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Cobalt ferrite dispersion in organic solvents for electrophoretic deposition: Influence of suspension parameters on the film microstructure

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HIGHLIGHTS

- Suspension parameters were investigated in the EPD of $CoFe_2O_4$ film.
- Among organic solvents acetylacetone is proper to prepare $CoFe_2O_4$ suspension.
- I_2 addition improved suspension stability but deteriorated the film structure.
- PEI addition improved both the suspension stability and the film structure.

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ABSTRACT

An electrophoretic deposition (EPD) method was applied for the preparation of $CoFe_2O_4$ (CFO) films on Al_2O_3/Pt substrates. A coprecipitation process was used to synthesize fine CFO powders with an average particle size of ~40 nm. Influences of suspension parameters such as solvents, iodine additive, and charged polymer on the suspension stability and film microstructure were investigated in detail. Three suspensions including CFO–acetylacetone, CFO–acetylacetone–0.08 wt% I_2 and CFO–acetylacetone –0.2 wt% polyethylenimine (PEI) were optimized, respectively. It was found that CFO was deposited uniformly and the potential required for the deposition was small for the three optimized suspensions. After sintering at 1250 °C for 2 h, the film from CFO–acetylacetone–0.08 wt% I_2 showed many cracks, which indicates this suspension is not suitable for preparing high quality CFO ceramic films. While the sintered films fabricated from the other two optimized suspensions exhibited dense structures. Based on the electric and magnetic properties of CFO ceramic films, it can be concluded that CFO–acetylacetone –0.2 wt% PEI is the proper suspension to prepare films with better microstructures and properties.

1. Introduction

Spinel ferrite with general formula $MnFe_2O_4$ (M = Mg, Ni, Zn, Mn, et al) is a magnetic material and it is extensively used for many technological applications such as ferrofluids, electro-optic devices, microwave devices, and magnetic storage units [1–4]. Among the spinel type ferrites, $CoFe_2O_4$ (CFO) is not much useful in high-frequency fields because of low permeability [5]. However, owing to the super magnetostrictive properties, more interests have been drawn in polycrystalline CFO which is considered as an alternative to the traditional Tb–Dy–Fe alloys based magnetostrictive smart materials [6]. Furthermore, CFO is a good candidate for ferromagnetic material which could be used to prepare multiferroic composite materials with ferroelectric materials (e.g., $BaTiO_3$ [7], $Pb(Zr,Ti)O_3$ [8], et al) in the preparation of multiferroic composite materials. Several methods including spray pyrolysis [9], sol–gel [10], laser deposition [11], and RF magnetron sputtering [12], et al have been applied to the preparation of CFO films. The processing and the resultant microstructure are quite different from each other.

As one of colloidal processes for ceramic production, electrophoretic deposition (EPD) is achieved via motion of charged particles in suspension towards an electrode under an applied electric field [13,14]. It shows the advantages of (1) precise controllability of composition, (2) simple deposition apparatus, (3) fast and even film growth rate, and (4) mild reaction condition [15]. EPD has been used to fabricate oxide films such as $Pb(Zr,Ti)O_3$, TiO_2, Al_2O_3, et al

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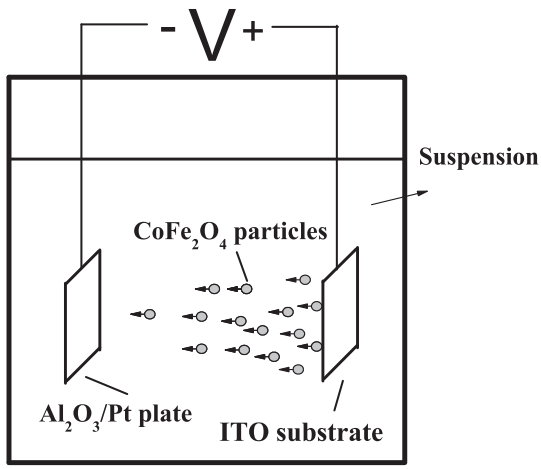

Fig. 1. Schematic diagram of the electrophoretic deposition apparatus used in this study.

[16–18]. The deposition of CFO by EPD has been previously reported [19,20]. However, the influence of suspension parameters on the film microstructure has not been fully understood. In CFO suspension, Magnetic particles are easy to form conglobation as van der Walls attraction and an additional magnetic attraction exist. Therefore exploring suitable conditions to supply enough interparticle repulsive forces become the key to avoid the aggregation.

Organic suspension is preferable to make dense ceramic films by organic suspension for its high thermal stability. However, particles cannot be charged easily due to small amounts of free ions in the organic solvent. The charging mechanism in organic suspension is a sophisticated process which depends mainly on the physical parameters of solvents such as ionizability, dielectric constant, and electron donicity [21–23]. The charging of the particles in organic suspension can also be adjusted through other approaches. It is reported that small amount of I_2 were added to acetone or acetylacetone for particle charging to prepare yttria-stabilized zirconia (YSZ) or $BaTiO_3$ films [24–26]. The protons are formed by a reaction between ketones and iodine. In addition, charged polymers such as polyethylenimine (PEI) was used as a dispersant and polyelectrolyte for particle charging and electrodeposition of various materials [27,28]. To successfully fabricate magnetic films by nonaqueous EPD, it is necessary to prepare stable suspensions with fully charged particles.

