Article

Migration and Enrichment Behaviors of Ca and Mg Elements during Cooling and Crystallization of Boron-Bearing Titanium Slag Melt

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Abstract: Synthetic rutile was prepared from titanium slag melt with low energy consumption and a small amount of additive (B_2O_3) in our previous work. The modification mechanism of titanium slag was not clear enough. The migration and enrichment behaviors of Ca and Mg elements during cooling and crystallization of boron-bearing titanium slag melt were characterized by XRF, FESEM, EMPA, and XPS. Results show that when additive (B_2O_3) is added, Ti elements are migrated and enriched in the area to generate rutile, while Ca, Mg, and B elements are migrated and enriched in another area to generate borate. With the additive (B_2O_3) amount increased, Ca and Mg element migration is complete and more thorough. Additive (B_2O_3) promotes rutile formation and inhibits the formation of anosovite during cooling and crystallization of titanium slag melt. With the additive (B_2O_3) amount increasing from 0% to 6%, the proportion of Ti^{3+} in the modified titanium slag reduces from 9.15% to 0%, and the proportion of Ti^{4+} increases from 90.85% to 100% under the same cooling and crystallization condition. The result will lay the foundation for the efficient preparation of synthetic rutile by adding B_2O_3 to the titanium slag melt.

Keywords: titanium slag; migration and enrichment; Ca and Mg element; additive (B_2O_3); titanium-rich material

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1. Introduction

Titanium white has been used in paint, plastic, paper, fiber, ink, rubber, food, and cosmetics [1–3]. Titanium alloy has been applied in the chemical industry, aerospace, electric power, ocean engineering, medicine, shipbuilding, sports, metallurgy, and salt making [4–7]. Titanium tetrachloride ($TiCl_4$) is an important intermediate to prepare titanium white from the chloride process and sponge titanium in the titanium metallurgy industry [8]. The mainstream process for preparing $TiCl_4$ is fluidized chlorination [9].

During the fluidized chlorination process, the mixed particles of petroleum coke and titanium-rich material are suspended by chlorine gas (Cl_2). Titanium dioxide (TiO_2) in the titanium-rich material is chlorinated to form $TiCl_4$, while other impurity oxides are chlorinated to form the corresponding chlorides. Calcium chloride ($CaCl_2$, melting point 1045 K) and magnesium chloride ($MgCl_2$, melting point 987 K) formed during the chlorination reaction process are in their liquid phase under the chlorination temperature range of 1073–1273 K [10]. The formation of liquid $CaCl_2$ and $MgCl_2$ during the chlorination reaction process will cause the agglomeration of solid particles and deteriorate the fluidization state, resulting in the cessation of the chlorination operation [11]; therefore, the fluidized chlorination process requires the total content of CaO and MgO in the titanium-rich material to be as low as possible, generally less than 1.50% [12].

The preparation of high-quality titanium-rich material is particularly important in the titanium metallurgy industry. With the gradual depletion of natural rutile, ilmenite has become the main raw material in the titanium metallurgy industry. Ilmenite accounts for 92.68% of the titanium mineral consumption around the world in 2020 [13]. The Panxi area in southwestern China holds 870 million tons of ilmenite reserves, accounting for 35.17% of the world's ilmenite reserves [14,15]. At present, ilmenite is mainly upgraded to titanium-rich material by several commercialized processes, such as reduction smelting [16], Becher [17], sulfuric acid leaching [18], and hydrochloric acid leaching [19]. The product of the former process is called titanium slag, while the product of the latter three processes is called synthetic rutile. The reduction smelting has become a dominant process for preparing titanium-rich material worldwide [20]. Titanium slag prepared by the reduction smelting from ilmenite in the Panxi area cannot meet the requirement of the fluidized chlorination process due to its high content of CaO and MgO. The preparation of high-quality titanium-rich material has become an urgent requirement for developing the titanium metallurgy industry in China; therefore, upgrading titanium slag with a high content of CaO and MgO to high-quality titanium-rich material has become a hot spot in the titanium metallurgy industry.

