Morphological Changes and Reduction Mechanism for the Weak Reduction of the Preoxidized Panzhihua Ilmenite

JIANBO ZHANG, GENGYU ZHANG, QINGSHAN ZHU, CHAO LEI, ZHAOHUI XIE, and HONGZHONG LI

Morphological changes and phase transition behaviors were investigated for the weak reduction (reduction of ferric iron-to-ferrous state) of preoxidized Panzhihua ilmenite by hydrogen at 873 K to 1073 K (600 °C to 800 °C). Ilmenite was preoxidized for 4 hours at 1023 K and 1173 K (750 °C and 900 °C), respectively, before the reduction. The results revealed that there were two competing reduction routes. At high reduction temperatures, *e.g.*, 1023 K and 1073 K (750 °C and 800 °C), ferric irons from both hematite and pseudobrookite would combine with rutile grains as formed in the preoxidation to form homogeneous ilmenite phase with pores immingled. However, at lower reduction temperatures, *e.g.*, 873 K (600 °C), hematite and pseudobrookite are reduced mainly through direct reduction without the participation of rutile. As a result, the as-reduced ilmenites show great differences in their phase components and microstructure, especially for the Ti species. For ilmenites preoxidized at 1023 K (750 °C), most of the Ti ions present in the needlelike rutile network, but for ilmenites preoxidized at 1173 K (900 °C), Ti distributed in both irregular rutile grains and ilmenite matrix.

I. INTRODUCTION

UPGRADING ilmenite to produce synthetic rutile, which is the main raw material for production of titania pigment and metallic titanium, is becoming increasingly important.[1] Hydrochloric acid leaching is one of the preponderant approaches to obtain synthetic rutile from ilmenite due to its advantages in the removal of impurities and its ability to recycle hydrochloric acid. Thermal pretreatments were broadly adopted to improve the reactivity of ilmenite toward hydrochloric acid or to prevent the pulverization of leaching products.[2–9] Strong oxidation–weak reduction, where the ferrous ions in ilmenite are oxidized to ferric ions first (the strong oxidation) and then reduced back to the ferrous state (the weak reduction), is one of the most effective pretreatment methods and has wide applicability for nearly all kinds of ilmenite concentrates.[2,5,6,9] A full understanding of the phase and microstructural changes of ilmenite during these thermal pretreatments is important and necessary for obtaining optimal process parameters. A systematic investigation on the ilmenite oxidation process has been reported in previous papers.[10,11] Therefore, this article addresses the weak reduction process of the preoxidized ilmenite.

Actually, the weak reduction of the preoxidized ilmenite has not been fully clarified yet, although it has been adopted as a pretreatment process for several years. On the one hand, researchers concentrated mainly on its phase transitions and reduction kinetic. Many articles in the literature proposed that the ferric iron of ilmenite was reduced to a ferrous state that presents as ilmenite phase in the weak reduction process.[2,3,5,6,12] This transformation was found to have a relatively high rate above 1073 K (800 °C)[13,14]; *e.g.*, Grey *et al.*[14] found that the reduction completed in ~1 minute in hydrogen at 1123 K (850 °C) for ilmenite that had been oxidized at 1223 K (950 °C) for 45 minutes. However, few investigations gave detailed information about the morphological changes accompanying the phase transition. On the other hand, the influence of oxidation and reduction temperatures on the weak reduction process has also not been studied. Most of the previous investigations were performed (not only the reduction but also the oxidation) at relatively high temperatures[2,5,6,9]; *e.g.*, in the study of Sinha, ilmenite was oxidized at 1173 K to 1223 K (900 °C to 950 °C) and then reduced at 1123 K to 1173 K (850 °C to 900 °C).[5] Nicholson *et al.*[6] suggested in their patent that the preferred temperature ranges for the oxidation and reduction steps were 1198 K to 1248 K (925 °C to 975 °C) and 1023 K to 1173 K (750 °C to 900 °C), respectively. The weak reduction process at lower temperatures has been seldom studied. Both the oxidation and reduction temperatures probably have great influence on the phase and microstructural changes. Significant temperature effects have actually been found in many heat thermal processes of ilmenite: In the study of direct reduction of synthetic ilmenite (ilmenite are

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directly reduced to metallic iron and rutile), de Vries et al.[5] found two different morphologies of ilmenite reduced at different reduction temperatures. In our studies of ilmenite oxidation, we found two kinds of typical thermodynamic stable oxidized ilmenites at 873 K to 1273 K (600 °C to 1000 °C), and their phase components were hematite + rutile; pseudobrookite + rutile, respectively.[10] The lack of studies on the morphological changes and temperature effects badly limit our understanding on the weak reduction because both of them can give necessary information on the reaction path and mechanism. Therefore, a systematic study to allow a comprehensive understanding would be necessary.

This article systematically investigates the weak reduction process of the two typical thermodynamic stable oxidized ilmenites, which were obtained through oxidation of the Panzhihua ilmenite for 4 hours at 1023 K and 1173 K (750 °C and 900 °C), respectively. The phase transitions and morphological changes during the weak reduction at 873 K to 1073 K (600 °C to 800 °C) by hydrogen were investigated and the reduction mechanisms were clarified.

