Selective Phase Transformation Behavior of Titanium-bearing Electric Furnace Molten Slag during the Molten NaOH Treatment Process

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In this paper, selective phase transformation for titanium-bearing phase (Ti-bearing phase) and impurity phase in titanium-bearing electric arc furnace molten slag (Ti-bearing EAF slag) was effectively realized during the molten NaOH treatment process. The phase transformation mechanism based on thermodynamic calculation was investigated in detail by X-ray diffraction, X-ray photoelectron spectroscopy and Raman spectrum. It is indicated that the Ti-bearing phases in Ti-bearing EAF slag such as anosovite solid solution and Mg_2TiO_4 can be easily converted to Na_2TiO_3 with NaCl-type crystal structure, whilst the main impurity phase such as MgAl_2O_4 was apt to be decomposed by molten NaOH to form NaAlO_2 and MgO . In addition, with increasing of roasting temperature and time, as well as decreasing of Ti-bearing EAF slag/NaOH mass ratio ($R_{\text{slag/NaOH}}$), the formed Na_2TiO_3 could be partly changed to NaMO_2 ($M=\text{Mg, Ti, Fe}$) with $\alpha\text{-NaFeO}_2$ -type crystal structure, due to the coexisting metal ions like Mg^{2+} and Fe^{3+} in the slag be doped into or even substituted the Ti atoms of Na_2TiO_3 to form NaMO_2 ($M=\text{Ti, Fe, Mg}$).

KEY WORDS: Ti-bearing electric arc furnace molten slag; molten NaOH treatment; phase transformation; thermodynamic; crystal structure.

1. Introduction

Ti-bearing slags such as Ti-bearing blast furnace slag (Ti-bearing BF slag) and Ti-bearing electric arc furnace molten slag (Ti-bearing EAF slag) *etc.*, are considered as valuable secondary resources in China due to their relatively higher TiO_2 contents. Since the Ti-bearing slags are produced from various raw ores by using different treating processes, the main chemical compositions and the phase structure of these slags are basically different. Therefore, how to extract titanium efficiently from the Ti-bearing slags has been attracted much attention, and various approaches have been utilized including acid process,^{1–3)} alkali fusion process,^{4,5)} carbonization and chlorination process,⁶⁾ selective crystallization process.^{7–11)} Comparing these methods, the alkali fusion process shows obvious advantage such as unrestricted raw slag materials, and easy recycling of alkali, *etc.* More importantly, after alkali fusion process, the Ti-bearing phases can be selectively separated from other impurity phases by only water leaching process based on the different water solubility of formed sodium salts instead of complicate dressing method.

However, no matter which Ti-bearing slags were used during the alkali fusion process, the attention of researchers was mainly focused on the extraction efficiency of titanium

and the decomposition kinetics of Ti-bearing slags in different alkali systems. None of the efforts have been taken on phase transformation mechanism for titanium and other elements in slags. Zhang *et al.*¹²⁾ studied the decomposition behavior of Ti-bearing slag in NaOH solution at 493 K for 4 h, and indicated that the hydrothermal product obtained under optimal conditions was $\text{Na}_4\text{Ti}_3\text{O}_8$. Scott Middlemas *et al.*¹³⁾ believed that the Ti-bearing phases in Ti-bearing slag could react with molten NaOH at 773 K for 4 h to form Na_2TiO_3 . Han *et al.*⁵⁾ also considered that Ti-bearing slag reacted with molten NaOH yielded only one kind of sodium titanate (Na_2TiO_3). In fact, it should be noted that the titania could react with molten NaOH to form various sodium salts.^{14–17)} However, the phase transformation mechanism of the Ti-bearing phases was not clear, especially the influence of metal ions such as Fe^{3+} , Al^{3+} , Mg^{2+} , *etc.* coexisting in the slags on the formation of Ti-bearing phases were seldom been investigated.

In this paper, Ti-bearing EAF slag was used as raw material to investigate the transformation mechanism of the Ti-bearing phases and impurity phases during the molten NaOH treatment process. The phase transformation mechanism was studied in detail based on thermodynamic calculation and crystal structure analysis. This paper may provide some essential thermodynamic information for Ti-bearing slags or other Ti-bearing materials in the molten NaOH system, and would also give a reference to comprehensive utilization of titanium resource treated by molten NaOH

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treatment process.