There are some studies on upgrading titanium slag with high content of CaO and MgO to high-quality titanium-rich material [21–27]. The essence of titanium slag upgrading technology is to enrich titanium through phase reconstruction of the titanium slag and subsequent impurity separation of the modified product. What is obtained after the phase reconstruction of the titanium slag is called a modified product. In these upgrading techniques, a certain amount of solid, liquid, or gas additives was used to cause phase reconfiguration of the titanium slag at higher temperatures to obtain the modified product. According to the literature on the upgrading technologies of titanium slag, the addition amount is 42.8% of the mass of titanium slag for a solid additive; the addition amount is 16% of the mass of titanium slag for a liquid additive; the addition amount is enough for a gas additive. The treating temperature of titanium slag is generally about 900 °C, which requires a high energy consumption to maintain such a high temperature. The high-quality titanium-rich material was prepared at the cost of high energy consumption and a large amount of additive. In our previous work, high-quality titanium-rich material was prepared with low energy consumption and a small amount of additive (B_2O_3) [28]. Upgrading titanium slag with high content of CaO and MgO to high-quality titanium-rich material included two processes: modification and leaching. During the modification process, additive (B_2O_3) was added into the titanium slag melt to obtain boron-bearing titanium slag melt. The modification was achieved by controlling the migration and enrichment behavior of elements in the melt to make alkali earth elements and Ti elements enriched in different phases. The modification was completed, and the modified titanium slag was obtained after the cooling and crystallization of boron-bearing titanium slag melt. During the leaching process, hydrochloric acid was used as a leaching agent to remove CaO and MgO impurity in the modified titanium slag to obtain high-quality titanium-rich material. CaO and MgO impurity in the modified titanium slag can be easily removed during the leaching process due to the different acid solubility between the titanium-rich phase and the alkaline earth-rich phase; therefore, the upgrading effectiveness depended largely on the modification effectiveness of titanium slag with high-content CaO and MgO. However, the modification mechanism of titanium slag with high-content CaO and MgO was not clear enough. Therefore, it is very valuable and necessary to investigate the migration and enrichment behavior of Ca and Mg during the cooling and crystallization of boron-bearing titanium slag melt.

In this work, the migration and enrichment behavior of Ca and Mg element during cooling and crystallization of boron-bearing titanium slag melt were characterized by X-ray fluorescence spectrometer (XRF), field emission scanning electron microscope (FESEM), electron microprobe analyzer (EMPA), and X-ray photoelectron spectroscopy analysis

instrument (XPS). The result will lay the foundation for the efficient preparation of synthetic rutile by adding B_2O_3 to the titanium slag melt.

2. Materials and Methods

2.1. Material

Titanium slag in this work was obtained from the city of Panzhihua in southwestern China. The chemical composition of the titanium slag was as follows (wt.%): TiO_2 = 73.81, CaO = 1.00, MgO = 2.51, FeO = 12.21, SiO_2 = 5.89, and MnO = 1.53, Al_2O_3 = 2.83. The total content of CaO and MgO in the titanium slag is 3.51%, which cannot meet the requirement of the fluidized chlorination process.

2.2. Experiment Producer

Although upgrading titanium slag with high content of CaO and MgO to high-quality titanium-rich material included modification and leaching, the modification process was focused on in this work. The experiment producer in the modification process was as follows. Firstly, titanium slag and additive (B_2O_3) with different mass ratios were weighed and mixed, respectively. The additive (B_2O_3) amount was 0%, 2%, 4%, and 6%, respectively. The mixture was pressed into a ball and the ball was placed into a cylindrical crucible made of metal molybdenum. The crucible containing titanium slag and additive (B_2O_3) was placed into a vacuum induction furnace. The protective atmosphere with argon gas was implemented in the vacuum induction furnace. Then, the vacuum induction furnace was turned on, and heating was started. When the input power of the induction furnace was maintained at 11.00 kW, the temperature of the melts in the crucible was 1700 °C. After the mixture was melted, the vacuum induction furnace maintained the input power at 11.00 kW and heated for 30 min to obtain boron-bearing titanium slag melt. After the predetermined time was reached, the crucible was taken out of the vacuum induction furnace and placed in the air for natural cooling. After cooling to room temperature, the modified titanium slag was obtained for characterization.