II. MATERIALS AND METHODS

A. Materials

Ilmenite concentrate from the Panzhihua area of China with particle sizes ranging from 50 μm to 150 μm was used as the raw ilmenite. The chemical compositions and X-ray diffraction (XRD) pattern of the raw Panzhihua ilmenite were reported in our previous paper.[10] Preoxidization of the ilmenite was performed in a muffle furnace in air for 4 hours at 1023 K and 1173 K (750 °C and 900 °C), respectively, and the preoxidized samples were referred to as sample A and B, correspondingly. As illustrated by the XRD pattern in Figure 1, the phase compositions are quite different for the two samples; i.e., the sample A is mainly composed of rutile and hematite, while the sample B is consisted of pseudobrookite and rutile with a small quantity of hematite. The microstructure of the two samples (see Figure 2) also shows significant difference as needlelike rutile network enwrapped by hematite grains can be found in sample A, and irregular rutile grains disperse in the pseudobrookite matrix with few isolated hematite grains in sample B.[10]

H_2 (purity 99.999 pct) and N_2 (purity 99.999 pct), which were from Beijing Huayuan Gas Chemical Industry Co., Ltd. (Beijing, China), were used as the reducing gas and the shielding gas, respectively.

B. Experimental

The isothermal reduction experiments of the preoxidized ilmenites were carried out in a horizontal tubular reactor that was heated by a resistant furnace at temperatures ranging from 873 K to 1073 K (600 °C to 800 °C). In each experiment, 10 g preoxidized ilmenite powder was placed in an alumina boat (about 8.5 × 2.5 × 1.5 cm^3), put into the reactor, and then
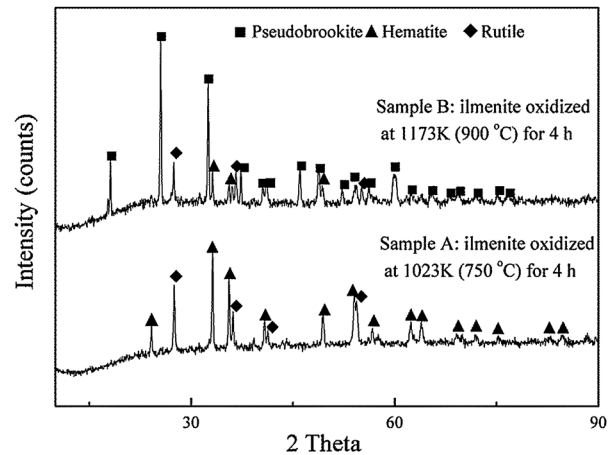

Fig. 1—XRD patterns of samples A and B.

preheated in the shielding gas atmosphere. When the temperature was stable, the gas flow was changed to hydrogen with a rate of 0.3 L/min. After a desired period of reduction, the gas flow was changed to the shielding gas again, and the power of the furnace was switched off. The boat was kept in the reactor until naturally cooled to room temperature.

C. Analysis and Characterization

The phases presented in the samples were analyzed by XRD (X' Pert MPD Pro, PANalytical, Almelo, The Netherlands) with Cu Kα radiation (λ = 1.5408 Å). Morphologies were characterized by field-emission scanning electron microscopy (FESEM; Quanta 200; FEI Company, Eindhoven, The Netherlands). Before XRD analyses, all samples were ground into fine powders with particle sizes smaller than 74 μm. For the SEM characterization, ilmenite specimens were mounted using epoxy resin first and then were ground and polished.

III. RESULTS AND DISCUSSION

A. Phase Transitions at High Temperatures

The phase transitions during weak reduction were first investigated at 1023 K and 1073 K (750 °C and 800 °C). Samples A and B reduced at 1023 K (750 °C) for 5, 15, and 30 minutes, respectively, were prepared and characterized by XRD. Their XRD patterns were displayed in Figures 3 and 4, respectively. As shown in these patterns, the intensity of peaks from both hematite and pseudobrookite decreases, while the peaks from ilmenite increase quickly with increasing reduction time, indicating changes from ferric irons, no matter hematite or pseudobrookite, to ferrous irons as the ilmenite phase in a fast rate. Besides, with the rapid formation of ilmenite, the intensity of peaks of rutile for both samples A and B also decreases, revealing that rutile takes part and is consumed uninterruptedly in the ferric-to-
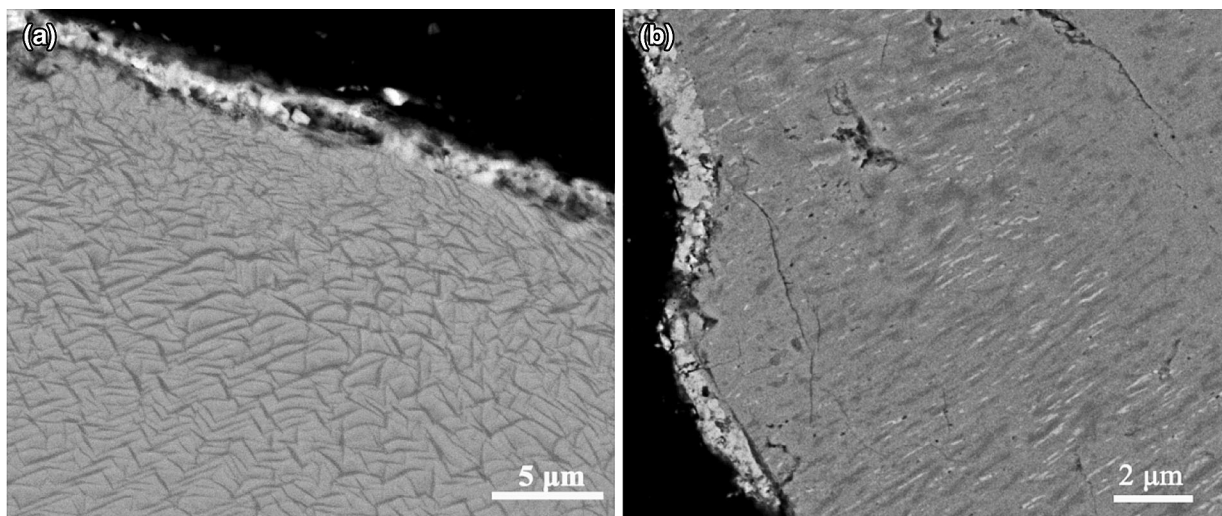
Fig. 2—Backscattered electron images of (*a*) sample A and (*b*) sample B. Needlelike rutile network enwrapped by hematite grains can be found inside of sample A, while irregular rutile grains (little dark) disperse into the pseudobrookite matrix (gray phase) with few isolated hematite grains (bright phase) in sample B.
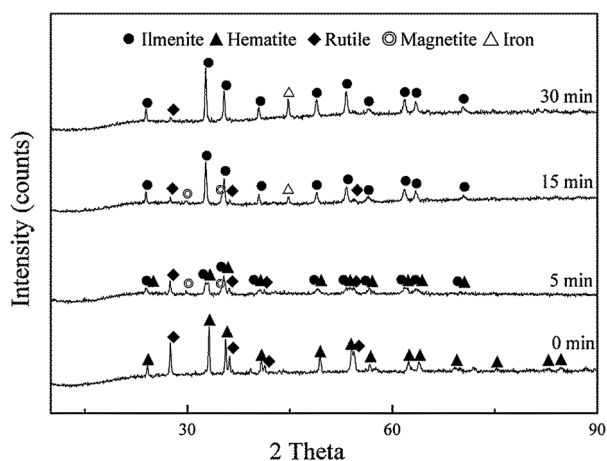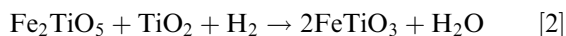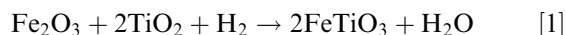

