Characteristcis of α-Fe_2O_3 Thick Film Fabricated by Screen Printing Method

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Abstract

Fine powders of α-Fe_2O_3 were prepared by precipitation method using iron(Ⅲ) nitrate in ethanol solvent and the thick film using this powder was made by the screen printing technology. Effects of the reaction temperature and concentration of the iron (Ⅲ) nitrate on the particle size and specific surface area were studied. Also, the relationship between the powder size and properties of the thick film was discussed.

I. Introduction

The α-Fe_2O_3 has been studied extensively because of its wide applicatioln in pigments, catalysts, electromagnetic materials, and gas sensors. Generally α-Fe_2O_3 has been produced by various techniques such as precipitation, sol-gel, pyrolysis, hydrothermal and spray drying process, etc.

Recently thick film of α-Fe_2O_3 has been studied for gas sensors[1-2]. Gas sensor can be broadly divided into three types : sintered pellet, thin film and thick film. Thin film sensors are prepared using various techniques like physical vapour deposition, chemical vapour deposition, RF sputtering, spray pyrolysis, laser ablation and electron beam evaporation. Thick film sensors are prepared using standard screen printing technology[3].

Thick film technology has been considerable progress in many electronic parts because it has many advantages such as circuit reliability, process economics, adaptability to circuit miniaturization and mass production than thin film technology[4].

In this study α-Fe_2O_3 fine powder was prepared by precipitation method. Then thick film based on α-Fe_2O_3 was made by screen printing technology. Effects of reaction temperature, solute concentration and aging condition on particle size and

specific surface area were examined. Also, the relationship between powder size and properties of the thick film was discussed

II. Experimental procedure

Powder Preparation in the Solution

The starting material was iron(Ⅲ) nitrate($Fe(NO_3)_3 \cdot 9H_2O$.) and ethanol(C_2H_5OH, 99.9%) was used as solvent for preparing homogeneous solution. The starting solutions were stirred at 100 rpm for 90 min in rotary evaporator. The concentration of iron (Ⅲ) nitrate was 0.2M, 0.5M, and 0.8M and the reaction temperature was 50℃ and 70℃ respectively. When the starting solution was stirred, it became supersaturated and precipitated at a certain time. For the solutions stirred at 50℃, pH variation was measured to examine hydrolysis rate and the spectra were obtained using FT-IR spectrometer to investigate reaction behavior of Fe^{3+} ion in the solution. All the spectra were measured in the region 4000-400 cm^{-1}. The precipitates obtained form above procedure were centrifuged repeatedly at 10,000 rpm for 10 minutes intervals and washed in ethanol to remove impurity ions. The separated precipitates were dried for 12 h in a oven at 60℃. The dried powders were calcined for 1 h in air at 200, 250, 300, 350, 400 and 450℃. The crystalline phase of dried and calcined powders were determined by X-ray diffractometry in the range of 20° ~70° and decomposition of impurity ions according to heat treatment was identified by FT-IR spectrometer. The morphology and the size of the resulting particles were examined by SEM and the specific surface area was measured by BET method.

Fabrication of Thick Film

Three types of α-Fe_2O_3 precipitated at 70℃ with different concentration(0.2M, 0.5M, and 0.8M respectively) and calcined at 350℃ for 1 h were mixed with organic vehicle to make paste. Variation of paste viscosity with shear rate was measured using rheometer. The pastes were screen printed on the α-Al_2O_3(96%) substrate with 0.5 mm thick. Mask frame was 250 mesh stainless steel and emulsion thickness was 30 ㎛. Printed thick films were dried in an oven at 100℃ for 20 min after 30 min predrying at room temperature in air and sintered at 400, 500, 600℃ for 1 h in air. The surface and cross section of thick film with sintering temperature were observed using SEM.