2. Experimental

2.1. Materials and Characterization

All the chemical reagents employed were analytical grade (Sinopharm Chemical Reagent Co. Ltd) and the distilled water was used throughout the experiment. The Ti-bearing EAF slag samples were provided by Panzhihua Steel Company (Sichuan Province, China), which were obtained from vanadium-titanium magnetite concentrate through direct reduction reaction by rotary hearth furnace and smelting separation by electric furnace. The main chemical compositions of the slag were analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES, TELEDYNE Leeman Labs) and listed in **Table 1**. The phase structure of the slag was investigated by X-ray diffraction using Cu K α radiation ($\lambda=0.154056$ nm) with 40 kV, 200 mA and a speed of 10°/min (XRD, M21X, MAC SCIENCE Co. Ltd, Japan). The results shown in **Fig. 1** indicated that the Ti-bearing phases of the slag were MgTi₂O₅, Ti₃O₅ and Mg₂TiO₄, while the main impurity phases were MgAl₂O₄ and amorphous CaSiO₃. The valences of transition elements were analyzed by X-ray photoelectron spectroscopy (XPS, Al K α , AXIS ULTRA), in which C1s binding energy value (284.8 eV) was chosen as standard for baseline correction and baseline subtraction method was Shirley-type. The XPS spectrum of Ti in Ti-bearing EAF slag was shown in **Fig. 2**. It is shown that about 15% Ti³⁺ and 85% Ti⁴⁺ coexisted in the slag, suggesting that the existence form of titanium element might be Ti₃O₅ or Ti₂O₃ anosovite solid solutions in the slag.

Measurements of Raman spectra were performed on a laser confocal Raman spectrometer (JY-HR800, Jobin Yvon). A blue line (514 nm) of the laser was taken as the excitation source.

Artificially synthesized MgTi₂O₅ was prepared by roast-

Table 1. Main chemical compositions of the Ti-bearing EAF slag (mass%).

Composition	TiO ₂	Al ₂ O ₃	MgO	SiO ₂	CaO	Fe ₂ O ₃
Content	50.9	19.4	12.9	8.0	5.4	2.9

Fig. 1. XRD pattern of the Ti-bearing EAF slag.

ing TiO₂ (anatase, analytical reagent) with MgO at 1 873 K for 3 h with TiO₂/MgO molar ratio at 2:1.

2.2. The Concrete Process of Extracting TiO₂ from Ti-bearing EAF Slag

Figure 3 illustrated the general flow sheet of whole extraction process of TiO₂ from Ti-bearing EAF slag, and the detailed procedure were described as follows.¹⁸⁾ It should be noted that this paper was mainly focus on the molten NaOH treatment process to elucidate the Ti-bearing EAF slag phase transformation mechanism clearly.

Firstly, 10 g Ti-bearing EAF slag was ground to about 120 mesh and mixed with NaOH homogeneously at different mass ratios in a nickel crucible. Then, the nickel crucible was placed into a muffle furnace when the temperature reached a preset value, holding for a required time with free

Fig. 2. XPS spectrum of Ti in the Ti-bearing EAF slag. (Online version in color.)

Fig. 3. Schematic flow diagram of extracting TiO₂ from Ti-bearing EAF slag.

access to air. After the molten NaOH treatment process, the nickel crucible was taken out rapidly and then cooled at room temperature. The obtained slag was called alkali fusion slag. For phase analysis, the alkali fusion slag was ground to about 200 mesh rapidly.

Secondly, as for hydrolysis reaction process, 3 g ground alkali fusion slag was dissolved in distilled water with electromagnetic stirring for 1 h. The sodium salts such as Na_2SiO_3 and NaAlO_2 formed in the alkali fusion slag were dissolved in water while the insoluble sodium titanate salts also formed in the alkali fusion slag were separated from the solution by filtration.

Finally, the obtained residue was mixed with HCl solution and refluxed at 373 K for 6 h to perform acidolysis reaction to get metatitanic acid. Then, the samples were calcined in the muffle furnace at 773 K for 1 h to obtain TiO_2 .

