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Preparation of ferromagnetic metal fine fibers by organic gel-thermal reduction process

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Abstract: The organic gel-thermal reduction process was used for the preparation of ferromagnetic metal Ni, Co and Fe fine fibers from the raw materials of citric acid, lactic acid and metal salts. The structure, thermal decomposition process and morphologies of the gel precursors and fibers derived from thermal reduction of these gel precursors were characterized by Fourier transform infrared spectroscopy, X-ray diffraction, thermo-gravimetric/differential scanning calorimetry and scanning electron microscopy. The results show that spinnability of gel largely depends on molecular structure of metal-carboxylate complex that is a linear-type structure formed in the gel. As a result, the gels exhibit a good spinnability. Metal Ni, Co and Fe fine fibers are featured with diameters of around 1 μm and a high aspect ratio up to 1×10^6.

Key words: ferromagnetic metal fiber; organic gel; thermal reduction; spinnability

1 Introduction

Ferromagnetic metal fine fibers showing anisotropic characteristics are attractive for use as fillers in polymer-matrix composites for advanced electromagnetic interference (EMI) shielding and radar absorbing materials[1−3]. Because electromagnetic radiation at high frequency penetrates only the near surface region of an electrical conductor, known as skin effect, the electric field of a plane wave penetrating a conductor drops exponentially with increasing depth into the conductor. The composite material as a conductive filler of metal fibers with a smaller diameter is better than that with a larger diameter. For effective use of the entire cross section of metal fibrous fillers for EMI shielding or radar absorbing materials, the diameter of the metal fiber should be comparable with or less than the skin depth[1]. Therefore, the filler of ferromagnetic metal fibers with a diameter of 1 μm or less than 1 μm and a high aspect ratio (ratio of fiber-length to fiber-diameter) is required technologically.

In recent years, several methods have been developed to prepare metal fine fibers, including electroplating[4], chemical vapor deposition[5], pyrolysis[6] and template synthesis[7]. However, these processing routes are expensive to make metal fine fibers, and the aspect ratio of fibers is small.

The sol-gel method based on hydrolysis of alkoxide compounds is a promising approach for fine ceramic fibers as it allows mixing of multiple components at an atomic or a molecular level, resulting in a homogenous precursor. Consequently, improved sintering rates at lower temperatures can be expected, leading to improved microstructure. TSAI[8] prepared Mg_2SiO_4 fibers by the sol-gel process using $Si(OC_2H_5)_4$ and $Mg(OCH_3)_2$ as the starting reagents and found that the gel's spinnability was improved by addition of linear-type molecular citric acid. Organic gel processes have been used to produce various ceramic oxide powders or coatings[8−12]. The aim of this investigation is to determine the feasibility of utilizing the organic gel-thermal reduction process to prepare metal Ni, Co and Fe fine fibers from the raw materials of citric acid, lactic acid and the metal salts.

2 Experimental

2.1 Preparation of metal fibers

The starting reagents were citric acid ($C_6H_8O_7 \cdot H_2O$, AR), lactic acid ($C_3H_6O_3$, AR), iron(III) nitrate ($Fe(NO_3)_3 \cdot 9H_2O$, AR), nickel basic carbonate ($NiCO_3 \cdot Ni(OH)_2 \cdot 4H_2O$, AR) and cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$, AR). The desired amounts of metal salts and citric acid or lactic acid were separately dissolved in deionized water to form 0.2 mol/L aqueous solutions. According to the required composition, the metal salt solution was then gradually added into the citric acid or lactic acid solution with continuous magnetic stirring. The solution pH was adjusted by addition of ammonia solution. The final solution was magnetically stirred at room temperatures for about 18 h and transferred to a rotary evaporator and evaporated

in a vacuum at 60−70 ℃ to remove surplus water until a viscous liquid was obtained. The resultant liquid was then poured into an evaporating basin and heated in vacuum at 75 ℃ until a spinnable gel could be used for drawing gel fibers by handling a glass rod. The spinning performance of the gel was estimated from the capability of fiber formation by immerging a glass rod with 2 mm in diameter into the gel and then pulling it up by hand.