2.3. Characterization Method

XRF (SHIMDZU, XRF1800, Kyoto, Japan) was adopted to characterize the chemical composition of the titanium slag. FESEM (JEOL, JSM7800F, Tokyo, Japan) was adopted to characterize the influence of additive (B_2O_3) amount on the micromorphology of the modified titanium slag. EMPA (JEOL, JXA8230, Tokyo, Japan) was adopted to characterize the influence of additive (B_2O_3) amount on the element distribution of the modified titanium slag. XPS (Thermo Fisher Scientific, ESCALAB250Xi, Waltham, MA, USA) was used to characterize the influence of additive (B_2O_3) amount on the valence state of titanium in the modified titanium slag.

3. Results and Discussion

3.1. The Micromorphology of the Modified Titanium Slag with Different Amounts of Additive (B_2O_3)

FESEM was used to characterize the influence of additive (B_2O_3) amount on the micromorphology of the modified titanium slag to reveal the migration and enrichment behavior of Ca and Mg elements during cooling and crystallization of boron-bearing titanium slag melt. The micromorphology of the modified titanium slag with different additive (B_2O_3) amounts is shown in Figure 1. In Figure 1, the surface of the modified titanium slag is compact and smooth, without cracks, holes, or flocculent substances. The modified titanium slag is mainly composed of an inter-connected flake structure. There are long strip structures among the gap of the flake structure. There is a clear boundary between the two types of structures. The flake structure in the modified titanium slag has a bright color, while the long strip structure has a dark color.

Figure 1. Micromorphology of the modified titanium slag with different additive (B_2O_3) amounts: (a) 0% B_2O_3 , (b) 2% B_2O_3 , (c) 4% B_2O_3 , and (d) 6% B_2O_3 .

The backscattered electron imaging can be used to display the micromorphology contrast and composition contrast. The contrast under FESEM is determined by the type of element in the enriched area. The backscattered electron imaging has become an important method to infer the element type and characterize the preliminary element's migration and enrichment behavior; therefore, the micromorphology of the modified titanium slag was characterized with the backscattered electron imaging in this section. The number of backscattered electrons increases as the corresponding atomic number increases. The area enriched with heavy elements receives more backscattered electrons and shows bright contrast; the area enriched with light elements receives fewer backscattered electrons and shows dark contrast.

Among the main constituent element in the modified titanium slag, B, Mg, Al, Si, and Ca are relatively light elements, while Ti is a relatively heavy element. When comparing to Figure 1, it can be seen that the Ti is concentrated in the flake and bright area, and elements such as B, Mg, Al, Si, and Ca are concentrated in the long strip and dark area. Combined with the phase characteristic of titanium slag, it can be deduced that the phase of rutile is formed in the flake and bright area, while the phase of borate is formed in the long strip and dark area. Moreover, Ti is concentrated with the form of rutile in the flake and bright area, and B, Mg, and Ca elements are concentrated with the form of borate in the long strip and dark area during cooling and crystallization of boron-bearing titanium slag melt.

3.2. Effect of Additive (B_2O_3) Amount on the Element Distribution of the Modified Titanium Slag

EPMA was used to characterize the influence of additive (B_2O_3) amount on the element distribution of the modified titanium slag to reveal the migration and enrichment behavior of Ca and Mg elements during cooling and crystallization of boron-bearing titanium slag melt. The backscattered electron image of the cross-section of block sample of modified titanium slag with different additive (B_2O_3) amounts is shown in Figure 2. In Figure 2, the bright areas may be enriched areas of Ti, and the dark areas are enriched areas of Si and B. Modified titanium slag mainly contains two types of phases: titanium-rich phases correspond to bright colored areas, such as Point 1, Point 3, Point 5, and Point 7; Si, B, Ca, Mg-rich phases correspond to dark areas, such as Point 2, Point 4, Point 6, and Point 8.

Figure 2. The backscattered electron image of the cross-section of block sample of modified titanium slag with different additive (B_2O_3) amounts.

