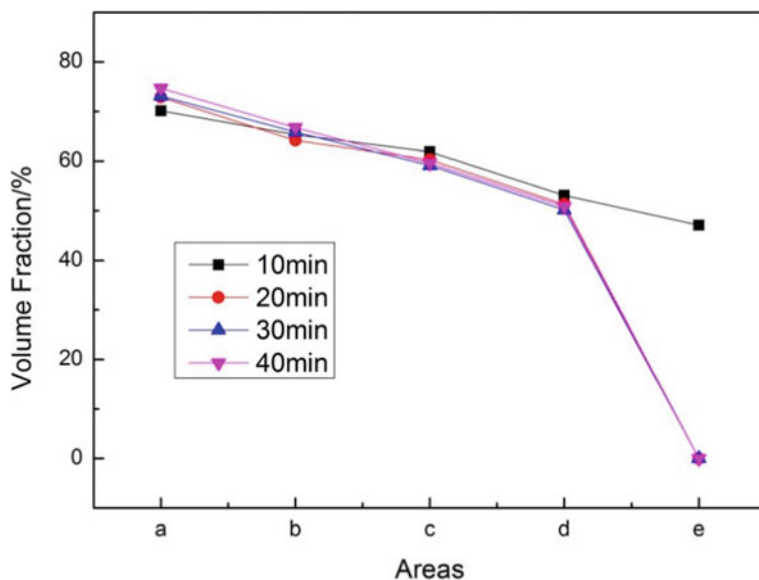


Fig. 6.19 Volume fraction of C_2S-C_3P in different areas of the layered samples with time at $G = 800$ and $T = 1663$ K

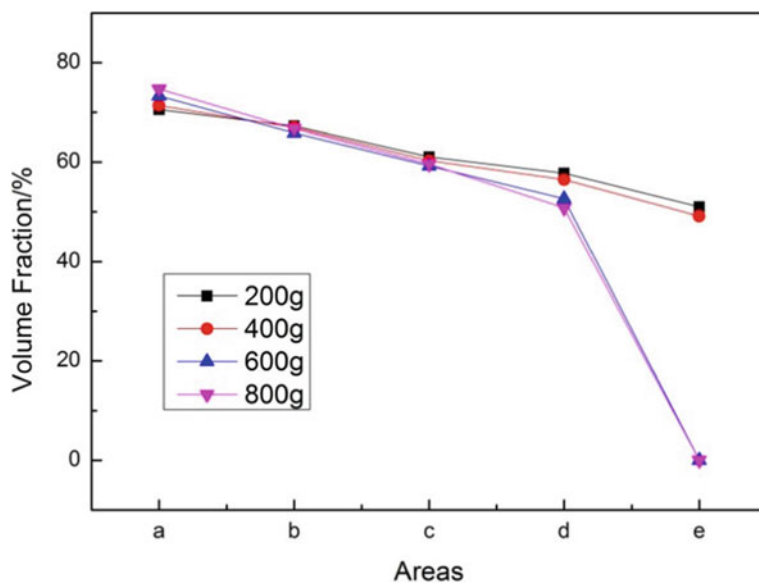


Fig. 6.20 Volume fraction of C_2S-C_3P in different areas of the layered samples with gravity coefficient at $t = 40$ min and $T = 1663$ K

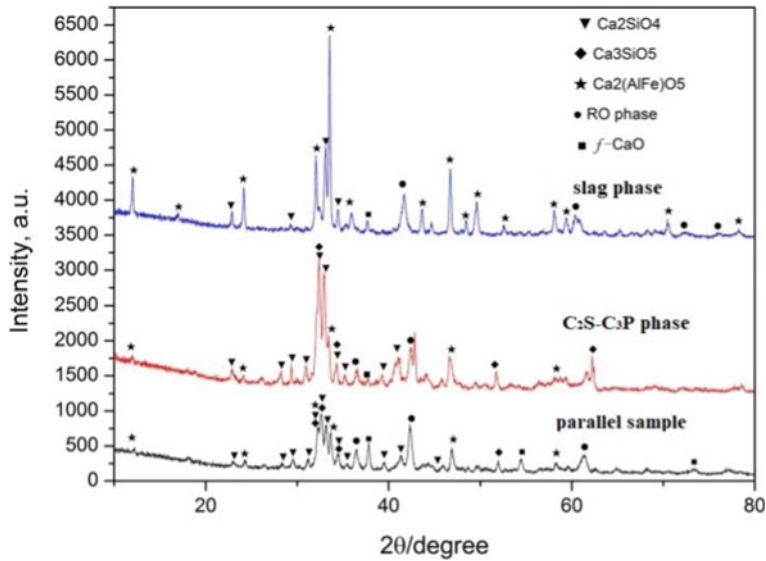


Fig. 6.21 XRD patterns of the sample obtained by super gravity

Table 6.13 Chemical compositions of separated C₂S–C₃P and slag phases by super gravity (wt%)

Phases	CaO	FeO	SiO ₂	MgO	P ₂ O ₅	MnO	Al ₂ O ₃	TiO ₂	CaF ₂
C ₂ S–C ₃ P phase	53.94	16.6	17.95	2.66	4.12	1.56	1.16	0.86	1.15
Slag phase	38.24	35.17	7.42	6.09	1.67	3.1	2.65	1.7	3.96
Parallel sample	47.37	24.38	13.56	4.1	3.1	2.16	1.8	1.21	2.32

Table 6.14 Recovery ratio of P₂O₅ and FeO in the C₂S–C₃P and slag phases

Phases	Recovery ratio of P ₂ O ₅ (%)	Recovery ratio of FeO (%)
C ₂ S–C ₃ P phase	77.56	–
Slag phase	–	60.07

6.3.2 Separation Behavior of C₂S–C₃P from Steelmaking Slag by Super Gravity

6.3.2.1 Experimental Procedure

On the basis of the crystallization and motion behaviors of the C₂S–C₃P in molten steelmaking slag under the super gravity, selective separation of C₂S–C₃P and slag phases from the steelmaking slag enhanced by super gravity were conducted further [39]. About 20 g steelmaking slag from the Laiwu Iron and Steel Corporation of China was ground and put into the upper magnesia crucible with the pores of 0.4 mm

at the bottom. And a carbon fiber felt with the thickness of 4 mm used as the filter was put inside and right above the bottom of the crucible, to intercept the C_2S-C_3P in molten steelmaking slag. Another magnesia crucible was put below to hold the slag melt that went through the filter. The steelmaking slag was heated to the desired temperature of $T = 1663$ K at a rate of 5 K/min and kept for 10 min, to ensure the slag phase in a molten state while the C_2S-C_3P in a solid state. The centrifugal apparatus was started, and the specified rotational speed was adjusted to 1465 r/min, namely $G = 600$, and then kept at the constant temperature of $T = 1663$ K for different time. After that, the centrifugal apparatus was turned off, and the sample was taken out to cool in air.

The samples that are separated into the upper and lower crucibles were both cut into two halves along the central axis. One part was polished and measured on the scanning electron microscope, and the other was characterized by XRF and XRD for the chemical components and mineral compositions of the separated samples. Comparatively, the parallel experiment was conducted at 1663 K for 15 min under the normal gravity. The recovery ratios of P_2O_5 and FeO were calculated further via Eqs. (6.3) and (6.4), respectively.

