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Phase transformation and the mechanism of combustion synthesis of ZnFe_2O_4 ferrite powders

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Abstract

The reaction mechanism of combustion synthesis of zinc ferrite, which belongs to the complex oxide combustion reaction was investigated using a combustion front quenching method (CFQM). Phase transformation and microstructural evolution of the quenched samples were observed by XRD, SEM, and Mössbauer spectroscopy. The results showed that the combustion proceeded by a dissolution-precipitation mechanism, viz the iron was burned to form Fe_2O_3 in an oxygen atmosphere and melting of the Fe_2O_3 led to the dissolving of the ZnO particles, then ZnFe_2O_4 precipitated out. In addition, a model of the mechanism was drawn.

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1. Introduction

Zinc ferrites have been a subject of great interest for a long time because of their importance in many technological applications. Traditionally, zinc ferrite is fabricated by solid-state reaction of ZnO and Fe_2O_3 powders. In recent years, combustion synthesis of ferrites has attracted the interest of many researchers as an energy and time-saving process [1–3]. The combustion synthesis of ferrite powders is a chemically complicated process in which many intermediate products can be formed. Synthesis of ZnFe_2O_4 ferrite proceeds according to the following equation:

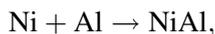


where k is the coefficient which controls the exothermicity of the mixture. The larger the k value, the higher the molar ratio $\text{Fe}/\text{Fe}_2\text{O}_3$ in the reactants should be.

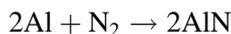
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The method usually used to reveal the mechanism of combustion synthesis is a combustion front quenching method (CFQM), which has been used in many simple combustion reaction systems including:



and



as reported in [4–6]. While combustion synthesis of ferrite is a more complex process compared to the reactions mentioned above due to more reactants and a gas reactant, oxygen, that participate in the reaction. However, to our knowledge, no systematic studies about the phase transformation and the combustion reaction mechanism of ferrite systems are reported in the literature. The purpose of our work is to elucidate the reaction mechanism of combustion synthesis of zinc ferrite, an example of a complex oxide combustion reaction, by using XRD, SEM, and Mössbauer spectroscopy.

2. Experimental procedure

The materials used in the experiments were iron (with the average particle size of 25 μm), iron oxide (with the average particle size of 0.8 μm), and zinc oxide (with the average particle size of 0.5 μm). The purity of the raw materials is more than 99%. The starting materials were weighed according to the required stoichiometric proportion, mixed in ethanol followed by ball milling for 8 h and then dried in air. The mixture was used for the following tests: (1) The combustion temperature was measured with Pt/Rh thermocouples pressed into the mixture. The procedure is identical with that given in a previous work [2]. (2) Phase transformation of the combustion-synthesized products were examined by an X-ray diffraction (XRD). (3) A CFQM was used to determine the initial, intermediate and end combustion reaction products. By this CFQM, oxygen gas was very rapidly released from the chamber while the combustion wave was proceeding along the sample. Because released oxygen gas carried a large amount of heat away, a combustion front that was self-propagating in a compact of reactant powders was quenched. Thus, the phase transformation and mechanism of the combustion reaction could be revealed by a microstructural observation of the quenched samples. (4) Morphology of the quenched samples was characterized by scanning electron microscopy (SEM). (5) The elemental compositions in several selected areas were analyzed using X-ray energy dispersive spectroscopy (EDS).

3. Results

3.1. Combustion temperature

The relationship between combustion temperature and reaction time is shown in Fig. 1. It should be noted that the temperature rises from the initial low temperature plateau, up to 1830 K (a little above the melting point of Fe) and then at a much lower rate up to the maximum temperature of 1880 K (a little above the melting point of Fe_2O_3).

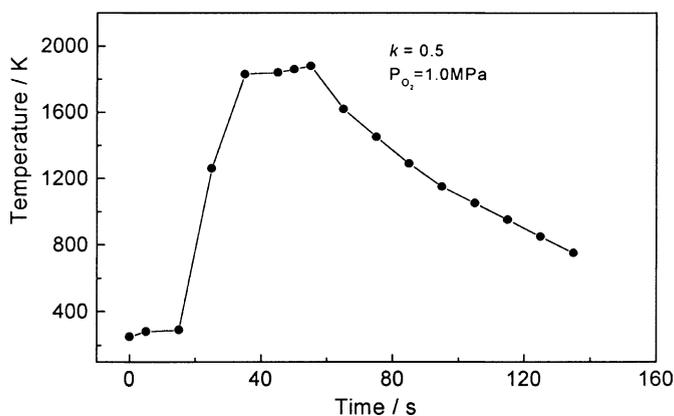


Fig. 1. The dependence of the combustion temperature on reaction time.