The chemical composition of the points in Figure 2 is shown in Table 1. In Table 1, when B_2O_3 is not added, most of the TiO_2 and MgO are distributed in the bright areas, and most of the CaO , SiO_2 , Al_2O_3 , and MnO are distributed in the dark areas in the modified titanium slag. This distribution law is consistent with the results of phase analysis in the raw titanium slag; therefore, when B_2O_3 is not added, the spatial distribution of elements in the modified titanium slag and the raw titanium slag has no significant differences. When B_2O_3 is added, the bright area in the backscattered image is almost pure TiO_2 ($\omega(TiO_2) > 97.5\%$), almost free of Ca , Mg , and other impurity oxides; the dark area contains very low content of TiO_2 ($\omega(TiO_2) < 3.80\%$), and contains high content of Ca , Mg , B , and other impurity oxides. Therefore, B_2O_3 promotes titanium and impurity elements in the molten titanium slag to enrich two different regions.

Table 1. The chemical composition of the points in Figure 2 (wt.%).

Point	TiO_2	CaO	MgO	B_2O_3	Al_2O_3	MnO	Fe_2O_3	SiO_2
1	74.36	0.10	3.63	0.00	2.49	1.21	18.12	0.09
2	6.76	10.34	1.56	0.00	10.51	3.39	16.42	51.03
3	98.54	0.25	0.00	0.13	0.09	0.09	0.81	0.10
4	3.79	7.76	3.00	19.67	9.17	3.50	19.35	33.77
5	97.69	0.22	0	0	0.09	0.18	1.69	0.09
6	5.26	5.43	3.65	24.71	8.18	4.22	25.90	25.61
7	99.43	0.09	0.00	0.00	0.10	0.05	0.29	0.03
8	3.90	4.77	4.71	27.30	8.56	4.22	23.42	23.12

WDS mapping analysis of the cross-section of block sample of the modified titanium slag with the additive (B_2O_3) amount of 0% is displayed in Figure 3. In Figure 3, the enrichment area of the Ca and Si elements clearly overlap each other, and the enrichment area of Ti and Mg elements distinctly overlap each other. The two overlapped areas do not overlap each other at all. Combined with the phase characteristic of titanium slag, it can be inferred that the phase of silicate is formed in the enrichment area of Ca and Si , while the solid solution of anosovite is formed in the enrichment area of Ti and Mg . The migration and enrichment behavior of Ca and Mg during cooling and crystallization of titanium slag melt with the additive (B_2O_3) amount of 0% are consistent with that of the raw titanium slag melt. Therefore, there are no obvious migration and enrichment behaviors of Ca and Mg during cooling and crystallization of titanium slag melt with the additive (B_2O_3) amount of 0%.

WDS mapping analysis of the cross-section of block sample of the modified titanium slag with the additive (B_2O_3) amount of 2% is displayed in Figure 4.

In Figure 4, the regional characteristic of element enrichment in the modified titanium slag with the additive (B_2O_3) amount of 2% is obvious. The enrichment area of Ti in the upper right area in Figure 3 contains almost no other elements except Ti and O . The enrichment area of Mg and Fe and the enrichment area of Ti overlap each other partially, while elements other than Ti are also enriched in the narrow and long area in Figure 3. Combined with the phase characteristic of titanium slag, it can be referred that the enrichment area of Ti is the phase of rutile, the overlapped enrichment area of Mg , Fe , and Ti is the solid solution of anosovite, and the long and narrow area is the phase of borate. It can be seen that the migration and enrichment behavior of Ca and Mg during cooling and crystallization of the titanium slag melt with the additive (B_2O_3) amount of 2% are more obvious than that of the titanium slag melt with the additive (B_2O_3) amount of 0%. This phenomenon indicates a slight migration and enrichment behavior of Ca and Mg during cooling and crystallization of titanium slag melt with the additive (B_2O_3) amount of 2%.

Figure 3. WDS mapping analysis of the cross-section of block sample of the modified titanium slag with the additive (B_2O_3) amount of 0%: (a) total, (b) Ti, (c) Ca, (d) Mg, (e) B, (f) Mn, (g) Fe, and (h) Si.

Figure 4. WDS mapping analysis of the cross-section of block sample of the modified titanium slag with the additive (B_2O_3) amount of 2%: (a) total, (b) Ti, (c) Ca, (d) Mg, (e) B, (f) Mn, (g) Fe, and (h) Si.

