Article

Microstructure and Chemical Transformation of Natural Ilmenite during Isothermal Roasting Process in Air Atmosphere

Gongjin Cheng 1,2,†, Zixian Gao 1,*,†, Songtao Yang 3, He Yang 1,2 and Xiangxin Xue 1,2,*

1 School of Metallurgy, Northeastern University, Shenyang 110819, China; successking123@gmail.com (G.C.); yangh@smn.neu.edu.cn (H.Y.)
2 Liaoning Key Laboratory of Recycling Science for Metallurgical Resources, Shenyang 110819, China
3 School of Materials and Metallurgy, University of Science and Technology Liaoning, Anshan 114051, China; yangsongtao1984@163.com
* Correspondence: gaozixian1992@stumail.neu.edu.cn (Z.G.); xuexx@mail.neu.edu.cn (X.X.)
† These authors contributed equally to this work and should be considered as co-first authors.

Abstract: Ilmenite is a vital raw material for the production of metal titanium and titanium-containing materials. In this paper, microstructure and chemical transformation of natural ilmenite in air atmosphere were investigated by the analysis of XRF, X-ray diffractometer, and SEM-EDS. Results showed that the untreated ilmenite had three layers after oxidation at 800 °C for 60 min, which were FeO·TiO2 and the inside mixture layer of Fe2O3 and TiO2 in turn. Subsequently, it was roasted at 900 °C, and Fe2TiO5 was firstly developed between Fe2O3 and TiO2 layers. With the increase in the roasting time, the Fe2TiO5 layer was decomposed into Fe3TiO5 and TiO2, and Fe3TiO5 continued to be formed along the diameter direction toward the center of the particle until Fe2TiO5 and TiO2 were formed as the final products in the center of particles. Pseudorutile in natural ilmenite was directly decomposed into TiO2 and FeO in the roasting process.

Keywords: ilmenite; chemical transformation mechanisms; oxidation; pseudorutile; synthesis

1. Introduction

Ilmenite as one of titanium-bearing ores is abundant and economical [1,2], being a vital material for the production of metal titanium and titanium-containing materials like ferrotitanium alloy [2–6], synthetic rutile [7–9], titanium dioxide nanomaterial [10–12] and anode material [Li2TiO3] [11,13]. The utilizing value of ilmenite is limited to this. Pseudobrookite and pseudorutile synthesized by pure reagents can be used as a photocatalyst material [14,15] and anode material [16]. Moreover, they are the key components of the oxidation product of natural ilmenite. If the pseudobrookite and pseudorutile is produced by ilmenite, the cost of which will be lower, which will promote the development of anode materials and photocatalytic materials. Therefore, the application of ilmenite in anode materials and photocatalytic materials has great potential. Moreover, it is meaningful for ilmenite to reveal its chemical transformation mechanisms in the oxidation process in order to produce pseudorutile and pseudobrookite by controlling reaction processes.

Ilmenite mainly consists of one or several phases of FeTiO3, FeO·TiO2, Fe2O3, TiO2, and pseudorutile (Fe3TiO5) [1,7,17–24]. There are two different crystal types of pseudorutile. One is the phase of unprocessed weathering ilmenite [20,22,23], and the other is obtained in oxidation process of ilmenite above 500 °C. In this paper, the latter is written as H239 in accordance with the previous paper [19]. Researchers did some investigations about the chemical transformation of ilmenite in an oxidizing atmosphere. The consensus was that the final oxidation product consisted of FeO·TiO2 or/and H239 below 800 °C.
(Reactions (1) to (4)) and it comprised Fe$_2$TiO$_5$ and TiO$_2$ above 900 °C (Reactions (5) to (7)) [19,24–26]. Besides that, there still were some differences owing to the various roasting temperatures, varying distributions of particle size and different initial phase compositions. Fu et al. indicated that H239 and rutile were formed by parallel reactions during the oxidation process of ilmenite and small particle size could enhance the formation of H239. Gupta et al. revealed pseudorutile in natural ilmenite could be decomposed to Fe$_2$TiO$_5$ and TiO$_2$ (Reaction (9)) [23]. With prolonged roasting time, Fe$_2$TiO$_5$ would decompose to FeO$_2$ and TiO$_2$ below 800 °C (Reaction (10)) and decompose to Fe$_2$TiO$_5$ and TiO$_2$ above 800 °C (Reaction (11)). Besides that, Zhang and Ostrovski also elucidated that ilmenite was able to be oxidized to FeO$_2$ between 600 and 800 °C (Reaction (8)), that Fe$_2$TiO$_5$ was able to decompose to FeO$_2$ and TiO$_2$ between 600 and 1000 °C, and that Fe$_2$TiO$_5$ was formed between 1000 and 1200 °C as Reactions (4) and (11) show [22].