Fig. 3—XRD patterns of sample A reduced at 1023 K (750 °C) for different times.

Fig. 4—XRD patterns of sample B reduced at 1023 K (750 °C) for different times.

ferrous transformation reactions. Therefore, the two preoxidized ilmenite samples underwent almost the same reduction paths, *i.e.*, they combined with rutile to form ilmenite even though they have different phase components. The main reactions, therefore, can be expressed as:

$$Fe_2O_3 + 2TiO_2 + H_2 \rightarrow 2FeTiO_3 + H_2O \qquad [1]$$

$$Fe_2TiO_5 + TiO_2 + H_2 \rightarrow 2FeTiO_3 + H_2O \qquad [2]$$

It should be noted that a small amount of magnetite was also found in the XRD patterns as shown in Figures 3 and 4, indicating that independent reduction of hematite and pseudobrookite[16,17] occurs together with the combining reactions. The independent reduction reactions will be further discussed in Section III–C. Ilmenite was not the final stable product in the reduction because the ferrous to metallic iron reduction took place
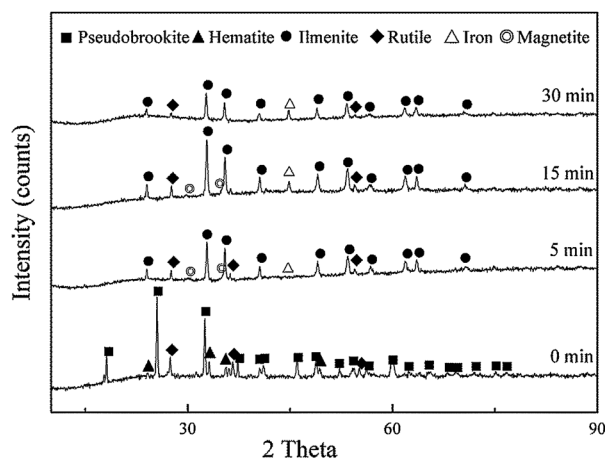
as a subsequent reaction. This metallization reaction of ilmenite has been studied by many researchers[14,17–19] and can be written as:

$$FeTiO_3 + H_2 \rightarrow Fe + TiO_2 + H_2O \qquad [3]$$

The XRD patterns of the two samples reduced at 1073 K (800 °C) for 5 and 15 minutes were shown in Figures 5 and 6. These XRD patterns show the same phase transitions as happened at 1023 K (750 °C) (see Figures 3 and 4). Rutile combines with hematite or pseudobrookite to form ilmenite. However, the temperature favors the reduction rate. At 1073 K (800 °C), hematite and pseudobrookite were reduced completely to ilmenite and metallic iron after only 15 minutes.

In summary, at these high reduction temperatures, the two preoxidized ilmenite samples undergo the similar reduction paths; the formation of ilmenite as Reactions [1] and [2] shows the main phase transitions in the
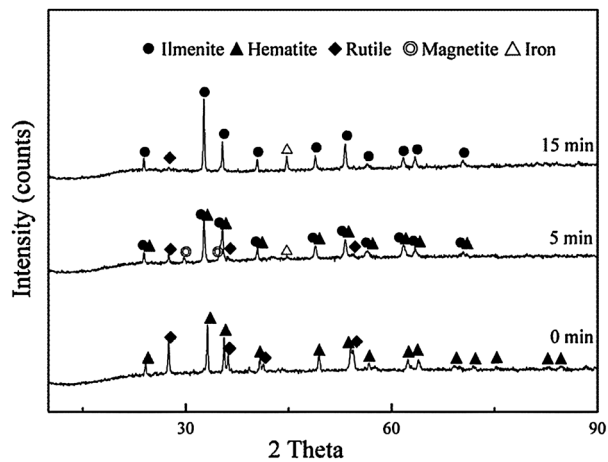
Fig. 5—XRD patterns of sample A reduced at 1073 K (800 °C) for different times.
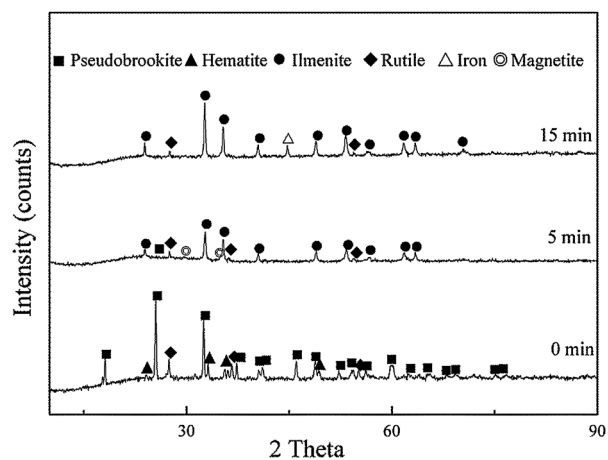