3. Results and Discussion

3.1. Thermodynamic Analysis

When the Ti-bearing EAF slag was mixed with NaOH and roasted at different temperatures in muffle furnace under atmospheric condition, the related reactions could be described as follows:

Therefore, the standard Gibbs free energy change (ΔG°) of the above reactions can be calculated according to Eq. (6).

$$\begin{aligned} \Delta G_T^\circ &= \Delta H_T^\circ - T\Delta S_T^\circ \\ &= \Delta H_{298}^\circ - T\Delta S_{298}^\circ + \int_{298}^{T_1} \Delta C_p dT + \int_{T_1}^{T_2} \Delta C_p' dT \quad \dots (6) \\ &\quad - T_1 \int_{298}^{T_1} \frac{\Delta C_p}{T} dT - T_2 \int_{T_1}^{T_2} \frac{\Delta C_p'}{T} dT \end{aligned}$$

Where ΔG° is the standard Gibbs free energy change, J/mol, ΔH° is the standard enthalpy change, J/mol, ΔS° is the standard entropy change, J/(mol K), C_p is the specific heat capacity at constant pressure, J/(mol K). Thereinto, ΔH_{298}° , S_{298}° and C_p could be obtained from the FactPS database of FactSage 6.3 software, respectively, and the related values were listed in **Table A1**. **Figure 4** gave the variation trend of ΔG° ranging from 573 K to 1173 K. It is shown that the ΔG° of all the reactions were negative and decreased with the roasting temperature increasing, indicating that all the reactions could be occurred above 573 K. Moreover, it should be noted that the ΔG° values of the reactions (1), (2) and (3) were more negative than that of the other reactions, while the ΔG° value of the reaction (5) was most positive

Fig. 4. The plot of $\Delta_r G^\circ \sim T$ for reactions between Ti-bearing EAF slag and molten NaOH.

among all the reactions, suggesting that the Ti-bearing phases in the slag would react with molten NaOH much earlier than other phases, especially the impurity phase MgAl_2O_4 during the molten NaOH treatment process based on thermodynamic calculation. Considering that MgAl_2O_4 was difficult to be decomposed by molten NaOH than other impurity phase, e.g. CaSiO_3 , so, the investigation on the transformation of the main impurity phases in this paper was only focus on the decomposition of MgAl_2O_4 during the molten NaOH treatment process.

Because NaOH can be used as an ionized solvent at higher temperature above 623 K,¹⁹⁾ it is reasonable to assume that the reactions between Ti-bearing EAF slag and molten NaOH may be considered as a solid-liquid reaction mechanism. In order to make sure the Ti-bearing phases or other impurity phases in Ti-bearing EAF slag convert to their corresponding sodium salts completely, Ti-bearing EAF slag/NaOH mass ratio ($R_{\text{slag/NaOH}}$) should be controlled at least below 1 according to the material balance calculation. Moreover, excess amount of NaOH is necessary to maintain the liquidity of the reactants and ensure their sufficient contact areas during the reactions. Based on the aforementioned analysis, all the experiments should be conducted above 673 K with $R_{\text{slag/NaOH}}$ below 1.

3.2. The Effect of Roasting Temperature on the Phase Transformation

The effect of roasting temperature on the Ti-bearing phases transformation was investigated from 773 K to 973 K for 1 h. **Figure 5** gives the XRD patterns of alkaline fusion slag obtained under different temperatures with $R_{\text{slag/NaOH}}$ fixed at 1:1. It can be seen that the diffraction peaks of anosovite solid solution and Mg_2TiO_4 completely disappeared while strong diffraction peaks of Na_2TiO_3 ($2\theta=40.1^\circ$) appeared. This case indicated that the anosovite solid solution (**Fig. 6(a)**) with orthorhombic crystal system was decomposed by molten NaOH and converted to Na_2TiO_3 (**Fig. 6(b)**) with cubic crystal structure (until cell parameters of $a=b=c=4.49 \text{ \AA}$, and $\alpha=\beta=\gamma=90^\circ$). Increasing the temperature to 873 K, a new phase named NaMO_2 ($M=\text{Ti, Mg, Fe}$) with hexagonal crystal system (unit cell parameters of $a=b=3.04 \text{ \AA}$, $c=16.26 \text{ \AA}$ and $\alpha=\beta=90^\circ$, $\gamma=120^\circ$) appeared, which was derived from

Fig. 5. XRD patterns of alkaline fusion slags obtained under different temperatures with $R_{\text{slag/NaOH}}$ fixed at 1:1.

Fig. 7. XRD patterns of the product prepared by pure TiO_2 with molten NaOH at 973 K for 1 h.

Fig. 6. The phase transformation relationship between Ti-bearing phases (a) MgTi_2O_5 , (b) Na_2TiO_3 , (c) NaMO_2 . (Online version in color.)

