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Preparation of fibrous nickel oxide particles①

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Abstract: The fibrous nickel oxide particles were prepared by chemical precipitation and pyrolysis method. The NiO precursors were firstly precipitated from nickel ions solution with addition of oxalate salt, and then the final NiO particles were obtained by pyrolysis of the precursor. The effects of the pH value, precipitation temperature, reactant concentration, addition of surfactant on the morphology of the precursor particles were investigated. The crystallinity, purity, morphology of the fibrous NiO were analyzed by XRD and SEM. The fibrous NiO particles with 100－120 in axis/diameter ratio may be produced under the optimal process conditions that are proposed: the Ni^{2+} concentration is 0.5－0.8 mol/L, pH value is 8.3－8.9, precipitation temperature is 60－75 ℃, pyrolysis temperature is 500－600 ℃.

Key words: chemical precipitation and pyrolysis; precursor; fibrous NiO particles; preparation

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1 INTRODUCTION

The nickel oxide (abbreviated as NiO thereafter) is a versatile material which has been found many applications in industrial fields. It is used as the key material in manufacture of battery electrode, catalyst, thermal sensitive element, gas sensitive element, functional ceramics, glass, electronic components and so on[1－8]. At present, the approaches available for ultrafine NiO particles production include carbonyl method, laser chemical method, pyrolysis by microwave, sol-gel method, pyrolysis by ultrasonic, precipitation-calcination etc[9－19]. The NiO particles produced by carbonyl method may be in high purity and narrow size distribution, however, the equipment and technology may be strictly required and emission of toxic gas is a potential problem and difficult to be avoided. The laser chemical method is a complicate process with high cost. Pyrolysis by microwave demands advanced equipment. Though the sol-gel method is available for production of spherical monor-dispersed NiO particles, the difficulties in washing and drying prevent it from industrial application. Certainly, owing to the relative simplicity and the low energy consumption, the chemical precipitation is a promising alternative in replace of the carbonyl method for NiO preparation. The common precipitation reagents are NaOH, Na_2CO_3 and $NaHCO_3$, which easily result in impure precipitates and excessive consumption of washing water. The above studies have been mainly focused on the spherical morphology. But only a limited research has been performed on a detailed introduction of the fibrous crystalline structure. Fibrous structures of powder are currently attracting considerable attention because of their potential applications in powder metallurgical field[20]. In order to obtain fibrous nanostructure of desired materials, various preparation methods have been developed including ultrasonic radiation, hydrothermal synthesis, in-situ method, γ-radiation method and other methods[21－26]. However, to the best of our knowledge, special conditions tedious procedures or complex apparatus may be required for these methods. In this study, the fibrous NiO particles were prepared by the method of wet chemical precipitation of nickel ions by oxalate salt followed by pyrolysis. The effects of the variable parameters in precipitation, such as solution pH value, temperature, reactant concentration, and surfactants(P) on the morphology, dispersion as well as the particle size of the precursor were investigated in detail, which are key factors for final product.

2 EXPERIMENTAL

The reagents $NiCl_2 \cdot 6H_2O$, ethanol, acetone,

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oxalate, surfactant (P) were all analytically pure. All the solutions were prepared elaborately by distilled water. In chemical precipitation, the ammonium oxalate solution was heated to certain temperature among 30 – 80 ℃, and sprayed into the bulk nickel ions solution with SONO-TEK modeled ultrasonic sprayer. The produced precipitation, so-called precursor, was washed with distilled water, then filtered and dried in a vacuum drier at 100 – 120 ℃. The precursor was input in a pipe-shaped furnace and heated at decomposition temperature of 500 – 600 ℃ in the air flow, and the final NiO particles was produced after the pyrolysis.

The crystalline phases of the as-precipitated and the sintered samples were characterized by D/max-rA10 powder X-ray diffractometer, using CuK_α radiation. The morphologies of the particles were observed with JSM-5600LV scanning microscopy. The thermogravimetric analysis and differential thermal analysis of the precursor were conducted with DUPont9900 thermal analyzer to detect the decomposition behavior of the as-precipitated samples.

