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Article

Crucial Mechanism to the Eutectoid Transformation of Wüstite Scale on Low Carbon Steel

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Abstract

It is important to realize the transformation behavior of wüstite because it greatly affects the final structure of the oxide layer and the surface quality of the steel products. In the present study, the transformation behaviors of the wüstite layer are examined under nearly-oxygen-free conditions, to simulate the cooling processes after the hot rolled strip is coiled. As the single phase wüstite was prepared at 950˚C, the 460˚C transformed oxide layer was composed of a mixture of iron and magnetite formed through eutectoid reactions. For the 750 ˚C -fabricated wüstite, only magnetite was observed after transformation, without iron precipitates and residual wüstite. It is speculated that the unusual transformation behavior of the low-temperature-made wüstite results from the pseudo-structural intermediate phase transformation between wüstite and magnetite. This pseudo-structure is a pre-transformed wüstite and of various concentration of ferrous ion, which is determined by the fabrication conditions. During the hot strip mill process, the so-called wet scale, wüstite, is produced continuously from finish mill to laminar flow sections and ended at 570˚C. Consequently, the final eutectoid transformation below 570˚C is dominantly controlled by the surface temperature ranged from 750˚C to 950˚C for low carbon steel.

Keywords: wüstite, magnetite, eutectoid transformation, oxide scale, hot strip mill.

1. Introduction

Much attention has been paid to the oxidation behavior of steel in hot rolling because it affects the mechanical adherence of steel products as well as chemical descaling performance [1, 2]. During hot rolling, the strip surface temperatures are usually in the range of 1000~1100˚C at the finishing mill entry, and in the range of 820~940˚C at the exit of the last finishing stand. After rolling, the strip is tightly coiled at the temperature in the range of 500~740˚C [3]. It usually takes tens of hours to cool down the strip to room temperature when no additional driving force is applied. The hot-rolled strip oxidized at high temperatures usually forms relatively thick iron oxides composed of three layers: wüstite, magnetite and hematite. Wüstite is unstable at temperatures below 570˚C and is transformed into magnetite and iron. In previous studies, the reactions of the wüstite transformations have been mainly categorized into three kinds: precipitation and growth of magnetite, formation of the magnetite seam at the scale/steel interface, and the eutectoid reaction [4-9]. The rate and the proportion of these transformations depend on the transformation conditions, such as wüstite formation temperature, cooling rate, and the transformation temperature. In practice, however, the wüstite transformation takes place in a limit space after the strip is tightly coiled. It is quite difficult to supply oxygen to the strip surface packed in the coil. Consequently, the wüstite transformation actually proceeds under the condition of a low equivalent oxygen pressure. However, only a few studies have been conducted to investigate the transformation behavior of wüstite under such a condition, especially for those on the steel surface [10-14]. In the present research, a device is designed to study both the growth and the transformation behaviors of wüstite in the environment with very low oxygen pressure. It is a useful tool for researchers if vacuum equipment is not available.

2. Materials and Methods

An on-line low carbon steel sheet (0.001%C, 0.15%Mn, 0.01%Si, 0.015%P, 0.002%S and

0.003%Al) was used as the substrate for the preparation of the wüstite layer. The low carbon steel sheet was first punched into disks of 10mm in diameter. Low carbon steel disks were mechanically polished (0.05-µm alumina powder) and cleaned in acetone. Grinded Fe_2O_3 powders of 99.5wt% in purity (Himag Magnetic Corporation) were pressed into a disk with the smaller diameter than that of a low carbon steel disk. After sintered at 1160˚C for 6 h, the Fe_2O_3 disk was used as the source of free oxygen. The container applied to the growth of the wüstite layer and the subsequent phase transformation process was illustrated in Figure 1. A Fe_2O_3 disk was positioned below a low carbon steel disk. The container and the cover were jointed with a thin spacer by welding. In this way, the Fe_2O_3 disk opposite to the low carbon steel disk would be the main source of free oxygen at a high temperature. To prepare the wüstite layers, the containers were put into a furnace and isothermally treated at 750˚C~950˚C for 2h. After the isothermal heat treatment, the containers were rapidly cooled down to room temperature. The cooling rate in this stage was about 250˚C/min above 200˚C. These containers were then put into another furnace, annealed at 460˚C for 72h, and rapidly cooled down to room temperature. The cooling rate in this stage was about 60˚C/min. The phase constitution of the oxide layer was determined by X-ray diffraction analysis (Bruker D8 Advance). The morphology of the oxide layer was examined by DB-FIB/SEM (FEI Nova-200 NanoLab). For the further investigation, it was used for the preparation of the TEM sample. The TEM analysis was conducted by using Titan-20 transmission electron microscope.

3. Results and Discussion

3.1 XRD Analysis

Figure 2 shows the XRD patterns of the low carbon steels isothermally treated at 750℃, 850℃ and 950℃ for 2h, respectively. As the device being heated, the original residual oxygen in the container will be gradually consumed by the surrounding materials, including the cover, the seal ring and the container wall. In the meanwhile, free oxygen will be created through the decomposition of the Fe_2O_3

bulk material during the heating process. Finally, a balanced atmosphere with a very low oxygen partial pressure will be established. Pursuant to the thermodynamic data base [15], the temperature and oxygen pressure conditions ranging from 570˚C (10^{-26}atm) to 1300˚C (10^{-10}atm) are appropriate to form a wüstite equilibrium phase, no matter through the oxidation of the iron base metal or the reduction of magnetite. The only oxide on the specimen surface is wüstite, indicating that the condition in the container is only favorable to the formation of wüstite. Besides, the specimens were rapidly cooled down as the isothermal processes was completed, suggesting that no obvious phase transformation occurred during cooling. The disappearance of the iron reflections reveals that a thicker oxide layer formed at 950˚C. Although the prefer orientation of (220) reflection is observed at 950˚C, this phenomena caused by the initial surface conditions such as roughness or rolling texture is unavoidable. According to a previous study [16], wustite is a non-stoichiometric structure which can be easily distinguished by the shoulder reflections. Figure 3 shows the enlargement of the (220) reflections which all reveal the separation phenomena. According to the definition of wüstite by American Mineralogist Crystal Structure Database (AMCSD) Code 0013893 and 0013894 [17], two kinds of structures can coexist in the same phase because the iron ions occupy in different proportions in the tetrahedral and octahedral sites. Consequently, the wüstite should be regarded as $Fe_{1-x}O$ formula because of the electrically neutrality of the crystal structures. Herein, the difference in two theta angles is slightly increased with the fabrication temperatures from 750˚C to 950˚C. It implies that the wüstite at higher temperature can accommodate greater mismatch between two non-stoichiometric structures. Therefore, the eutectoid transformation of wustite is easier to occur in the higher temperature-made $Fe_{1-x}O$ structure.