α - NaFeO_2 -type crystal structure (Fig. 6(c)).¹⁴⁾ Further increasing the temperature to 973 K, the diffraction peaks of NaMO_2 ($2\theta=16.4^\circ, 41.1^\circ$) became stronger, whereas the diffraction peaks of Na_2TiO_3 ($2\theta=40.1^\circ$) turned to weaker, suggesting that relatively higher temperature (>873 K) may be benefit for Ti-bearing phases (e.g. MgTi_2O_5 and Mg_2TiO_4) transformation to NaMO_2 instead of Na_2TiO_3 during the molten NaOH treatment process.

It is known that the compositions of Ti-bearing EAF slag are very complex and various elements including Fe^{3+} and Mg^{2+} etc. coexist in the slag system. Therefore, with the roasting temperature increasing, some Fe^{3+} or Mg^{2+} ions would be doped into Na_2TiO_3 , or even substituted the Ti atom of Na_2TiO_3 to form a class of layered ionic structure called α - NaFeO_2 -type crystal structure.¹⁴⁾ In this paper, the M in NaMO_2 with α - NaFeO_2 -type structure phase can be Fe, Mg or Ti elements due to their similar ion radius ($\text{Fe}^{3+}=0.064$ nm, $\text{Mg}^{2+}=0.066$ nm and $\text{Ti}^{4+}=0.068$ nm). With

increasing the roasting temperature, more and more Fe^{3+} or Mg^{2+} would be doped into Na_2TiO_3 to make Na_2TiO_3 convert to NaMO_2 ($\text{M}=\text{Fe}^{3+}, \text{Ti}^{4+}, \text{Mg}^{2+}$), so the amount of NaMO_2 increased whereas the amount of Na_2TiO_3 decreased. According to the analysis above, nearly all the Ti-bearing phases in Ti-bearing EAF slag could convert to Na_2TiO_3 or NaMO_2 during the molten NaOH treatment process, implying the Ti-bearing phase transformation can be realized effectively as illustrated in Fig. 6.

Based on the experimental results, one problem need to be elucidated clearly, that is to say, Fe^{3+} or Mg^{2+} doping into Na_2TiO_3 would promote Na_2TiO_3 to be transformed to NaMO_2 ($\text{M}=\text{Fe}^{3+}, \text{Ti}^{4+}, \text{Mg}^{2+}$). In order to confirm the key influence factors on the phase transformation between Na_2TiO_3 and NaMO_2 , pure TiO_2 (anatase, analytical reagent) was used as raw material to react with NaOH. Meanwhile, other experimental conditions were controlled the same as that during molten NaOH treatment reaction process. **Figure 7** shows the XRD patterns of the product obtained at 973 K for 1 h. It can be seen that the main phases of the product were only Na_2TiO_3 and excess NaOH. None diffraction peaks of NaMO_2 appeared, indicating that TiO_2 reacted with molten NaOH could not be reduced to form NaTiO_2 in air atmosphere.

However, as shown in Fig. 5, when Ti-bearing EAF slag was used as raw material to react with molten NaOH, the diffraction peaks of NaMO_2 did exist at 873 K and their intensities became stronger with the roasting temperature increasing to 973 K. The results were basically different from each other, suggesting that coexisting elements such as Fe^{3+} and Mg^{2+} in the Ti-bearing EAF slag determined the formation of NaMO_2 or Na_2TiO_3 . In order to further investigate the transformation mechanism between Na_2TiO_3 and NaMO_2 , artificially synthesized MgTi_2O_5 was used as raw material to react with molten NaOH under the same experimental conditions. **Figure 8** gives the XRD patterns of the products obtained under different roasting temperatures. It can be clearly seen that the main phases of the product were Na_2TiO_3 and MgO when the temperature was fixed at 773 K, while NaMO_2 with α - NaFeO_2 -type crystal structure appeared when the temperature increased to 973 K. So it is

Fig. 8. XRD patterns of the product prepared by artificially synthesized MgTi_2O_5 with molten NaOH under different roasting temperatures for 1 h.

reasonable to assume that the synthesized MgTi_2O_5 could be decomposed by molten NaOH according to the following equations:

Considering that the M in NaMO_2 is trivalence, it might be assumed that Ti^{3+} should be formed during the alkali fusion process. It is known that X-ray photoelectron spectroscopy (XPS) is often utilized to detect elements and confirm their corresponding valence state. **Figure 9** illustrated the XPS of Ti element in the product obtained at 973 K for 1 h. The binding energies of the double peaks are 458.1 eV and 463.6 eV for $\text{Ti } 2p_{3/2}$ and $\text{Ti } 2p_{1/2}$, respectively. The energy position of this doublet only corresponds to the Ti^{4+} oxidation state, suggesting that none of Ti^{3+} existed in the product.