In the present work, CFO films on Al_2O_3/Pt substrate were prepared using EPD in organic suspensions. Various suspension parameters such as solvents, iodine additive, and polymers were selected to explore the influences of suspension compositions on the film microstructure. The suspensions were subsequently optimized to improve the quality of the films. In addition, the electric and magnetic properties of CFO films obtained by EPD were also investigated.

2. Experimental

2.1. Synthesis of CFO powder

CFO powders were synthesized using chemical co-precipitation method as the following process. $FeCl_3 \cdot 6H_2O$ (99.9%, Aladdin, China) and $CoCl_2 \cdot 6H_2O$ (99.95%, Aladdin, China) were selected as

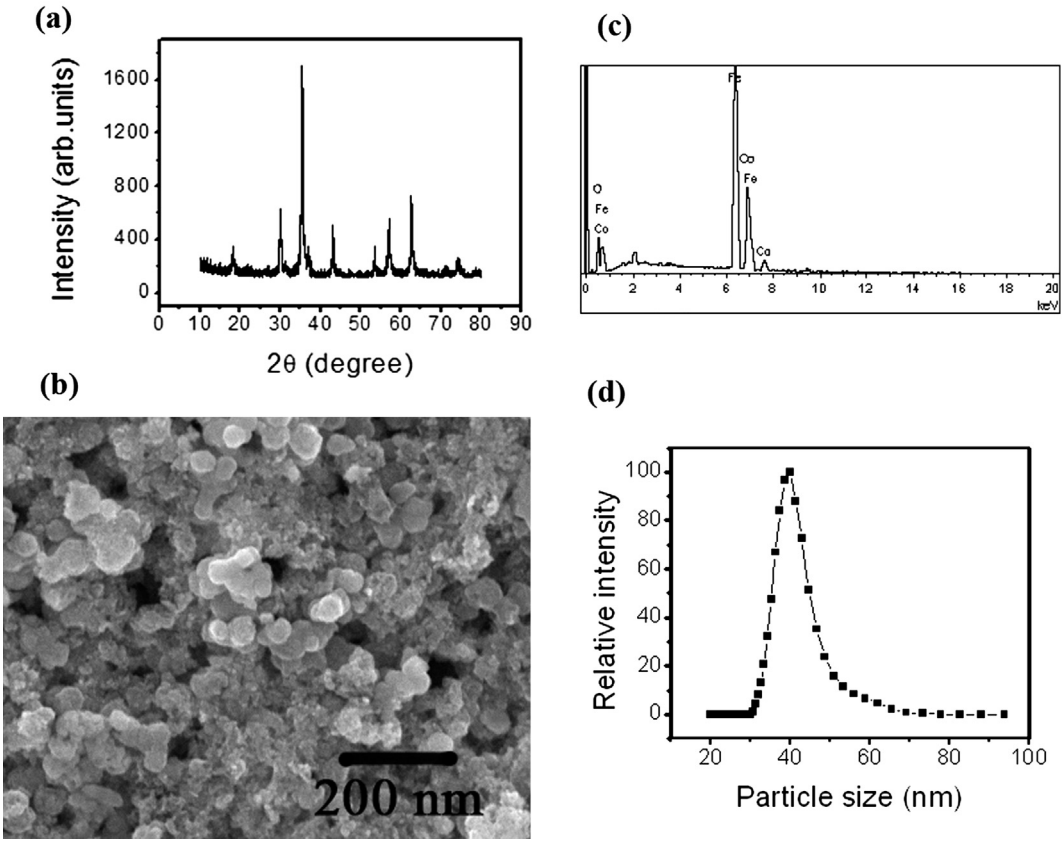

Fig. 2. Characteristics of the CFO powders derived from co-precipitation method after being calcined at 700 °C for 2 h: (a) an XRD pattern, (b) a SEM micrograph, (c) an EDX pattern, and (d) the particle size distribution measured by a laser particle size analyzer.

Table 1
Effects of solvent on the quality of CFO films prepared using EPD method.

Solvent	Dielectric constant ε_r	Sediment volumes (cm^3 0.2 g^{-1})	Voltage/time (V min^{-1})	Deposited CFO (mg cm^{-2}	Quality of film
Ethanol	24.55	0.51	20/10	2.9	Porous
n-Propanol	27	0.53	20/10	2.8	Porous
Acetic acid	6.15	0.5	20/10	3.2	Porous
Acetylacetone	25.7	0.2	20/10	7.2	Uniform
Isopropyl ether	3.9	0.7	50/10	1.2	Porous
Turpentine	2.2	1.8	90/10	–	Scarcely deposited

precursors. Stoichiometric amount of the chlorides (forming the composition of $CoFe_2O_4$) were dissolved into de-ionized water to make a solution. As an oxidizer and pH adjuster, excessive NaOH at Na/Cl ratio of 1.1:1.0 was dissolved into de-ionized water and then heated to 80 °C. The chlorides solution was slowly added into the hot alkali solution with continuous stirring to generate precipitation. After washing, the precipitate was dried at 100 °C for 2 h and then calcined at 700 °C for 2 h to get CFO powders, which were characterized by X-ray diffraction (XRD, X'Pert PRO, PANalytical B.B., Holland), field emission gun scanning electron microscope with energy dispersive X-ray spectrometry (FEG-SEM-EDX, Sirion 200 PRO, Holland), and laser scattering size analysis (Zetasizer 3000 HAS, Malvern Instruments Ltd., UK).