3 RESULTS AND DISCUSSION

3.1 Effect of pH value

In order to obtain the fibrous NiO particles, the precursor particles should be precipitated with fibrous shape in morphology. It is considered that control of the solution pH in precipitation is significant. The results of the precursor particles obtained at different solution pH are shown in Fig. 1, from which it can be seen that when pH is less than 8, the precursor particles are in spherical-like shape. When pH is higher than 8, the particles are in fibre with satisfactory dispersion, and the optimum ratio in axis/diameter is 100 – 120. However, when pH is higher than 9.0, the length of the fibrous is become less and the cluster of the fiber tend to be corroded.

It is well known that the formation of the precursor particles includes the crystal nuclear formation and growth. Generally, if these two stages may be divided, the monodisperse particles with specific morphology may be anticipated. In the initial stage, the circumstance to promote the nuclear formation instead of the stable nuclear growth should be created; in the successive stage, the solution conditions to promote the stable nuclear growth and to prevent formation of new nuclear should be created. In solution with relatively low pH value, the precursor is certainly easier to grow as spherical-like particles (Fig. 1(a)), because of the low over-saturation resulting in low rate for the nuclear formation and growth. In suitable pH condition, the nuclear formation and growth may be divided and the monodisperse particles are formed. The produced fibrous shape may be due to the complexation action of the ammonia with nickel