Fig. 6—XRD patterns of sample B reduced at 1073 K (800 °C) for different times.

whole weak reduction processes. Their reduction rates increase with increasing reduction temperature. The increase of reaction rates should be attributed to the acceleration of both the hydrogen diffusion rate and the rates of solid-state diffusion of ions. It has been reported that Ti cations had a fast diffusion rate at high temperatures as revealed by the formation of pseudo-brookite during oxidation of ilmenite.[10,20] It is there-fore reasonable to infer that the diffusion of Ti cations plays an important role during the formation of ilmenite through the combination Reactions [1] and [2].

B. *Morphological Changes at High Temperatures*

The cross-section SEM images of reduced ilmenites were observed carefully to investigate the morpholog-ical changes along with the phase transitions. Figure 7 show morphologies of sample A reduced at 1023 K (750 °C) for 30 minutes. These ilmenite powders vary in the reduction extent with their particle sizes. Powders with greater particle sizes were only partially reduced and their typical cross-section morphology was

displayed in Figure 7(a). The three distinctive regions from the interior to surface of the particle are the unreacted core, the ferric-to-ferrous reaction zone, and the ferrous to metal iron zone (the metalized rim), respectively. The unreacted core remains its dense structure, but several micropores are present in the reacted zones as the result of the removal of O ions during the reduction process. In the second layer, *i.e.*, the ferric-to-ferrous reaction zone, the network struc-ture of rutile grains has been completely destroyed due to the fact that the reduction reaction needs rutile to form ilmenite as Reaction [1]. As shown in Figure 7(b), the reduction product ilmenite (gray) becomes the main phase, while few residual rutile (relatively dark) and hematite (relatively bright) grains disperse in the ilmenite matrix (gray). The boundaries of these grains are blurry, reflecting that rutile and hematite are gradually "dissolved" during the formation of ilmenite. It is worth mentioning that the thickness of the outmost rim is obviously much thinner than that of the second layer, reflecting that the metallization reaction has a much slower reduction rate than that of the ferric-to-ferrous reduction. As the reduction process goes on, the unreacted core disappears and the whole particle becomes porous as shown in Figure 7(c), which is the typical cross-section morphology of those completely reduced ilmenite particles that have smaller particle sizes. In these small particles, rutile grains in needle-like structure disappear and homogeneous ilmenite phase is formed, as shown in Figure 7(d).

Similar morphological changes were observed from the partially and completely reduced ilmenite particles of sample B. Figures 8(a) and (b) are the SEM images of ilmenite particles from sample B reduced at 1023 K (750 °C) for 5 minutes. These particles have just been partially reduced and show layered microscopic mor-phologies. However, they only exhibit two zones: the unreduced regions and the ferric-to-ferrous reaction zone. In these reacted zones, the number of rutile grains decreases significantly; large numbers of micropores and ilmenite grains, which are in a little brighter color, replace the dense and gray pseudobrookite matrix. Figures 8(c) and (d) are the SEM images of completely reduced ilmenite particles from sample B that were reduced for 30 minutes. Similar to that shown in Figures 7(c) and (d), the particle consists of ferric-to-ferrous and ferrous-to-metallic iron reduction zones. Ilmenite grains with micropores have completely replaced the dense, pseudobrookite matrix.