WDS mapping analysis of the cross-section of the block sample of the modified titanium slag with the additive (B_2O_3) amount of 4% is displayed in Figure 5.

Figure 5. WDS mapping analysis of the cross-section of block sample of the modified titanium slag with the additive (B_2O_3) amount of 4%: (a) total, (b) Ti, (c) Ca, (d) Mg, (e) B, (f) Mn, (g) Fe, and (h) Si.

In Figure 5, the element enrichment in the modified titanium slag with the additive (B_2O_3) amount of 4% has a relatively distinct regional characteristic. The backscattered electron imaging in the modified titanium slag includes two distinct areas: the bright leaf-shaped area and the dark area. Ti is concentrated in the bright leaf-shaped area in the middle of the visual field, while almost no other elements except Ti and O are concentrated in this area. Ca, Mg, B, and other impure elements are concentrated in the dark area. The element distribution in the modified titanium slag is spatially consistent with the two areas with different brightness and darkness on the backscattered electron imaging. Combined with the phase characteristic of titanium slag, the bright area is the phase of rutile enriched with Ti, and the dark area is the phase of borate enriched with Ca, Mg, and B elements. It can be seen that the migration and enrichment behavior of Ca and Mg during cooling and crystallization of the titanium slag melt with the additive (B_2O_3) amount of 4% is more obvious than that of the titanium slag melt with the additive (B_2O_3) amount of 2%. There are fairly significant migration and enrichment behaviors of Ca and Mg during cooling and crystallization of titanium slag melt with the additive (B_2O_3) amount of 4%.

WDS mapping analysis of the cross-section of block sample of the modified titanium slag with the additive (B_2O_3) amount of 6% is displayed in Figure 6. In Figure 6, the

element distribution in the modified titanium slag with the additive (B_2O_3) amount of 6% presents extremely significant regional characteristics. The backscattered electron imaging in the modified titanium slag includes two fairly distinct areas: a bright area and a dark triangular area. Ti is concentrated in the bright area, while only Ti and O elements are concentrated in the bright area. A small amount of Mg, Ti, and Fe are enriched at the border of the bright area. Ca, Mg, B, and other impurity elements are enriched in the dark triangle area. The element distribution in the modified titanium slag is spatially consistent with the distribution of slight and dark areas on the backscattered electron imaging. The bright area is the rutile phase, the border of the bright area is the solid solution of anosovite, while the dark triangle area is the borate phase. It can be seen that the migration and enrichment behaviors of Ca and Mg during cooling and crystallization of the titanium slag melt with the additive (B_2O_3) amount of 6% are much more obvious than that of the titanium slag melt with the additive (B_2O_3) amount of 4%. There are extremely significant migration and enrichment behaviors of Ca and Mg during cooling and crystallization of titanium slag melt with the additive (B_2O_3) amount of 6%.

Figure 6. WDS mapping analysis of the cross-section of block sample of the modified titanium slag with the additive (B_2O_3) amount of 6%: (a) total, (b) Ti, (c) Ca, (d) Mg, (e) B, (f) Mn, (g) Fe, and (h) Si.

When no additive (B_2O_3) is added, there are no obvious migration and enrichment behaviors of Ca and Mg during the cooling and crystallization of titanium slag melt. When additive (B_2O_3) is added, Ti migrates and enriches in one area to form the rutile phase, while Ca, Mg, and B elements migrate and enrich in another area to form the borate phase. The elements that are too late to migrate stay at the boundary between the two enrichment areas, leading to the formation of the “residual” solid solution of anosovite. With the additive (B_2O_3) amount increased, the migration and enrichment of Ca and Mg are complete and more thorough. The obvious migration and enrichment behavior of Ca and Mg element during cooling and crystallization of titanium slag melt will contribute to the modification of titanium slag and the removal of Ca and Mg impurity. This is consistent with the experimental results on the modification of titanium slag melt and the removal of Ca and Mg impurity in the titanium slag. It is worth noting that Ca and Mg elements have obvious migration and enrichment behavior during cooling and crystallization of boron-bearing titanium slag melt. It can be seen that B_2O_3 has the effect of promoting the formation of the rutile phase and at the same time inhibiting the formation of the solid solution of anosovite during cooling and crystallization of titanium slag melt.