The gel fibers were drawn from the spinnable gels and dried in a vacuum oven at 80 ℃ for about 10 h. The dried gel fibers were then aligned into a quartz crucible and subsequently reduced into metal fibers under an atmosphere of N_2 (80%, volume fraction)+H_2(20%) in a tubular oven at appropriate temperatures.

2.2 Characterization of fibers

The structure, composition and morphology of the gel precursors and the products derived from thermal reduction of the precursors at different temperatures were examined by Fourier transform infrared spectroscopy(FTIR) using a model of Nexu670 spectrometer, X-ray diffraction (XRD) using a D/max2500PC diffractometer(RIGAKU), and scanning electron microscopy using a XL-30ESEM instrument (JEOL). The decomposition process of the gel precursors was investigated by thermo-gravimetric(TG) analysis and differential scanning calorimetry(DSC) using a SDT2960 (TA) system.

3 Results and discussion

3.1 Formation and spinnability of gel precursors

The XRD patterns of iron lactate, nickel citrate, and cobalt citrate gel precursors are shown in Fig.1. It can be seen that these gel precursors are amorphous and do not contain crystalline inorganic salts. The FTIR spectra and peak positions for these gel precursors shown in Fig.2 confirm the formation of complexes between Fe^{3+} and lactic acid, Ni^{2+} and citric acid, and Co^{2+} and citric acid. C═O characteristic frequencies of the carboxylic acid shift to low frequencies of 1 618 cm^{-1} and 1 385 cm^{-1} for Ni-citrate, 1 618 cm^{-1} and 1 384 cm^{-1} for Co-citrate, 1 618 cm^{-1} and 1 384 cm^{-1} for Fe-lactate. The two bands at 1 350−1 650 cm^{-1} result from the C═O symmetric and asymmetric stretching vibration, which are the characteristic absorption peaks for the citrates. The carbonyl peak at 1 720 cm^{-1} could be attributed to surplus citric acid or lactic acid in the gel precursors.

According to Ref.[13], there are three possible ligand types between carboxylate and metal ions. It is believed that the single-dentate ligand leads to formation of linear molecular structures and the other two ligand types are beneficial to net-work molecular structures between metal ions and carboxylate. The value

$\Delta(\Delta=\nu_a−\nu_s)$ can be used to classify the ligand type: the single-dentation corresponds to a higher value Δ, the double-dentation corresponds to a lower value Δ and the bridge corresponds to an approximately equal value Δ of C═O in the complex compared to the free carboxylate. So that, referring to the value Δ obtained from FTIR data as shown in Table 1, the single-dentation between metal ions and carboxylic acid would be dominative and linear molecular structures for these complexes can be expected.
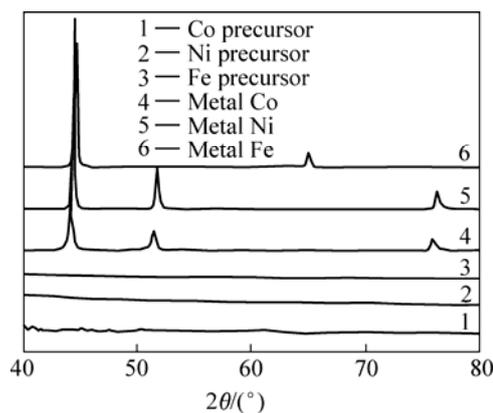

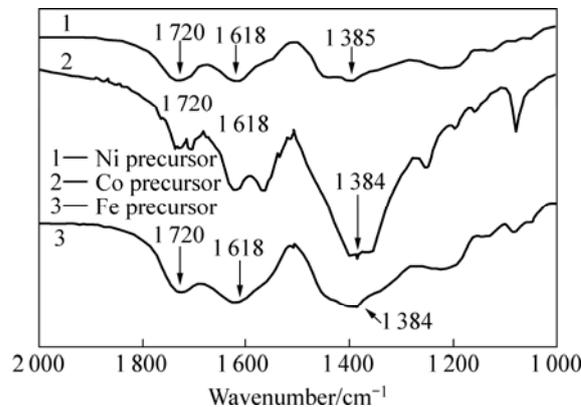**Fig.1** XRD patterns of gel precursors and products derived from thermal reduction of precursors