\[
\begin{align*}
4\text{FeTiO}_3(s) + \text{O}_2(g) & \rightarrow 2\text{FeO}_2(s) + 4\text{TiO}_2(s) \quad (1) \\
12\text{FeTiO}_3(s) + 3\text{O}_2(g) & \rightarrow 4\text{Fe}_2\text{TiO}_5(s) + 2\text{FeO}_2(s) \quad (2) \\
4\text{FeTiO}_3(s) + \text{O}_2(g) & \rightarrow 2\text{Fe}_2\text{TiO}_5(s) + 2\text{TiO}_2(s) \quad (3) \\
\text{Fe}_2\text{TiO}_5(s) (\text{H}_2\text{O}_3) & \rightarrow \text{Fe}_2\text{TiO}_5 + 2\text{TiO}_2(s) \quad (4) \\
\text{TiO}_2(s) + \text{FeO}_2(s) & \rightarrow \text{Fe}_2\text{TiO}_5(s) \quad (5) \\
\text{Fe}_2\text{TiO}_5(s) (\text{H}_2\text{O}_3) + 2\text{FeO}_2(s) & \rightarrow 3\text{Fe}_2\text{TiO}_5(s) \quad (6) \\
4\text{FeTiO}_3(s) + 2\text{FeO}_2(s) + \text{O}_2(g) & \rightarrow 4\text{Fe}_2\text{TiO}_5(s) \quad (7) \\
4\text{FeTiO}_3(s) + \text{O}_2(g) & \rightarrow 2\text{Fe}_2\text{TiO}_5(s) \quad (8) \\
\text{Fe}_2\text{TiO}_5(s) (\text{pseudorutile}) & \rightarrow \text{Fe}_2\text{TiO}_5(s) + \text{TiO}_2(s) \quad (9) \\
\text{Fe}_2\text{TiO}_5(s) & \rightarrow \text{FeO}_2(s) + 2\text{TiO}_2(s) \quad (10) \\
\text{Fe}_2\text{TiO}_5(s) & \rightarrow \text{Fe}_2\text{TiO}_5(s) + \text{TiO}_2(s) \quad (11)
\end{align*}
\]

With regard to the microstructure of ilmenite in oxidation process, Zhang et al. revealed ilmenite was oxidized to form hematite and rutile, with a morphology of needlelike rutile grains intermingled by hematite grains below 800 °C [18]. When temperature increased to 800 °C, hematite and rutile were constantly consumed to form the morphology with irregular rutile grains and isolated hematite grains dispersed in the pseudobrookite matrix.

From the studies of previous researchers, there are some uncertainties for the chemical transformation mechanisms of ilmenite like the formation processes of H239 above 800 °C, the actual formation paths of Fe$_2$TiO$_5$ and the chemical transformation processes of Fe$_2$TiO$_5$ in air atmosphere. In addition, development processes of microstructure for ilmenite are also unclear in oxidation processes. Thus, this paper investigated the microstructure and chemical transformation of natural ilmenite without pseudorutile phase above 800 °C. After that, chemical transformation processes of pseudorutile were studied alone in order to eliminate the interference of existing compounds and the oxidation products of ilmenite.
2. Experimental

2.1. Materials

Ilmenite, in this study, was from Liaoning, China, whose chemical composition is shown in Table 1. Ilmenite A0 and A1 were obtained by a sample crusher for 0 s and 240 s; the average grain diameters are 64.5 and 19.8 μm, respectively. Pseudorutile powder was synthesized by a hydrothermal method via tetra-n-butyl titanate (Ti(OBu)₄) and ferric nitrate (Fe(NO₃)₃·9H₂O) [27]. The synthetic product consists of pseudorutile and a small amount of titanium dioxide, as indicated in Figure 1. Figure 2 revealed microstructure of ilmenite and synthesis pseudorutile, and SEM-EDS of pseudorutile. From Figure 2a, the surface of ilmenite is smooth and dense. The incomplete separation of gangue and ilmenite leads to the high SiO₂ content, with a mass fraction of 5.11%. For the synthesis pseudorutile particles, their size is below 10 μm, as shown in Figure 2b. By the analysis of SEM-EDS presented in Figure 2c,d, it is found that the particles are pseudorutile phases in accordance with the analysis results of Figure 1.