6.3.2.2 Separation Behavior of C_2S-C_3P from Steelmaking Slag

Figure 6.22 shows the cross sections of the samples obtained by super gravity under the conditions of gravity coefficient of $G = 600$ and temperature of $T = 1663$ K for different time $t = 1$ min, 5 min, 10 min, and 15 min, compared with the parallel sample under the conditions of $G = 1$, $T = 1663$ K, and $t = 15$ min. It is noted from Fig. 6.22a that all of the molten steelmaking slag is blocked on the filter, and a uniform structure is appeared in the parallel sample under the normal gravity field. In comparison, the slag melts efficiently pass through the filter as driven by super gravity, which is separated into the lower crucible, as shown in Fig. 6.22b–e. More slag melt is fully separated from the C_2S-C_3P , and the mass of the separated slag phase into the lower crucible is increased significantly with the increase of gravity coefficient. Figure 6.23 shows the microstructure of the separated samples obtained by super gravity, and Fig. 6.24 shows the XRD patterns of the two separated samples. It indicates that a large number of elliptical C_2S-C_3P are fully concentrated in the upper crucible, while there is not any C_2S-C_3P particles found in the slag phase in the lower crucible.

Table 6.15 shows further the chemical compositions of the separated samples by super gravity with $G = 600$, $T = 1663$ K, and $t = 15$ min. The mass fraction of P_2O_5 in the C_2S-C_3P phase is up to 3.56 wt%, while that in the slag phase is just 1.04 wt%. The opposite results appeared on the distribution of FeO in the separated samples, where the mass fraction of FeO in the slag phase is up to 38.67 wt%, while that in the C_2S-C_3P phase is just 13.18 wt%. Accordingly, the recovery ratio of P_2O_5 in the C_2S-C_3P phase is 82.2%, and that of FeO in the slag phase is to 68.5%, as shown in Table 6.16. It can be concluded that the phosphorus is selectively precipitated into the C_2S-C_3P , while most of iron forms the molten slag phase, and thus the C_2S-C_3P

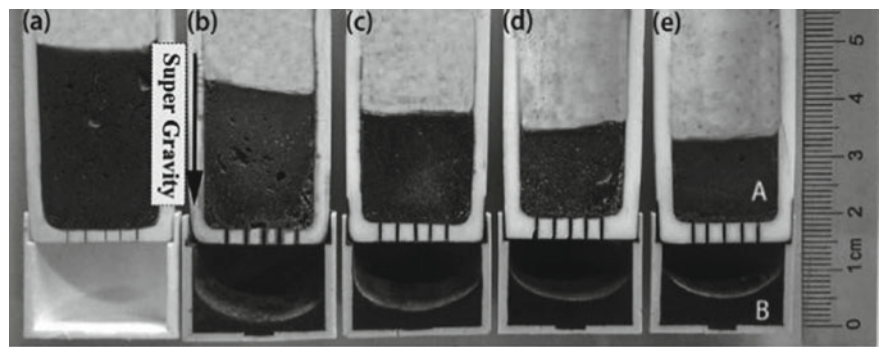


Fig. 6.22 Macrographs of the samples obtained by super gravity with time compared with normal gravity: **a** $G = 1$ and $t = 15$ min; **b** $G = 600$ and $t = 1$ min; **c** $G = 600$ and $t = 5$ min; **d** $G = 600$ and $t = 10$ min; **e** $G = 600$ and $t = 15$ min

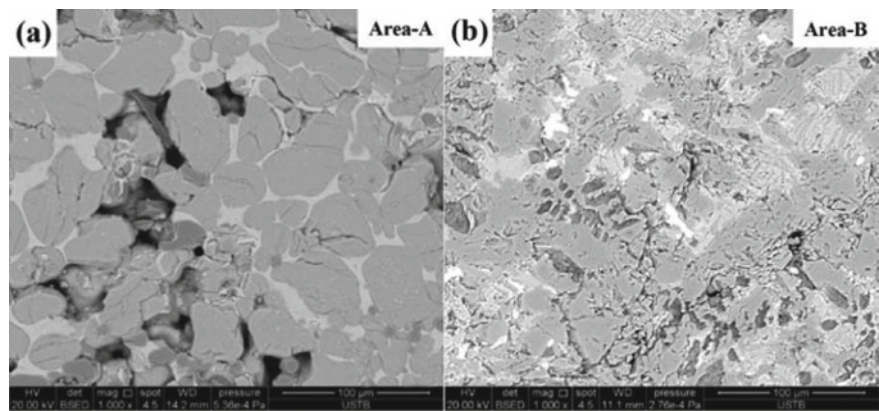


Fig. 6.23 Microstructures of the separated C_2S-C_3P and slag phases by super gravity: **a** and **b** C_2S-C_3P and slag phases

and Fe-rich slag phases are efficiently separated from the molten steelmaking slag in a solid-liquid existing state under the force of super gravity.

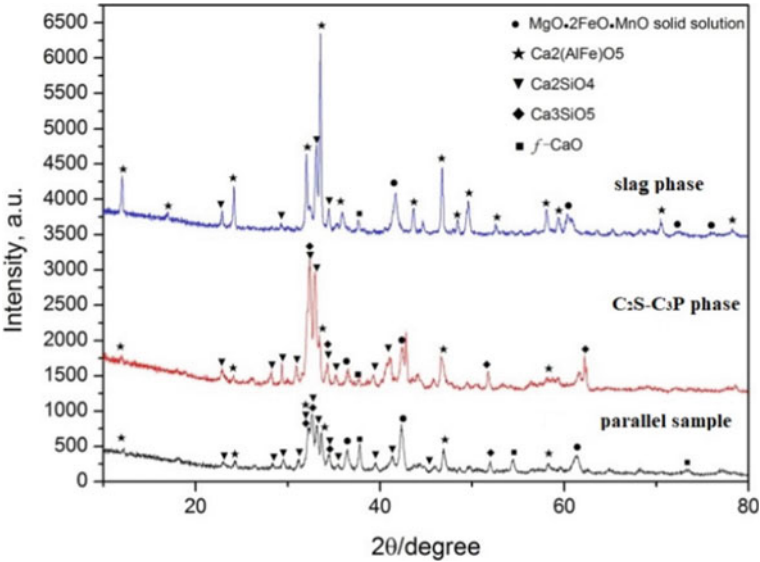


Fig. 6.24 XRD patterns of the separated sample by super gravity

Table 6.15 Chemical compositions of the separated samples by super gravity (wt%)

Phases	CaO	FeO	SiO ₂	MgO	P ₂ O ₅	MnO	Al ₂ O ₃	TiO ₂
C ₂ S–C ₃ P phase	54.20	13.18	20.78	4.59	3.56	1.85	1.08	0.76
Slag phase	39.97	38.67	6.35	6.47	1.04	2.77	2.94	1.79
Parallel slag	48.13	23.99	14.67	5.39	2.49	2.24	1.87	1.20

Table 6.16 Recovery ratios of P₂O₅ and FeO in the separated C₂S–C₃P and slag phases by super gravity (%)

Phases	Mass fraction	Recovery ratio of P ₂ O ₅	Recovery ratio of FeO
C ₂ S–C ₃ P phase	57.5	82.2	–
Slag phase	42.5	–	68.5

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Chapter 7

Selective Crystallization and Separation of V in V-Bearing Slag



Abstract Reports the selective crystallization and separation of V in V-bearing slag. The selective crystallization behavior of V-containing spinel in $\text{FeO-SiO}_2\text{-V}_2\text{O}_3\text{-TiO}_2\text{-CaO-MgO}$ system is reported in Sect. 7.1. The study on selective separation of V in V-bearing slag, including the motion and separation behaviors of V-containing spinel in molten V-bearing slag, is included in Sect. 7.2.

Vanadium (V), as one of the most important alloying elements, is widely used in metallurgy, chemical engineering, and aerospace fields due to its enhancement of mechanical properties on metal materials, such as tensile strength, hardness, and fatigue resistance [1]. Therefore, vanadium consumption in the iron and steel industry represents about 85% of the vanadium-bearing products produced worldwide [2], and with gradual increase of special steel production in the twenty-first century, the requirement of vanadium is rapidly increased.