It should be noted that the images of reduced sample A and B (see Figures 7(d) and 8(d)) show different characteristics; *i.e.*, the ilmenite phase of reduced sample A has a network structure, while ilmenite phase of reduced sample B shows micron-sized grains scattered by micropores. These pores are much smaller than those of sample A. This phenomenon is understandable. The diffusion of Ti cations of rutile control the formation of ilmenite as Reactions [1] and [2], structures of rutile grains as-formed in the preoxidation determine the morphology of ilmenite phase. As a result, both reduced samples "inherited" some original morphological char-acteristics of the oxidized ilmenites.
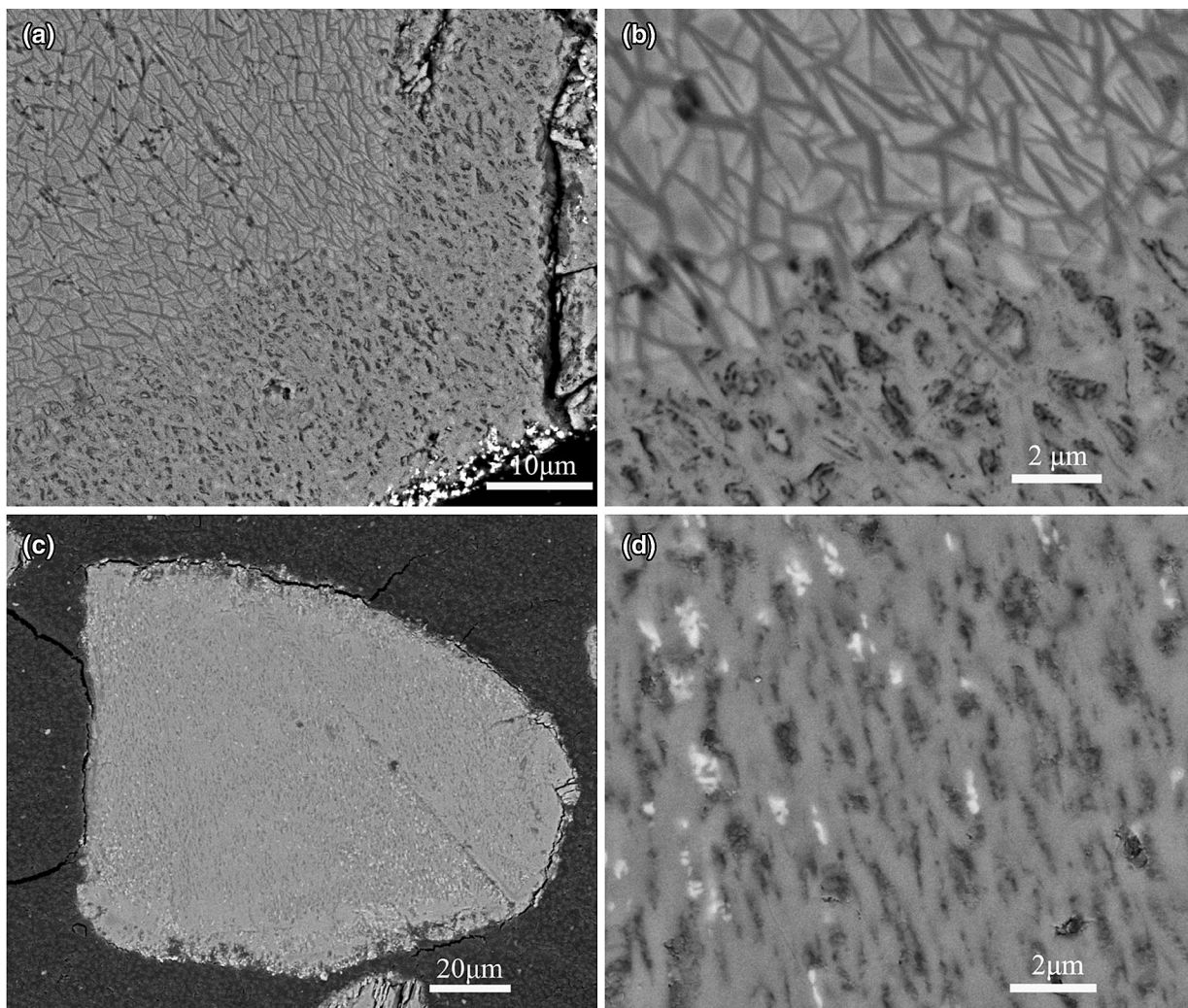
Fig. 7—Backscattered electron images of sample A reduced at 1023 K (750 °C) for 30 min. Image (*a*) shows three distinctive regions from the inside to surface of the partially reduced powders, which are the unreacted core (hematite + rutile), the ferric-to-ferrous reaction zone (ilmenite with few rutile and hematite), and the ferrous-to-metal iron reaction zone (the metalized rim), respectively. Image (*b*) is a higher-magnification image of image (a). Images (*c*) and (*d*) show a completely reduced particle with different magnifications.

The above investigation demonstrates that the oxidation temperature has a marginal effect on the phase constitution; *e.g.*, the phases formed during oxidation at low and high temperature would all be reduced to ilmenite. However, the oxidation temperatures have a significant influence on the microstructure of reduced ilmenite, where the morphology of the reduced sample tends to "inherit" some morphological characteristics of the preoxidized sample.

C. Phase Transitions and Morphological Changes at Low Temperature

To study the influence of reduction temperature on the phase and microstructure, samples A and B were reduced at 873 K (600 °C) for up to 2 hours. Phase changes during the low-temperature reduction are illustrated by the XRD patterns in Figures 9 and 10. Both samples exhibit obvious different phase transitions at such low temperatures compared with those discussed

above. As shown in Figures 9 and 10, the intensity of peaks from both hematite and pseudobrookite decreases with an increase of reduction time, while no evident decline of the intensity of peaks of rutile can be observed, indicating that rutile did not take part in the reduction reactions. Moreover, for sample A, the formation of ilmenite is negligible; relatively strong peaks of metallic iron have appeared when there are still strong peaks of hematite (see Figure 9).