![Figure 1. XRD pattern of synthetic pseudorutile powder.](image)

![Figure 2. Microstructure of natural ilmenite and synthesis pseudorutile powder for (a) ilmenite; (b) synthesis pseudorutile powder; (c) SEM-EDS of point A in (b); (d) SEM-EDS of point B in (b).](image)
Table 1. Chemical composition of ilmenite (mass %).

| TFe | FeO | CaO | SiO2 | MgO | Al2O3 | TiO2 | MnO | V2O3 | P   | S    |
|-----|-----|-----|------|-----|-------|------|-----|------|-----|------|
| 34.52 | 26.85 | 0.86 | 5.11 | 0.95 | 1.06 | 44.44 | 0.65 | 0.28 | 0.024 | 0.006 |

2.2. Experimental Methods

Ilmenite or pseudorutile powder, approximately 2 g, was placed flat on the bottom of a porcelain boat (3 cm × 6 cm × 1.5 cm). When muffle furnace reached the required temperature, the loaded porcelain boat was put into the constant temperature zone for a prepared time. Meanwhile, 1 L/min air was injected into the furnace. After oxidation roasting, it was taken out, and cooled to room temperature in air.

The chemical composition of ilmenite was analyzed by chemical analysis and X-ray fluorescence (XRF; ZSXPrimus-II, Rigaku, Tokyo, Japan), and the particle size composition of ilmenite was obtained by a Laser Diffraction Particle Size Analyzer (Mastersizer 3000, Malvern Panalytical, Malvern, UK). The X-ray diffractometer (XRD; X’Pert Pro, PANalytical, Almelo, the Netherlands) was used to measure phases both before and after oxidation roasting. In addition, SEM linked with EDS (SEM-EDS; Ultra Plus, Carl Zeiss GmbH, Oberkochen, Germany and MIRA3 XMH, TESCAN, Brno–Kohoutovice, Czech Republic) was applied to observe microstructure and obtain the compositions of different phases.

3. Results and Discussion

3.1. Confirmation of Oxidation Roasting Products of Natural Ilmenite

As is known to us, TiO2, FeO, Fe2TiO5, H239 and Fe2TiO7 are the oxidation roasting products of ilmenite. There is no debate for TiO2, FeO and Fe2TiO5. With regard to Fe2TiO5 and H239, they do not emerge simultaneously in the previous studies. When oxidation temperature is below 800 °C, some researchers found H239 is one of the oxidation roasting products of FeTiO3 [19,24,25], while others found Fe2TiO5 is one of the oxidation roasting products of FeTiO3 [22,23]. In order to confirm which one is the oxidation product in this work, the ilmenite A1 which is oxidized at 600 °C for 180 min and then is oxidized at 800 °C for 60 min is chosen as the analysis object due to less overlap of peaks, as presented in Figure 3. Reference pattern of Cr2TiO7 is chosen as the reference pattern of Fe2TiO5 because of the similarity [23,26]. The three diffraction peaks at 21.7° , 39.1° , and 56.0° are only matched with H239; the diffraction peak of Fe2TiO5 at 46.7° does not appear. As a result, H239 is one of the oxidation products of FeTiO3, not Fe2TiO5 in this work. In addition, the main diffraction peak of Fe2TiO5 at 25.6° does not match with the XRD pattern, so Fe2TiO5 is not formed at 800 °C.
3.2. Chemical Transformation of Natural Ilmenite above 800 °C