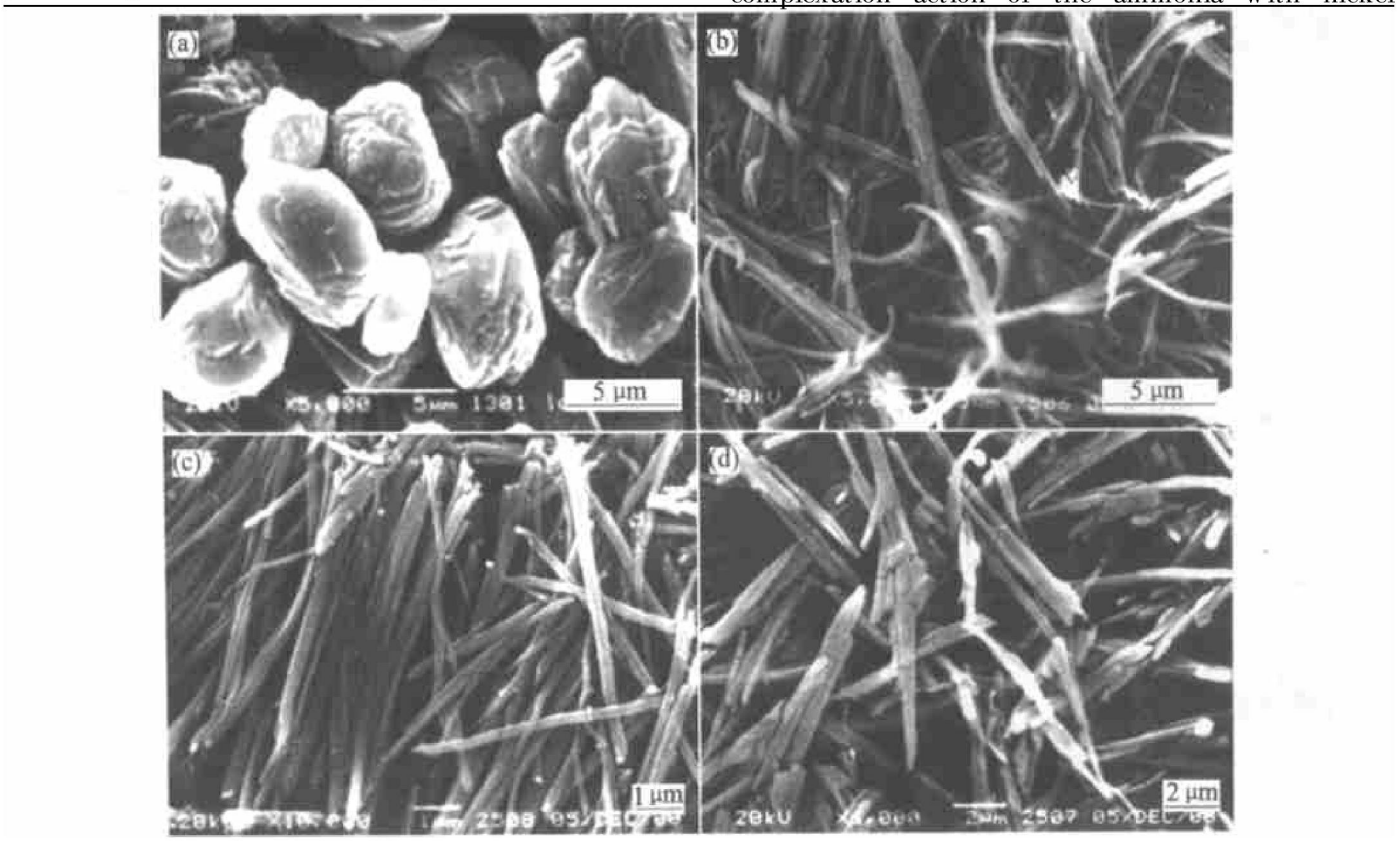

Fig. 1 SEM morphologies of precursor particles precipitated at different pH values
(a) —pH= 7.6; (b) —pH= 8.3; (c) —pH = 8.7; (d) —pH= 9.1

ions, which promote the particle growth dominant toward one direction. These specific morphology characteristics are shown in Fig. 1(b) and(c). However, in relatively higher pH condition, the growth of the particle is fast in the dominant direction, and the simultaneous growth in diameter direction is in relatively slow speed, by this way, the fibers grow in short length and the ratio in axis/diameter is smaller (Fig. 1(d)).

3.2 Effect of precipitation temperature

With the other conditions being kept constant, the temperature in precipitation exerts significant effect on the morphology and particle size of the precursor. It can be seen from Fig. 2 that at relatively low temperature, for example 60 ℃, the obtained particles are coarse (Fig. 2(a)). At 65 ℃, the fine and long fibrous particles are produced (Fig. 2(b)). With the temperature elevated, for example 75 ℃, the uniform fibrous particles are precipitated(Fig. 2(c)).

