Effect of Heat Treatment on Preparation of Ferrite Magnetite Hollow Beads by Self-Propagating Method

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Abstract: The characterization results of hollow ceramic beads show that oxidant KClO₃ had a great influence on the preparation of hollow ceramic beads. The morphology picture and XRD analysis showed that the surface of hollow beads without KClO₃ was smooth, and the particle size analysis results show that the particle size was 10 ~ 50μm. Without KClO₃, the average particle size is 28.08 μm; After adding KClO₃, dense dendritic crystal structure was distributed on the surface of hollow beads, and the phase is mainly BaFe₂O₄, and the distribution range of hollow beads is 5 ~ 40 μm, and the average particle size is 16.02 μm. It could be inferred from the analysis that the quenching reaction is fully carried out after the addition of KClO₃, resulting in a large amount of gas, reducing the volume of ceramic droplets and reducing the particle size of hollow beads.

1. Introduction

Magnetoplumbite ferrite had c-axis anisotropy, and its crystal symmetry makes its own properties better than spinel ferrite with cubic symmetry. In terms of electromagnetic properties, magnetoplumbite ferrite had higher saturation magnetization and higher curie temperature. Compared with spinel ferrite, magnetoplumbite ferrite has both hard magnetic and high-frequency soft magnetic properties. Compared with other ferrite materials, magnetoplumbite ferrite had smaller anisotropic field and lower natural resonance frequency, which was closer to the electromagnetic wave band to be absorbed. It was more suitable for application in microwave absorbing materials. The most common magnetoplumbite ferrite in application was BaFe₁₂O₁₉. The preparation of hollow ceramic beads with magnetoplumbite ferrite BaFe₁₂O₁₉ phase structure was realized through high temperature self-propagating combustion synthesis, and the electromagnetic properties of hollow ceramic beads with magnetoplumbite ferrite BaFe₁₂O₁₉ was deeply studied in this paper.

2. Test materials and methods

2.1 Test materials

With a molecular weight of 197.35, insoluble in water and a density of 4.43g/cm³, the melting point of Barium carbonate was 1740 °C, and it decomposes at 1450 °C.

Potassium chlorate potassium chlorate was shiny or white particles or powder. The melting point was 356 °C and the boiling point is 368 °C. It was decomposed into potassium perchlorate above the melting point, and oxygen is generated by the decomposition of potassium perchlorate at 400 °C. It
was slightly soluble in ethanol, soluble in water and alkali solution, and will burn when ground with oxides, sulfur phosphorus, nitrite, hypophosphite and other easily oxidized substances. The reason why potassium chlorate is selected instead of potassium perchlorate was to ensure the stability and safety of combustion synthesis reaction.

Potassium perchlorate white powder or colorless orthorhombic crystal, density 2.52g/cm³, Melting point 610℃. Slightly soluble in water, it would decompose into potassium chloride and oxygen at the melting point. Decomposition also occurs when mixed with organics or combustibles. Table 4-1 shows the basic information of raw materials used in the test, such as purity, particle size and chemical composition. The basic parameters were shown in Table 1.

| Material | Purity          | Particle size/μm | Chemical composition/wt.%       |
|----------|-----------------|------------------|----------------------------------|
| Fe       | Analytical purity | ≤45              | Fe≥98 Cu<0.005                   |
| Fe₂O₃    | Analytical purity | ≤5               | Fe₂O₃≥98.5 Cu<0.01               |
| BaCO₃    | Analytical purity | ≤5               | BaCO₃≥98.5                       |
| KClO₃    | Analytical purity | ≤50              | KClO₃≥98                        |
| Sucrose  | Analytical purity | ≤5              | C₁₂H₂₂O₁₁≥99.9 H₂O<0.1          |
| Epoxy resin | E-44 Type       | -                |                                  |

2.2 Experimental method
According to the reaction molar ratio of raw materials required in the system, the reaction raw materials were accurately weighed with an electronic scale, and the good reaction raw materials were divided into two parts. One part was added with an appropriate amount of KClO₃, and the other part was not added with KClO₃. The two parts of raw materials were respectively put into the ball milling tank, added anhydrous ethyl alcohol as the medium, ball milled for 6 hours, and then carbonized, crushed. After screening and other processes, it was made into agglomerated powder for use. When fusing the agglomerated powder, use a double oxygen cylinder, one of which was powder feeding gas with a pressure of 0.5MPa; The other cylinder of oxygen and acetylene form an oxyacetylene flame, the pressure is set to 0.6MPa and 0.11MPa respectively, and the flame maintains the oxidation flame. The quenching distance is set to 450mm. Whether to further increase the heat treatment process was determined according to whether the phase composition of the quenched product reaches the preparation purpose.