More importantly, from Fig. 8, it also should be noted that both diffraction peaks of MgO ($2\theta=43.1^\circ$) and Na_2TiO_3 ($2\theta=40.1^\circ$) decreased a lot, while the diffraction peaks of NaMO_2 ($2\theta=16.4^\circ$, 41.1°) increased correspondingly with roasting temperature increasing from 773 K to 973 K. This phenomenon may be ascribed to that the Mg^{2+} ionized at relatively high temperature could partially dope into or even substitute the Ti atom of Na_2TiO_3 to form solid solution $\text{Na}(\text{Mg}^{2+}, \text{Ti}^{4+})\text{O}_2$, that is to say, the apparent trivalence of M in NaMO_2 might be displayed by Ti^{4+} together with Mg^{2+} . The results agreed well with XRD patterns (Fig. 8) and it can be inferred that higher temperature would be benefit for Mg^{2+} doping into/substituting the Ti atoms of Na_2TiO_3 , leading to Ti-bearing phase transformation from Na_2TiO_3 to NaMO_2 ($\text{M}=\text{Mg}^{2+}, \text{Ti}^{4+}$).

In order to verify the assumption, the Raman spectra were used to investigate the change of chemical bonds in the molten NaOH treatment process. **Figure 10** is the Raman spec-

Fig. 9. XPS spectrum of Ti in the alkali fusion slag obtained at 973 K for 1 h. (Online version in color.)

Fig. 10. Raman spectra of MgTi_2O_5 and alkali fusion slags obtained under different roasting temperatures for 1 h.

tra of synthesized MgTi_2O_5 (Fig. 10(a)) and its corresponding alkali fusion slags obtained under different roasting temperatures (Figs. 10(b) and 10(c)). It can be clearly seen that the Raman spectrum of MgTi_2O_5 shows three peaks at 281, 445 and 605 cm^{-1} , respectively. Some researchers suggested that the peak near 600 and 445 cm^{-1} should be ascribed to Ti–O stretching vibrations in 6-coordinated Ti^{4+} .^{20,21)} Meanwhile, the peaks near 281 cm^{-1} correspond to the bending and stretching vibration of Mg–O bonds.²²⁾ When MgTi_2O_5 reacted with molten NaOH at 773 K for 1 h, the peaks of the alkali fusion slag (Fig. 10(b)) didn't show obvious change comparing to that of MgTi_2O_5 (Fig. 10(a)). However, the intensity of peak at 281 cm^{-1} decreased a lot, and in the meantime, a weak vibration peak appeared at 800 cm^{-1} (Fig. 10(b)). This phenomenon may be ascribed to that Ti–O band still existed as 6-coordinated Ti^{4+} in the obtained Na_2TiO_3 , but the type of Mg–O bonds changed from covalent bond in MgTi_2O_5 to ionic bond in MgO, since MgTi_2O_5 can be decomposed by molten NaOH to form Na_2TiO_3 and MgO (Eq. (7)). Further increasing temperature to 973 K, the bending and stretching vibration peaks of Mg–O bonds at 281 cm^{-1} and Ti–O stretching vibration 445 and

Fig. 11. MgAl_2O_4 decomposed by molten NaOH to form NaAlO_2 and MgO . (Online version in color.)

600 cm^{-1} disappeared obviously, on the contrary, the intensity of vibration peak at 790 cm^{-1} increased dramatically (Fig. 10(c)). According to the references,^{20,23,24)} it is known that the vibration peak at 790 cm^{-1} should be assigned to $\text{Ti}-\text{O}^{2-}$ stretching vibrations in TiO_4^{4-} tetrahedral monomers. As a result of Mg^{2+} intercalating into $\text{Ti}-\text{O}$ bonds, titanyl bond did not exist as 6-coordinated Ti^{4+} , but demonstrated as $\text{Ti}-\text{O}^{2-}$ in TiO_4^{4-} tetrahedral monomers, which combined together to form $\text{O}-\text{Ti}-\text{O}$ or $\text{O}-(\text{Mg},\text{Ti})-\text{O}$ chain units. According to the analysis of the Raman spectra, it is reasonable to conclude that MgTi_2O_5 can be decomposed by molten NaOH to form 6-coordinated Ti^{4+} and Mg^{2+} at 773 K . Then they combined with Na^+ and O^{2-} supplied by molten NaOH to form NaTiO_3 and MgO , respectively. However, as the reaction temperature increased to 973 K , some Mg^{2+} would become ionized state and insert into $\text{Ti}-\text{O}$ bonds, which made 6-coordinated Ti^{4+} tetrahedron become to TiO_4^{4-} tetrahedral monomers and then form $\text{O}-(\text{Mg},\text{Ti})-\text{O}$ chain units. During this process, the crystal structure of Na_2TiO_3 changed from NaCl -type crystal structure system to $\alpha\text{-NaFeO}_2$ -type crystal structure, further confirming the transformation from Na_2TiO_3 to NaMO_2 ($\text{M}=\text{Mg}^{2+}$ and Ti^{4+}).