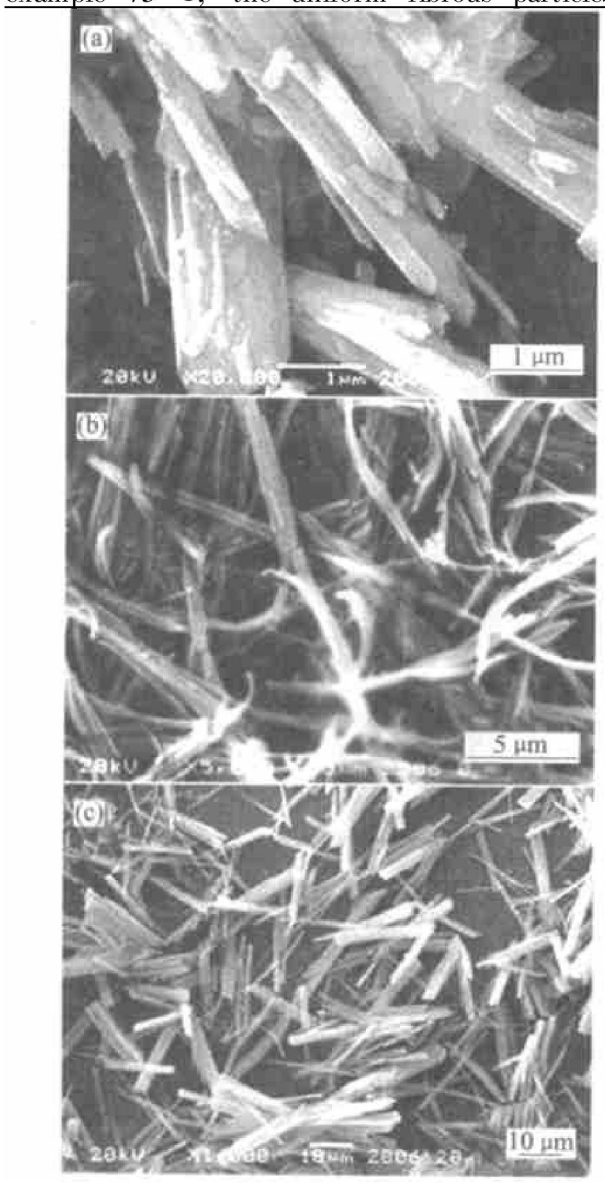

Fig. 2 SEM morphologies of precursor particles precipitated at different temperatures
(a) —t= 60 ℃; (b) —t= 65 ℃; (c) —t= 75 ℃

The morphology of the crystal is eventually determined by the relatively competitive growth of the different crystal plane orientation. The fast growing crystal plane will certainly disappear and the slow growing crystal plane may appear gradually. With the change of the physico-chemical condition the solution structure changes, that may lead to the change of the unit structure pattern of the crystal growth and the growing morphology of the particles to be different. Furthermore the temperature affects the nuclear formation and growth, because increasing temperature is beneficial for lowering the viscosity and increasing the diffusion of ions, and promotes the crystal growth as fibre[27].

3.3 Effect of reactant concentration

Under the condition of the precipitation conducted at same temperature, the change of the reactant concentration has obvious impact on the morphology of precursor particles, and the results obtained at different reactant concentrations are shown in Fig. 3. In this case, the precipitating reagent is in the excess of chemical stoichiometry. It can be found from the results that when the molar ratio of Ni^{2+} to $C_2O_4^{2-}$ is 1.0∶1.1, the reaction may be conducted completely. In this excessive ratio, the concentration of the nickel ions exerts pronounced influence on the morphologies of the precursor particles, that is, with increase of Ni^{2+} concentration, there are different morphological features of the produced particles. When Ni^{2+} concentration equals 0.4 mol/L, the specific morphology of the particles is in stick-like shape, and the axis/diameter ratio is relatively small(Fig. 3(a)); when Ni^{2+} concentration exceeds 0.5 mol/L, the fibrous precipitation with satisfactory dispersion and small diameter is produced (Fig. 3(b) and (c)). However, from Fig. 3(d), it is found that at even higher concentration, i.e., Ni^{2+} concentration equals 1.0 mol/L, the short stick particles are produced. Conclusively, adoption of suitable nickel salt concentration is important to produce the fine particles with satisfactory performance. The optimum Ni^{2+} concentration is 0.5－0.8 mol/L in this study.

3.4 Effect of surfactant

It is commonly realized that addition of suitable surfactant is useful for improving the dispersion of the particles and producing small size particles with specific morphology. The effect of the surfactant on the precursor was investigated and the results are shown in Fig. 4. It is clear that the fibrous particles are obtained with the addition of 0.2% (mass fraction) surfactant (P) (Fig. 4(a)). However, in the case of no surfactant addition, the