3.2. Phase transformation

Fig. 2 shows the XRD patterns of the samples obtained at different distances from the combustion front. The diffraction lines are mainly attributable to the ZnFe_2O_4 -based spinel-type ferrite, ZnO and $\alpha\text{-Fe}_2\text{O}_3$. In addition, two diffraction lines, are found at $2\theta = 42.2^\circ$ and 61.1° , respectively that are attributable to Fe_{1-x}O ($x < 1$) and these two diffraction lines disappear gradually. It can be concluded that a non-stoichiometric composition, Fe_{1-x}O , is formed during the oxidation of iron when the k value is 0.5 and the oxygen pressure is 1.0 MPa. The relative intensity of the diffraction lines assigned to Fe, ZnO, and Fe_2O_3 tends to decrease sharply with the increase of the distance from the combustion front, while the line intensity of ZnFe_2O_4 increases.

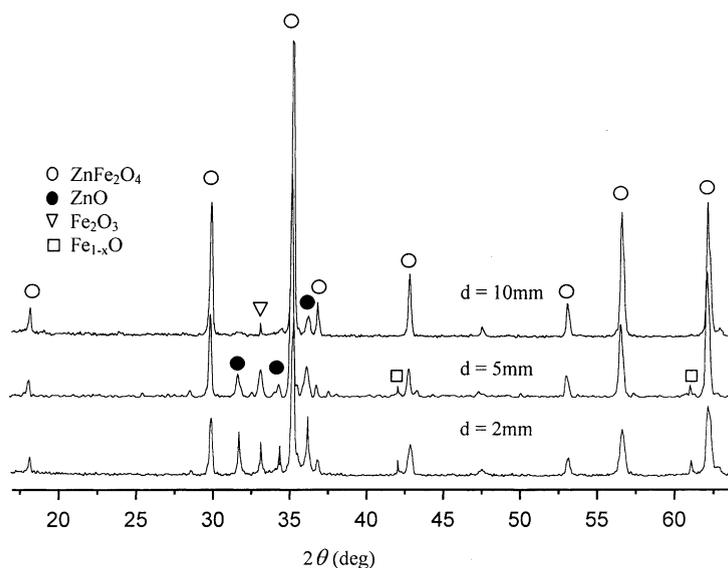


Fig. 2. XRD patterns of the quenched samples obtained at the different distances from the combustion front.

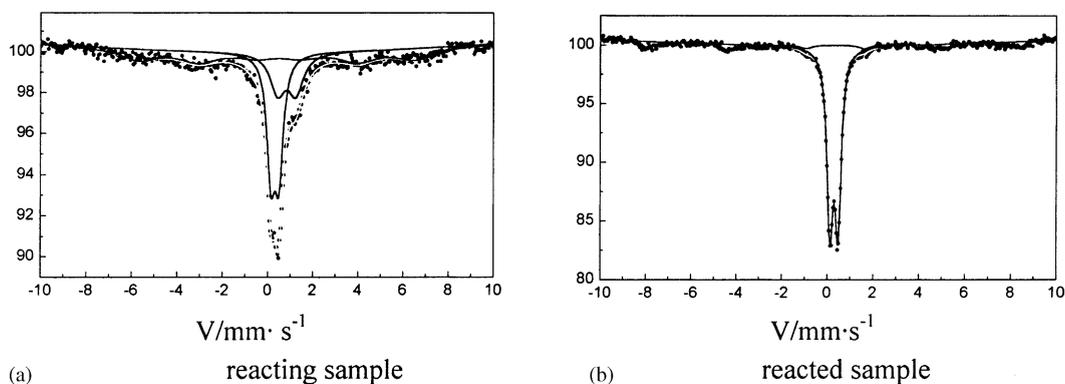


Fig. 3. Mössbauer spectra of the quenched samples.

Mössbauer spectra of the quenched samples corresponding to a reacting and a reacted sample, respectively, measured at room temperature, are shown in Fig. 3. In Fig. 3a, the spectrum displays three components: a sextet and two doublets. One of the doublets is related to ZnFe_2O_4 , the other is Fe_{1-x}O . The sextet is similar to that of $\gamma\text{-Fe}_2\text{O}_3$, as reported in reference [7], and indicates that $\gamma\text{-Fe}_2\text{O}_3$ is formed as an intermediate phase during the oxidation of iron. In Fig. 3b, the doublet is related to ZnFe_2O_4 and the sextet is related to $\alpha\text{-Fe}_2\text{O}_3$ [8].