To investigate the eutectoid decomposition behaviors of wüstite fabricated on low carbon steel, the high temperature treated specimens were located in another furnace, heated at 460˚C for 72h and then cooled down rapidly to keep the original status of the reactions. These conditions are meant to simulate the cooling processes of on-line hot rolled coils cooled down in the warehouse, about 350˚C~550˚C in an average duration of 3 days. The cooling process of a hot rolled coil in the warehouse is actually dynamic. It is known that the eutectoid decomposition reaction rate is higher within 400˚C~500˚C, especially as the temperature is close to 480˚C [9]. Therefore, 460˚C was the better temperature chosen for the second isothermal treatment in this study to facilitate the observation of the eutectoid decomposition reactions. Figure 4 shows the XRD patterns of specimens annealed at 460˚C for 72h. The only oxide obtained in this stage is magnetite. The oxide thickness for all specimens is expected to be nearly unchanged under such low oxygen partial pressures and relatively low reaction temperatures. As a result, the signals from the iron base metal should be almost the same as those obtained before the transformation. It is worth to notice that, for the 950˚C-made wüstite, the iron reflection (110) becomes apparent after the transformation, which is almost absent for the as-received wüstite. These variations of the iron reflections indicate that additional iron is produced during the transformation. Theoretically, wüstite will fully decompose into magnetite and iron during isothermal heat treatment at 400˚C~500˚C if the time is sufficient enough. The precipitation of α-Fe is considered to be the main source of iron in the transformed oxide layer. Nevertheless, for the 750˚C-made and 850˚C-made wüstite, no obvious iron was generated after the transformation. The determined lattice parameter of magnetite is 8.4Å for all the specimens. It is suggested that the decomposed magnetite may be a stoichiometric structure.

3.2 SEM Analysis

Figure 5(a) to 5(c) show the outer surface morphologies of wüstite prepared at different temperatures. For the 750˚C-made wüstite, polyhedral grains with clear crystal planes formed on the outer surface. The average grain size is about 2um. When the reaction temperature increases, dramatic grain growth occurs and the outer surface of wüstite became smoother, as shown in Figure 5(b) and 5(c). Figure 5(d) to 5(f) reveal the outer surface morphologies of the transformed oxide layers. The average grain size of the oxide layer seems to be unchanged after the transformation; however, some variations in outer surface morphologies could be observed. The outer surface of the 750˚C-made wüstite becomes rough after the transformation, and the grain boundaries are difficult to be identified (Figure 5(d)). For the 850˚C-made wüstite, the outer surface is somewhat uneven after the transformation, accompanying with the formation of protrusions along grain boundaries (Figure 5(e)). When wüstite is prepared at 950˚C, the roughening of the outer surface and the formation of protrusions along grain boundaries also take place after the transformation (Figure 5(f)), but of a less extent compared with those described in Figure 5(e).

Figure 6(a), 6(b) and 6(c) show the cross section morphologies of the as-received wustite layers. The wustite layer was composed of columnar grains and the grain size increased with the increasing preparation temperature. Figure 6(d) to 6(e) show the cross section morphologies of the transformed oxide layers. The oxide layer thickness of each specimen is similar to that before the transformation. Precipitation through the whole oxide layer only occurs for wüstite prepared at 950˚C. When wüstite is prepared at a lower temperature (750˚C or 850˚C) , the feature of the oxide layer seems to be unchanged before and after the transformation. Some protrusions at the grain boundaries near the outer surface can be observed (indicated by white arrows), coincident with the characteristics obtained from the top views. The protrusions have been confirmed to be magnetite. It is believed that the protrusions also form on the transformed oxide layer of the 750˚C-made wüstite, which is hard to identified as a result of the small grain size.

3.3 TEM Analysis

To further investigate the transformation mechanisms, TEM analyses are conducted. Figure 7 shows the TEM images of the transformed oxide layers. For the 950˚C-made wüstite (Figure 7(c)), a lamellar structure (dark arrows) mixed with some iron particles (white arrows) can be discerned. In contrast, no obvious iron precipitate is observed after the transformation for the low-temperature-made wüstite. The main phases in Figure 7(a) and 7(b) are identified to be magnetite, containing no remaining wüstite.

3.4 mechanism of Eutectoid transformation of wüstite

In the previous literatures [4-9], the wüstite used to examine the transformation behavior was generally prepared at the temperature in the range of 700˚C~900˚C in air. The transformation process of wüstite finished in about 10h at most even when the oxide thickness was thick [14]. The transformation described by chemical formula has been reported to proceed in two steps [16]:

$$(1\text{-}4y)Fe_{1\text{-}x}O \rightarrow (1\text{-}4x)Fe_{1\text{-}y}O + (x\text{-}y)Fe_3O_4 \ldots\ldots(1)$$

$$x > y$$

$$4Fe_{1\text{-}y}O \text{ (iron rich)} \rightarrow Fe_3O_4 + (1\text{-}4y)\alpha\text{-}Fe\ldots\ldots(2)$$

The final structure of the oxide layer typically consists of a granular mixture of iron and magnetite, a lamellar mixture of iron and magnetite, or a mixture of both the two types mentioned above. In the present study, the 950˚C-made wüstite transformed to a lamellar structure mixed with some granular participates, connoting that both the reaction (1) and (2) occurred during the transformation. However, no participates could be observed by SEM after the transformation for the low-temperature-made wüstite. The only source of oxygen in this study came from the decomposition of hematite. It could be expected that the decomposition rate of hematite was quite low due to its low specific surface area (for a bulk material), especially at a low reaction temperature (750˚C and 850˚C). Under such a condition, the establishment of a very low equivalent oxygen pressure in the container was reasonable. The low oxygen concentration made the unfavorable environment for the wusitie to be oxidized to magnetite or hemitite. Consequently, a possible phase transformation mechanism is deduced here for the low-temperature-made wüstite.