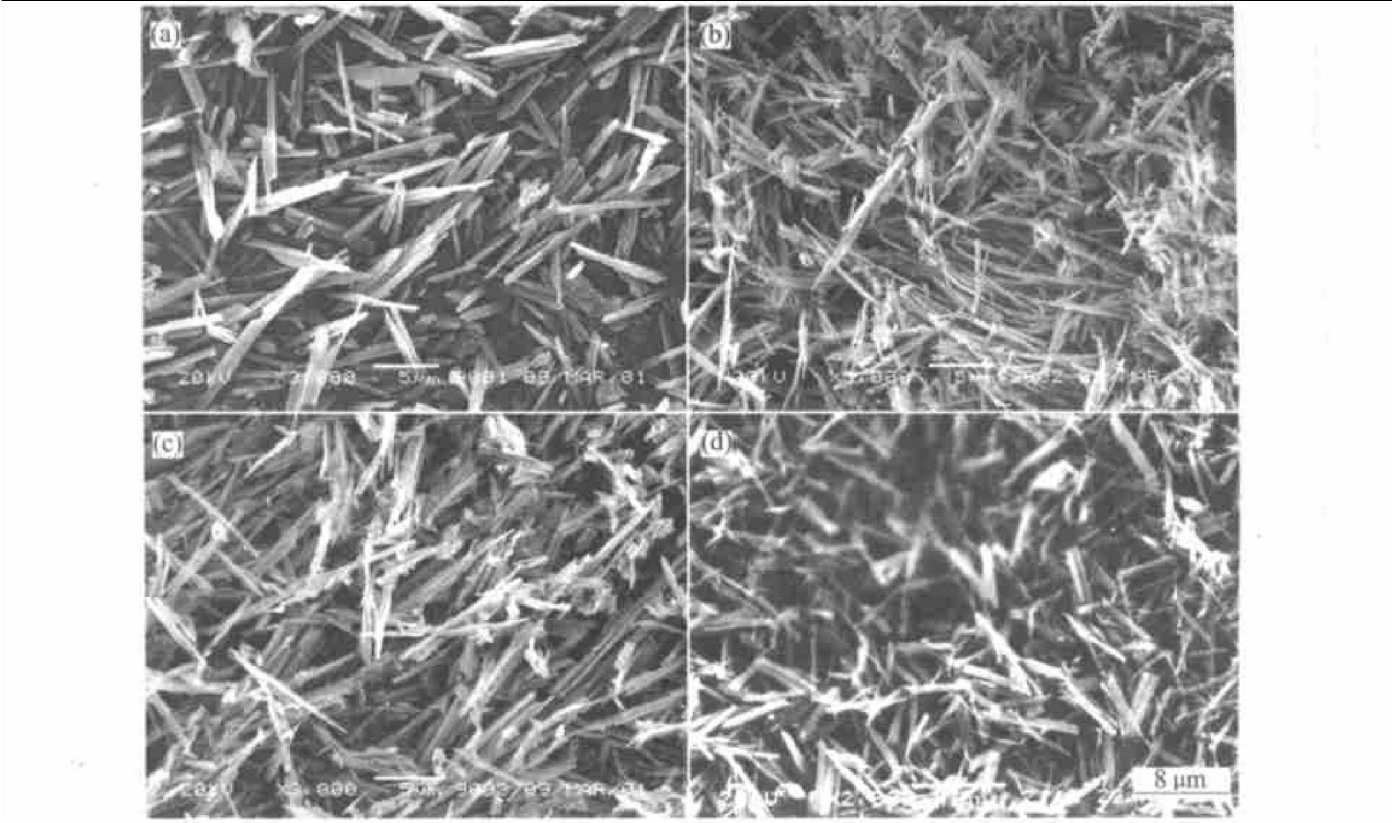

Fig. 3 SEM morphologies of precursor particles precipitated at different Ni^{2+} concentrations
(a) $-c(Ni^{2+}) = 0.4$ mol/L; (b) $-c(Ni^{2+}) = 0.6$ mol/L;
(c) $-c(Ni^{2+}) = 0.8$ mol/L; (d) $-c(Ni^{2+}) = 1.0$ mol/L