Vanadium exists mainly in the vanadium-titanium magnetite (VTM), which specifically contains various elements of titanium, vanadium, and iron, and mainly distributes in the Panzhihua and Chengde areas in China [3]. Generally, the vanadium-titanium magnetite has primarily relied on the blast furnace ironmaking and converter steelmaking process, where the vanadium-bearing hot metal and titanium-bearing blast furnace slag are firstly produced in the blast furnace ironmaking process. And then the produced vanadium-bearing hot metal is preoxidized further in a vanadium extraction converter (VEC) by blowing oxygen, where the semi-steel and vanadium-bearing slag are produced further [4, 5].

A representative leaching process is primarily used for vanadium extraction from vanadium (V) bearing slag, which mainly consists of three steps: the salt roasting and leaching, the solution purification, and the precipitation and V_2O_5 fusion [6]. The spinel phase, silicate phase, and the inclusion phase are the main mineral phases in vanadium-bearing slag, where most of vanadium is commonly existed in the spinel phase like Fe_2VO_4 [7–9], which is hard to directly leach out from the spinel. Therefore, the leaching process for extraction of vanadium from V-bearing slag is firstly to oxidize V(III) to acid-soluble V(IV) compounds and/or water-soluble V(V) compounds by calcification roasting and sodium roasting and then to dissolve it by acid leaching and/or water leaching [10–12]. Recently, there are serious pollution

problems in sodium roasting, the calcification oxidizing roasting-alkaline and acid leaching methods is a hot point for the extraction of vanadium from V-bearing slag [3, 13–15]. However, the small size of V-containing spinel and large amount of silicate phases in V-bearing slag result in a low oxidation rate of vanadium during roasting [16], and the large amount of silicate phases would also be dissolved into the leaching solution, which causes some difficulty for the filtration and purification process.

In recent years, several studies on pyrometallurgy for phase transition and enrichment of vanadium in V-bearing slag have been reported. Li et al. [17] studied the effect of CaO addition on phase formation in the Fe–Fe₂O₃–V₂O₃ system and found that the major phases of CaV₂O₅ and CaVO₃ were appeared in the V-bearing system instead of Fe₂VO₄ and Fe₃O₄ with the increase of CaO addition from 0 to 30 wt%. Fang et al. [18] also reported that the V-containing phase transformed from the V-containing spinel ((Mn, Fe, Mg)V₂O₄) to goldmanite (Ca₃V₂(SiO₄)₃) with the increase of CaO addition in V-bearing slag. Diao et al. [19, 20] investigated the growth behavior of spinel in V-bearing slag and reported that the temperature of 1200–1250 °C and the holding time over 45 min was beneficial for the growth of spinel in V-bearing slag. Lindvall et al. [21] reported that most of the vanadium was precipitated into the spinel, and the solubility of V in the liquid phase was generally less than 1 wt%.

Considering the density of V-containing spinel (Mn, Fe)(V, Cr)₂O₄ at room temperature is 4.64×10^3 kg/m³ according to the databases of XRD standard pattern, while the high temperature density of the slag melt is 3.92×10^3 kg/m³ as calculated by Archimedeian method [22], and the solid and liquid phases in V-bearing slag have a density difference. Based on the previous studies of super gravity technology applied in the preparation of functionally gradient materials [23, 24] and removing impurities from alloy melt [25, 26], the significant enhancement of super gravity field on phase separation and mass transfer in high-temperature process is confirmed. In this chapter, selective crystallization and separation of V-containing spinel in V-bearing slag enhanced by super gravity are conducted [27, 28].

In this chapter, selective crystallization and separation of V in V-bearing slag are proposed, and the crystallization, motion, and separation behaviors of V-containing spinel in the FeO–SiO₂–V₂O₃–TiO₂–CaO–MgO system and the V-bearing slag are included in the following sections, respectively:

Section 7.1 reports the selective crystallization of V-containing spinel in FeO–SiO₂–V₂O₃–TiO₂–CaO–MgO system.

Section 7.2 reports the selective separation of V-containing spinel in V-bearing slag, including the motion and separation behaviors of V-containing spinel in V-bearing slag produced from the Panzhihua Iron and Steel Corporation of China enhanced by super gravity.

7.1 Selective Crystallization of V-Containing Spinel in $\text{FeO-SiO}_2\text{-V}_2\text{O}_3\text{-TiO}_2\text{-CaO-MgO}$ System

Based on the main compositions of V-bearing slag produced from the steelmaking process in the Panzhihua Iron and Steel Corporation of China, $\text{FeO-SiO}_2\text{-V}_2\text{O}_3\text{-TiO}_2\text{-CaO-MgO}$ system is conducted for V-bearing slag, and the crystallization behavior of V-containing spinel in the V-bearing slag is studied.

7.1.1 *Thermodynamic Analysis for V in $\text{FeO-SiO}_2\text{-V}_2\text{O}_3\text{-TiO}_2\text{-CaO-MgO}$ System*

The variations of equilibrium phases in $\text{FeO-SiO}_2\text{-V}_2\text{O}_3\text{-TiO}_2\text{-CaO-MgO}$ system with temperature calculated through FactSage 7.2 are shown in Fig. 7.1. It is found that the V-containing spinel (FeV_2O_4) is the first equilibrium phase formed in the molten V-bearing slag, and the vanadium mainly crystallizes into the V-containing spinel at the temperature below 1723 K in thermodynamics. With the decrease of temperature, the titanium (Ti) bearing spinel starts to form in the molten V-bearing slag at 1623 K. As the temperature decreases from 1623 to 1373 K, the amount of V-containing spinel is decreased with the increase of Ti-containing spinel thermodynamically. With the further decrease of temperature from 1373 to 1273 K, the silicates phase also starts to form in the molten V-bearing slag. Thus, the liquid slag phase decreases significantly at 1623–1523 K and 1373–1273 K, respectively, as the successive formation of Ti-containing spinel and silicates phases in the molten V-bearing slag.

7.1.2 *Crystallization Behavior of V-Containing Spinel in $\text{FeO-SiO}_2\text{-V}_2\text{O}_3\text{-TiO}_2\text{-CaO-MgO}$ System*

7.1.2.1 Experimental Procedure

The $\text{FeO-SiO}_2\text{-V}_2\text{O}_3\text{-TiO}_2\text{-CaO-MgO}$ system was firstly prepared by mixing the chemical agents powders of FeO, SiO_2 , V_2O_3 , TiO_2 , CaO, and MgO, based on the main compositions of the V-bearing slag produced from Panzhihua Iron and Steel Corporation of China, as shown in Table 7.1. Subsequently, the V-bearing slag was put into some graphite crucibles lined with molybdenum sheet and heated to 1773 K under high-purity argon atmosphere in muffle furnace, to avoid the possible oxidation of elements in the V-bearing slag. After heating at the constant temperature for 30 min to make the V-bearing slag fully melted, the temperatures were rapidly decreased to 1673 K, 1573 K, 1473 K, and 1373 K at a cooling rate of 20 K/min, and then the melted V-bearing slags were water-quenched, respectively. The samples obtained at

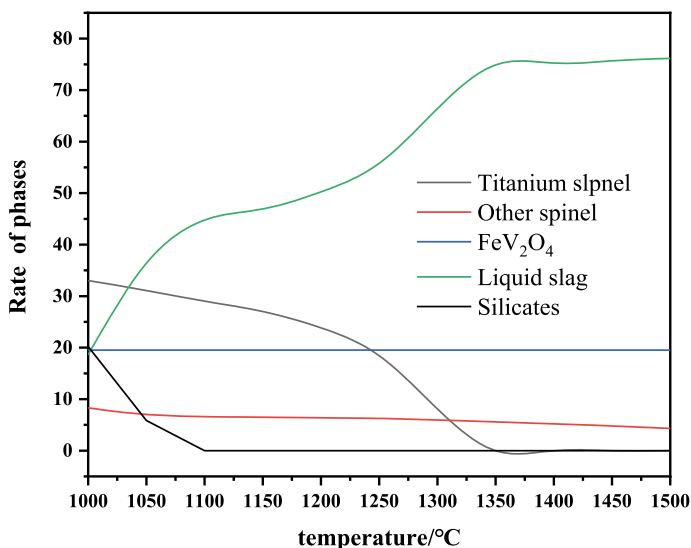


Fig. 7.1 Equilibrium phases in FeO–SiO₂–V₂O₃–TiO₂–CaO–MgO system with temperature

Table 7.1 Chemical composition of V-bearing slag (wt%)

Composition	FeO	SiO ₂	V ₂ O ₃	TiO ₂	CaO	MgO
Content	45.38	19.32	25.44	13.0	3.28	2.86

the different temperatures were characterized by XRD and SEM–EDS methods for the microstructures and mineral compositions formed in the V-bearing slag at the different temperatures.