2.3 analysis and characterization methods
(1) Morphology characterization methods the morphology of hollow microspheres was observed by quanta feg-250 scanning electron microscope.
(2) The particle size characterization method was Beckman Coulter LS 13 320 (the particle size test range is 0.04 ~ 2000) μm) The particle size of hollow beads was analyzed.
(3) Phase characterization method the phase of hollow microspheres was analyzed by Bruker D2 phase X-ray diffractometer, Cu, Kα 1 ray wavelength λ= 0.15456 nm, scanning step 0.05°, scanning angle 10-80°.

3. Results and analysis
3.1 The SEM characterization of Morphology
Fig. 1 showed the SEM images of quenched products of Fe+ Fe₂O₃ + BaCO₃ system, where A₁, A₂ and A₃ were the results of 500, 3000 and 10000 times magnification of SEM images of products without KClO₃ oxidant, and B₁, B₂ and B₃ were the results of 500, 3000 and 10000 times magnification of products with KClO₃ oxidant. From the comparison of figures A₁ and B₁, it could be seen that the size of quenched products after adding oxidant was significantly reduced, and through the comparison, it
was found that the particle size uniformity of products after adding oxidant is reduced, and products with finer particle size appear. In addition, it could be found from figures A1, A2 and B2 that some surfaces of products after adding oxidant were broken in complete spherical particles with holes on the surface appear. Through the analysis of the pre-designed reaction, it could be inferred that after adding oxidant, KClO3 could decompose to produce oxygen at high temperature. In addition, BaCO3 would decompose and produce gas CO2 when the temperature reached 1450 °C. The generation and release of these gases would lead to the breaking of the surface of some hollow beads. These broken hollow beaded also prove the hollow structure of the beads to a certain extent. The density of quenching products measured by Archimedes drainage method is 2.6g/cm³. Much less than the density of the same solid powder of 5.6 g / cm³, It could be further confirmed that there are a large number of hollow beads in the prepared product. From A2 and B2 diagrams and A3 and B3 diagrams, it could be seen that when KClO3 oxidant is not added, the quenched product surface was relatively smooth, and dendritic crystals are distributed on the product surface after oxidant is added, which should be that oxidant promotes the full progress of self propagating reaction. In order to further study the particle size and phase composition of the prepared hollow beads, the products need to be deeply studied by means of laser particle size analyzer, EDS and XRD.

3.2 Particle size characterization

Figure 2 showed the particle size analysis results of hollow beads, A4 is the result without oxidant, and B4 was the result after oxidant added. It could be seen from the figure that the particle size of hollow beads without KClO3 was 5-40 μm. The average particle size was 28.08 μm. After adding oxidant, the distribution range of hollow beads was larger, ranging from 5 to 50 μm, and the average particle size decreases to 16.02 μm. This was consistent with the situation reflected in figures A1 and B1. Through analysis, we could know that after adding KClO3, KClO3 decomposes at 1450 °C to produce oxygen, the Oxygen could promote the full quenching reaction, prolong the reaction time, and correspondingly increased the cooling and solidification time of ceramic droplets, so that the gas had time to escape, which reduces the volume of ceramic droplets and reduces the particle size of hollow beads. It can be seen that the addition of oxidant KClO3 to promote quenching reaction was conducive to the refinement of hollow ceramic beads and the formation of ideal ferrite phase after full high temperature self propagating combustion synthesis reaction.

Fig.1 The SEM of quenching products
4. Conclusion
The results of hollow ceramic beads showed that oxidant KClO₃ had a great influence on the preparation of hollow ceramic beads. The morphology picture and XRD analysis showed that the surface of hollow beads without KClO₃ was smooth, and the particle size analysis results show that the particle size was 10-50μm. Without KClO₃, the average particle size is 28.08 μm. After adding KClO₃, dense dendritic crystal structure was distributed on the surface of hollow beads, and the phase was mainly BaFe₂O₄, and the distribution range of hollow beads was 5-40 μm, and the average particle size was 16.02 μm. It could be inferred from the analysis that the quenching reaction was fully carried out after the addition of KClO₃, resulting in a large amount of gas, reducing the volume of ceramic droplets and reducing the particle size of hollow beads.

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