III. Results and discussion

Charaterization of Fine Powder

When the starting solutions were stirred at a certain temperature, the pH of iron (Ⅲ) nitrate solution was observed to decrease with time as shown in Fig. 1. It was reported that Fe^{3+} ions existed in the form of $Fe(OH)^{2+}$, $Fe(OH)_2^{+}$ and $Fe_2(OH)_2^{4+}$ in iron(Ⅲ) salt solution[5] hence the decrease of the pH was due to the substitution of NO_3^- with OH^-. The pH graph was divided into two steps. At first above mentioned specises were formed and the pH was rapidly droped. Then these species were condensed and precipitation occurred. During this step the solution became turbid and mud yellow precipitates were formed.

Fig. 2 showed the reaction behavior of iron(Ⅲ) nitrate solution during stirring. The absorption bands in the region 500 cm^{-1} were mainly associated with the Fe-O groups and the strong bands in the range 1740-1200 cm^{-1} were assigned to nitrate ion(NO_3^-). The other strong bands in the range 1050-1100 cm^{-1} was due to C-O stretching in ethanol. According to this observation, ethanol was not decomposed and OH^- which composed with Fe^{3+} in the solution was supplied from H_2O of iron(Ⅲ) nitrate.

The result of the x-ray diffraction analysis was reported in Fig. 3. An amorphous pattern without any detectable crystalline phase was found for the sample heat-treated at 200℃. After heating at 250℃ a diffraction peak at 33.2° and 35.4° appeared in the spectrum and was attributed to the (104) and (110) crystallographic plane.

The FT-IR spectra of the calcined powders were displayed in Fig. 4. The absorption bands in the range 400-600 cm^{-1} associated with Fe-O bonding became stronger in accordance with the increase of calcined temperature. The spectrum of powders calcined less than 300℃ showed particular bands at 1380 cm^{-1} associated with NO_3^- ion.

Fig. 5 shows the specific surface area of powders calcined at 350℃. As the concentration of iron(Ⅲ) nitrate increased, the specific surface area increased but effect of reaction temperature was not so significant. Typical morphology and size of powders prepared at 50℃ and calcined at 350℃ were observed in Fig. 6. The powders were composed of agglomerates of relatively uniform particles and the size decreased with the increase of iron(Ⅲ) nitrate concentration. According to DLVO theory, the energy barrier between two particles which inhibited agglomeration was proportional to the dielectric constant of the liquid medium[6]. Considering that the solution was composed of ethanol and water dissolved from solute, as the concentration of iron(Ⅲ) nitrate increased the content of water increaed and the

amount of ethanol decreaed relatively. The dielectric constant of water and ethanol at 20℃ was 80.37 and 25.00 respectively. Therefore an increase of energy barrier was attributed to an increase of dielectric constant of the starting solution. As a result the particle size decreased with an increase of concentration of iron(Ⅲ) nitrate.

Charaterization of Thick Film

Variation of paste viscosity with shear rate was measured(Fig. 7). All the paste displayed typical pseudoplastic behavior - a decreasing viscosity with an increasing shear rate. The paste of finer powder had a good condition for screen printing such as high viscosity at low shear rate and low viscosity at high shear rate.

Fig. 8 showed the surface of thick films dried at 100℃ and sintered at various temperatures. Thick film was composed of many clusters of powders and was not changed significantly until 500℃. After sintered at 600℃ grain growth was occured and thick film was densified. The change of thick film with sintered temperature was observed by SEM micrographs of fracture surface(Fig. 9). The thickness of dried film was about 10.6 ㎛ and almost same after sintered at 500℃. But there was distinct shrinkage of thick film to 8.7 ㎛ after sintered at 600℃. Therefore properties of thick film such as density, porosity and specific surface area might be significantly changed after 600℃.

IV. References

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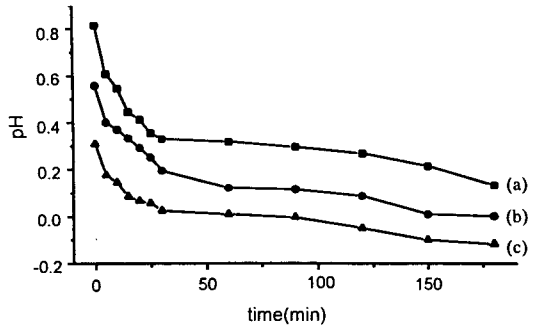

Fig. 1 Variation of pH values with reaction time ; (a) 0.2M, (b) 0.5M and (c) 0.8M.