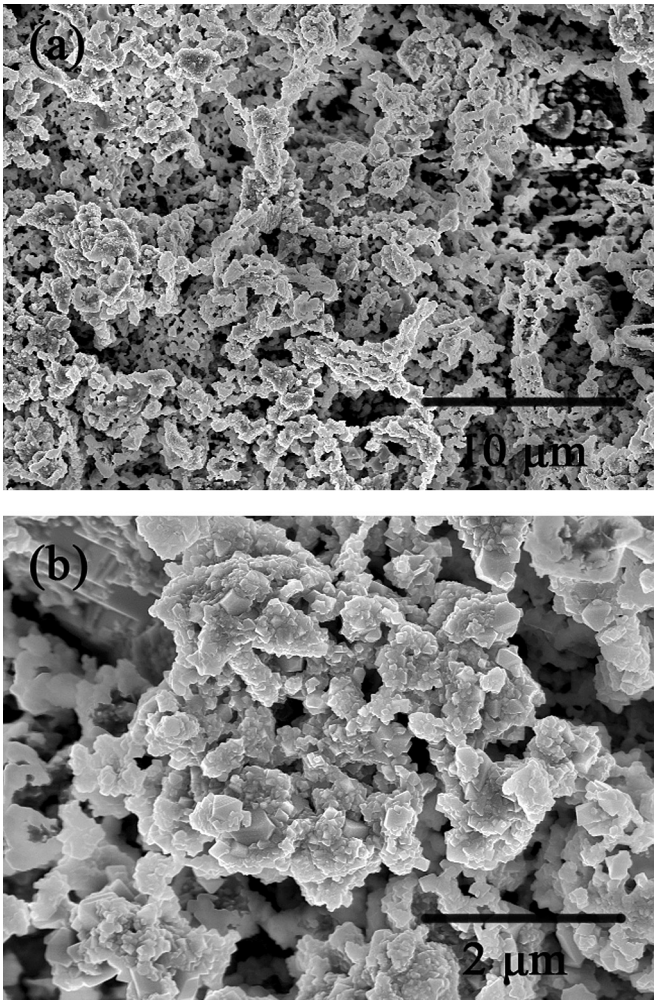

Fig. 3. SEM micrograph of the as-deposited films fabricated from CFO dispersion in ethanol.

2.2. Preparation of suspensions

CFO suspension was obtained by dispersing CFO powders in various organic solvents (AR, Sinopharm, China) with or without additives. To be thoroughly dispersed, the dispersion was stirred by an electric stirring apparatus (JJ-1, JinTan Instruments, China) and ultrasonicated by a high intensity ultrasonic probe (KQ2200E, Kun Shan Ultrasonic Instruments Co., Ltd., China). Iodine (99.5%, Aldrich, China) and polyethylenimine (PEI, M_w = 40,000, Nuotai Chemical, China) were used as the additives. The sediment volumes of suspensions were measured in 10 mL cylinders after being settled for 3 weeks. The concentration of suspension was 20 g L^{-1}. The CFO suspension was diluted to 10 mg L^{-1} to measure zeta potential by means of electrophoretic light scattering technique (Zetasizer 3000 HAS, Malvern Instruments Ltd., UK). Viscosity of suspensions was evaluated by a rotary viscometer (NDJ-7, Mydream Electronic Ltd., China) with a shear rate of 350 s^{-1}. The conductivity was measured by a conductivity meter (DDB11-A, Bridgesi Instruments, China).

2.3. Fabrication of CFO films

The experimental arrangement for EPD is schematically illustrated in Fig. 1. The polished ITO ($InSnO_3$, Indium tin oxide) conductive substrate and Al_2O_3/Pt plate (1.5 cm × 2.5 cm in plane dimension, placed 1.5 cm apart) were used as the cathode and anode, respectively. By means of magnetron sputtering, the Pt layer with thickness of ~1 μm was deposited on the Al_2O_3 plate (purity 99.5%; density 3.88 g cm^{-3}), which was made by solid phase sintering. Charged CFO particles were electrophoretically deposited onto the Al_2O_3/Pt electrode in a constant voltage mode. The deposition weight (mg cm^{-2}) was calculated by dividing the increased weight of the electrode after deposition by the deposition area. As-deposited CFO films were dried in air for ~24 h and characterized by SEM for surface morphology.