Figure 8(a) to (c) plot the unit cells of wüstite and magnetite based on the crystal information from AMCSD. Essentially, the change from wüstite to magnetite is caused by the oxidation of the Fe^{2+}

ions. Based on Fjellvag's definition [17], the difference in stoichiometric and non-stoichiometric wüstite is the partial Fe^{3+} at tetrahedral sites as shown in Figure 8(a). It implies that stoichiometric wüsitie is not a stable structure and can coexist with another non-stoichiometric phase. In order to investigate the structure change during the eutectoid transformation of wüsitie, a metastable phase between typical wüsitie and magnetite can be simply derived. A pseudo-structure based on 2×2×2 wüstite drawn in Figure 8(b) is suggested to be estimated because of the similar lattice symmetry to space group *Fm3m* or *Fd3m*. For simplification, this pseudo structure can be also dismantled by octahedral-based and tetrahedral-based polyhedral as the insets shown in the insets of Figure 7(b). Apparently, the wüstite cannot support all the octahedral and tetrahedral sites for iron ions in the unit cell owing to the coordination conditions of O^{2-}. It is suggested that the absence of tetrahedral sited Fe^{3+} in the wüstite lattice will lead to further structure change. As the Gibb's free energy of wüstite decreases more rapidly than iron and magnetite at the temperatures below 570˚C, a thermo- dynamical condition of eutectoid transformation will be established [17,18]. According to the magnetite structure shown in Figure 8(c) [18], all the sits in the unit cell is similar to the as-estimated pseudo structure which is based on Figure 7(a). Hence the structural change between wüstite and magnetite can be figured out to be a balance behavior of polyhedral because the O^{2-} sites remain unchanged. For the electrical neutrality, oxidation of Fe^{2+} to Fe^{3+}, reduction of Fe^{2+} to Fe and diffusion of Fe^{2+} should be carried out to complete the structural transformation [20-22]. Herein, the formation of magnetite and precipitation of iron leads to the so-called eutectoid transformation. Based on this mechanism, original structural conditions such as cation vacancy or substitutional solute of wüstite are suggested to dominate the transformation. In this work, the variation of lattice parameter caused by fabrication temperature makes further various phenomena of eutectoid transformation reliable. In addition, final phase composition of oxide scale on the hot roll coil is controlled mainly by the hot strip mill process rather than afterward air cooling when coiling temperature is below 570˚C which is the limited temperature of wüstite formation.

4. Conclusion

Based on the investigation of the phase transformation from wüstite to magnetite in this work, the eutectoid transformation mechanism can be derived from structural change and precipitation of Fe. Since the coordination of Fe^{2+} and O^{2-} is not strong enough to support rock salt unit cell, the structural change can be regarded as the movement tendency of Fe^{2+} from octahedral site to tetrahedral site to balance the lattice energy. Consequently, the Fe^{2+} should be further oxidized to Fe^{3+} and reduced to Fe spontaneously. Therefore, matrix wüstite, magnetite and iron can approach eutectoid equilibrium. During the hot strip mill process, wüstite is always fabricated on the steel surface under cooling water spray. In addition, following heat recovery, phase transformation and grain orientation from the matrix steel will also affect stability of the wüstite scale. As the result, the eutectoid reaction naturally takes place after the strip is coiled because it will be kept at the temperature below 570˚C for 1 or 2 days. According to the investigation in this work, it can be emphasized that the structural stability of the wüstite scale will dominate the final eutectoid reaction.

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Author Contributions:

Szu-Ning Lin conceived and designed the experiments; Min-Tao Wu and Wei-Lin Wang performed the experiments; Chao-Chi Huang analyzed the data; Szu-Ning Lin wrote the paper. Ker-Chang Hsieh is the Advisor.

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

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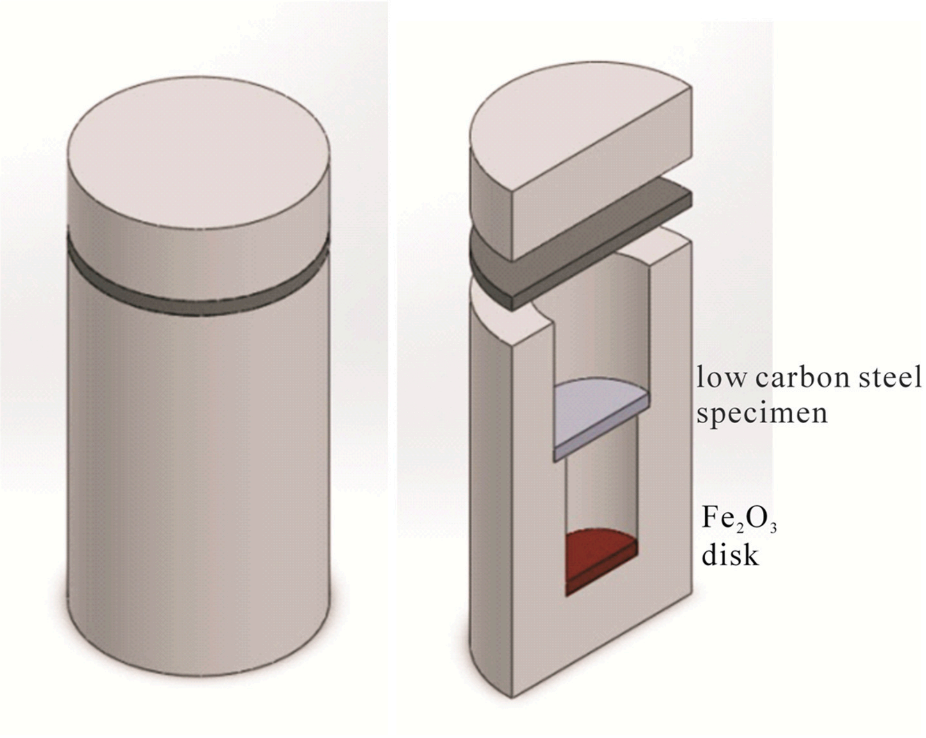