7.1.2.2 Crystallization Behavior of V-Containing Spinel

The variation in XRD patterns of the V-bearing slag melt after cooling at different temperatures is shown in Fig. 7.2, and the variation of microstructures for the V-bearing slag melt with temperature is shown in Fig. 7.3. It is indicated that the V-containing spinel is the first crystal phase formed in the molten V-bearing slag, which are wrapped in the slag melt. The equiaxed crystals of V-containing spinel are firstly precipitated in the molten V-bearing slag with the temperature decreasing from 1773 to 1473 K, as shown in Fig. 7.3a–c. The only diffraction peaks of V-containing spinel appear in the XRD pattern of the V-bearing slag for the temperature range of 1773–1473 K, as shown in Fig. 7.2. When the temperature decreased to 1373 K, the pyroxene and quartz start to appear in the V-bearing slag melt, which are closely included among the first precipitated spinel phases, as shown in Fig. 7.3d. Thus, the mixed diffraction peaks of V-containing spinel, pyroxene, and quartz are all appeared

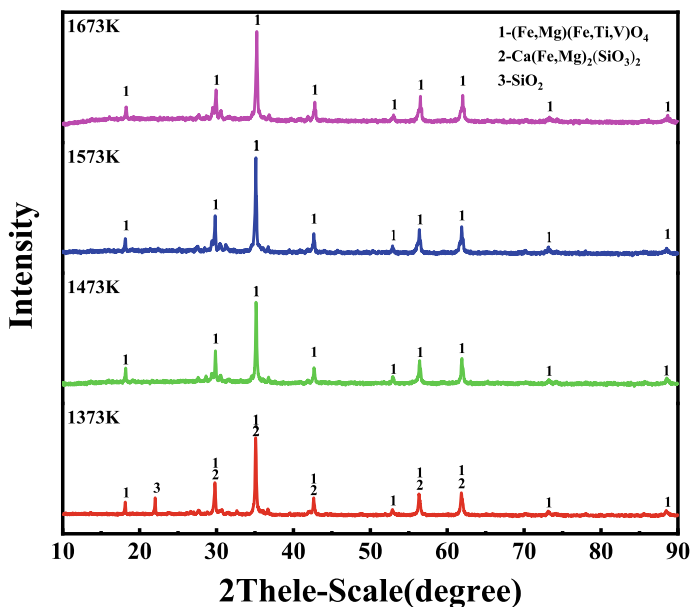


Fig. 7.2 Variation in XRD patterns of the V-bearing slag melt after cooling at different temperatures

in the XRD pattern of the V-bearing slag at the temperature at 1473–1373 K, as shown in Fig. 7.2.

With the help of EDS data for the various phases precipitated in molten V-bearing slag as displayed in Table 7.2, it indicates that the vanadium is mainly enriched into the V-containing spinel phase, in which some Fe, Mg, and Ti are also precipitated into the spinel phase. Moreover, the concentration of vanadium in the V-containing spinel is decreased, while the concentration of titanium in which is gradually increased with the decrease of temperature from 1773 to 1473 K. Accordingly, the temperature above 1473 K is confirmed to be the favorable crystallization temperature range for the single V-containing spinel in molten V-bearing slag.

7.2 Selective Separation of V-Containing Spinel in V-Bearing Slag

7.2.1 Motion Behavior of V-Containing Spinel in V-Bearing Slag Under Super Gravity

On the basis of the crystallization behavior of V-containing spinel in the $\text{FeO-SiO}_2\text{-V}_2\text{O}_3\text{-TiO}_2\text{-CaO-MgO}$ system, selective separation of V-containing spinel in V-bearing slag is conducted by super gravity at the temperature above 1473 K, at

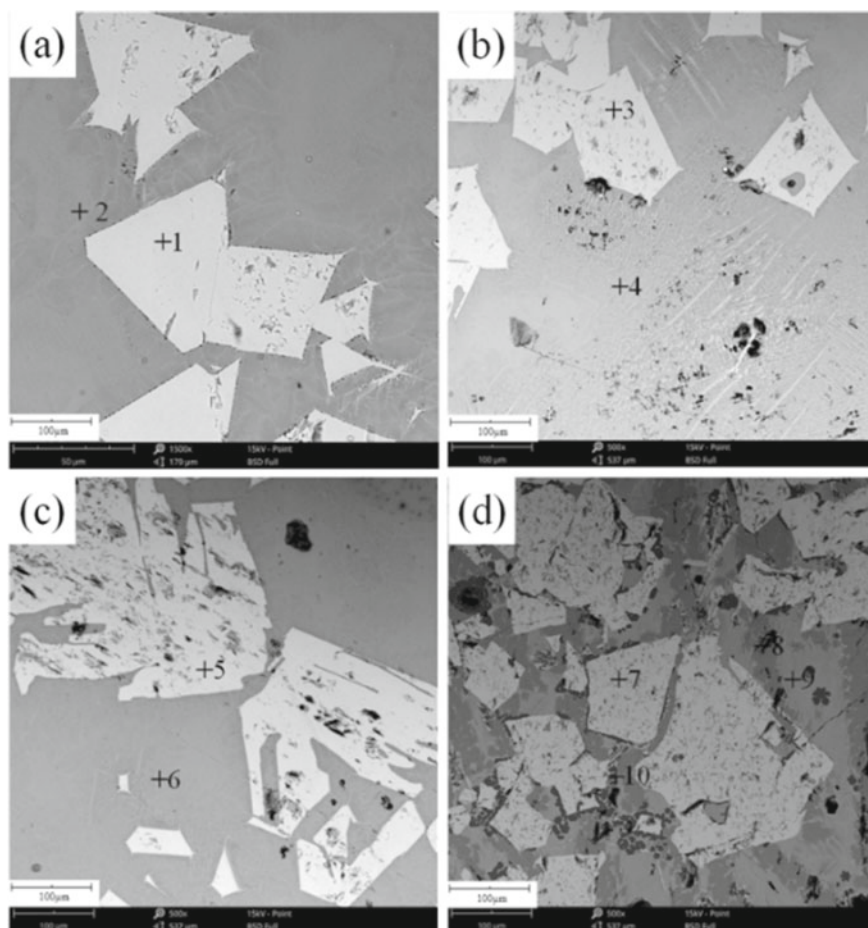


Fig. 7.3 Variation in microstructures of the V-bearing slag melt after cooling at different temperatures: **a** 1673 K; **b** 1573 K; **c** 1473 K; **d** 1373 K

which the vanadium is fully enriched into the V-containing spinel, while the slag phase is in a molten state [27].