From previous studies, ilmenite without pseudorutile phase is very explicit below 800 °C. H239 and rutile were formed by parallel reactions during oxidation process of ilmenite, and small particle size, low temperature and high oxygen pressure are favored for the formation of H239 [19]. However, chemical transformation of natural ilmenite is not very clear above 800 °C. Thus, the chemical transformation mechanisms of natural ilmenite are revealed above 800 °C in this part. As shown in Figure 4, the oxidation roasting products of ilmenite A0 are TiO$_2$, Fe$_2$O$_3$, H239 and Fe$_2$TiO$_5$ at 900 °C. There is no doubt that TiO$_2$ and Fe$_2$O$_3$ are produced by Reaction (1). Because low temperature is beneficial to the formation of H239 in the oxidation process [19] and there are no H239 diffraction peaks at 800 °C in Figure 5a, H239 is most likely to be formed by combination of TiO$_2$ and Fe$_2$O$_3$ on the basis of the interdiffusion of ion [28]. In order to verify this possibility, ilmenite A0 is oxidized to TiO$_2$ and Fe$_2$O$_3$ at 800 °C for 60 min firstly and then the oxidation products are roasted at 900 °C for 30 min, 60 min and 450 min. The phases of roasting products are shown in Figure 5b–d, in which H239 and Fe$_2$TiO$_5$ arise. After the oxidation at 800 °C for 60 min, FeO content of ilmenite, measured by chemical analysis, is only 0.29%. So H239 is formed by the combination of TiO$_2$ and Fe$_2$O$_3$ rather than the oxidation of FeTiO$_3$ at 900 °C, as shown in Reaction (12).

$$3\text{TiO}_2(s) + \text{FeO}_2(s) \rightarrow \text{Fe}_2\text{TiO}_5(s) \ (\text{H239}) \quad (12)$$

Owing to the same content of SiO$_2$ in oxidation products, changes of objective oxides contents is revealed by the characteristic peak intensity ratios of objective oxides to SiO$_2$ [29]. Figure 6 presents the changes of objective oxides of the oxidation products in Figure 5. Fe$_2$TiO$_5$ content increases with the decrease in Fe$_2$O$_3$ content and TiO$_2$ content. However, TiO$_2$ content has an increasing trend while Fe$_2$TiO$_5$ content continues to increase after roasting for 60 min. At the same time, H239 content decreases. So, it is certain that Reaction (4) works on the formation of Fe$_2$TiO$_5$, not Reaction (6). As shown in Figure 4, H239 is formed and Fe$_2$TiO$_5$ is not detected when the roasting time is below 30 min. Therefore, TiO$_2$ and FeO$_2$ are combined to generate H239 firstly at 900 °C, and then Fe$_2$TiO$_5$ is formed by Reactions (4). H239 and Fe$_2$TiO$_5$ are not formed simultaneously. H239 is an intermediate phase for the formation of Fe$_2$TiO$_5$. Therefore, the formation of Fe$_2$TiO$_5$ is owed to Reaction (4), not Reactions (3) and (5)–(7).
Figure 4. Chemical transformations of ilmenite A0 with the increase in roasting time.

Figure 5. Combination of TiO$_2$ and FeO$_3$ for (a) ilmenite A0 oxidized at 800 °C for 60 min, (b) ilmenite A0 roasted at 900 °C for 30 min after it was oxidized at 800 °C for 60 min, (c) ilmenite A0 roasted at 900 °C for 60 min after it was oxidized at 800 °C for 60 min, and (d) ilmenite A0 roasted at 900 °C for 450 min after it was oxidized at 800 °C for 60 min.
3.3. Microstructure Transition of Natural Ilmenite above 800 °C

Figure 7 shows the XRD patterns of the oxidation products of A0 and A1 at 800 °C for 60 min. Compared with phases of A0, A1 has a new phase, H239, formed by the oxidation of natural ilmenite. The microstructure of A0 in Figure 8a displays that a dark TiO$_2$ layer forms with the ferrous ions migrating to the surface of particles to form a ferric oxide layer. After full oxidation, ilmenite A0 forms three layers, which are Fe$_2$O$_3$, TiO$_2$ and the inside mixture layer of Fe$_2$O$_3$ and TiO$_2$ in turn. When particle size decreases, a H239 layer is formed instead of TiO$_2$ layer, as shown in Figure 8b. The main reason is that oxygen diffusion rate decreases with the increase in the diameter of ilmenite particle [30,31]. So oxygen partial pressure increases with the decrease in particle size for a simple ilmenite particle, which is beneficial to the formation of H239.
Figure 8. Microstructures of ilmenites with different diameters at 800 °C for 60 min for (a) A0 64.5 μm and (b) A1 19.8 μm.