3.3. Microstructural evolution

The quenched samples could be divided into three zones: an unreacted zone, a reacting zone, and a reacted zone. Fig. 4a shows a SEM photograph of the reactants in the unreacted zone. The EDS results indicate that the large particles are Fe, and the smaller ones are Fe_2O_3 and ZnO, which are too fine to be distinguished. Fig. 4b shows the reactants in the reacting zone. The large spherical products are the molten Fe and Fe_2O_3 that coagulate on cooling. In Fig. 4c, the bright larger ones “A” are Fe unreacted, and the small particles “B” are ZnO particles which suspend in the molten liquid. Fig. 4d shows that during the oxidation of iron, an acicular crystal, $\gamma\text{-Fe}_2\text{O}_3$, also appears. In Fig. 4e, the white lineations are ZnFe_2O_4 ferrite powders that have precipitated out of the liquid as it cooled. Fig. 4f shows the microstructure of the region “D” of the ZnFe_2O_4 in Fig. 4e. According to the results of XRD, Mössbauer spectra and SEM of the quenched samples, a mechanism for the combustion synthesis of ZnFe_2O_4 ferrite powders can be proposed as follows. In the reacting zone, the iron powder is ignited and is oxidized in a highly exothermic reaction which leads to a sharp increase in the temperature–time profile (Fig. 1). Then, a part of the iron, iron oxide both in the reactants and that formed from the burning iron begin to melt as the combustion temperature increases, while the higher melting point of particles of zinc oxide, are suspended in the molten liquid. Intermediate phases, Fe_{1-x}O and Fe_2O_3 appear due to the non-equilibrium phase-transformation under the high heating rate. Finally, the zinc oxide particles start to dissolve in the molten Fe_2O_3 and zinc ferrite grains gradually precipitate out. As the zinc ferrite is being formed, heat will continue to be given out by the oxidation of unreacted iron powders. At this stage, heat of oxidation causes the temperature of the reaction to keep increasing, although at a reduced rate, up to the maximum value (Fig. 1). As the oxidation of iron powder continues, the quantity of unreacted iron decreases and ultimately disappears which means that the quantity of heat released decreases gradually.

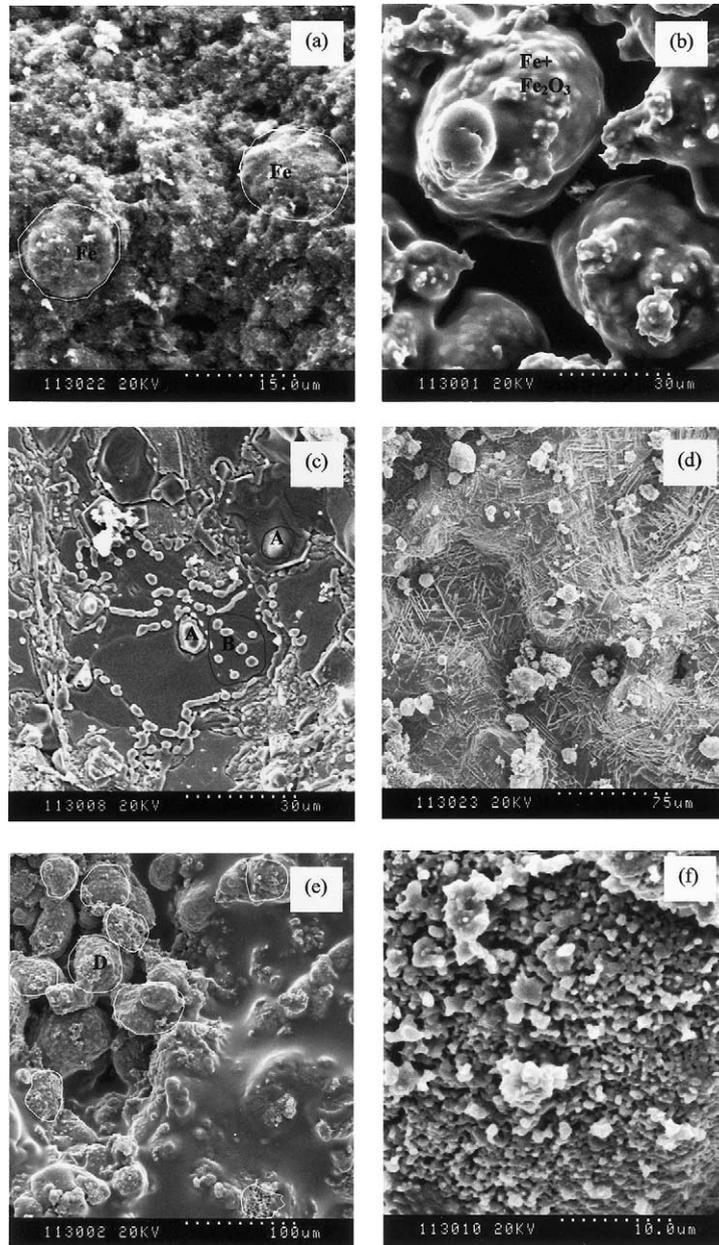


Fig. 4. SEM photographs of the quenched samples: (a) the reactants in the unreacted zone; (b) the reactants in the reacting zone; (c) Fe particle unreacted and ZnO particle; (d) an acicular crystal, γ -Fe₂O₃; (e) ZnFe₂O₄ ferrite powders precipitated out of the molten liquid as it cooled; (f) the microstructure of the region “D” of the ZnFe₂O₄ in (e).