3.3. Effect of Additive (B_2O_3) Amount on the Valence State of Titanium in the Modified Titanium Slag

XPS was used to characterize the influence of additive (B_2O_3) amount on the valence state of titanium in the modified titanium slag to reveal the migration and enrichment behavior of Ca and Mg elements during cooling and crystallization of boron-bearing titanium slag melt. The C1s of externally contaminated carbon are always used as the reference peak for calibration. The difference between the measured value and the reference value (284.8 eV) was used as the charge correction value (Δ) to correct other elements in the spectrum. The narrow scanning spectrum of Ti in the modified titanium slag with different additive (B_2O_3) amounts is shown in Figure 7. In Figure 7, there are two peaks on the total scanning spectrum of the Ti. The energy level splitting is caused by spin-orbit coupling. Two valence states of the Ti can be obtained by performing peak fitting on the spectral lines of the Ti.

XPS results of the modified titanium slag with different additive (B_2O_3) amounts are shown in Table 2. In Table 2, the proportion of Ti^{3+} is 9.15%, and the proportion of Ti^{4+} is 90.85% in the modified titanium slag with the additive (B_2O_3) amount of 0%. It can be seen that the modified titanium slag with the additive (B_2O_3) amount of 0% still contains a small proportion of Ti^{3+} . Ti^{3+} accounts for 6.65%, and Ti^{4+} accounts for 93.35% in the modified titanium slag with the additive (B_2O_3) amount of 2%. Compared with the modified titanium slag with the additive (B_2O_3) amount of 0%, the proportion of Ti^{3+} in the modified titanium slag with the additive (B_2O_3) amount of 2% is significantly reduced. Ti^{3+} accounts for 4.46%, and Ti^{4+} accounts for 95.54% in the modified titanium slag with the additive (B_2O_3) amount of 4%. Compared with the modified titanium slag with the additive (B_2O_3) amount of 2%, the proportion of Ti^{3+} in the modified titanium slag with the additive (B_2O_3) amount of 4% is lower. The proportion of Ti^{3+} is 0%, and the proportion of Ti^{4+} is 100% in the modified titanium slag with the additive (B_2O_3) amount of 6%. Compared with the modified titanium slag with the additive (B_2O_3) amount of 4%, the proportion of Ti^{3+} in the modified titanium slag with the additive (B_2O_3) amount of 6% is further reduced. The addition of B_2O_3 causes the self-diffusion coefficient of each ion in titanium slag melt to increase, and subsequently, the viscosity of the system to decrease. As the B_2O_3 content increases, the contact probability of Ti^{3+} and O_2 increases, and the oxidation reaction of low-valent titanium is strengthened during the cooling and crystallization of boron-bearing titanium slag melt; therefore, as the B_2O_3 content increases, low-valent titanium in the system is more easily contacted with O_2 , and the TiO_2 -rich phases from titanium slag melt are promoted.

Figure 7. XPS patterns of detail scan of Ti in the modified titanium slag: (a) 0% B_2O_3 , (b) 2% B_2O_3 , (c) 4% B_2O_3 , and (d) 6% B_2O_3 .

Table 2. XPS results of modified titanium slag with different additive (B_2O_3) amounts.

B_2O_3 Addition Amount (%)	Content	$Ti^{4+}2p_{1/2}$	$Ti^{3+}2p_{1/2}$	$Ti^{4+}2p_{3/2}$	$Ti^{3+}2p_{3/2}$
0	binding energy (eV)	464.5	463.8	458.9	458.3
	peak area	4491.3	452.5	8982.7	905.0
	proportion (%)	90.85	9.15	90.85	9.15
2	binding energy (eV)	464.5	463.7	458.9	458.2
	peak area	5998.2	427.3	11996.5	854.7
	proportion (%)	93.35	6.65	93.35	6.65
4	binding energy (eV)	464.5	463.6	458.9	458.1
	peak area	4883.2	228.2	9766.3	456.3
	proportion (%)	95.54	4.46	95.54	4.46
6	binding energy (eV)	464.5	463.6	458.9	458.1
	peak area	4818.3	0.05	9636.6	0.1
	proportion (%)	100	0	100	0