The morphological changes arose during the weak reduction at 873 K (600 °C) were given in Figures 11 and 12. Figure 11 displays the morphologies of partially reduced ilmenite particle from sample A. These morphologies show two evident differences compared with those reduced at 1023 K (750 °C). The first difference is that there are only two distinctive layers in one particle; both of the two reduction steps take place in the same reacted zones, and no evident ilmenite grains are formed. The second difference is that rutile grains with needle-like structure remain, demonstrating that rutile
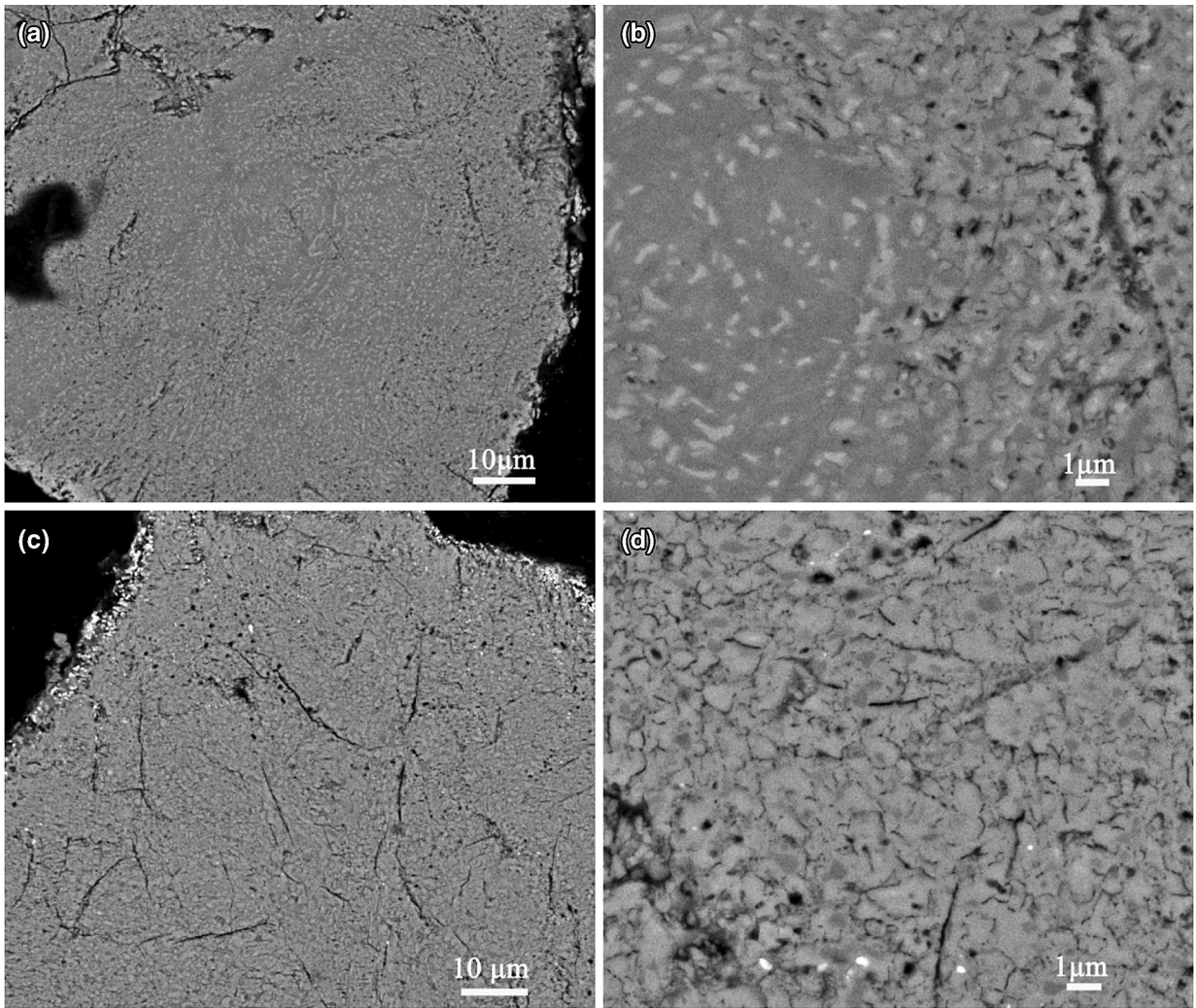
Fig. 8—Backscattered electron images of sample B reduced at 1023 K (750 °C). (*a*) and (*b*) Partially reduced particles reduced for 5 min. (*c*) and (*d*) Completely reduced powders reduced for 30 min. (b) Is a higher-magnification image from (a) and shows the morphological change during reduction from pseudobrookite to ilmenite: Large numbers of micropores and ilmenite grains in micron sizes and a little brighter color has replaced the pseudobrookite matrix and the number of rutile grains (little dark phase) decreases.
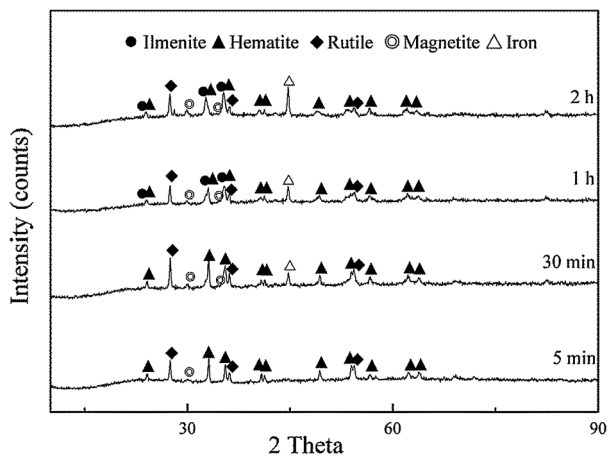

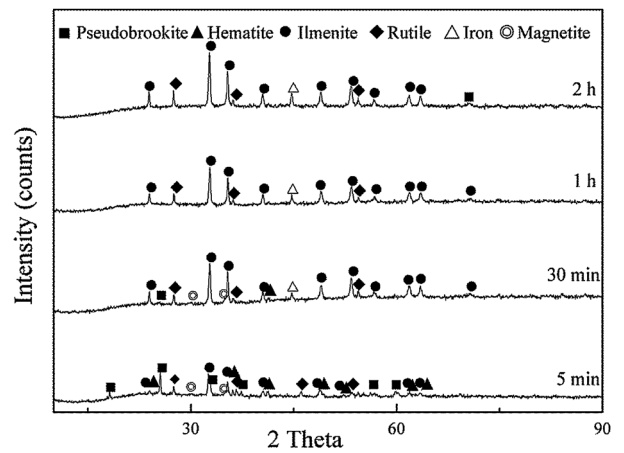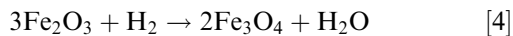Fig. 9—XRD patterns of sample A reduced at 873 K (600 °C) for different times.