Figure 9 illustrates microstructure of oxidation roasting ilmenite, in which points A, C and F are Fe$_2$O$_3$; points B, E and H are TiO$_2$; D and G are iron–titanium oxides by analyzing the atomic percentage in Table 2. When ilmenite A0 oxidized at 800 °C for 60 min continues to be roasted at 900 °C for 30 min, an iron–titanium oxides layer is formed between Fe$_2$O$_3$ and TiO$_2$ layers in Figure 9b. The schematic diagram is shown in Figure 10a,b. The iron–titanium oxides layer is Fe:TiO$_2$ layer according to the atomic percentage of point D in Table 2. When the roasting time continues to increase, the outermost Fe:Ti:O$_5$ begins to be decomposed into Fe:TiO$_5$ and TiO$_2$, and Fe:Ti:O$_5$ continues to be formed along the diameter direction toward the center of the particle until Fe:TiO$_5$ and TiO$_2$ are as the final products in the center of particles, as shown in Figure 10c,d. The wider iron–titanium oxides layer also certifies it, as shown in Figure 9c.

Figure 9. Microstructure of oxidation roasting ilmenite for (a) ilmenite A0 oxidized at 800 °C for 60 min, (b) ilmenite A0 roasted at 900 °C for 30 min after it was oxidized at 800 °C for 60 min and (c) ilmenite A0 roasted at 900 °C for 60 min after it was oxidized at 800 °C for 60 min.
3.4. Chemical Transformation Mechanisms of Pseudorutile

Pseudorutile is the characteristic phase of the weathering ilmenite, for which the chemical transformation mechanisms are not clear due to the interference of oxidation products of ilmenite. As mentioned in the introduction, the pseudorutile was able to decompose to Fe₂Ti₂O₇. However, Fe₂Ti₂O₇ is also one of the oxidation products of natural ilmenite. Thus, effect of temperature and roasting time on chemical transformation of pseudorutile is investigated in this section. Figure 11 shows the chemical transformation mechanisms of pseudorutile in roasting processes at 600 °C and 800 °C. The pseudorutile is directly decomposed to TiO₂ and Fe₂O₃ in Figure 11a–d, as Reaction (13) shows and no new phase is formed with the increase in roasting time, like Fe₂Ti₂O₇. When the roasting temperature increases to 800 °C, it can be seen that the decomposition processes of pseudorutile is the same, and the decomposed products, TiO₂ and Fe₂O₃, combine to form H239 and Fe₂Ti₂O₇ at 800 °C with increasing time, as showed in Figure 11f,g. Therefore, pseudorutile in natural ilmenite is directly decomposed into TiO₂ and Fe₂O₃ instead of being decomposed into Fe₂Ti₂O₇ firstly and then into TiO₂ and Fe₂O₃ in the roasting process.

\[
\text{Fe}_2\text{Ti}_3\text{O}_9 \text{(pseudorutile)} \rightarrow 3\text{TiO}_2 + 2\text{Fe}_2\text{O}_3 \quad (13)
\]
In this work, microstructure and chemical transformation of natural ilmenite during an isothermal roasting process in air atmosphere was investigated. H239 not only can be formed by the oxidation of FeTiO3, but it also can be generated by the combination of TiO2 and FeO in turn. When it is roasted at 900 °C, Fe2TiO5 is firstly developed between FeO and TiO2 layers. With the increase in roasting time, the Fe2TiO5 layer is decomposed into FeTiO3 and TiO2, and FeTiO3 continues to be formed along the diameter direction toward the center of the particle until Fe2TiO5 and TiO2 are as the final products in the center of particles. FeTiO3 is formed by the decomposition of H239, not by the oxidation of FeTiO3 and combination of TiO2 and FeO. Pseudorutile in natural ilmenite is directly decomposed into TiO2 and FeO instead of being decomposed into Fe2TiO5 firstly and then into TiO2 and FeO in the roasting process.

