EFFECTIVENESS OF AMORPHOUS CITRATE GEL PRECURSORS FOR PLASMA SYNTHESIS OF COMPLEX FERRITE FINE PARTICLES

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Abstract
In order to prepare complex ferrite fine particles(Y-Fe-O, Ba-Fe-O, M-Zn-Fe-O (M = Mn, Ni, Cu)) with good stoichiometry and crystallinity, the authors adopted the precursors of amorphous citrate gel for plasma powder synthesis. The precursors yielded almost mono-phase ferrites(YFe5O8Ti, x=3.5)[1], hexagonal YFeO3, BaFe12O19, M6Zn11Fe2O17). EDX microanalysis of precursors showed that the distribution of elemental content ratio of gel particles was much sharper than that of co-precipitated particles. The properties of complex ferrite fine particles are also presented.

1. Introduction
For the plasma synthesis of complex oxide fine particles with good stoichiometry and crystallinity, the preparation of their precursors is of crucial importance.

Although gaseous precursor would be most suitable, gaseous compounds are either difficult to obtain or highly expensive, in many systems. Liquid precursors can be applicable in almost all systems and yielded good stoichiometric particles [2, 3]. However, the heat loss due to the solvent (water) is inevitable, which might lead to an upper limit in their feed rate for a given plasma power. In order to eliminate this heat loss and attain high through-put, powder precursor would be better. However, co-precipitated powder shows sometimes segregation of each component, especially in the system where the solubility products are widely separated in each other.

The authors have been studying the plasma synthesis of Y-Fe-O fine particles [4]. During this work, they adopted amorphous citrate gel [5] as a precursor and compared with other types of precursors, including liquid(mist) and solid(co-precipitated powder) precursors. As a result, the amorphous citrate gel precursor was found to be a most promising.

In this Symposium, the detail of the comparison and the results of the application of the amorphous citrate gel precursor to another binary system (Ba-Fe-O, Y-Fe-O) and ternary system (M-Zn-Fe-O) are presented.

2. Experimental
2.1 Preparation of Precursors
Citrate gel precursors were prepared as follows after Matsumoto [6]. Nitrates of each metal element were dissolved in an aqueous solution of citric acid, where total metal ions and citric acid were the same molar amount. A small amount of ethylene glycol was added to promote gel reaction. The solution was kept at 80 °C in a rotary evaporator until the gel reaction was completed, typically for 9 h. The gel was successively heated at 110 °C for 36 h in a vacuum oven, then was pulverized to powder less than 40 μm and kept in dry until being fed to RF plasma.
2.2. Plasma Powder Synthesis

The RF plasma reactor was the same as previous works[1, 4] and schematically shown in Fig.1. The collected powder products were characterized with XRD, TEM/EDX, VSM, etc. Typical experimental conditions and some results are shown in Table 1.

Table 1. Typical experimental conditions and some results

<table>
<thead>
<tr>
<th>Plasma Power</th>
<th>22-30kW (plate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasma Gas</td>
<td>Ar 61-65 slpm</td>
</tr>
<tr>
<td>Pressure</td>
<td>1 atm</td>
</tr>
<tr>
<td>Gel Powder Feed Rate</td>
<td>18-38 g/h</td>
</tr>
<tr>
<td>UFP Production Rate</td>
<td>3.1-6.8 g/h</td>
</tr>
<tr>
<td>Yield (net)</td>
<td>63.81%</td>
</tr>
</tbody>
</table>

3. Results and Discussions

3.1. M-Fe-O Binary Systems

In Y-Fe-O system, in which the authors found a new cubic phase with the composition around Fe/Y = 3.5[1, 4], three types of precursors were entrained into RF Ar-O2 plasma. Figure 2 shows the XRD patterns of product powder synthesized from each precursor. As shown in the figure, amorphous citrate gel yielded almost mono-phase new cubic ferrite with good crystallinity (particle size: 20-50 nm). EDX microanalysis of precursor powders also confirmed that Fe/Y ratio distribution of citrate gel particles was much sharper than that of co-precipitated particles as shown in Fig.3.

The authors applied this precursor in other
binary systems (Ba-Fe-O, Y-Fe-O). The XRD patterns of each product were shown in Fig. 4 a) and b), respectively.