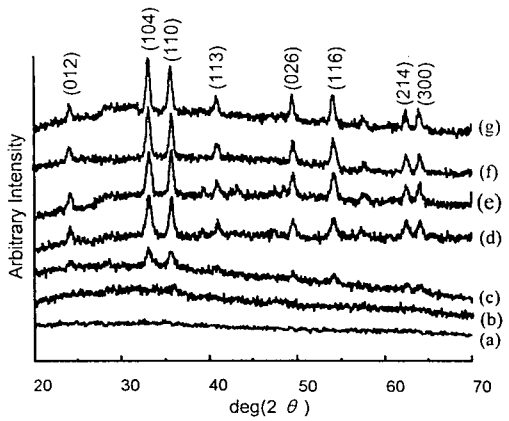

Fig. 3 XRD patterns of powders dried at (a) 60℃ and calcined at (b) 200, (c) 250, (d) 300, (e) 350, (f) 400 and (g) 450℃.

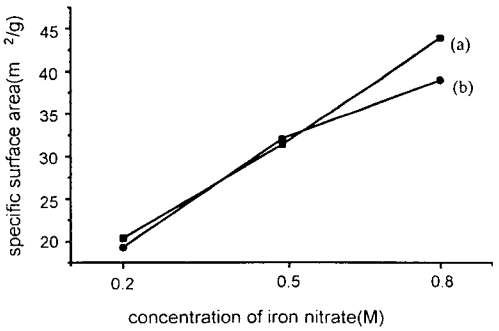

Fig. 5 Effect of the concentration of iron nitrate and reaction time on the specific surface area of α-Fe_2O_3 powders : (a) 50℃ and (b) 70℃.

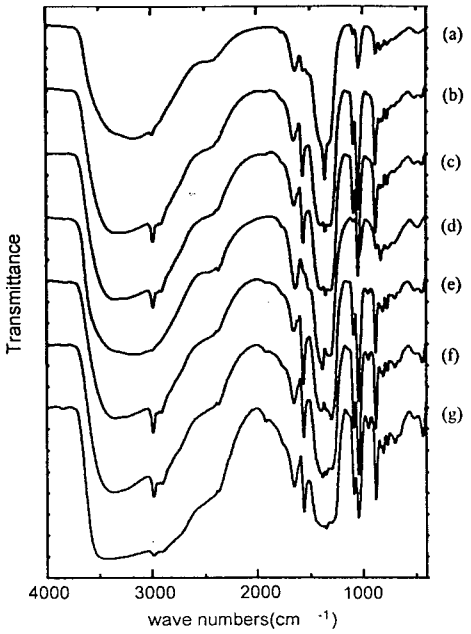

Fig. 2 FT-IR spectra of iron nitrate solution with the reaction time ; (a) 0, (b) 15, (c) 30, (d) 45, (e) 60, (f) 75 and (g) 90 min.

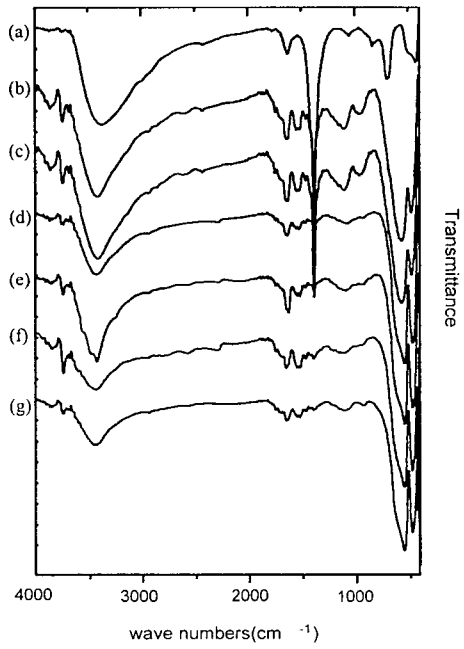

Fig. 4 FT-IR spectra of powders dried at (a) 60℃ and calcined at (b) 200, (c) 250, (d) 300, (e) 350, (f) 400 and (g) 450℃.