7.2.1.1 Experiment Procedure

The V-bearing slag produced from Panzhihua Iron and Steel Corporation of China was employed, whose chemical compositions are listed in Table 7.1. The V-bearing slag was milled to 120 μm and put into an alumina crucible, which was heated in the muffle furnace that was controlled by a program controller with an R-type thermocouple, within the observed precision range of ± 3 K. The V-bearing slag

Table 7.2 EDS data for various phase formed in V-bearing slag

No	Phases	Fe	V	Si	Ca	Mg	Ti	O
Pt.1	V-containing spinel	39.35	40.09	0.00	0.12	1.75	7.55	11.12
Pt.2	Slag phase	40.23	0.93	23.25	5.99	3.75	8.47	17.38
Pt.3	V-containing spinel	41.24	34.40	0.00	0.00	1.74	9.17	13.44
Pt.4	Slag phase	38.25	0.86	22.31	5.86	4.17	7.36	21.20
Pt.5	V-containing spinel	46.79	30.65	0.31	0.00	1.89	11.17	9.20
Pt.6	Slag phase	43.19	1.51	21.43	5.65	3.55	9.95	14.72
Pt.7	V-containing spinel	50.47	31.19	0.00	0.12	1.53	10.25	6.43
Pt.8	Pyroxene	35.89	0.95	32.78	4.83	10.32	2.26	12.98
Pt.9	Slag phase	42.24	0.85	23.79	9.24	0.91	11.33	11.63
Pt.10	Quartz	2.09	0.22	72.64	0.00	0.03	0.82	24.20

was heated in the muffle furnace under argon gas at 1723 K for 30 min to make it fully melted and then rapidly cooled to 1523 K at a cooling rate of 20 K/min. After keeping at 1523 K for 60 min to promote the fully crystallization of V-containing spinel, the molten V-bearing slag was water-quenched.

An amount of 30 g of the V-bearing slag in which the V-containing spinel was fully precipitated, was put into an alumina crucible (ID = 16 mm), and heated to 1473, 1498, 1523, 1548, and 1573 K in the heating furnace of the centrifugal apparatus. And then the centrifugal apparatus was started and adjusted to the gravity coefficients of $G = 450, 650, 850, 1050$, and 1250 , respectively. The centrifugal apparatus was not shut off until the target time of $t = 10, 20, 30, 40$, and 50 min, and then the alumina crucible was taken out and the V-bearing slag melt was water-quenched.

The samples obtained under super gravity with various gravity coefficients, temperatures, and time were sectioned longitudinally along the center axis. One part was crossly divided into two parts along the interface between the gray area and black area, as illustrated in Fig. 7.4b, which were characterized by XRD and XRF methods to obtain the respective mineral and chemical compositions of different parts in the layered sample. The other was measured on the metallographic microscope and image analyzer by the line intercept method (average of 20 fields) to gain the variations in volume fraction and equivalent diameter of V-containing spinel in the layered sample. Simultaneously, the parallel experiment was carried out at 1523 K for 30 min under the normal gravity of $G = 1$.

7.2.1.2 Motion Behavior of V-Containing Spinel

Figure 7.4 shows cross sections of the sample obtained by super gravity with the gravity coefficient of $G = 1050$, $t = 30$ min, and $T = 1523$ K compared with the parallel sample with the conditions of $G = 1$, $t = 30$ min, and $T = 1523$ K. As shown in Fig. 7.4a, the parallel sample shows a homogeneous dark gray structure under the

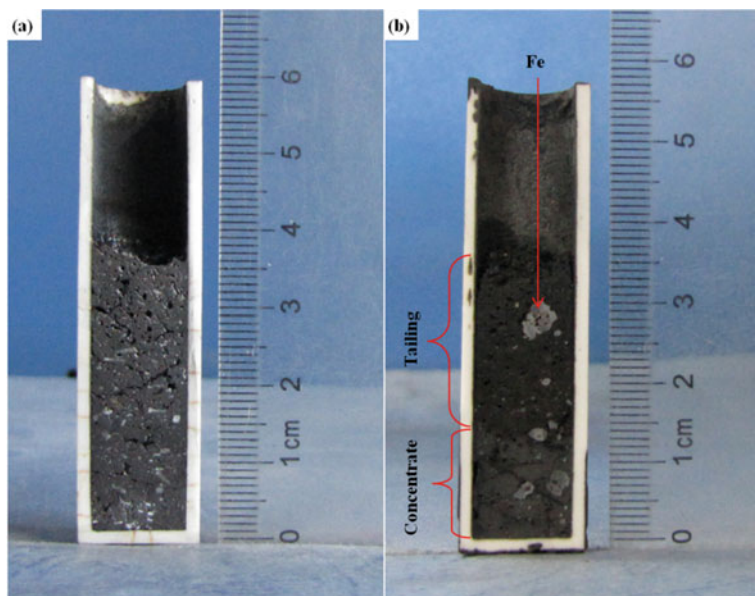


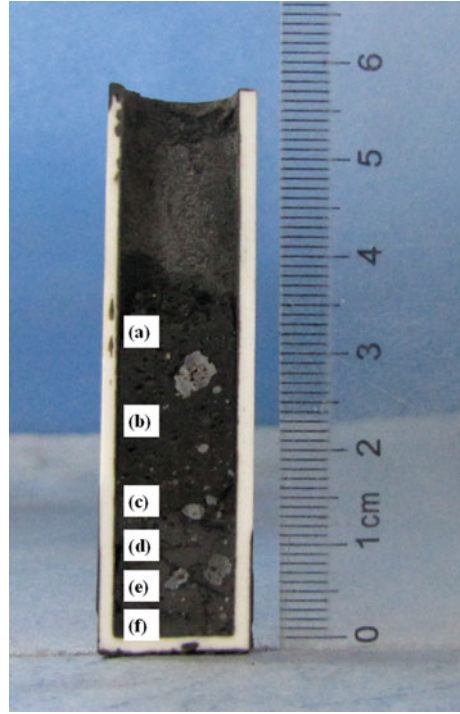
Fig. 7.4 Cross sections of the sample obtained by super gravity compared with normal gravity: **a** $G = 1$, $t = 30$ min, and $T = 1523$ K; **b** $G = 1050$, $t = 30$ min, and $T = 1523$ K

normal gravity, while a significant two-layered structure appears significantly in the sample under the super gravity, with the upper area black and the bottom area gray, as shown in Fig. 7.4b. In addition, there are some metallic iron grains appearing in the section of the two samples.

Figure 7.5 presents the position of different regions in longitudinal section of the layered sample attained by super gravity under the condition of $G = 1050$, $t = 30$ min, and $T = 1523$ K, each area is characterized by the metallographic microscopy for the respective microstructure, and the corresponding results are given in Fig. 7.6. It is confirmed that the slag melt is efficiently migrated to the upper layer as shown in Fig. 7.6a, b, while all of the V-containing spinel are driven to move to the lower layer along the super gravity direction as shown in Fig. 7.6d, f, respectively. A significant interface between the slag melts and V-containing spinel is appeared in the middle region (c), as shown in Fig. 7.6c. Meantime, the size of V-containing spinel crystals significantly increases with the area approaching to the bottom of the layered sample, and the gradient size distribution of V-containing spinel crystals is presented in the samples along the direction of super gravity.

XRD patterns of the different phases in the layered sample obtained by super gravity compared to normal gravity are shown in Fig. 7.7. It indicates that an overwhelming majority of V-containing spinel $(\text{Mn}, \text{Fe})(\text{V}, \text{Cr})_2\text{O}_4$ accumulates in the lower part of the layered sample along the direction of super gravity, while the slag melt moves to the upper part which form the Fe_2SiO_4 and $(\text{Mn}_{0.113} \text{Fe}_{0.977} \text{Ti}_{0.91})(\text{Ti}_{0.09} \text{Fe}_{0.815} \text{Mn}_{0.095})\text{O}_4$ phases during the cooling process.