Accordingly, a sudden decrease in slope of the temperature–time profile appears which indicates that the sum of heat released by the oxidation of iron is less than that of radiating to the environment.

Oxygen gas also plays an important role in the combustion process. Since Fe and Fe₂O₃ both melt during the combustion reaction, hindering the permeation of oxygen into the solid samples, the oxygen



Fig. 5. Morphology of the combustion products ($k = 0.5$, $P_{O_2} = 1.0$ MPa).

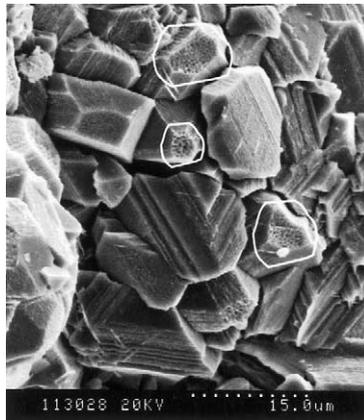


Fig. 6. SEM photograph of the reacted sample.

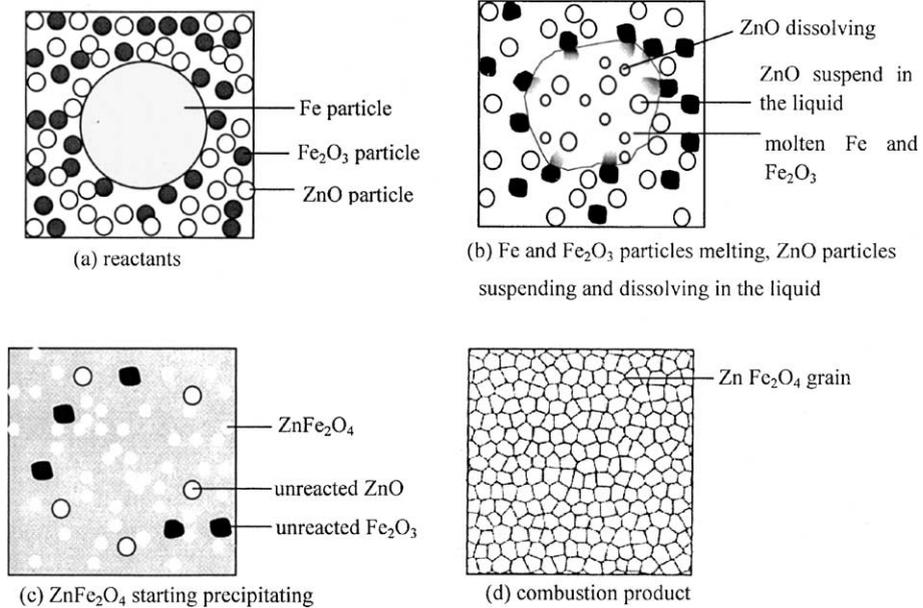


Fig. 7. A model of combustion synthesis of zinc ferrite.

pressure inside the sample should be lower than outside. Only when the oxygen pressure reaches to a certain value, can the iron burn which results in a product with a layered morphology as shown in Fig. 5. It can be seen from the layered nature of the products that the reactants are burned layer by layer. The microstructure of the reacted product is shown in Fig. 6 and clearly shows many small voids visible on the surface of the grains. These voids most likely resulted from the excess oxygen, which is dissolved in the liquid system that was released as the products cooled. Similar results were obtained by Steinberg et al. [9] in research on the combustion of iron rods.

From the microstructural and phase transformation during the combustion synthesis of zinc ferrite as mentioned above, a model corresponding to the mechanism is proposed as a schematic, Fig. 7.

4. Conclusions

A dissolution-precipitation mechanism of the combustion synthesis of zinc ferrite is proposed according to the results of XRD, SEM, and Mössbauer spectra of the quenched samples. The results suggest the following sequence for the formation of ZnFe_2O_4 through combustion synthesis: the iron is first burned in the oxygen, then part of the iron and iron oxide in both reactants, and that formed from the burning iron, begin to melt. Zinc oxide particles dissolve in the molten Fe_2O_3 and zinc ferrite grains precipitate out. During the combustion synthesis of zinc ferrite, intermediate phases of iron oxide, Fe_{1-x}O and $\gamma\text{-Fe}_2\text{O}_3$, also appear due to the non-equilibrium phase-transformations as a result of the high heating-rate.

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