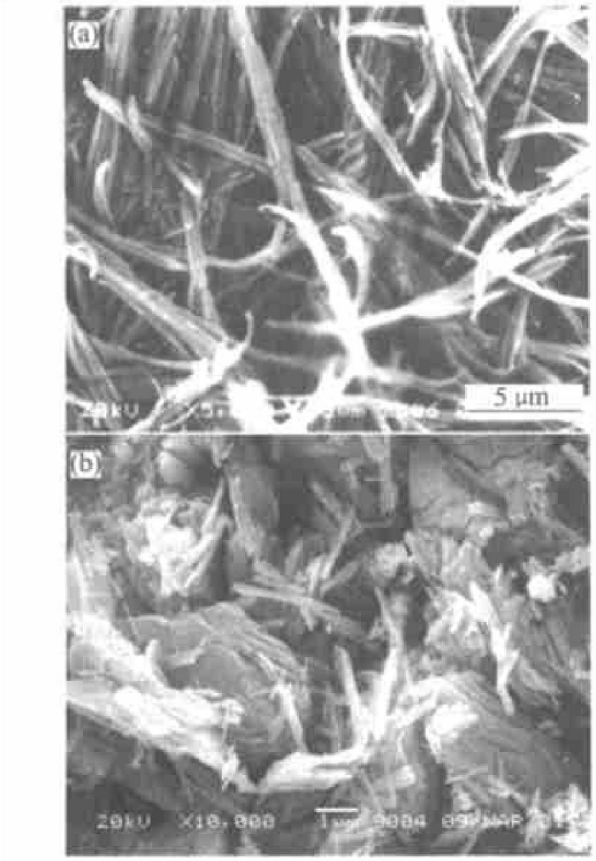

Fig. 4 SEM morphologies of precursor particles precipitated with(a) or without(b) surfactant (P)

obtained particles accumulate very seriously (Fig. 4 (b)). The surfactant(P), though added in less content, may covers on the surface of the particle to form a thin film, which is useful for improving the dispersion of the particles. The optimum content of the surfactant (P) should be controlled in the range of 0.1% - 0.5%. Too less in the content, the effectiveness is not obvious; whereas too high in its content, the solution composition may be changed and it is difficult for ions diffusion.

3.5 X-ray diffraction analysis of precursor

Fig. 5 illustrates the X-ray diffraction patterns of the precursor. It can be found that the diffraction peaks are quite complicate, suggesting that the precursors are poor crystal.

3.6 TGA and DTA curves of precursor particle

Fig. 6 shows the thermogravimetric analysis (TGA) and differential thermal analysis (DTA) curves of the precursor particle. From the TGA curve, it can be calculated that the mass loss terminated at about 400 ℃ and the total mass loss is about 64.24%. In corresponding DTA curve, there are two thermal adsorption peaks, one is in the range of 62.7 - 100 ℃, and the mass loss is 15% - 16%, which may be caused by the release of the ammonia in the NiC_2O_4-$(NH_3)_z \cdot nH_2O$; the other peak is relative wide between 200 ℃ and 250 ℃, with about 11% - 12% of corresponding mass loss, which may be caused by the release of the crystal water molecules contained in NiC_2O_4-