In addition, as for the main impurity in Ti-bearing EAF slag (e.g. MgAl_2O_4), the corresponding phase transformation trend was also shown in Fig. 5. It can be seen that with temperature increasing from 773 K to 973 K , the intensity of diffraction peaks of MgAl_2O_4 decreased obviously, suggesting higher temperature would be benefit for MgAl_2O_4 decomposition by molten NaOH according to the following equation:

Because NaOH can be used as an ionized solvent when the reaction temperature is higher than 623 K , it is reasonable to assume that the solid-liquid reaction process between MgAl_2O_4 and NaOH was a diffusion controlled process.¹⁸⁾ Moreover, MgAl_2O_4 belongs to the cubic crystal system (unit cell parameters are $a=b=c=8.09\text{ \AA}$ and $\alpha=\beta=\gamma=90^\circ$), and it has a relative stable and dense structure since Al ions uniformly dispersed in $\text{Mg}-\text{O}$ bonds as shown in Fig. 11(a). Therefore, increasing the amount of NaOH during the molten NaOH treatment reaction, namely, adjusting $R_{\text{slag/NaOH}}$, would lead to complete phase transformation of MgAl_2O_4 by molten NaOH to form NaAlO_2 and MgO as illustrated in Fig. 11.

Fig. 12. XRD patterns of alkaline fusion slag obtained at 973 K for 1 h with $R_{\text{slag/NaOH}}$ ranging from $1:1$ to $1:1.5$.

3.3. The Effect of Ti-bearing EAF Slag/NaOH Mass Ratio ($R_{\text{slag/NaOH}}$) on the Phase Transformation

Figure 12 gave the XRD patterns of alkaline fusion slags obtained at 973 K for 1 h when $R_{\text{slag/NaOH}}$ was controlled from $1:1$ to $1:1.5$, respectively. It can be clearly seen that none of the diffraction peaks of anosovite solid solution or Mg_2TiO_4 existed in the alkali fusion slags, while some strong diffraction peaks of Na_2TiO_3 and NaMO_2 appeared accordingly, indicating that all the Ti-bearing phases in Ti-bearing EAF slag could realize the effective phase transformation even when $R_{\text{slag/NaOH}}$ was at $1:1$. In addition, it is also found that the intensity of diffraction peaks of MgAl_2O_4 decreased dramatically when $R_{\text{slag/NaOH}}$ was controlled from $1:1.2$ to $1:1.5$ at 973 K . This case may be ascribed to that much more amount of molten NaOH could ensure sufficient contact areas between reactants (Ti-bearing EAF slag and NaOH), leading to MgAl_2O_4 complete decomposition under the condition.

More importantly, it should be noted that with $R_{\text{slag/NaOH}}$ decreasing from $1:1$ to $1:1.5$, the intensities of diffraction peaks of Na_2TiO_3 ($2\theta=40.1^\circ$) decreased gradually while the intensities of diffraction peaks of NaMO_2 ($2\theta=16.4^\circ, 41.1^\circ$) increased correspondingly, suggesting that some previously formed Na_2TiO_3 would be spontaneously converted to NaMO_2 . This phenomenon may be explained as follows: when the $R_{\text{slag/NaOH}}$ was adjusted from $1:1$ to $1:1.5$, according to Eq. (9), almost all MgAl_2O_4 in the slag could react with enough molten NaOH , liberating amounts of free Mg^{2+} . In

Fig. 13. XRD patterns of alkali fusion slag obtained at 973 K under different roasting time with $R_{\text{slag/NaOH}}$ fixed at 1:1.2.

the meantime, such free Mg^{2+} would prefer to dope into/substitute Ti atoms of Na_2TiO_3 to form NaMO_2 ($\text{M}=\text{Mg}^{2+}, \text{Ti}^{4+}$), rather than combine with O^{2-} by ionic bond to produce MgO . This result agrees well with XRD patterns as shown in Fig. 12, that is to say, hardly any diffraction peaks of MgO appeared when MgAl_2O_4 was completely decomposed by molten NaOH . In addition, there were obvious diffraction peaks of NaAlO_2 existed in XRD patterns, indicating that Al atoms in NaAlO_2 could not be substituted by Mg^{2+} ion due to their different ionic radius ($\text{Mg}^{2+}=0.066$ nm, $\text{Al}^{3+}=0.051$ nm).