4. Conclusions

Author Contributions: Writing—original draft, G. C. and Z.G.; Data curation, G. C. and S. Y.; Investigation, G. C. and Z.G.; Methodology, Z.G.; Project administration, H.Y. and X.X.; Resources, H.Y.; Supervision, X.X.; Visualization, S.Y. All authors have read and agreed to the published version of the manuscript.

Funding: National Natural Science Foundation of China (Grant No. U1908226); Fundamental Research Funds for the Central Universities (Grant No. N182503035).

Data Availability Statement: Data is contained within the article.

Conflicts of Interest: The authors declare no conflict of interest.
References

1. Chen, M.; Tang, A.; Xiao, X. Effect of milling time on carbothermic reduction of ilmenite. Trans. Nonferrous Met. Soc. China 2015, 25, 4201–4206.

2. Panigrahi, M.; Shibata, E.; lizuka, A.; Nakamura, T. Production of Fe-Ti alloy from mixed ilmenite and titanium dioxide by direct electrochemical reduction in molten calcium chloride. Electrochim. Acta 2013, 93, 143–151.

3. Xiong, L.; Hua, Y.; Xu, C.; Li, J.; Li, Y.; Zhang, Q.; Zhou, Z.; Zhang, Y.; Ru. J. Effect of CaO addition on preparation of ferrotitanium from ilmenite by electrochemical reduction in CaCl2NaCl molten salt. J. Alloy. Compd. 2016, 676, 383–389.

4. Zhou, Z.; Hua, Y.; Xu, C.; Li, J.; Li, Y.; Gong, K.; Ru, J.; Xiong. L. Preparation of Ferrotitanium from Ilmenite by Electrolysis-Assisted Calciothermic Reduction in CaCl2NaCl Molten Salt. Jom 2015, 68, 532–539.

5. Gao, Z.; Cheng, G.; Yang, H.; Xue, X.; Ri. J. Preparation of Ferrotitanium Using Ilmenite with Different Reduction Degrees. Metals 2019, 9, 962.

6. Dou, Z.; Wang, C.; Fan, S.; Shi, G.; Zhang, T.-A. Al Control in High Titanium Ferro with Low Oxygen Prepared by Thermite Reaction. In the 6th International Symposium on High-Temperature Metallurgical Processing, Springer: Berlin/Heidelberg, Germany, 2015; 11–17.

7. Akhgar, B.; Pazouki, M.; Ranjbar, M.; Hosseinnia, A.; Salarian, R. Application of Taguchi method for optimization of synthetic rutile nano powder preparation from ilmenite concentrate. Chem. Eng. Res. Des. 2012, 90, 220–228.

8. Wu, L.; Li, X.; Wang, Z.; Guo, H.; Wang, X.; Wu, F.; Fang, J.; Wang, Z.; Li, L. A novel process for producing synthetic rutile and LiFePO4 cathode material from ilmenite. J. Alloy. Compd. 2010, 506, 271–278.

9. Hiraki, T.; Maruyama, Y.; Suzuki, Y.; Itoh, S.; Nagasaka, T. Up-grading of natural ilmenite ore by combining oxidation and acid leaching. Int. J. Miner. Metall. Mater. 2018, 25, 729–736.

10. Li, Z.; Wang, Z.; Li, G. Preparation of nano-titanium dioxide from ilmenite using sulfuric acid-decomposition by liquid phase method. Powder Technol. 2016, 287, 256–263.

11. Wu, F.; Li, X.; Wang, Z.; Guo, H.; Wu, L.; Xiong, X.; Wang, X. Preparation of TiO2 nanosheets and Li4Ti5O12 anode material from natural ilmenite. Powder Technol. 2011, 213, 192–198.

12. Palliyaguru, L.; Kulathunga, U.S.; Jayarathna, L.I.; Jayaweera, C.D.; Jayaweera, P.M. A simple and novel synthetic route to prepare anatase TiO nanopowders from natural ilmenite via the H3PO4/NH3 process. Int. J. Miner. Metall. Mater. 2020, 27, 846–855.