Fig.2 FTIR data for gel precursors

Table 1 Characteristic frequencies of FTIR spectra for gel precursors

Gel precursor	ν_a(C═O)/cm^{-1}	ν_s(C═O)/cm^{-1}	Δ/cm^{-1}
Ni-citrate gel	1 618	1 385	233
Fe-lactate gel	1 618	1 384	234
Co-citrate gel	1 618	1 384	234
Free carboxylate	1 588	1 392	196

In aqueous solutions, the citric acid can be disassociated and exists in four species in the sequence of H_3Cit, $H_2Cit^−$, $HCit^{2−}$ and $Cit^{3−}$. The species are present in different amounts at different pH values and the complex formation depends on solution pH values[14]. $HCit^{2−}_a$ is dominant when pH is in the range of 2.8−4.5

and Cit^{3-} largely exists when pH>4.5. The metal ions (such as Ni^{2+}, Co^{2+}) mainly coordinate with $HCit^{2-}$ species in aqueous solutions at pH of 2.8−4.5[15]. When $HCit^{2-}$ reacts with Ni^{2+}, or Co^{2+}, a dimeric unit is formed, which is interconnected through the terminal carboxylate group, leading to an infinite chain. So, the molecular structure as shown in Fig.3 can be deduced. The experimental results show that the gel precursor formed at pH of 3.0−4.0 exhibits good spinnability with a molar ratio of H_3Cit to M^{2+} of 1:1.

In the experiments, using critic acid and iron (III) nitrate as the starting reagents to prepare iron fibers was attempted. But the gel exhibited no spinnability and failed to form iron fibers. This phenomenon can be attributed to a three-dimensional network structure for Fe^{3+}–citrate complexes formed[16]. It was found that using lactic acid and iron (III) nitrate as the starting reagents (in a molar ratio of 3.025:1 and at pH1.5) in aqueous solutions the Fe-lactate gel with a good spinnability was prepared. The complexes for lactic acid and Fe^{3+} might exist in the form of molecular structures as shown in Fig.3(b), with the molar ratio of 3:1 for lactate and Fe^{3+}, which is close to the optimized molar ratio used for the spinning gel precursor. These complexes are possibly linked each other to form larger molecules with a linear-type or chain-like structure through hydrogen bonds.
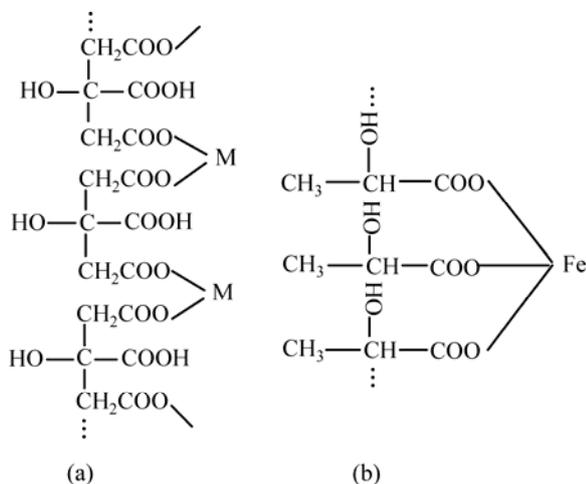

Fig.3 Possible molecular structures for various gel precursors (a) $[(C_6H_6O_7)M]_n$ for Co or Ni fibers; (b) $[(C_3H_5O_3)_3Fe]_n$ for Fe fibers

3.2 Thermal decomposition process of gel precursors

Fig.4 shows the TG/ DSC data for the various gel precursors. For all the compositions investigated, the thermal decomposition process consists of the following three stages.