Figure 1. Schematic diagram of the container for nearly-oxygen-free oxidation process

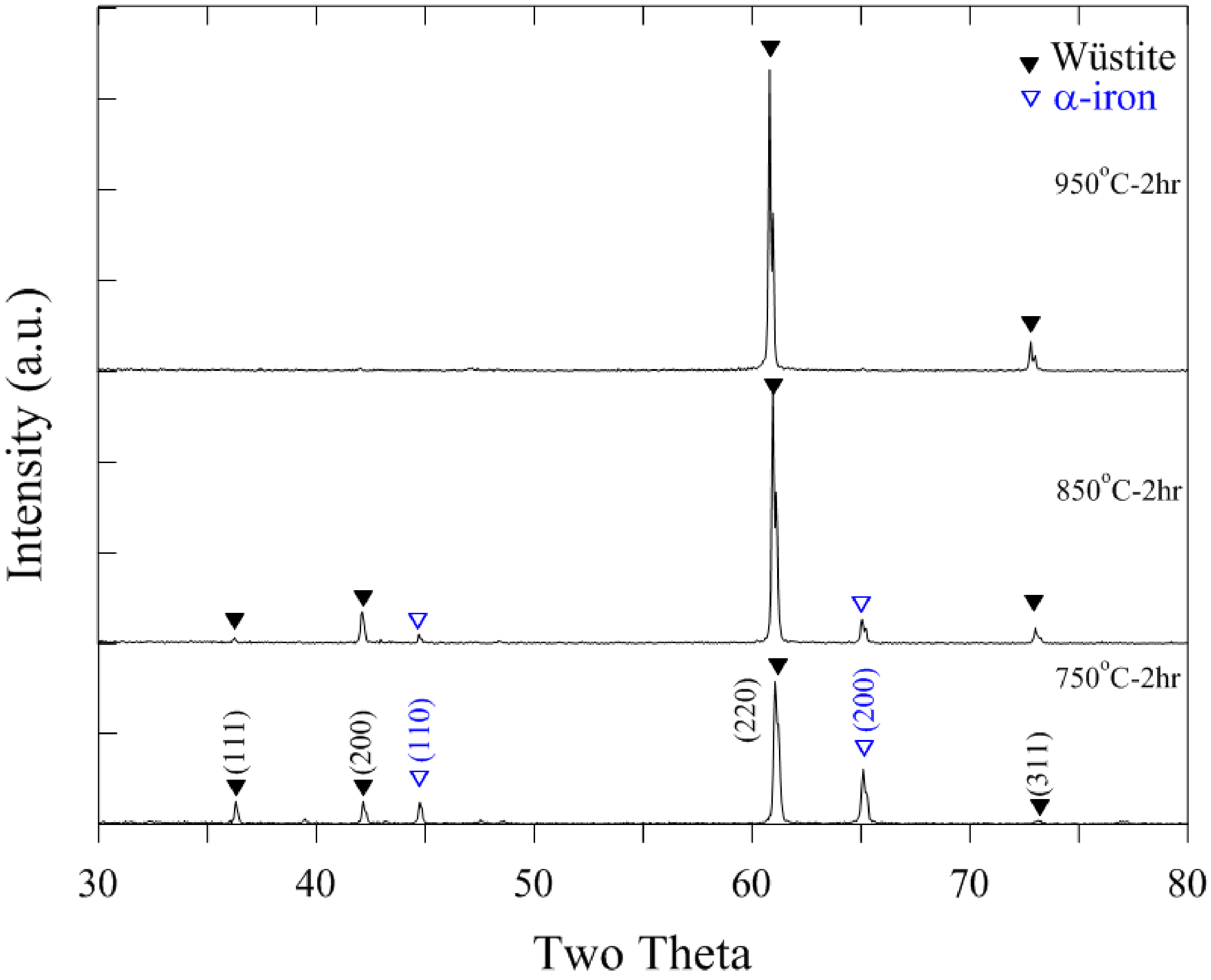


Figure 2. XRD pattern of oxidized low carbon steel at (a)750˚C, (b)850˚C and 950˚C.