Finally, the as-deposited films on Al_2O_3/Pt were sintered at temperatures of 1250 °C for 2 h and then cooled to ambient temperature, with a heating and cooling rate of 5 °C min^{-1}. The surface microstructures of the sintered films were observed by SEM. The leakage current measurement was conducted on a ferroelectric materials measurement system (Multiferroic, Radiant Ltd., USA). For electric measurement, Ag electrodes on the top surface of CFO films were made by screen-printed method. Magnetic hysteresis loops at room temperature were measured via a vibrating sample magnetometer (VSM, Model 4HF, ADE Ltd., USA) in a magnetic field ranging from −15 to 15 kOe.

3. Results and discussion

3.1. Characterization of CFO powder

The XRD pattern of the as-calcined CFO powder at 700 °C for 2 h is shown in Fig. 2a, which indicates that the powder corresponds to a pure spinel phase with JCPDs no. 01-1121. Its average grain size is about 40 nm, as calculated from the line broadening according to

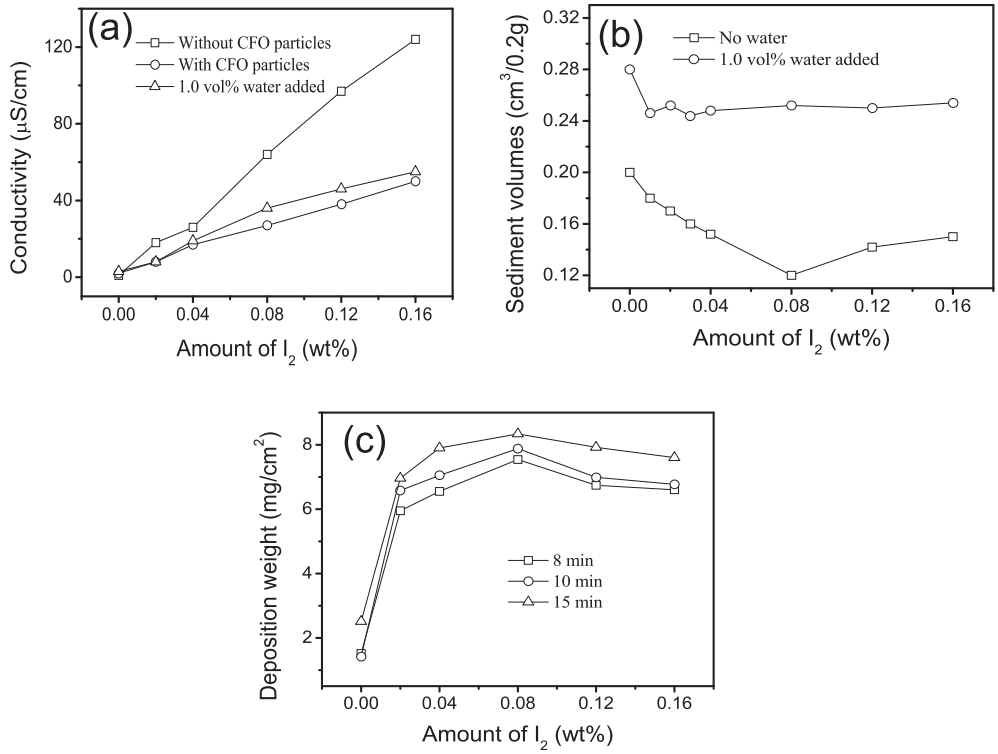

Fig. 4. Effect of I_2 on the properties of CFO–acetylacetone suspension. (a) Conductivity, (b) sediment volumes, and (c) deposition weight as a function of the addition amount of I_2.

Scherrer formula. Fig. 2b is a typical CFO powder SEM image, characterized by particles with uniform size. Results from EDX show that Co, Fe, and O are the main elemental components of the ferrite particles (Fig. 2c). It also confirms the expected Co:Fe atomic ratio, which approximately equals to 1:2. From Fig. 2d, the particle size analysis result of the CFO powder, it is proved that an average size of ~40 nm could be achieved by the coprecipitation method. It is also believed that the narrow size distribution will enhance the uniformity of particle arrangements in the films prepared by EPD.

3.2. Effect of the solvents on CFO suspensions

The stability and chargeability of the CFO dispersion depend mainly on the physical parameters of the solvent such as ionizability and the dielectric constant, and the interactions between the particles and the solvent. A homogeneous ceramic film made by EPD requires a fully charged and stable suspension. Therefore the selection of a solvent plays a fundamental role in the development of suitable suspensions. Different solvents were considered to investigate their effects on the suspension stability and film structure and the results listed in Table 1 give an overview of the different solvents.

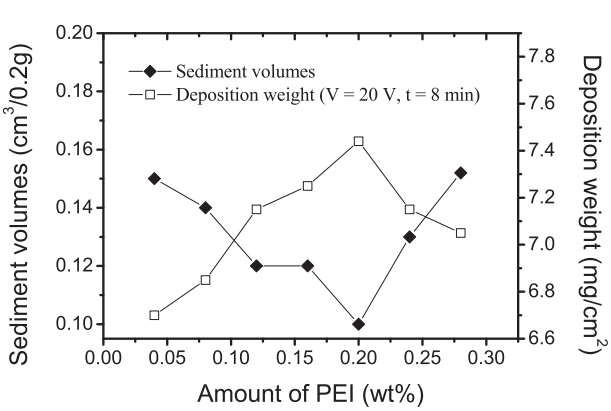

Fig. 5. Sediment volumes and deposition weight as a function of PEI amounts.