The binding energy of Ti^{3+} and Ti^{4+} photoelectron peaks in the modified titanium slag with different additive (B_2O_3) amounts change within a small range. The binding energy of $Ti^{3+}2p_{1/2}$ is 463.8~463.6 eV, and the binding energy of $Ti^{3+}2p_{3/2}$ is 458.3~458.1 eV. The binding energy of $Ti^{4+}2p_{1/2}$ is 464.5 eV, and the binding energy of $Ti^{4+}2p_{3/2}$ is 458.9 eV. The spacing of the spin-orbit splitting peak of the photoelectron peak of Ti^{3+} is 5.5 eV, and the spacing of the spin-orbit splitting peak of the photoelectron peak of Ti^{4+} is 5.6 eV. The peak positions of Ti^{3+} and Ti^{4+} photoelectron peaks of titanium oxide in the literature are shown in Table 3. Ti^{3+} and Ti^{4+} photoelectron peaks obtained in this work are consistent

with those in the literature, which shows the accuracy of XPS characterization and peak fitting in this work.

Table 3. Peak positions of photoelectron peaks of Ti^{3+} and Ti^{4+} in titanium oxide in the literature.

Researcher	Ti_2O_3 (eV)			TiO_2 (eV)		
	$Ti2p_{1/2}$	$Ti2p_{3/2}$	Peak Spacing	$Ti2p_{1/2}$	$Ti2p_{3/2}$	Peak Spacing
Albert F. Carley et al. [29]	462.5	457.5	5.0	465.0	459.0	6.0
B. Siemensmeyer et al. [30]	463.6	457.9	5.7	465.2	459.4	5.8
T. Choudhury et al. [31]	463.4	457.6	5.8	465.0	459.1	5.9
T. Godfroid et al. [32]	463.1	457.2	5.9	464.7	458.8	5.9
J. Pouilleau et al. [33]	463.1	457.4	5.7	464.8	459.1	5.7
Yu Qian et al. [34]	462.8	457.0	5.8	464.0	458.1	5.9
B. Siemensmeyer et al. [35]	463.4	457.7	5.7	465.0	459.2	5.8
Y. S. Liu et al. [36]	463.4	457.6	5.8	465.0	459.1	5.9
B. V. R. Chowdari et al. [37]	464.2	458.7	5.5	465.3	459.8	5.5
Liu Qianqian et al. [38]	463.7	458.2	5.5	464.8	459.3	5.5

With the additive (B_2O_3) amount increasing from 0% to 6%, the proportion of Ti^{3+} in the modified titanium slag reduces from 9.15% to 0%, and the proportion of Ti^{4+} increases from 90.85% to 100% under the same cooling and crystallization conditions. It can be deduced that the addition of B_2O_3 can promote the oxidation of Ti^{3+} and precipitation of the rutile phase during cooling and crystallization of titanium slag melt, facilitating the modification of titanium slag and the removal of Ca and Mg impurity.

4. Conclusions

The migration and enrichment behaviors of Ca and Mg during the cooling and crystallization of boron-bearing titanium slag melt were characterized by XRF, FESEM, EMPA, and XPS. The results are as follows.

- (1) Ti was concentrated with the rutile form in the flake and bright areas, and B, Mg, and Ca elements were concentrated with the borate form in the long strip and dark areas during the cooling and crystallization of boron-bearing titanium slag melt.
- (2) When additive (B_2O_3) is added, Ti migrated and enriched in one area to form the rutile phase, while Ca, Mg, and B migrated and enriched in another area to form the borate phase. When the additive (B_2O_3) amount increased, Ca and Mg migration was complete and more thorough.
- (3) Additive (B_2O_3) has the effect of promoting the formation of the rutile phase and at the same time inhibiting the formation of the solid solution of anosovite during the cooling and crystallization of titanium slag melt.
- (4) With the additive (B_2O_3) amount increasing from 0% to 6%, the proportion of Ti^{3+} in the modified titanium slag reduces from 9.15% to 0%, and the proportion of Ti^{4+} increases from 90.85% to 100% under the same cooling and crystallization condition.

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