Fig. 7.5 Positions of six areas in the layered sample obtained by super gravity with $G = 1050$, $t = 30$ min, and $T = 1523$ K



The chemical compositions of the separated samples by super gravity are shown further in Table 7.3. It is confirmed that the mass fraction of V_2O_3 in the V-containing spinel phase is up to 18.92 wt%, where the mass fraction of SiO_2 is only 7.42 wt%. In contrast, the mass fraction of V_2O_3 in the slag phase is decreased to 6.86 wt%, in which the mass fraction of SiO_2 is increased to 24.48 wt%. As calculated via Eqs. 7.1 and 7.2, the recovery ratio of V in the V-containing spinel phase is 74.60%, and the removal ratio of Si in which is 75.59% under the condition of $G = 800$, which is listed in Table 7.4.

$$\varepsilon_i = \frac{m_c \omega_c}{m_r \omega_r + m_c \omega_c} \times 100\% \quad (7.1)$$

$$\varepsilon_j = \frac{m_r \omega_r}{m_r \omega_r + m_c \omega_c} \times 100\% \quad (7.2)$$

where ε_i and ε_j are the recovery ratio of V in the V-containing spinel and slag phases, or the removal ratio of Si in the slag and V-containing spinel phases, wt%; m_c and m_r are the mass fractions of the V-containing spinel and slag phases, wt%; and ω_c and ω_r are the mass fractions of V_2O_3 or SiO_2 in the V-containing spinel and slag phases, wt%.

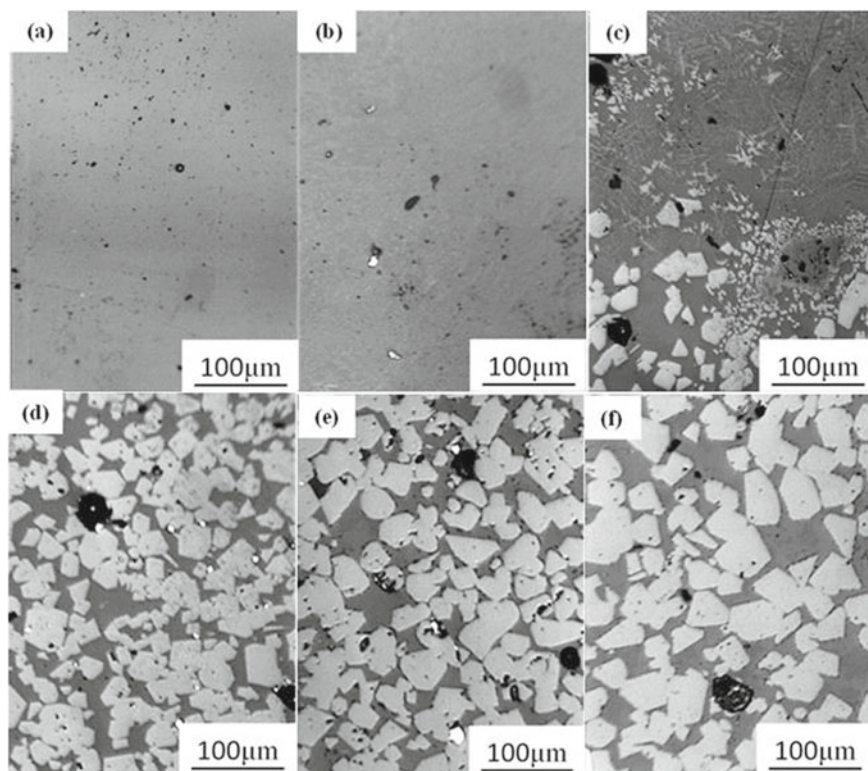


Fig. 7.6 Micrographs of six areas in the layered sample achieved by super gravity with $G = 1050$, $t = 30$ min, and $T = 1523$ K

Tables 7.5, 7.6 and 7.7 present the variations in volume fraction of V-containing spinel crystals obtained in different areas of the layered samples with different gravity coefficient at $t = 30$ min and $T = 1523$ K, with different time at $G = 1050$ and $T = 1523$ K, and with different temperature at $G = 1050$ and $t = 30$ min, respectively. The corresponding equivalent diameter of V-containing spinel crystals in the different areas of the layered samples is showed further in Figs. 7.8, 7.9 and 7.10. It is in evidence that the volume fraction of V-containing spinel crystals is approaching to zero from the upper area (a) to area (b) with the gravity coefficient of $G \geq 1050$, $t \geq 30$ min, and $T \geq 1523$ K, as shown in Tables 7.5, 7.6 and 7.7. Moreover, the volume fraction of V-containing spinel crystals increases slightly from the lower area (d) to area (f), and the peak value appears in the bottom area (f), as shown in Figs. 7.8, 7.9 and 7.10. This confirms the directional concentration behaviors of V-containing spinel in the molten V-bearing slag under the force of super gravity.

It can be included from the motion behavior of V-containing spinel with the gravity coefficient, time, and temperature that the gravity coefficient of $G \geq 1050$, time of $t \geq 30$ min, and temperature of $T \geq 1523$ K are the necessary conditions for the

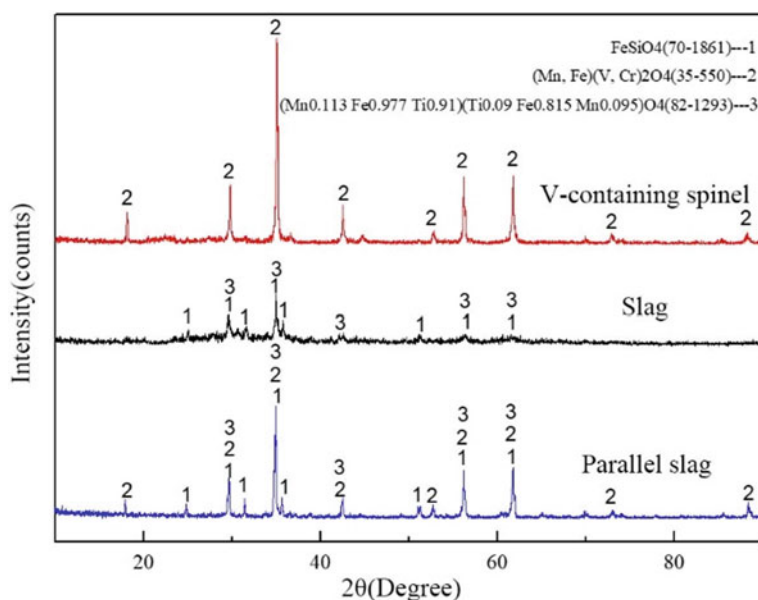


Fig. 7.7 X-ray diffraction of the samples obtained by super gravity

Table 7.3 Chemical compositions of the separated samples by super gravity (wt%)

Phases	FeO	SiO ₂	V ₂ O ₃	TiO ₂	MnO	Cr ₂ O ₃	Al ₂ O ₃	MgO	CaO
V-containing spinel phase	41.24	7.42	18.92	13.16	8.81	3.01	3.03	2.35	2.06
Slag phase	32.48	24.88	6.86	11.32	10.04	5.01	3.54	3.19	3.08
Parallel sample	37.02	15.25	13.34	12.49	9.22	3.94	3.23	2.84	2.67

Table 7.4 Recovery ratio of V and removal ratio of Si in the separated samples by super gravity

Phases	Mass fraction of V ₂ O ₃ (wt%)	Mass fraction of SiO ₂ (wt%)	Recovery ratio of V (%)	Removal ratio of Si (%)
V-containing spinel phase	18.92	7.42	74.60	75.59
Slag phase	6.86	24.48	25.40	24.41

efficient separation of V-containing spinel crystals in molten V-bearing slag, where the V-containing spinel crystals can be fully separated from the molten V-bearing slag and efficiently concentrated into the lower areas along the super gravity direction.