1) At 50−170 ℃, the TG/DSC data exhibit a broad endothermic event corresponding to a mass loss of about 2%−10%, which is attributed to the loss of free water and bound water in the gels.
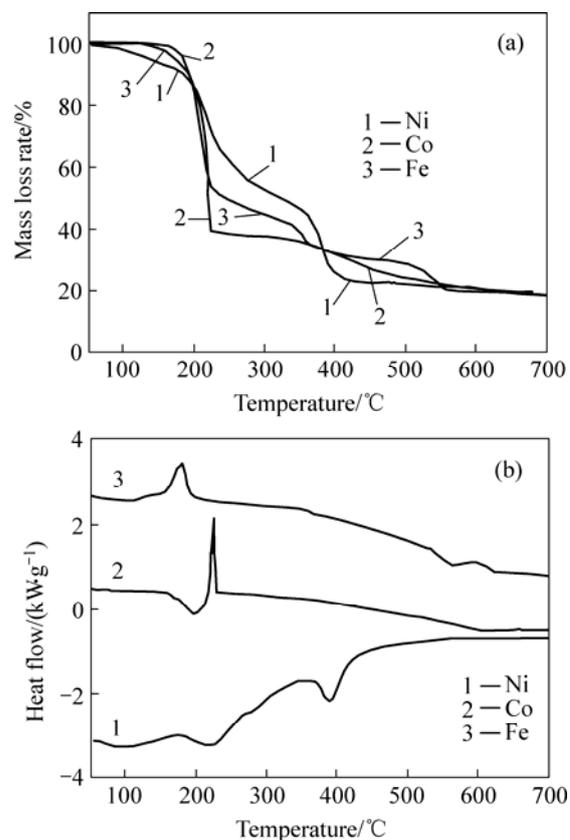

Fig.4 TG(a) and DSC(b) curves for gel precursors

2) At 170−350 ℃, large and sharp peaks occur in DSC curves, accompanying a substantial mass loss of 45%−60%, which is owing to the initial decomposition of the complexes and spontaneous combustion liberating H_2O, CO_2 and NO_x. Ni-citrate and Co-citrate gel exhibit a small and broad endothermic peak at about 225 and 200 ℃, respectively, caused by the decomposition of the complexes. At a light higher temperature, a large and sharp exothermic event occurs in the Co-citrate gel and Fe-lactate gel, corresponding to a quick mass loss, which is attributed to the spontaneous combustion between the nitrate ions and the carboxylate. The increase in the ratio of nitrate to carboxylate would result in an increase of the spontaneous combustion, because the nitrate ions provide an in situ oxidizing environment for the combustion of the organic materials[17]. The molar ratios of nitrate to carboxylate in the Ni-citrate, Co-citrate and Fe-lactate gel precursors are 0, 2:1 and 1:1 correspondingly. Therefore, the exothermic event due to the spontaneous combustion in the cobalt citrate gel is the most intensive.

3) At 350−600 ℃ and over, the decomposition of gel experiences a mass loss of 10%−15%. The decomposition at this stage comprises the oxidation of the residual organic materials, and the formation of the

corresponding metal oxides with an endothermic event. Ni-citrate gel exhibits a sharp endothermic peak at about 400 ℃, associated with the formation of NiO. A small endothermic peak occurring at about 550 ℃ for the Fe-lactate gel might be attributed to the formation of iron oxides.

Since the gel precursors contain amounts of organics, removal of these organics during the gel precursor to metal fiber conversion usually results in a large shrinkage and cracking of the fibers. Therefore, in order to produce dense and crack-free fibers, it is necessary to optimize heating rates and atmospheric conditions during the decomposition and reduction process.

According to the above analysis, the decomposition and reduction procedure was worked out. The maximum temperature of 700 ℃ for the thermal decomposition-reduction of the gel fibrous precursor was used to form metal fibers at a heating rate of 3 ℃/min under

atmosphere of N_2 (80%, volume fraction) + H_2(20%) for 1 h.