Based on above analysis, in order to make the main impurity phase MgAl_2O_4 convert to water soluble NaAlO_2 completely, and then separate from insoluble sodium titanates (Na_2TiO_3 and NaMO_2) by water leaching, excessive amount of NaOH should be added to maintain a good reaction kinetic condition. Considering the energy consumption and material cost comprehensively, the roasting temperature and $R_{\text{slag/NaOH}}$ should be controlled at 973 K and 1:1.2, respectively during the molten NaOH treatment process.

3.4. The Effect of Roasting Time on the Phase Transformation

Figure 13 illustrates XRD patterns of alkali fusion slags obtained under different time when roasting temperature was controlled at 973 K and $R_{\text{slag/NaOH}}$ fixed at 1:1.2. It is shown that the diffraction peaks of all the Ti-bearing phases in Ti-bearing EAF slag (anosovite solid solution and Mg_2TiO_4) disappeared just within 10 min. Meanwhile, obvious diffraction peaks of corresponding sodium titanates (Na_2TiO_3 and NaMO_2) emerged, suggesting that all the Ti-bearing phases in Ti-bearing EAF slag could be converted to sodium titanates (Na_2TiO_3 and NaMO_2) promptly at the initial stage. Moreover, with prolonging the roasting time from 10 to 45 min, the intensities of diffraction peaks of MgAl_2O_4 decreased. Further increasing the time to 60 or 90 min, nearly all of the diffraction peaks of MgAl_2O_4 vanished, implying that relatively longer reaction time (>60 min) would benefit for complete decomposition of MgAl_2O_4 .

In addition, it is worth noting that the diffraction peaks of NaMO_2 with weak intensity appeared within 10 min. When

Fig. 14. The schematic diagram of phase transformation during the molten NaOH treatment process.

the roasting time increased to 30 min and further to 90 min, the intensity of diffraction peaks of NaMO_2 increased gradually whereas that of Na_2TiO_3 decreased, and finally, even NaMO_2 became the main phase in the alkali fusion slag as shown in Fig. 13. The same phenomenon also appeared when the alkali fusion process was conducted at different roasting temperatures and $R_{\text{slag/NaOH}}$. According to the above analysis, it is believed that some trivalence or divalent metal ion like Fe^{3+} or Mg^{2+} existed in Ti-bearing EAF slag could dope into/substitute the Ti atoms of Na_2TiO_3 to form NaMO_2 ($\text{M}=\text{Ti}, \text{Fe}, \text{Mg}$) due to their similar ionic radius ($\text{Fe}^{3+}=0.064$ nm, $\text{Mg}^{2+}=0.066$ nm and $\text{Ti}^{4+}=0.068$ nm). Therefore, NaMO_2 ($\text{NaFeO}_2, \text{Na}(\text{Mg}^{2+}, \text{Ti}^{4+})\text{O}_2$) appeared within 10 min should be ascribed to the doped of these metal ions with low content from Ti-bearing EAF slag. With increasing of roasting time, more MgAl_2O_4 was decomposed to liberate more Mg^{2+} , therefore enhanced the chance of Mg^{2+} doping into/substituting the Ti atoms of Na_2TiO_3 to form solid solution $\text{Na}(\text{Mg}^{2+}, \text{Ti}^{4+})\text{O}_2$. By this way, the amount of Na_2TiO_3 decreased while NaMO_2 increased with roasting time prolonging.

Based on the aforementioned analysis, the phase transformation mechanism during the alkali fusion process can be illustrated as Fig. 14. It is shown clearly that the main Ti-bearing phases and impurity phases in Ti-bearing EAF slag can be decomposed by NaOH to form their corresponding sodium salts. Meanwhile, some cations may dope into/substitute the Ti atoms of Na_2TiO_3 to form NaMO_2 ($\text{M}=\text{Ti}, \text{Fe}, \text{Mg}$) due to their similar ionic radius. During the doping or substitution process, these cations originated from two sources. One is existing in the initial Ti-bearing EAF slag such as Fe^{3+} or Ti^{3+} , which occupied a small fraction. The other (Mg^{2+}) is from decomposition of MgTi_2O_5 or MgAl_2O_4 by NaOH with ionic state at high temperature (>873 K), which occupied high content.