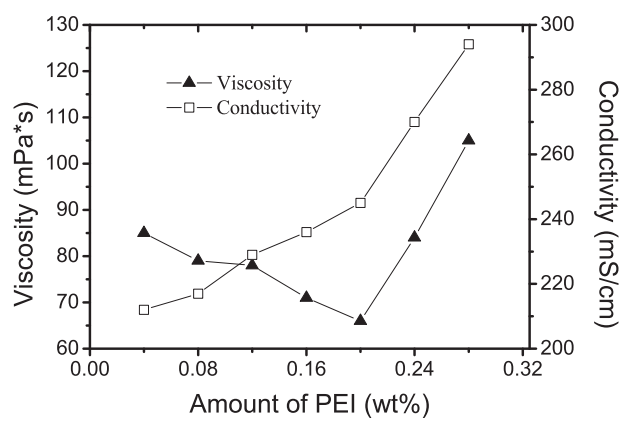

Fig. 6. Viscosity and conductivity of CFO suspensions as a function of PEI amounts.

It is found that the sediment volume (cm^3 0.2 g^{-1}) of suspension in turpentine was the highest, and with scarcely deposited CFO film. For solvents of ethanol, n-propanol, acetic acid, and isopropyl ether, the sediment volumes of corresponding suspensions were

Table 2
Comparison of properties of the optimized CFO suspensions.

Solvent	Additives/ amounts	Sediment volumes (cm^3 0.2 g^{-1})	Zeta potential (mV)
Acetylacetone	–	0.2	38
Acetylacetone	I_2/0.08 wt%	0.12	48
Acetylacetone	PEI/0.2 wt%	0.1	44

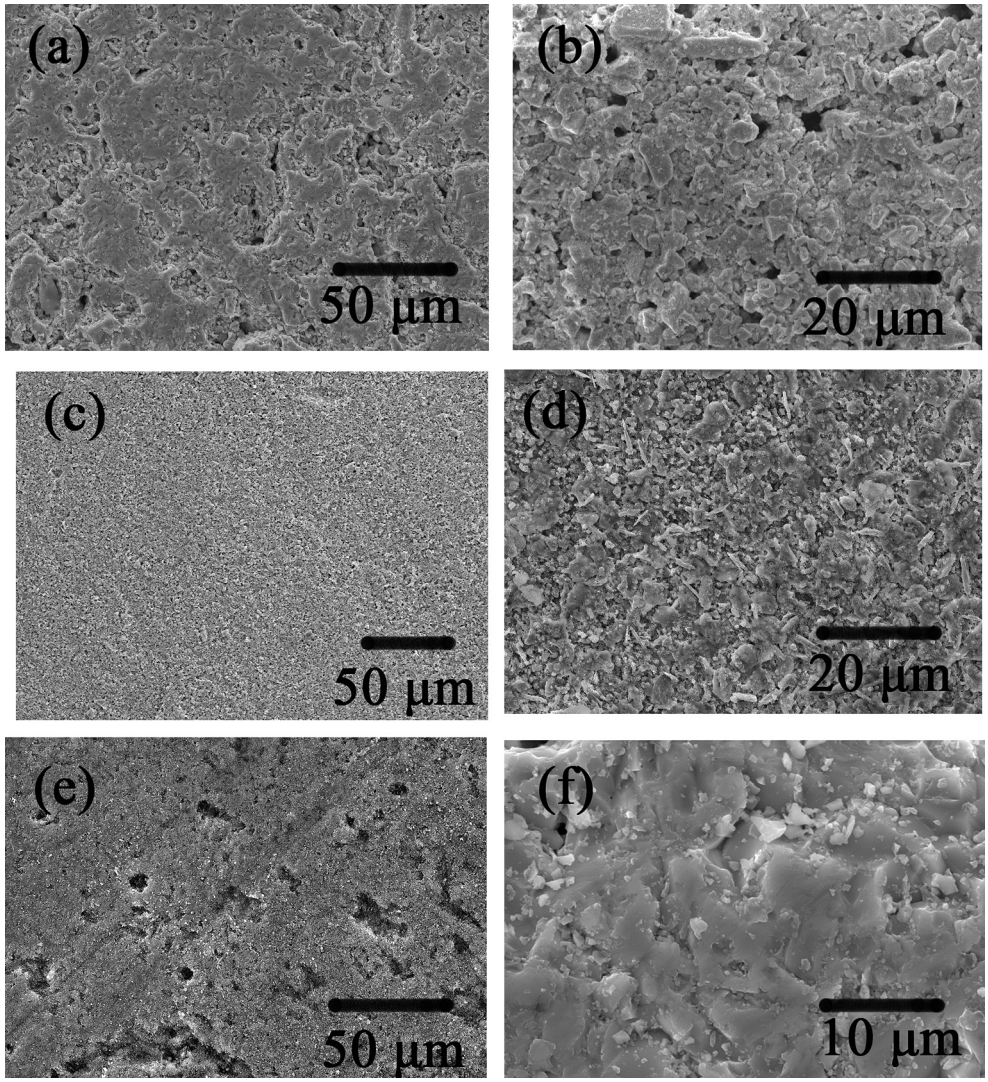

Fig. 7. SEM micrograph of the as-deposited films fabricated from various suspensions: (a) and (b) CFO–acetylacetone, (c) and (d) CFO–acetylacetone–0.08 wt% I_2, (e) and (f) CFO–acetylacetone–0.2 wt% PEI.