13. Wang, X.; Li, X.; Wang, Z.; Wu, L.; Yue, P.; Guo, H.; Wu, F.; Ma, T. Preparation and characterization of Li4Ti5O12 from ilmenite. Powder Technol. 2010, 204, 198–202.

14. Deng, Y.; Xing, M.; Zhang, J. An advanced TiO2 /Fe2TiO5 /Fe2O3 triple-heterojunction with enhanced and stable visible-light-driven fenton reaction for the removal of organic pollutants. Appl. Catal. B: Environ. 2017, 211, 157–166.

15. Jin, L.; Zhou, C. Electronic structures and optic properties of Fe2TiO5 using LSDA+U approach. Prog. Nat. Sci. Mater. Int. 2013, 23, 413–419.

16. Zeinali Moghadam, H.; Sharifitabar, M.; Roudini, G. Microstructure and wear properties of Fe–TiC composite coatings produced by submerged arc cladding process using ferroalloy powder mixtures. Surf. Coat. Technol. 2019, 361, 91–101.

17. Gou, H.-P.; Zhang, G.-H.; Chou, K.-C. Influence of Pre-oxidation on Carbothermic Reduction Process of Ilmenite Concentrate. Isi Int. 2015, 55, 928–933.

18. Zhang, J.; Zhu, Q.; Xie, Z.; Lei, C.; Li, H. Morphological changes of Panzhihua ilmenite during oxidation treatment. Metall. Mater. Trans. B 2013, 44, 897–905.

19. Fu, X.; Wang, Y.; Wei, F. Phase Transitions and Reaction Mechanism of Ilmenite Oxidation. Metall. Mater. Trans. A 2010, 41, 1338–1348.

20. Teufer, G.; Temple, A. Pseudorutile—a new mineral intermediate between ilmenite and rutile in the N alteration of ilmenite. Nature 1966, 211, 179.

21. Lv, W.; Lv, X.; Zhang, Y.; Li, S.; Tang, K.; Song, B. Isothermal oxidation kinetics of ilmenite concentrate powder from Panzhihua in air. Powder Technol. 2017, 320, 239–248.

22. Zhang, G.; Ostrovski, O. Effect of preoxidation and sintering on properties of ilmenite concentrates. Int. J. Miner. Process. 2002, 64, 201–218.

23. Gupta, S.K.; Rajakumar, V.; Grieveon, P. Phase transformations during heating of ilmenite concentrates. Metall. Trans. B 1991, 22, 711–716.

24. Rao, D.B.; Rigaud, M. Kinetics of the oxidation of ilmenite. Oxid. Met. 1975, 9, 99–116.

25. Xiao, W.; Lu, X.-g.; Zou, X.-l.; Wei, X.-m.; Ding, W.-z. Phase transitions, micro-morphology and its oxidation mechanism in oxidation of ilmenite (FeTiO3) powder. Trans. Nonferrous Met. Soc. China 2013, 23, 2439–2445.

26. Grey, J.; Reid, A. Shear structure compounds (Cr, Fe)Ti2-xOy derived from the α-PbO2: structural type. J. Solid State Chem. 1972, 4, 186–194.

27. Lin, F.; Song, H.; Tian, S.; Chen, X.; Zhou, J.; Wang, F. Fe:Ti5O3 nanoparticles as an anode material for lithium-ion batteries. Electrochim. Acta 2012, 83, 305–310.

28. Ren, Z.-s.; Hu, X.-j.; Li, S.-y.; Xue, X.-x.; Chou, K.-c. Interdiffusion in the FeO-TiO2 system. Int. J. Miner. Metall. Mater. 2013, 20, 273–278.

29. Zhang, X.; Fang, D.; Song, S.; Cheng, G.; Xue, X. Selective leaching of vanadium over iron from vanadium slag. J. Hazard Mater. 2019, 368, 300–307.
30. Zhang, H.-Q.; Fu, J.-T. Oxidation behavior of artificial magnetite pellets. *Int. J. Miner. Metall. Mater.* **2017**, *24*, 603–610.

31. Surzhikov, A.P.; Frangulyan, T.S.; Ghyngazov, S.A.; Lysenko, E.N. Investigation of oxidation processes in non-stoichiometric lithium–titanium ferrites using TG analysis. *J. Therm. Anal. Calorim.* **2010**, *102*, 883–887.