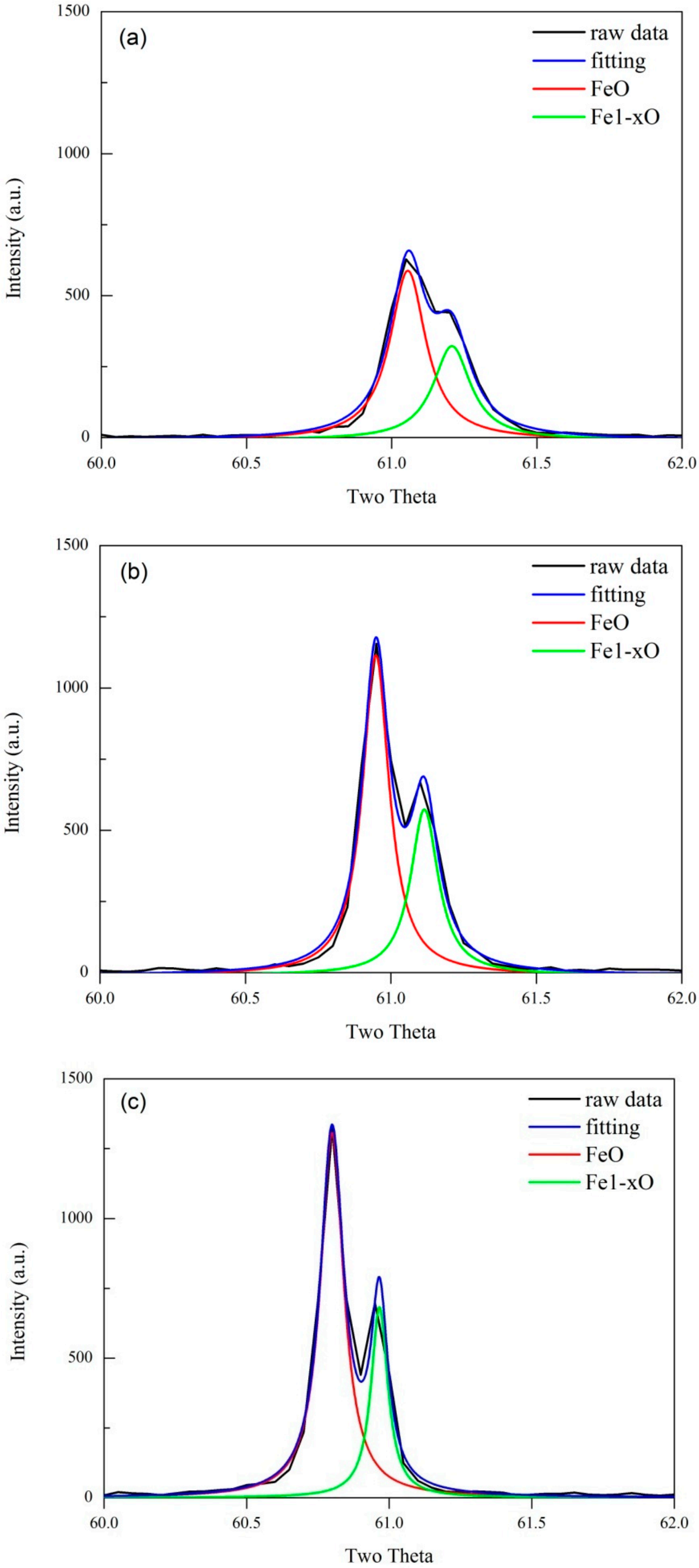


Figure 3. (220) reflections of wüstite prepared at (a)750˚C, (b)850˚C and 950˚C.