large and the deposited films were porous and nonuniform. SEM micrographs of the as-deposited CFO film obtained from ethanol suspension are shown in Fig. 3, which demonstrate a porous structure with some aggregation. The poor film quality is attributed to a not sufficient dispersion of the suspension and its low stability. Obviously, the solvents mentioned above are not suitable for obtaining dense CFO films. On the other hand, suspension with CFO dispersed in acetylacetone showed the highest stability (with the smallest sediment volume) among the suspensions. As-deposited films with uniform and good quality were obtained in acetylacetone suspension. So acetylacetone was selected as the solvent to make CFO suspension in this step. In acetylacetone (CH_3COCH_2-$COCH_3$), H^+ ions can be ionized from the $-CH_2-$ functional groups, which charge the CFO particles and stabilize the suspension [29]. The different effects between acetylacetone and other solvents may also relate to the physical properties of solvents such as dielectric constant and electron donicity.

3.3. Effect of I_2 on CFO suspensions

It is reported that small amount of I_2 was added to acetone or acetylacetone to charge particles for preparation of oxide films [23–25]. Protons were formed by a reaction between ketones and I_2: $CH_3COCH_2COCH_3 + I_2 \leftrightarrow ICH_2COCH_2COCH_2I + 2I^- + 2H^+$. The addition of I_2 increased the protons in suspension, so that the charging of particles was enhanced. It is also reported that small amount of water which acted as a catalyst was added in acetylacetone–I_2 suspension system for further enhancement of particles charging [26]. Thus in this study, the effects of I_2 and water on the properties of CFO–acetylacetone suspension were also investigated.

Conductivity measurement of pure acetylacetone, acetylacetone with CFO loaded, and acetylacetone with CFO loaded and 1.0 vol% water as a function of I_2 was conducted and the results are shown in Fig. 4a. It is found that the conductivity increases almost linearly with increased I_2 amount for all the curves and the conductivity of CFO–acetylacetone suspension is lower than that of pure acetylacetone. It indicates the free ions had been adsorbed onto the CFO particles in CFO–acetylacetone. Fig. 4b shows the sediment volumes as a function of amount of I_2 with and without water. It was obvious that sediment volumes of CFO suspensions with water were higher than those of suspensions without water, which indicates that the addition of water has little effect in enhancing the suspension stability. On the other hand, the sediment volumes of suspensions without water decrease at first with the increase of I_2

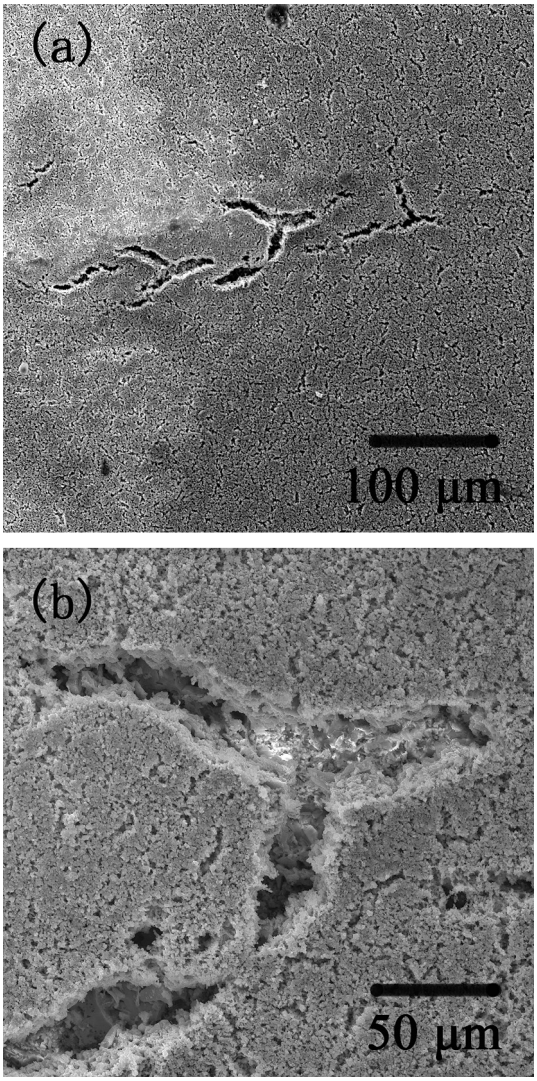

Fig. 8. SEM micrograph of the crack structures of CFO films prepared using EPD in suspension of CFO–acetylacetone–0.08 wt% I_2 followed by sintering at 1250 °C, 2 h.

amount and then increase, with the smallest sediment volume obtained at 0.08 wt% I_2 amount. Furthermore, for CFO suspensions with I_2 amount of 0.04, 0.08, and 0.12 wt%, zeta potential of 39, 48, and 34 mV were observed, respectively. The deposition weight of CFO films (Fig. 4c; $V = 20$ V, $t = 8$, 10, and 15 min) confirms the highest suspension stability of CFO–acetylacetone–0.08 wt% I_2, which could be a good choice for the EPD process.