4. Conclusion

The present work shows that the Ti-bearing phases and the main impurity phases in Ti-bearing EAF slag can realize phase transformation effectively in molten NaOH fusion process. The phase transformation mechanism was studied systematically by thermodynamic calculation and crystal structure analysis. It is indicated that the Ti-bearing phases in Ti-bearing EAF slag can be decomposed by molten

NaOH much earlier and easier than the main impurity phase MgAl_2O_4 . The Ti-bearing phases transformed from anosite solid solution or Mg_2TiO_4 to Na_2TiO_3 with NaCl-type crystal structure easily when the alkali fusion process was above 773 K with Ti-bearing EAF slag/NaOH mass ratio ($R_{\text{slag/NaOH}}$) below 1:1. However, the main impurity phase MgAl_2O_4 could not be decomposed by molten NaOH to form NaAlO_2 and MgO completely until the alkali fusion reactions were conducted at 973 K for 1 h with $R_{\text{slag/NaOH}}$ below 1:1.2. In addition, with increasing roasting temperature and time or decreasing $R_{\text{slag/NaOH}}$, the formed Na_2TiO_3 with NaCl-type crystal structure could convert to NaMO_2 ($M=\text{Mg, Ti, Fe}$) with $\alpha\text{-NaFeO}_2$ -type crystal structure, due to that some metal ions like Mg^{2+} or Fe^{3+} might dope into/substitute the Ti atoms of Na_2TiO_3 to form NaMO_2 ($M=\text{Ti, Fe, Mg}$).

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Appendices

Table A1. Thermodynamic data.

Composition	ΔH_{298}° (J/mol)	S_{298}° (J/mol K)	C_p (J/mol K)	T (K)
MgTi_2O_5	-2 504 887	137.34	$232.58-5\,660\,800\,T^{-2}-755.50\,T^{-1/2}+5.8*10^8\,T^{-3}$	298–1 930
Ti_3O_5	-2 452 465	157.62	$158.99+5.02*10^{-2}T$	298–1 991
Mg_2TiO_4	-2 156 788	115.10	$226.11-1\,701\,100\,T^{-2}-1\,380.10\,T^{-1/2}+41\,280\,000\,T^{-3}$	298–2 029
NaOH(S)	-425 931	64.44	$74.57-0.13T+2.55*10^{-4}T^2$	298–573
NaOH(L)	-413 211	86.32	$167.64-2.90T-1\,824\,129.7T^{-2}+35\,363.80T^{-1}-2\,929.24T^{-1/2}$	593–2 500
O_2	0	205.04	$26.92+1.70*10^{-2}T+229\,329.26T^{-2}-79.161659T^{-1/2}$	298–1 000
Na_2TiO_3	-1 587 877	121.75	$198.91-5\,948\,599.90\,T^{-2}-644.30\,T^{-1/2}+8.5*10^8\,T^{-3}$	560–1 238
MgAl_2O_4	-2 300 313	84.53	$235.90-1\,710\,415\,T^{-2}-1\,766.58\,T^{-1/2}+40\,616\,928\,T^{-3}$	298–2 381
NaAlO_2	-1 133 190	70.40	$89.15+1.53*10^{-2}T-1\,793\,262.4T^{-2}$	298–3 000
MgO	-601 500	26.95	$61.11-621\,154\,T^{-2}-296.20\,T^{-1/2}+5\,844\,612\,T^{-3}$	298–3 098
CaSiO_3	-1 634 676	79.81	$149.07-3\,659\,348\,T^{-2}-690.29\,T^{-1/2}-4.84*10^8\,T^{-3}$	298–2 000
Na_2SiO_3	-1 561 430	113.85	$234.77-2\,218.90\,T^{-1/2}+1.35*10^8\,T^{-3}$	298–1 363
CaO	-635 090	37.75	$58.79-1\,147\,146\,T^{-2}-133.90\,T^{-1/2}+1.03*10^8\,T^{-3}$	298–2 845
H_2O	-241 834	188.72	$25.78+1.49*10^{-2}\,T-27\,999.32\,T^{-2}$	298–1 100