Fig. 10—XRD patterns of sample B reduced at 873 K (600 °C) for different times.

does not take part in the reduction reactions, which agrees with the XRD results. Figure 12 displays the morphologies of ilmenite particle from sample B reduced at 873 K (600 °C) for 1 hour. As expected, there are also island-like rutile grains remaining in the reacted zone (see Figure 12(b)).

Therefore, both of XRD patterns and SEM images prove that, the combination reactions of rutile and ferric compounds as Reactions [1] and [2] were restricted at 873 K (600 °C). In this condition, both ferric irons of the two samples, hematite and pseudobrookite, were reduced independently without the participation of rutile. The independent reduction of hematite has been studied for many years, and magnetite was proven to be the weak reduction product of hematite when the reduction temperature is above 843 K (570 °C).[16] Therefore, the reduction reaction of sample A at 873 K (600 °C) can be written as:

$$3Fe_2O_3 + H_2 \rightarrow 2Fe_3O_4 + H_2O \qquad [4]$$

Magnetite is also one product of the independent reduction of pseudobrookite, because it is also found in the XRD patterns of reduced sample B. Similarly, the reduction reaction of sample B at 873 K (600 °C) can be written as:

$$3Fe_2TiO_5 + 2H_2 \rightarrow 3FeTiO_3 + Fe_3O_4 + 2H_2O \qquad [5]$$

However, the magnetite formed as Reactions [4] and [5] is probably reduced to metallic iron quickly because the contents of magnetite in both the reduced samples are very low as indicated by the XRD patterns (see Figures 9 and 10). This metallization reaction can be written as:

$$Fe_3O_4 + 8H_2 \rightarrow 3Fe + 4H_2O \qquad [6]$$
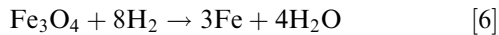
The high metallization rate of magnetite can explain why relatively strong peaks of metallic iron have appeared when there are still evident peaks of hematite (see Figure 9) and both two reduction steps of sample A take place in the same reacted zone (see Figure 11).

Weak reduction of preoxidized ilmenite has been extensively investigated and it was generally reported that the weak reduction proceeded through Reactions [1] and [2].[2,3,5,6,12] Through the above detailed phase and microstructural investigations, we found, however, that that there were two competing reduction routes during the weak reduction of preoxidized ilmenite at 873 K to 1073 K (600 °C to 800 °C): The combination reactions (Reactions [1] and [2]) compete with the independent reduction reactions (Reactions [4] and [5]). At high temperatures, combination reactions of ferric phases and rutile grains are the main reactions, while at a lower temperature, i.e., 873 K (600 °C), most ferric phases are reduced independently with the participation of rutile. The competition between combination reactions and independent reduction reactions may be related to the difference in the solid-state diffusion rate of Ti cations. At high temperatures, the diffusion rate of

Ti cations is relatively high, and Reactions [1] and [2], therefore, have greater rates than those of Reactions [4] and [5]. In contrast, at a low temperature, the low diffusion rate of Ti cations restricts the participation of rutile in the reduction reactions, and independent reductions of hematite and pseudobrookite as Reactions [4] and [5] become the main reactions. A similar phenomenon is that the variation in the solid-state diffusion rate of Ti cations with temperature caused changes in phase transitions, and morphological change was also observed previously. For instance, de Vries et al.[15] found that different morphologies of ilmenite disks reduced at different reduction temperatures due to the variation in the diffusion rate of Ti cations.

In addition, because most rutile grains as-formed in the preoxidation remained in the weak reduction process at 873 K (600 °C), particles of reduced samples A and B show significant differences in their phase compositions and microstructure, especially their Ti compounds. For reduced sample A, a large proportion of Ti ions still present in the needlelike rutile network formed during oxidation, while irregular rutile grains are dispersed in the ilmenite matrix for reduced sample B. In other words, the effect of the oxidation temperature on the rutile phase of ilmenite is completely "inherited" in the weak reduction process at 873 K (600 °C).

The current investigations revealed that the weak reduction has a competing reaction mechanism. The competition between the two different reaction routes depends on the reduction temperatures and determines the phase transitions and morphological changes of Ti compounds that occur during the weak reduction, just like the influence of oxidation temperature in the oxidation process. Therefore, temperature is probably one of the most important factors in the strong oxidation–weak reduction process. By adopting different oxidation and reduction temperatures, we can obtain different phase components and microstructure of ilmenite, which probably have different leaching behaviors. For instance, if both the oxidation and reduction are performed at high temperatures, i.e., the oxidation temperature is higher than 1073 K (800 °C) and the reduction temperature is higher than 1023 K (750 °C), then porous particles with ilmenite as the main phase can be obtained. However, at relatively low temperatures, the altered particles are also porous, but a large proportion of Ti ions is present in the rutile network. The former is helpful for increasing the leaching rate,[3,12] yet the latter is helpful for inhabiting the pulverization of leaching products.[2]