3.4. Effect of PEI on CFO suspensions

PEI is an effective cationic polymer dispersant to disperse ceramic particles in organic solvents. This is because there exists a stabilization of both electrostatic and steric in suspension with PEI, which may promote the inter-particle repulsive forces. And it was proved that PEI is dissolvable in acetylacetone. So the effect of PEI on the CFO suspension was also studied, as shown in Fig. 5. The sediment volumes reduced with the increase in PEI amount until 0.20 wt%, and then turned to increase. On the contrary, the deposition weight ($V = 20$ V, $t = 8$ min) grew up at first, and then decreased. The results indicate that the highest stability suspension exists at PEI amount of 0.20 wt%. It is well known that the sediment volume and deposition weight of material in EPD depend on the amount of dispersants since they play a fundamental role in the stabilization and in the surface charging of particles. However, excessive dispersant beyond the saturation adsorption point of particles could not further improve the dispersion properties. The viscosity and conductivity measurements (as shown in Fig. 6) confirm that the saturation adsorption amount of PEI is around 0.20 wt%. Therefore, it is concluded that the optimal suspension system with PEI was CFO–acetylacetone–0.20 wt% PEI.

Table 2 lists the properties of the three optimized CFO suspensions for comparison. It shows that all suspensions are characterized with low sediment volume (0.10–0.20 cm^3 0.2 g^{-1}) and big zeta potential (38–48 mV) which indicates that they are all good candidates for preparation of CFO film.

3.5. Microstructure of as-deposited and sintered CFO films

Fig. 7 presents SEM micrographs of the as-deposited films fabricated from the three optimal CFO suspensions (see Table 2) of CFO–acetylacetone (Fig. 7a–b), CFO–acetylacetone–0.08 wt% I_2 (Fig. 7c–d), and CFO–acetylacetone–0.2 wt% PEI (Fig. 7e–f). All the as-deposited films show rather dense and uniform structures.

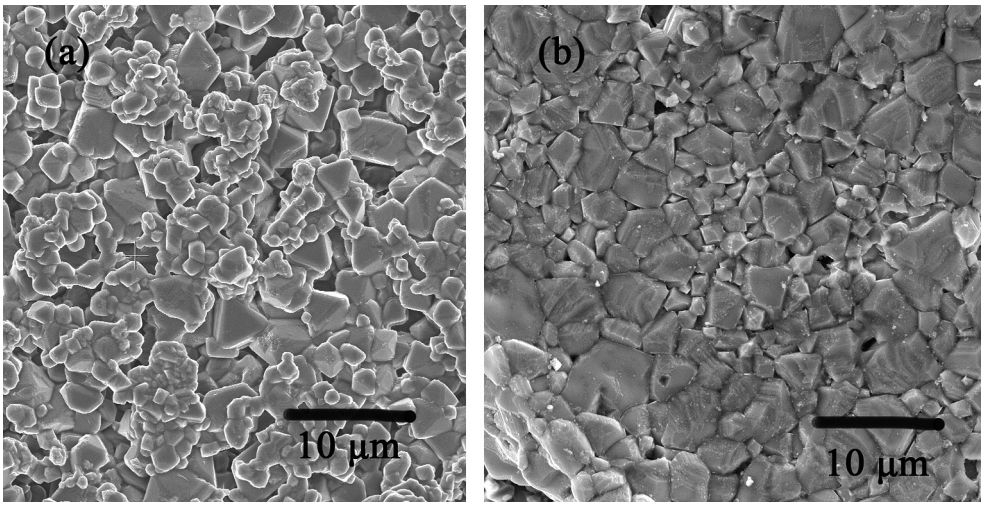

Fig. 9. SEM micrograph of the CFO films prepared using EPD in suspensions of (a) CFO–acetylacetone and (b) CFO–acetylacetone–0.2 wt% PEI, followed by sintering at 1250 °C, 2 h.

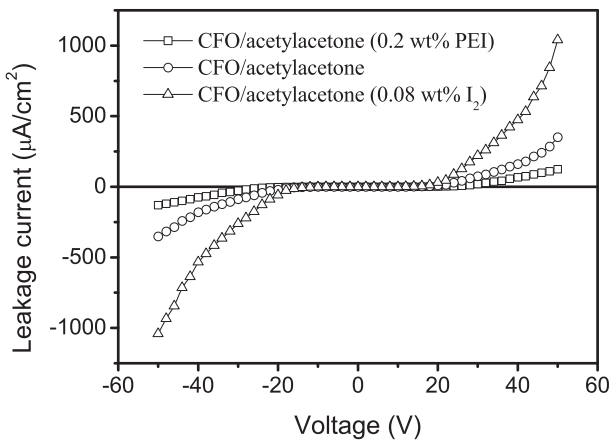

Fig. 10. Leakage current curves of the CFO films (sintered at 1250 °C for 2 h) obtained from suspension of CFO–acetylacetone, CFO–acetylacetone–0.08 wt% I_2, and CFO–acetylacetone–0.2 wt% PEI.