In Ba-Fe-O (Ba:Fe=1:12) system, hexagonal ferrite BaFe₁₂O₁₉ appeared as a main phase though not mono phase. Through TEM observation, round-shaped spheres were predominant and some particles showed hexagonal crystal habit. Mizoguchi also tried to prepare BaFe₁₂O₁₉ fine particles using Ar RF plasma with mist precursor and obtained almost same XRD pattern [7].

In Y-Fe-O (Y:Fe=3:5) system, hexagonal YFe₂O₅ appeared almost mono phase as shown in Fig. 4b). Hexagonal YFe₂O₅ is a metastable phase in Y-Fe-O system, and appeared only in sol-gel reaction of double alkoxydes [8], glycothermal reaction [9], and plasma reaction [3].

3.2 M-Zn-Fe-O Ternary Systems

In the ternary system of M-Zn-Fe-O (M: Mn, Ni, Cu), the authors require spinel type ferrites with a certain coercive force and Curie point range for the application of environmental use, that mean fine particles with the size of several ten nanometer and controlled Zn contents are necessary. Although there are many works for spinel ferrite fine particles, such as hydrothermal synthesis [10], microemulsion synthesis [11], and DC plasma method [2], the authors applied the amorphous citrate gel precursors to this system in order to examine crystallinity and controllability of size and composition.

First, the distribution of the ratios of Mn/Fe and Zn/Fe of citrate gel precursor was confirmed in the case of Mn-Zn-Fe-O (Mn:Zn:Fe=1:1:4). The results showed also sharp distribution as seen in Fig. 5.

The products were mono-phase spinel type MnₓZn₁₋ₓFe₂O₄ (x=0.3,0.5) ferrite fine particles with good crystallinity and desired magnetic properties. Figure 6 shows the typical TEM image of MnₓZn₁₋ₓFe₂O₄ and Figs. 7 and 8 show the XRD patterns and M-H curves, respectively.

However, some variation was observed depending on the powder collection port. Powder collected from "PY" (see Fig.1) showed smaller saturation magnetization and broader XRD peak width. Powder collected from "T" contained ZnO peaks in XRD. Moreover, the distribution of Zn/Fe ratio of powder collected from "S" became wider than precursor, as shown in Fig.9.

![Fig. 4 XRD patterns of plasma synthesized products. a) from Ba-Fe-O gel (Ba:Fe=1:12), b) from Y-Fe-O gel (Y:Fe=3:5).](image)

![Fig. 5 Histogram of Mn/Fe and Zn/Fe ratio of precursor particles. (Mn-Zn-Fe-O system, Mn:Zn:Fe=1:1:4).](image)
These facts imply that the flow field within the reaction chamber is not so uniform and that product powder experienced wide variety of temperature history. This is the subject to be resolved in future work.

Fig. 6 TEM image of plasma synthesized Mn$_0.5$Zn$_{0.5}$Fe$_2$O$_4$.

Fig. 7 XRD patterns of plasma synthesized M$_x$Zn$_{1-x}$Fe$_2$O$_4$ (M = Mn, Ni, Cu, x = 0.3 or 0.5).

Fig. 8 M-H curves of plasma synthesized M$_x$Zn$_{1-x}$Fe$_2$O$_4$ (M = Mn, Ni, Cu, x = 0.3 or 0.5).

Fig. 9 Histogram of Mn/Fe and Zn/Fe ratio of plasma synthesized particles. (Mn-Zn-Fe-O system, Mn:Zn:Fe=1:1:4)

**Conclusion**

In order to prepare complex ferrite fine particles, the authors adopted the precursors of amorphous citrate gel for plasma powder synthesis. The precursors yielded almost monophase ferrites such as YFe$_3$O$_5$[1], hexagonal YFeO$_3$, BaFe$_{12}$O$_{19}$, M$_x$Zn$_{1-x}$Fe$_2$O$_4$ (M = Mn, Ni, Cu, x = 0.3 or 0.5) with good crystallinity.

Since amorphous citrate gel can be easily prepared in almost all reaction system, this citrate gel is concluded to be a versatile promising precursor for plasma powder synthesis in the viewpoint of composition uniformness of precursor and good crystallinity of product powder.
References