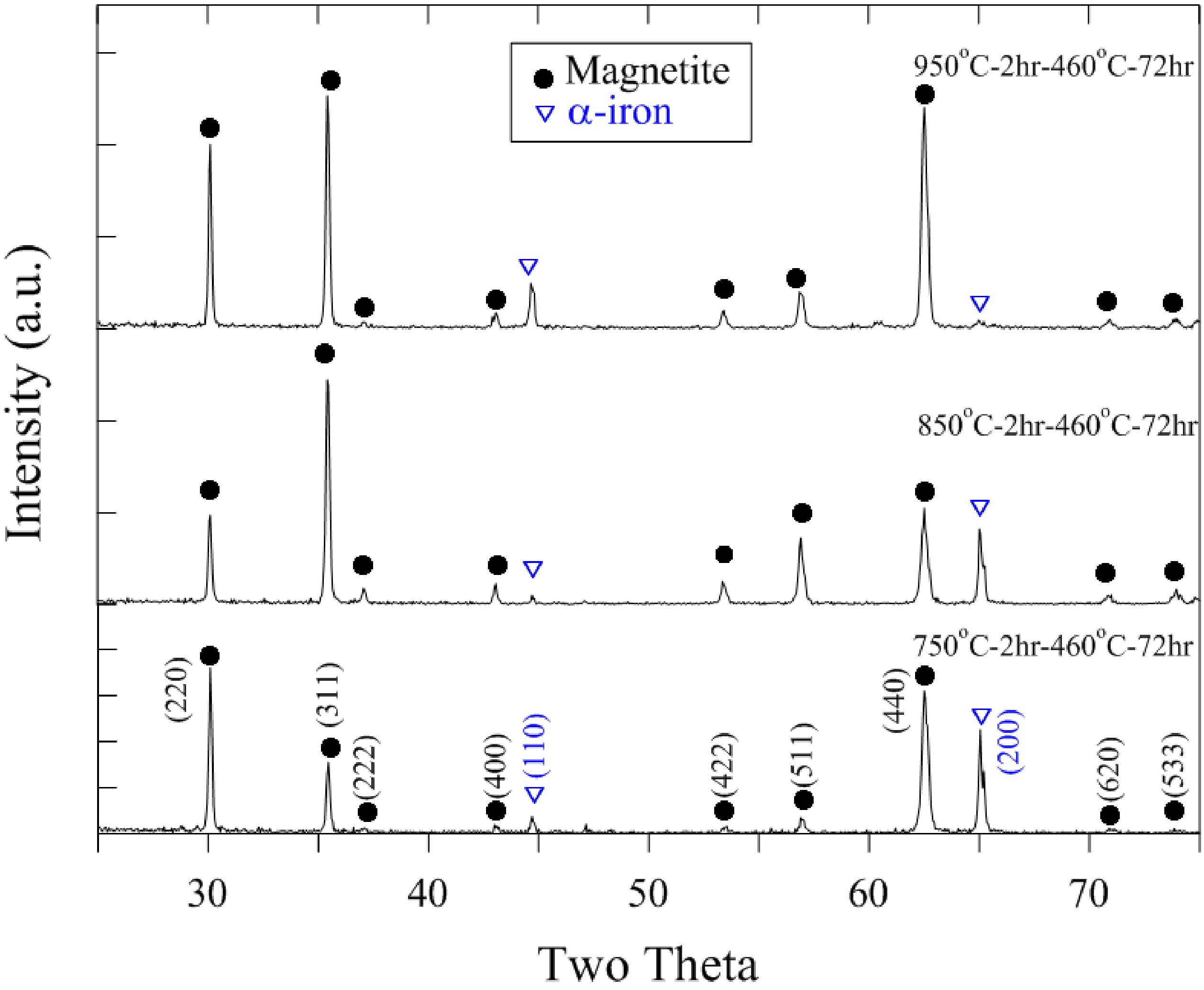


Figure 4. XRD patterns of specimens isothermal treated at 460˚C for 72h

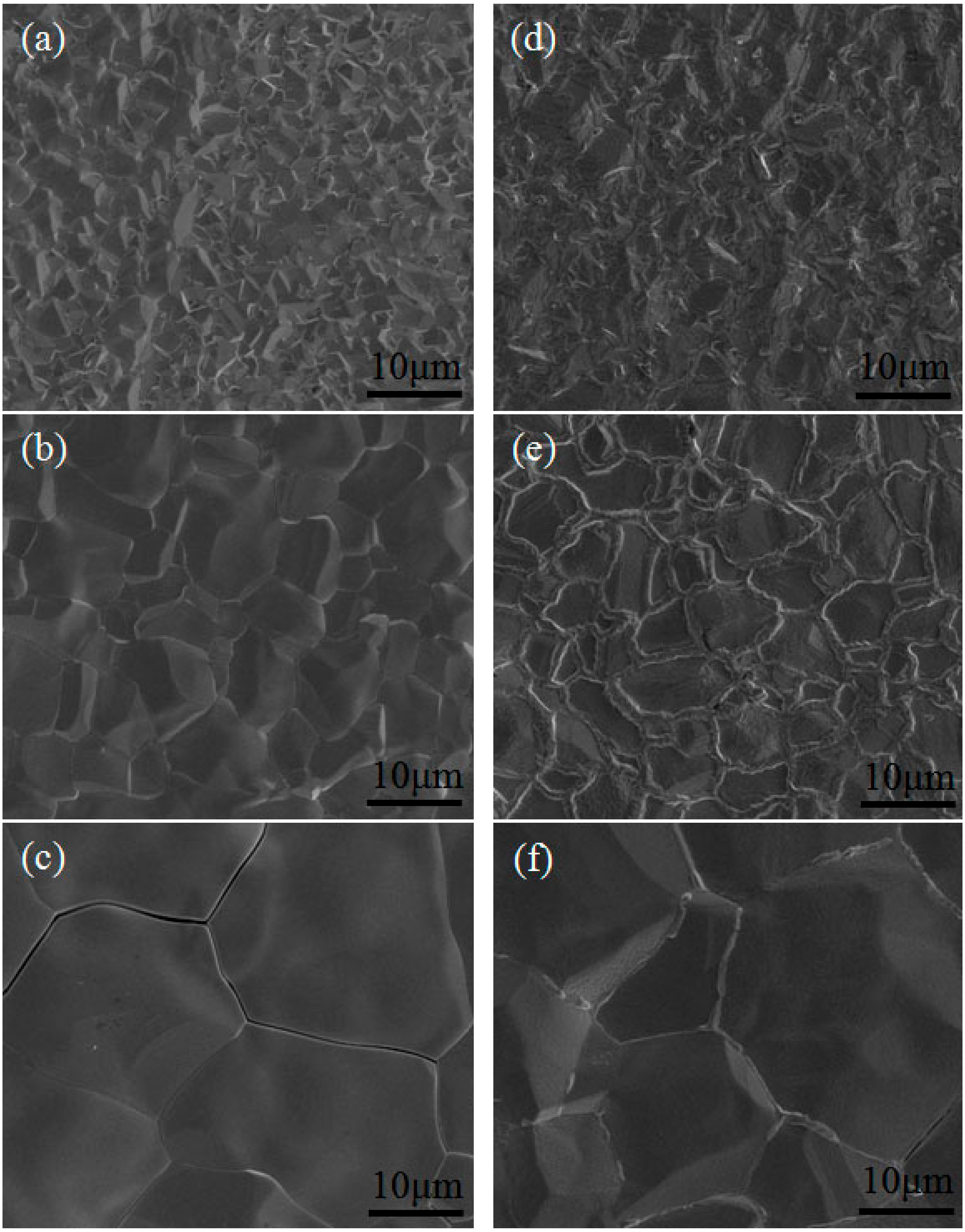


Figure 5. Outer surface morphologies of oxide layers: (a), (b) and (c) for the as-received wustite obtained at 750˚C, 850˚C and 950˚C, respectively; (d), (e) and (f) for the transformed oxide layers correspondent to (a), (b) and (c).