Especially the CFO film from CFO–acetylacetone–0.08 wt% I_2 exhibits smooth and crack free structure owing to the higher suspension stability.

The as-deposited films were sintered at 1250 °C for 2 h for further densification. Shown in Fig. 8 are SEM micrographs of CFO sintered films with suspension of CFO–acetylacetone–0.08 wt% I_2. Both big and tiny cracks are obviously found in the sintered films, which is rather contrary with the film microstructure before sintering. It is considered that the residual I_2 in the films may damage the CFO films during the sintering process and may result in the unusual change of the film structure. Caballero et al. [30] have reported that the residual phosphorus left by phosphate ester changed the sintering behavior and properties of the $BaTiO_3$ deposits using EPD. In the present work, different sintering temperatures (1150 and 1200 °C) were also employed, cracks were still found in the CFO films fabricated from CFO–acetylacetone–0.08 wt % I_2, which indicates this kind of suspension is not suitable for preparing high density CFO films. The mechanism will be studied in our future research.

Fig. 9 shows the SEM micrographs of sintered CFO films from suspensions of CFO–acetylacetone (Fig. 9a) and CFO–acetylacetone–0.2 wt% PEI (Fig. 9b), from which dense film structures are observed. The film prepared in CFO–acetylacetone–0.2 wt% PEI showed better structure than that in pure acetylacetone suspension.

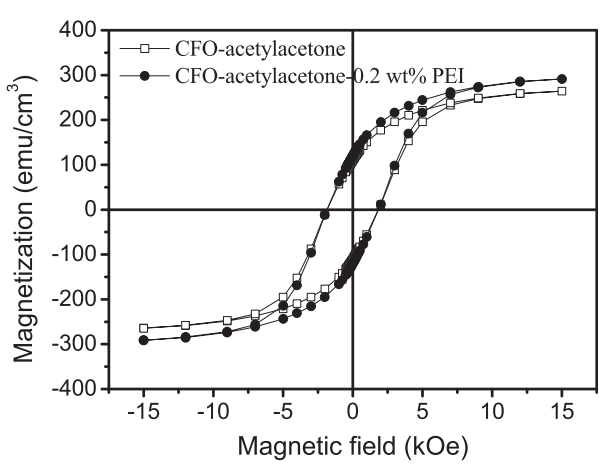

Fig. 11. Magnetic hysteresis loops (in-plane) measured at room temperature of the obtained CFO films deposited in suspensions of CFO–acetylacetone and CFO–acetylacetone–0.2 wt% PEI, followed by sintering at 1250 °C, 2 h.

3.6. Electric and magnetic properties of sintered CFO films

From Fig. 10, big value of leakage current is found in sintered film from CFO–acetylacetone–0.08 wt% I_2. The low resistivity is mainly related to the cracks inside the entire film, as shown in Fig. 8. On the other hand, the leakage current is small for the film obtained from CFO–acetylacetone (0.2 wt% PEI) or CFO–acetylacetone which can be attributed to the dense structure of the CFO films obtained in the corresponding suspensions. Moreover, Fig. 10 indicates that resistivity of film obtained from suspension of CFO–acetylacetone–0.2 wt% PEI is larger than that from CFO–acetylacetone suspension. The magnetic properties of the sintered films obtained from suspensions of CFO–acetylacetone and CFO–acetylacetone–0.2 wt% PEI were measured at room temperature. Magnetic hysteresis loops (in-plane) of the CFO films obtained from the two suspensions are shown in Fig. 11. Both films exhibit evident magnetic properties with saturation magnetization M_s higher than the reported values of CFO thick films prepared by spray pyrolysis [9] or sol–gel [31] method. Furthermore, the M_s value (312 emu cm^{-3}) of the film obtained from suspension with PEI is larger than that from the pure acetylacetone suspension (264 emu cm^{-3}). The improved electric and magnetic properties demonstrate that the proper addition of PEI is of help to enhance the stability of the pure acetylacetone suspension.

4. Conclusions

Acetylacetone was proved to be the suitable solvent for preparing CFO suspensions among several organic solvents. The addition of iodine and PEI can enhance the particle charging in organic suspensions so that CFO–acetylacetone–0.08 wt% I_2 and CFO–acetylacetone–0.2 wt% PEI were optimized as the other two suspensions to prepare CFO powders. Though uniform deposit of CFO can be obtained at a smaller potential in all the three optimized suspensions, CFO–acetylacetone–0.08 wt% I_2 cannot guarantee a crack free sintered film (1250 °C, 2 h) with high quality. On the other hand, sintered ceramic films from the other two optimized suspensions were obtained with dense structure and good electric and magnetic properties. Finally it is concluded that CFO–acetylacetone–0.2 wt% PEI is the proper suspension which may fabricate CFO films with better microstructure and properties.

Acknowledgments

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