Table 7.5 Variations in volume fractions of V-containing spinel crystals in different areas of the layered samples with different gravity coefficient at $t = 30$ min and $T = 1523$ K

Gravity coefficient	Areas				
	(a)	(b)	(d)	(e)	(f)
450	3.16	8.44	43.22	46.53	48.99
650	1.68	5.59	47.73	50.84	53.59
850	0	2.28	53.01	55.78	57.03
1050	0	0	54.82	57.43	58.49
1250	0	0	57.85	59.11	60.74

Table 7.6 Variations in volume fractions of V-containing spinel crystals in different areas of the layered samples with different time at $G = 1050$ and $T = 1523$ K

Time (min)	Areas				
	(a)	(b)	(d)	(e)	(f)
10	5.86	10.24	40.24	44.29	45.98
20	0	7.82	45.56	49.44	52.57
30	0	0	54.82	57.43	58.49
40	0	0	57.09	59.65	60.34
50	0	0	59.14	61.87	62.48

Table 7.7 Variations in volume fractions of V-containing spinel crystals in different areas of the layered samples with different temperature at $G = 1050$ and $t = 30$ min

Temperature (K)	Areas				
	(a)	(b)	(d)	(e)	(f)
1473	3.95	8.42	43.07	47.28	49.02
1498	0	5.33	49.91	53.76	55.68
1523	0	0	54.82	57.43	58.49
1548	0	0	56.24	58.35	59.22
1573	0	0	57.53	60.06	61.61

7.2.2 Separation of V-Containing Spinel from V-Bearing Slag by Super Gravity

Based on the crystallization of V-containing spinel in the $\text{FeO-SiO}_2\text{-V}_2\text{O}_3\text{-TiO}_2\text{-CaO-MgO}$ system and motion behavior of V-containing spinel in the molten V-bearing slag under the super gravity, selective separation of V-containing spinel from V-bearing slag by super gravity is conducted further [28].

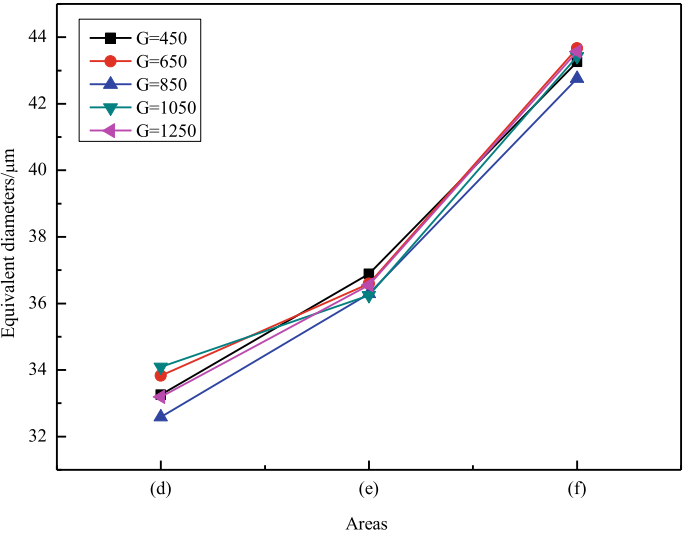


Fig. 7.8 Variations in equivalent diameters of V-containing spinel crystals in different areas of the layered samples with different gravity coefficient at $t = 30 \text{ min}$ and $T = 1523 \text{ K}$

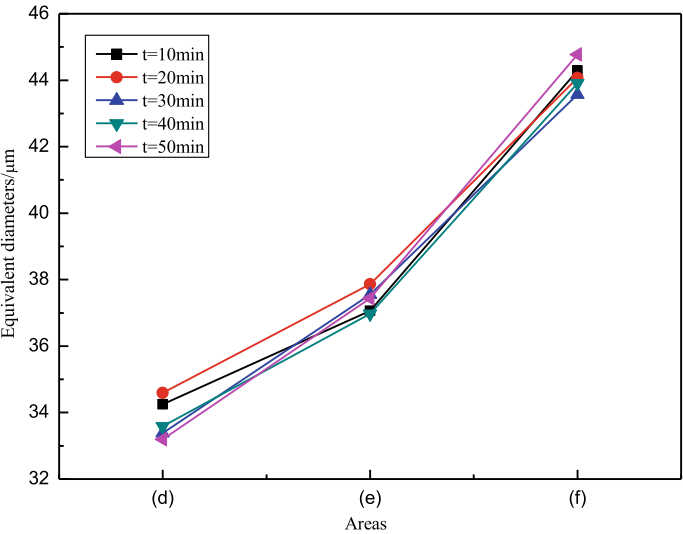


Fig. 7.9 Variations in equivalent diameters of V-containing spinel crystals in different areas of the layered samples with different time at $G = 1050$ and $T = 1523 \text{ K}$

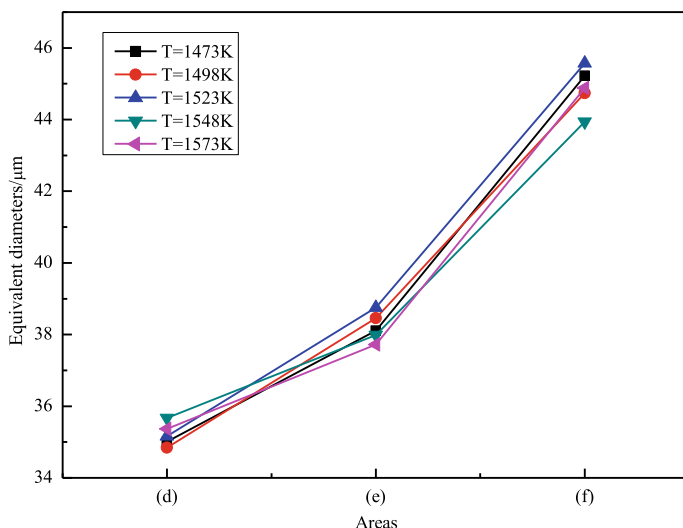


Fig. 7.10 Variations in equivalent diameters of V-containing spinel crystals in different areas of the layered samples with different temperature at $G = 1050$ and $t = 30$ min

7.2.2.1 Experimental Procedure

The V-bearing slag produced from the Panzhihua Iron and Steel Corporation of China was put into an alumina crucible and melted to 1723 K holding for 10 min in the muffle furnace, and then the melted V-bearing slag was rapidly cooled to 1557 K at a cooling rate of 20 K/min. Then the melted V-bearing slag was cooled slowly with a cooling rate of 0.5 K/min for the fully crystallization of V-containing spinel. After slowly cooling for 100 min, the V-bearing slag melt was quenched into water.

An amount of 20 g of the V-bearing slag where the V-containing spinel was fully precipitated was put into a graphite crucible (ID = 19 mm) with the pore size of $d = 0.5$ mm at the bottom, which was used as the filter to intercept the V-containing spinel in molten V-bearing slag. Another graphite crucible below was employed for holding the slag melt passing through the filter. The V-bearing slag was heated to 1557 K in the heating furnace of the centrifugal apparatus, and then the centrifugal apparatus was started and adjusted to the specified angular velocity of 1794 r min^{-1} , namely $G = 900$ at the constant 1557 K. After super gravity separation for 20 min, the centrifugal apparatus was shut off, and the graphite crucible was water-quenched. The separated samples from the V-bearing slag were sectioned longitudinally along the center axis. One part was characterized by XRD and XRF methods, while the other part was measured on the SEM and EDS methods. Simultaneously, the parallel experiment was carried out further at 1557 K for 20 min in the normal gravity.