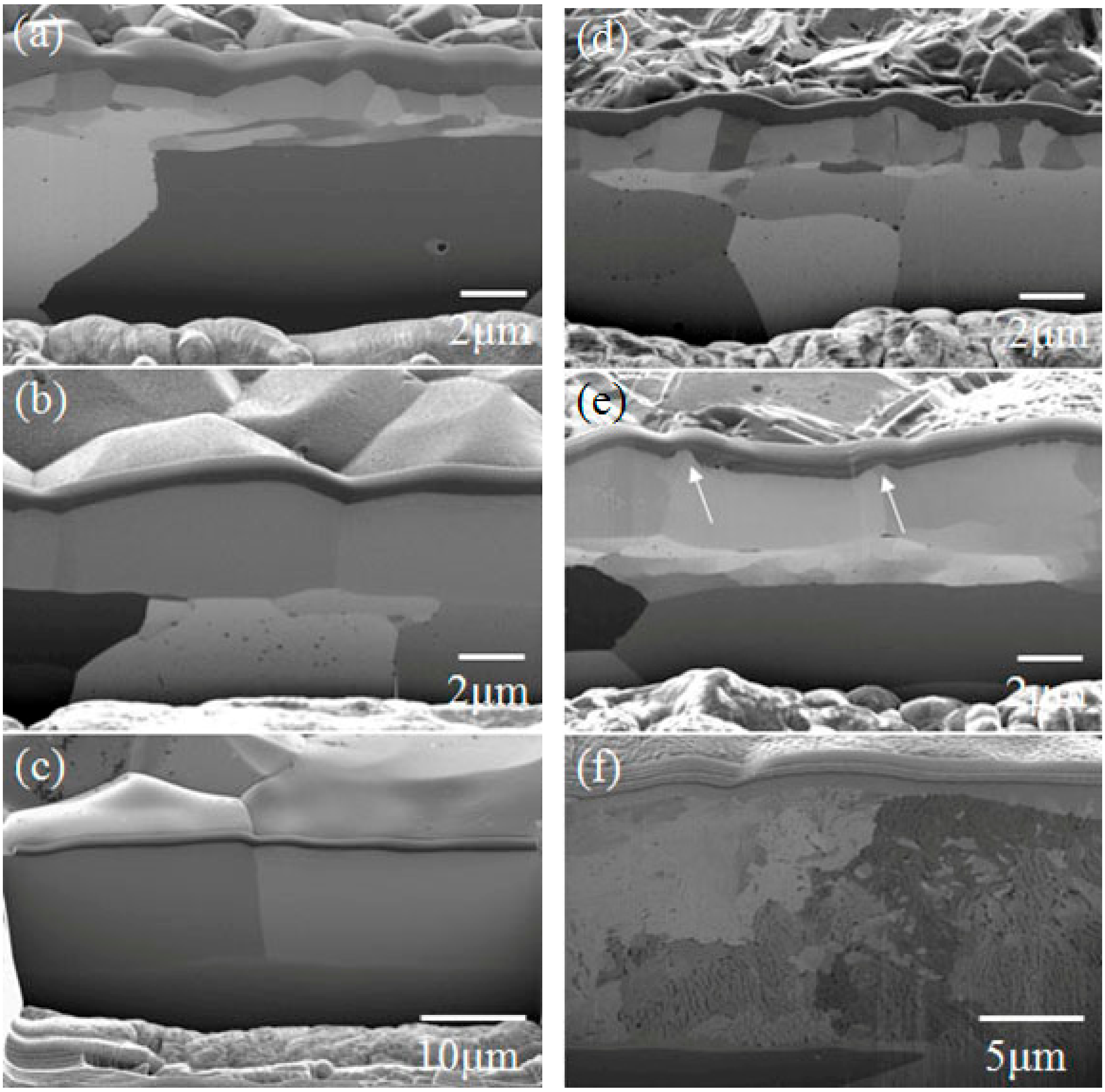
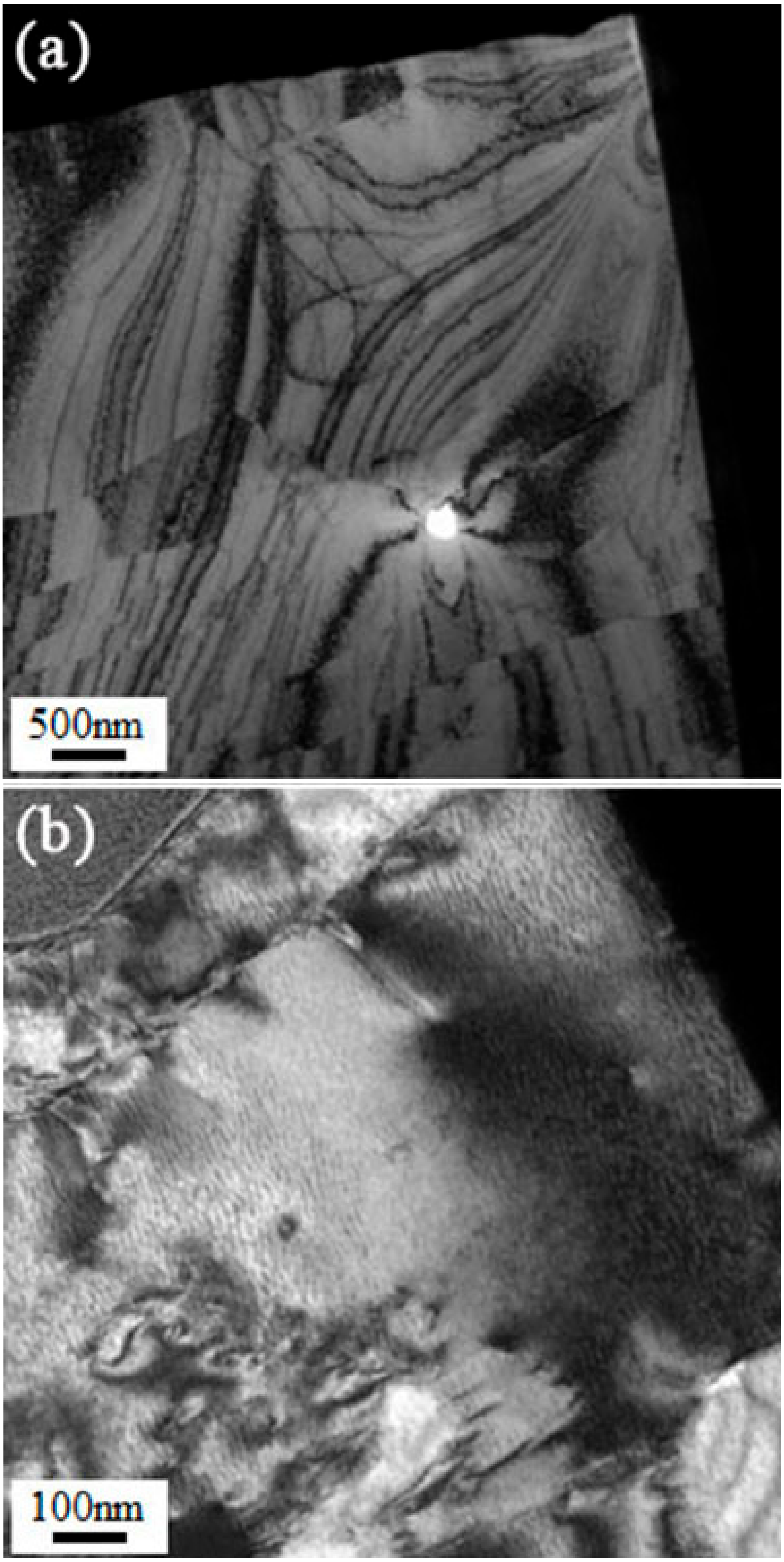


Figure 6. Cross section morphologies of oxide layers: (a), (b) and (c) for the as-received wustite obtained at 750˚C, 850˚C and 950˚C, respectively; (d), (e) and (f) for the transformed oxide layers correspondent to (a), (b) and (c).