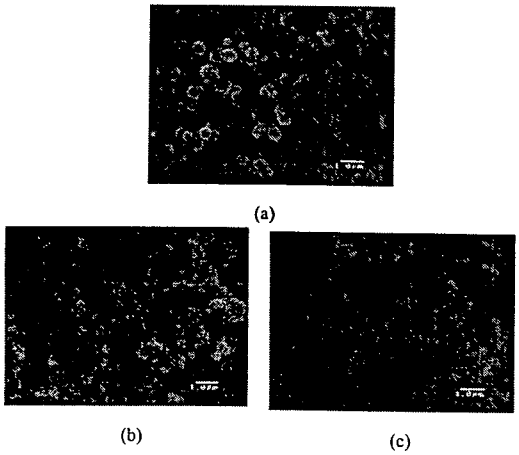

Fig. 6 SEM micrographs of α-Fe_2O_3 powders calcined at 350℃ with the concentration of iron nitrate ; (a) 0.2M, (b) 0.5M and (c) 0.8M.

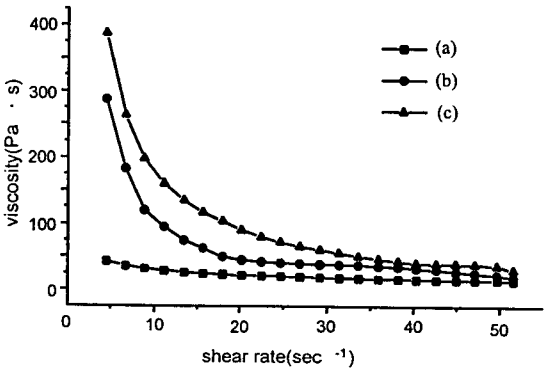

Fig. 7 Variation of paste viscosity via shear rate as a function of the concentration of iron nitrate ; (a) 0.2M, (b) 0.5M and (c) 0.8M

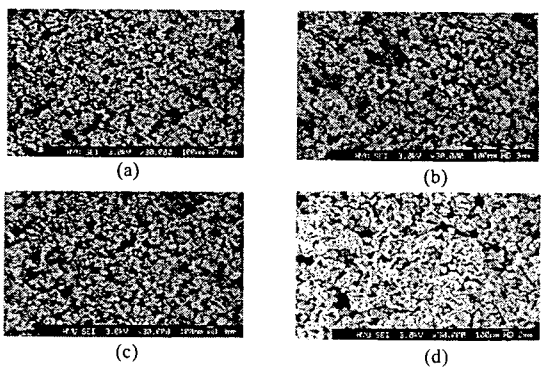

Fig. 8 The surface of thick film (a) dried at 100 ℃ and sintered at (b) 400, (c) 500 and (d) 600 ℃.

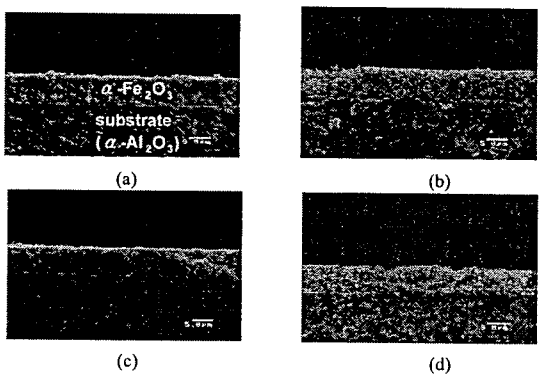

Fig. 9 The fracture surface of thick films (a) dried at 100 ℃ and sintered at (b) 400, (c) 500 and (d) 600 ℃.