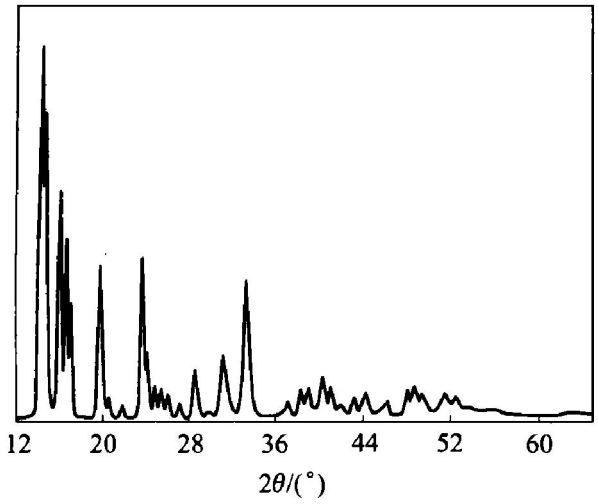

Fig. 5 XRD pattern of precursor particle

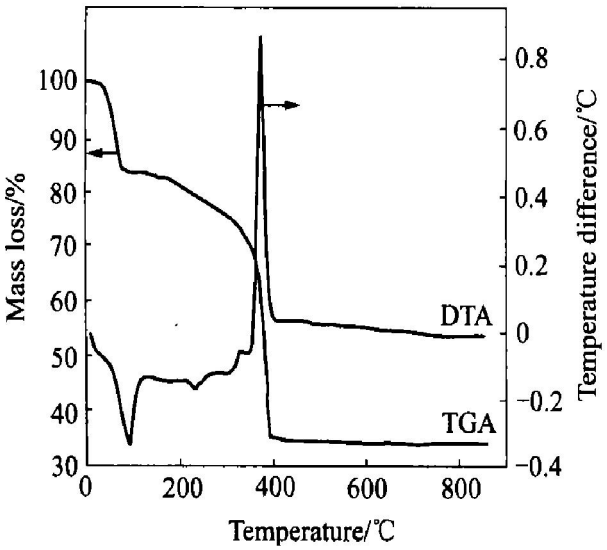

Fig. 6 TGA and DTA curves of precursor

$(NH_3)_z \cdot nH_2O$. In the temperature of 350 - 400 ℃, there is acute thermal release peak and correspondingly about 40% of the mass loss occurs, which is certainly the process of decomposition of the precursor and formation of crystal NiO. The acute peak originates from the exothermic reaction in the oxidation, and by this way, the precursor particles are decomposed at high temperature to produce the fine crystal NiO from the poor precursor. Thereafter, there is no peak appearing, proving that the pyrolysis may be completed at 400 ℃ and the stable product is obtained.

3.7 X-ray diffraction and morphology of fibrous NiO particles

Fig. 7 shows the X-ray diffraction pattern of the finial product. It can be seen that there are peculiar peaks for the decomposed product, indicating that the precursor in low crystallinity has been converted into fine crystal product after pyrolysis. By comparing the positions and the standard JCPDS card of cubic NiO, it is found that both are quite consistent, proving that the decomposed product is cubic NiO. The morphology of the fibrous NiO is observed by scanning electron microscope(SEM) as shown in Fig. 8. It can be seen that NiO crystal may inherit morphology of the precursor particles displaying fibrous shape.

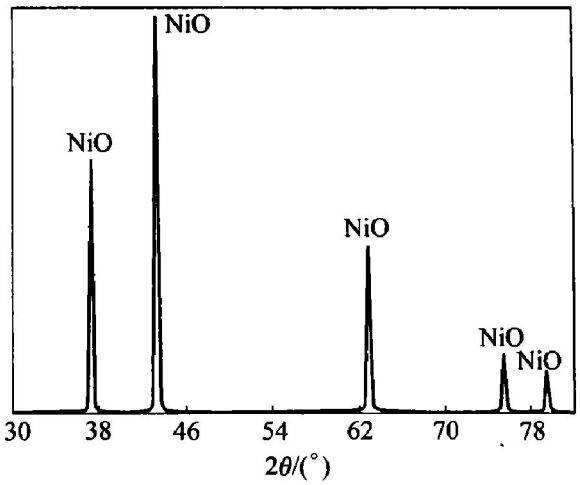

Fig. 7 XRD pattern of fibrous NiO particle

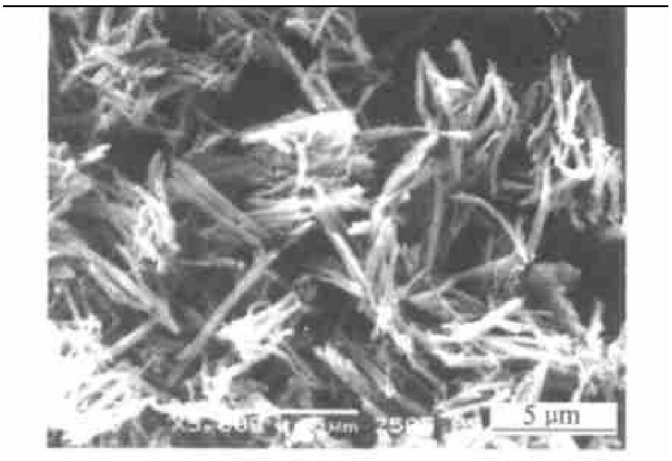

Fig. 8 SEM morphology of fibrous NiO particle
(Pyrolysis condition: 600 ℃, 40 min, in air)

4 CONCLUSIONS

1) The fibrous NiO precursor particles may be precipitated from the solution of nickel ion reacted with oxalate salt; and the precursor can be decomposed to NiO particles in the air. The final decomposed particles may inherit the morphology of the precursor particles.

2) In the condition of pH= 8.3 - 8.9, precipitation temperature 60 - 75 ℃, initial nickel salt concentration 0.5 - 0.8 mol/L and with addition of surfactant reagent (P), the precursor particles with specific fibrous morphology and fine dispersion may be produced.

3) The final product NiO may be produced with fine dispersion, 100 - 120 in axis/diameter ratio.

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