(a)
500nm
(b)
100nm

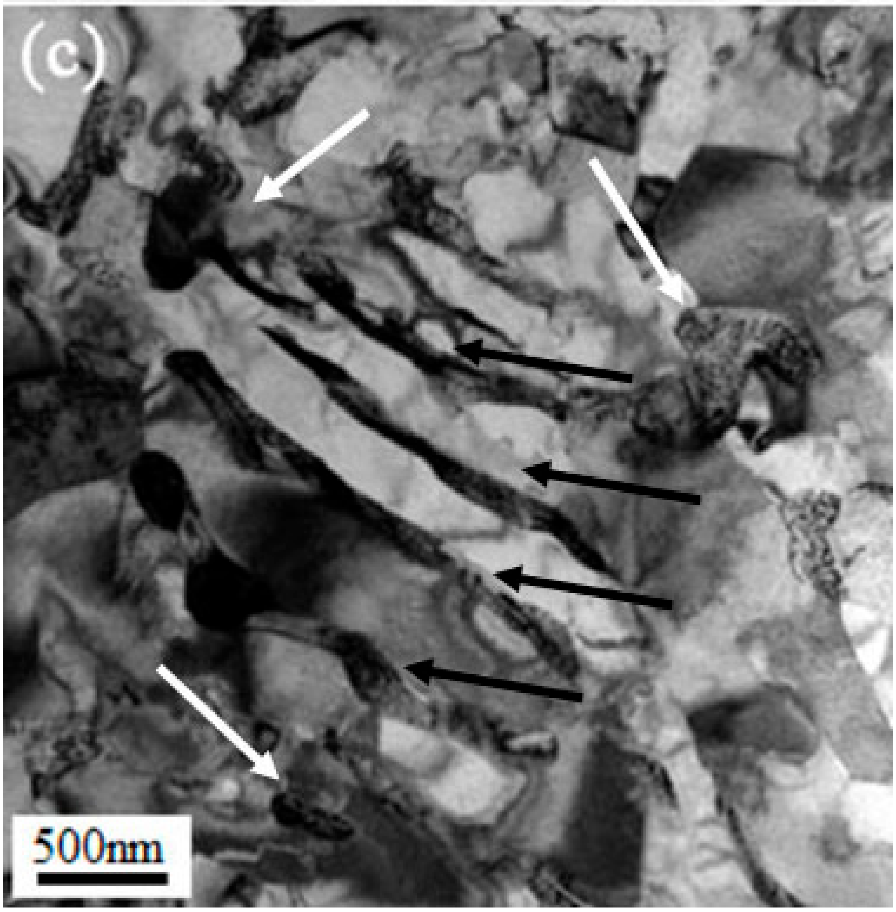
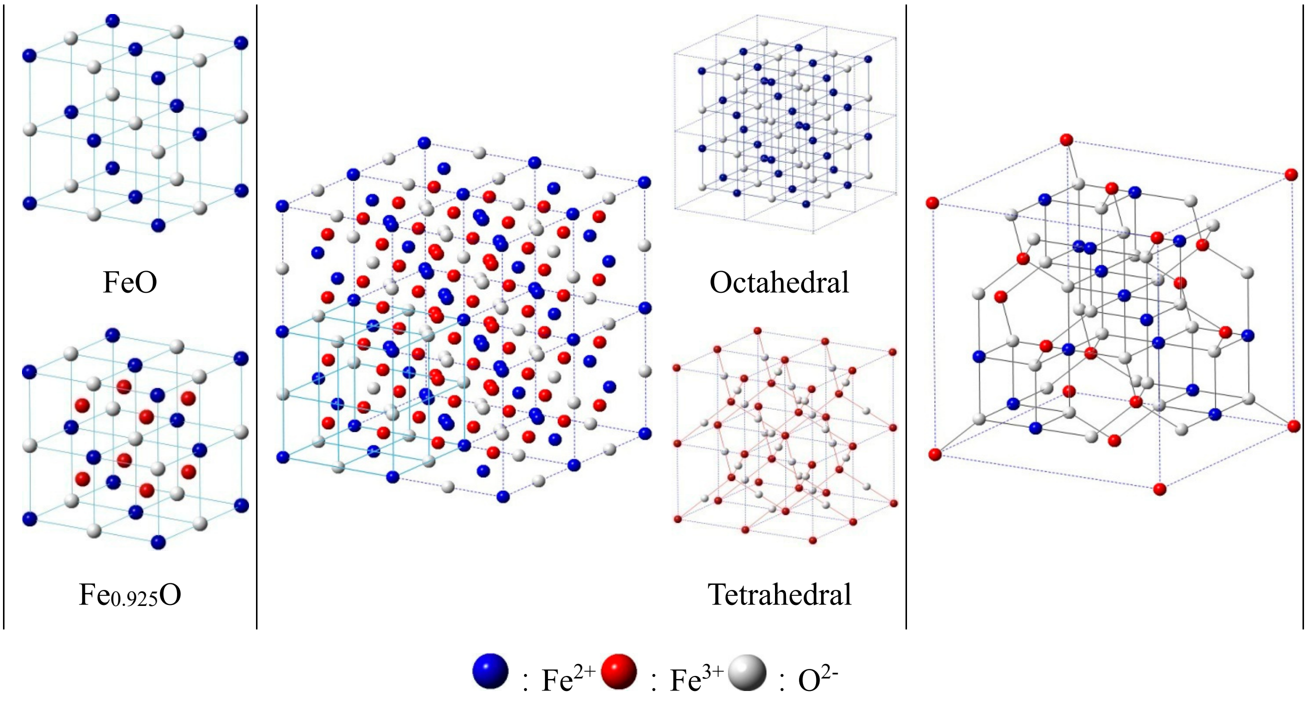


Figure 7. TEM images of oxide layers after transformation at 460˚C for 72h. The as-received wustite was prepared at (a)750˚C, (b)850˚C and (c)950˚C, respectively.



(a) Wüstite[17] (b) Pseudo Wüstite (c) Magnetite[18]

Figure 8. Schematic diagrams of structure change from wüstite to magnetite.