3.3 Characterization of metal fibers

The fibrous gel precursors after heat-treatment at 700 ℃ for 1 h, the nickel (curve 5 in Fig.1, JCPDS04-0850), cobalt (curve 4 in Fig.1, JCPDS15-0806) and iron (curve 6 in Fig.1, JCPDS06-0696) fibres were obtained. Fig.5 shows morphologies of the metal fibers with various diameters derived from the corresponding gel precursors under the above processing conditions. These metal fibers are flexible, dense and smooth in surfaces. Diameters of these metal fibers vary from 1 to 20 μm with a circular cross-section and the thinnest metal fiber is about 1 μm in diameter (Figs.5(b), (d), (f)) and an aspect ratio up to 1×10^6 and consists of nanosized grains at about 35−45 nm calculated by Scherrer equation from XRD data in Fig.1).
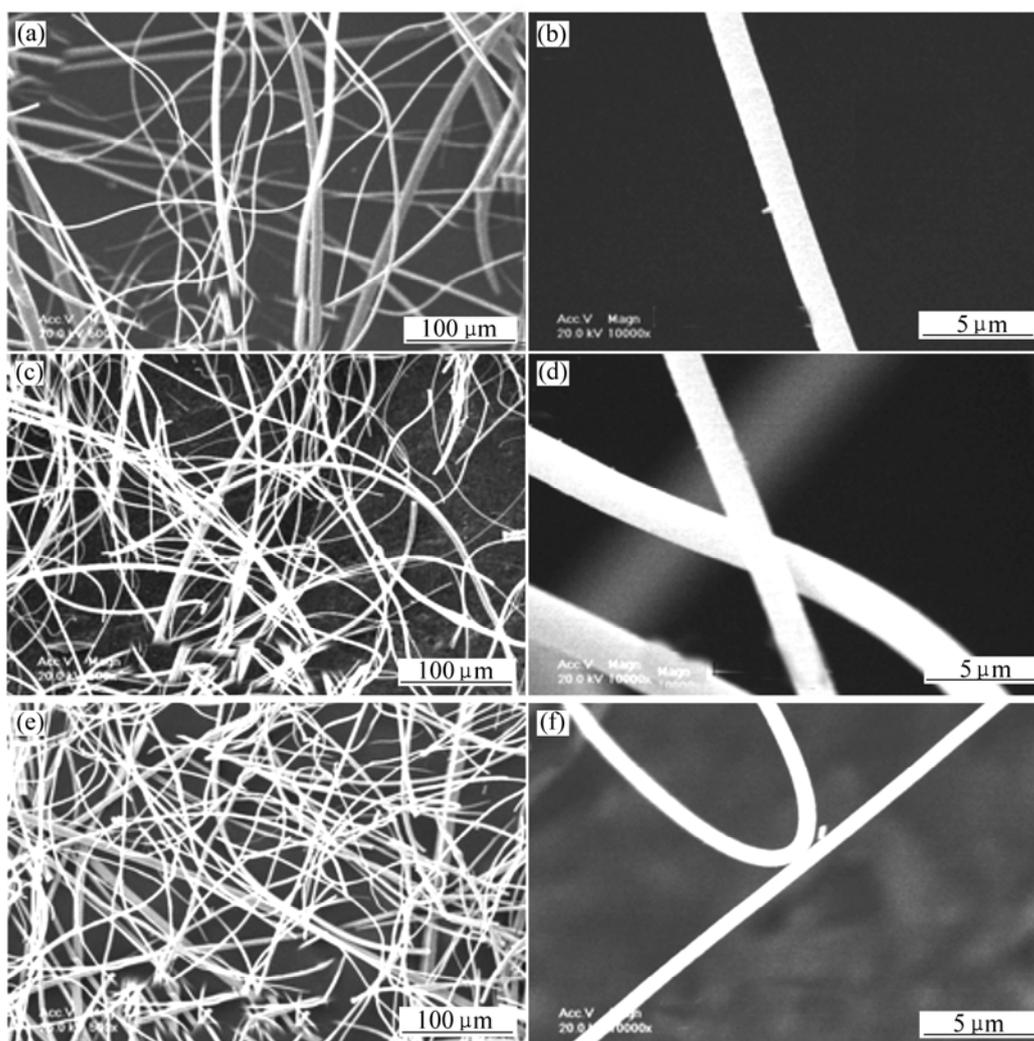

Fig.5 Morphologies of metal fibers
(a), (b) Ni-fibers; (c), (d) Co-fibers; (e), (f) Fe-fibers

4 Conclusions

1) The organic gel-thermal reduction process was successfully used for the preparation of ferromagnetic metal Ni, Co and Fe fine fibers using citric acid or lactic acid and metal salts as the starting reagents.

2) These ferromagnetic metal fibers consist of nanosized grains with small diameters and high aspect ratios.

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