7.2.2.2 Separation Behavior of V-Containing Spinel

Figure 7.11 shows vertical sections of the samples obtained by super gravity with the gravity coefficient of $G = 900$, $t = 20$ min, and $T = 1557$ K, compared with the parallel sample with the conditions of $G = 1$, $t = 20$ min, and $T = 1557$ K. Apparently, the entire sample is completely blocked by the filter, and a uniform porous structure is observed for the sample attained in the normal gravity field ($G = 1$), as presented in Fig. 7.11a. In contrast, the V-bearing slag is separated into two different parts by the filter in a super gravity field ($G = 1050$). The sample that held on the filter appears porosity with some metallic iron grains in the section, while the sample goes through the filter presents a gray glassy state, respectively.

Combined with the SEM and random EDS analysis for the separated samples by super gravity as shown in Fig. 7.12, it indicates that the V-containing spinel crystals with an average equivalent diameter of $30\text{ }\mu\text{m}$ are efficiently intercepted on the filter, while the slag melts fully pass through the filter and separate from the V-containing spinel in the lower crucible, where it is hard to find any spinel crystals included in the sample that are below the filter.

With the help of EDS analysis for the separated V-containing spinel and slag phases as shown in Table 7.8, it indicates that vanadium is mainly enriched into the V-containing spinel and separated from the molten V-bearing slag, in which the mass fractions of Fe, V, and O are in agreement with the chemical formula of Fe_2VO_4 . In contrast, the Fe, Ti, Mn, Mg, Al, Ca, Cr, and O are mainly transformed into the slag melt and separated from the V-containing spinel phase as driven by super gravity.

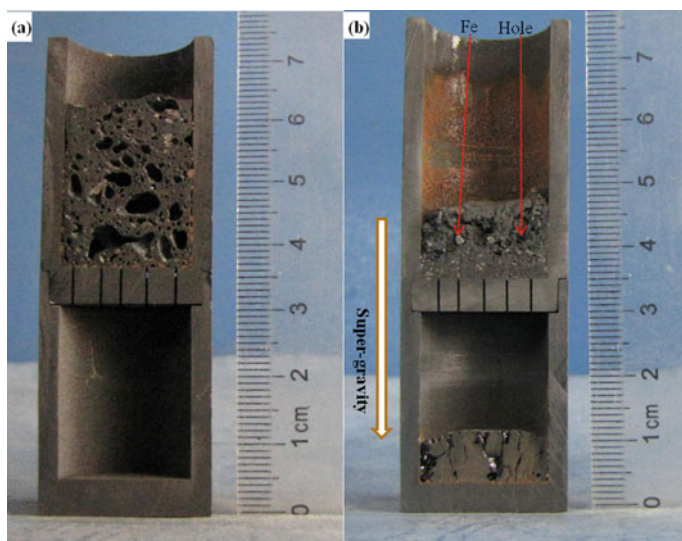


Fig. 7.11 Vertical profile of the samples obtained by super gravity compared with normal gravity: **a** $G = 1$, $t = 20$ min, and $T = 1557$ K; **b** $G = 900$, $t = 20$ min, and $T = 1557$ K

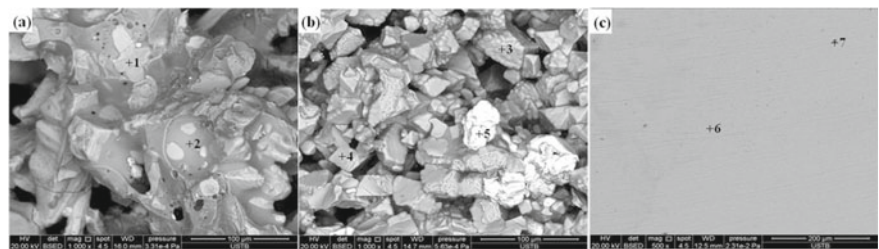


Fig. 7.12 Microstructure of separated samples compared with normal gravity: **a** normal gravity; **b** V-containing spinel phase; **c** slag phase

Combined with the XRD patterns for the separated two samples attained by super gravity and normal gravity as shown in Fig. 7.13, it is confirmed that the separated V-containing spinel phase on the filter shows the only strong diffraction peak value of V-containing spinel, while the slag phase below the filter shows a weak diffraction peak value of silicate and spinel. This confirms that the V-containing spinel crystals slag melt is efficiently separated from the molten V-bearing slag by super gravity, and the separated slag melt is transformed further to Fe_2SiO_4 , Fe_2TiO_4 , and Mn_2VO_4 phases during the cooling process.

Chemical compositions of the separated V-containing spinel and slag phases from molten V-bearing slag are shown further in Table 7.9. The mass fraction of V_2O_3 in the separated V-containing spinel phase is up to 25.19 wt%, while the mass fraction of SiO_2 in which is only 2.17 wt%. In contrast, the mass fraction of V_2O_3 is decreased to 0.81 wt% and that of SiO_2 is increased to 32.23 wt% in the separated slag phase. The recovery ratio of V and removal ratio of Si in the V-containing spinel and slag phases are calculated further via Eqs. 7.1 and 7.2. It confirms that the recovery ratio of V in the V-containing spinel phase is high up to 97.40%, and the removal ratio of Si in which also reaches 92.50%, respectively.

Table 7.8 EDS data of the V-containing spinel and slag phases

No	Fe	V	Ti	Mn	Al	Mg	Si	Ca	Cr	O
Pt.1	32.29	20.72	11.31	7.68	1.55	1.75		2.96	3.02	18.72
Pt.2	15.34	1.50	5.32	7.82	4.52	2.53	18.09	5.38	5.11	34.39
Pt.3	41.92	21.57	2.16	3.24	1.68	1.70		0.81	0.55	26.37
Pt.4	40.33	19.54	3.32	2.38	2.06	1.29		1.19	0.81	29.08
Pt.5	100									
Pt.6	19.02	0.77	15.12	13.46	6.16	5.09	16.28	5.92	5.49	12.69
Pt.7	7.87	0.59	4.47	5.98	6.46	3.60	15.75	8.79		46.48

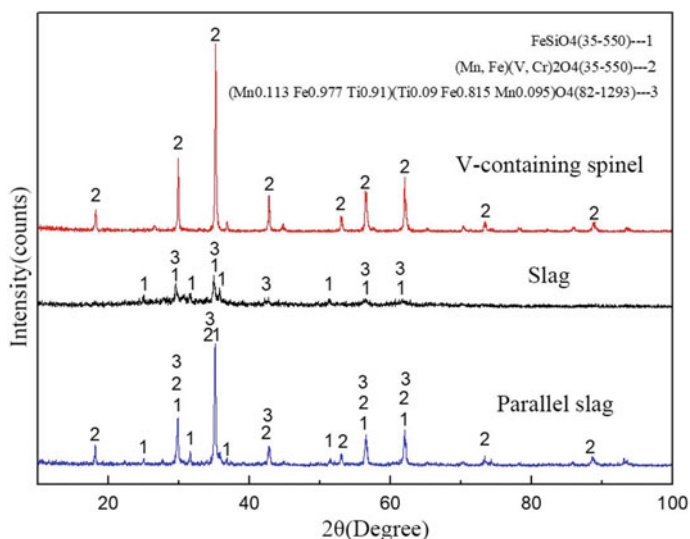


Fig. 7.13 XRD patterns of the separated V-containing spinel and slag phases

Table 7.9 Chemical compositions of the separated V-containing spinel and slag phases (wt%)

Phases	FeO	SiO ₂	V ₂ O ₃	TiO ₂	MnO	Cr ₂ O ₃	Al ₂ O ₃	MgO	CaO
V-containing spinel phase	42.22	2.17	25.19	13.42	8.45	2.01	2.19	2.23	2.35
Slag phase	30.36	32.23	0.81	10.07	10.11	5.16	5.02	3.54	3.30
Parallel sample	37.18	15.15	14.23	12.00	9.16	3.35	3.39	2.79	2.75

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