IV. CONCLUSIONS

This work systematically investigated morphological changes with the phase transitions during the weak reduction of preoxidized ilmenite. From the result, we can conclude that there are two different weak reduction routes at temperatures ranging from 873 K to 1073 K (600 °C to 800 °C). At relatively high reduction temperatures, e.g., 1023 K and 1073 K (750 °C and
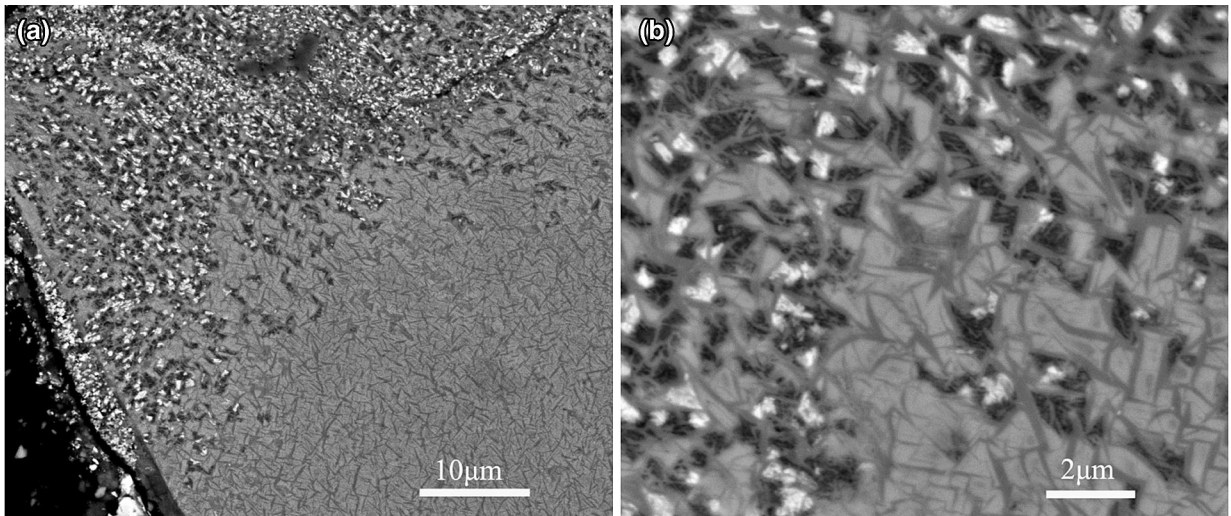
Fig. 11—Back-scattered electron images of sample A reduced at 873 K (600 °C) for 1 h. Image (*a*) displays that there is only one reacted zone and no distinct boundary between reduction rims of the ferric-to-ferrous and the ferrous to metallic iron. Image (*b*), which is a higher-magnification image from image (a), shows the rutile grains largely remain in the reacted zones.
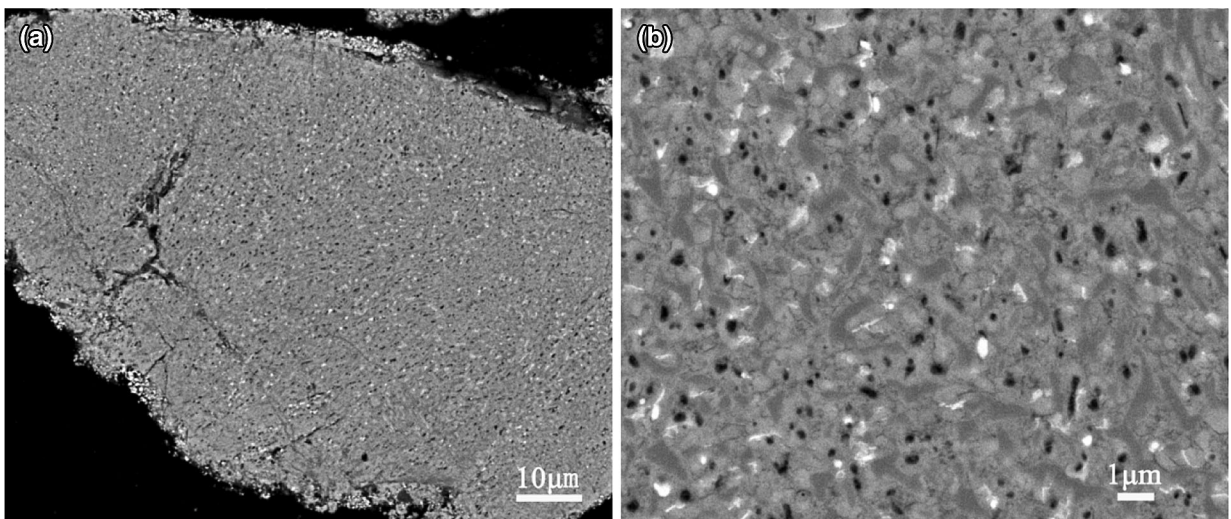

Fig. 12—Backscattered electron images of sample B reduced at 873 K (600 °C) for 1 h. Image (*b*), which is a higher-magnification image from image (*a*), shows that rutile grains with island like are also reserved in the reacted zones.

800 °C), both hematite and pseudobrookite combine with rutile grains to form ilmenite, while at a lower reduction temperature, *i.e.*, 873 K (600 °C), most of the ferric phases are reduced independently and rutile grains remain. As a result, reduced ilmenites show great differences in their phase components and microstructure, especially for the Ti species, after being reduced at different temperatures. At 1023 K and 1073 K (750 °C and 800 °C), both the two preoxidized ilmenites gradually become almost homogeneous ilmenite phase with porous structure. However, at 873 K (600 °C), a large proportion of Ti ions still present in the needlelike rutile network for ilmenites preoxidized at 1023 K (750 °C), while Ti element distributes both in irregular rutile grains and ilmenite matrix for ilmenites preoxidized at 1173 K (900 °C).

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