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ARTICLE

Guidance Evolution Mechanism of Nickel Oxalate Micro-structure for Formation of Polycrystalline Nickel Nano-fibers

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Abstract: Nickel oxalate nano-fibers were controllably synthesized via a restricted self-assembly growth process in a liquid phase precipitation system. Nickel nano-fibers were prepared by decomposing nickel oxalate under the guidance of fiber micro-structure in Ar gas atmosphere. The characteristics of the samples were measured by X-ray powder diffraction (XRD), scanning electron microscope (SEM) and transmission electron microscope (TEM). Result show that the existence of ammonia changes the growth behavior of nickel oxalate from free self-assembly mode to a restricted one. The nickel oxalate crystal nano-fibers with monoclinic geometry are 100~200 nm in diameter, and 1~5 μm in length. The nickel nano-fibers with face-centered cubic geometry are also 100~200 nm in diameter, and 1~5 μm in length, and the surface is very rough. Nickel nano-fibers are formed via a process of nucleation, grain growth and aggregation under the guidance of long and narrow space provided by nickel oxalate nano-fibers.

Key words: nickel; fibers; guidance evolution mechanism; chemical synthesis, thermal-decomposition

Nickel nano-materials with good properties of electrics, magnetics and chemistry, also with various external morphological characteristics (nano-powders, nano-fibers, nano-plates, nano-tubes, etc.), are widely applied in diverse fields such as internal electrodes of Multi-layer Ceramic Capacitor (MLCC)[1,2], storage media[3,4], catalysts[5-7], and fillers of conductive components[8,9]. With the electromagnetic pollution becoming a severe problem, the microwave absorbing materials develop very quickly. Among the microwave absorbing materials, nickel based nano-fibers, due to their unique fundamental of large aspect ratios, sensibility of microwave, and easily forming fibrous network, were usually used as microwave absorbing and shielding materials [10-13].

Among the preparation methods of nickel nano-fibers, oxidation-reduction, template and thermal decomposition were facile and widely used. Chou et al[14] used $NiCl_2 \cdot 6H_2O$ as oxidant and $N_2H_2 \cdot H_2O$ as reductant for preparing nickel nano-fibers with 0.5~2.0 μm in diameter, and very long in length. Zeng et al[15] obtained the nickel hollow fibers with trilobed structure and 20 μm in diameter, by calcining Ni/cellulose acetate hollow fibers. Motoyama et al[16] used track-etched polycarbonate (PC) membranes as the template, by electro-deposition, to synthesize nickel nano-wires with diameter from 15 nm to 200 nm. Wang et al[17] obtained polycrystalline nickel fibers with 93 nm in diameter and 1.866 μm in length, by self-assembly process in ethylene glycol solution. Otherwise, in the application of thermal decomposition method, preparation of fiber-like precursors by the common methods of electro-spinning, organic-gel, and precipitation, was the key procedure. By the thermal decomposition method, the basic characteristics of precursors once are formed, such as fibroid morphology, which can be maintained for a long time. Barakat et al[18] obtained nickel fibers with diameter 25 nm by electro-spinning and thermal treatment. Shen et al[19] prepared nickel fibers with less than 1 μm in diameter, and 2 m in length. Li Tao et al[20,21] have indicated that nickel oxalate nano-fibers and nickel nano-sheets can be prepared by liquid phase precipitation and thermal decomposition. As a result, the thermal decomposition of preparing nickel fibers were studied for many

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systems; however, the mechanism of crystal grain growth and the inner structure evolution were investigated less.

In the present work, on the basis of preparation of the nickel nano-fibers by the method of liquid phase precipitation and thermal decomposition [20-23], we further investigated the restricted and guidance growth mechanism of synthesis of nickel oxalate nano-fibers precursor and the inner structure evolution of nickel nano-fibers.

1 Experiment

The $NiCl_2$ $6H_2O$, PVP, NH_4OH, and C_2H_6O were analytically pure regents (AR) which were purchased and used without further purification. In a typical synthesis, 0.4 mol/L ammonium oxalate aqueous solution was prepared by dissolving ammonium oxalate monohydrate and moderate PVP into de-ion water. 0.42 mol/L nickel dichloride ethanol solution was prepared by dissolve nickel dichloriding hexahydrate into ethanol. The two solutions above were heated to 50 ℃ in baking box. Then, ammonium oxalate aqueous solution was sprayed into nickel dichloride ethanol solution under continuous stirring, and ammonia water was dropped into the mixed turbid liquid quickly for adjusting the pH value to 7.0. After that, the turbid liquid after reaction was put aside for 24 h at the temperature of 50 ℃. Finally, the light blue precipitate was filtered and washed multiple times with water and n-butyl alcohol, and then was dried in a vacuum oven at 90 ℃ for 12 h.

In a tubular oven filled with Ar gas, the dried nickel oxalate powders were decomposed into metal nickel powders at the temperature of 350 ℃ for 40 min.

XRD (X-ray powder diffraction) patterns were recorded by an X’Pert Pro (Holland Philips) using Cu radiation (Kα, λ= 0.154 18 nm) operating at 40 kV and 40 mA with 2θ ranging from 10 ° to 120 ° and continuous scanning mode. The SEM (Scanning electron microscope) images were taken with an Ultra 55 (German ZEISS) Field-emission scanning electron microscope. TEM (Transmission electron microscopy) images were taken with a Libra 200FE (German ZEISS) transmission electron microscope at an accelerating voltage of 200 kV.

2 Results and Discussion

2.1 Characteristics of nickel oxalate nano-fibers

Fig.1 shows the significant diffraction peaks located at 18.69 °, 22.72 °, 29.95 °, and 35.57 °, which correspond to the $(\bar{2}02)$, (002), $(\bar{4}02)$, and (021) crystal planes of nickel oxalate hydrate, respectively, indicating the formation of nickel oxalate crystal with monoclinic geometry (JCPDS: 25-0581). The strongest diffraction peak $(\bar{2}02)$ implies that the crystal growth direction of nickel oxalate seed is favorably oriented parallel to the $[\bar{2}02]$ direction. According to the values of the $(\bar{2}02)$ and $(\bar{4}02)$ peaks, calculated with Scherrer formula $D=0.89\lambda/(\beta\cos\theta)$, the nickel oxalate crystal size is about 35 nm. λ is the X-ray wavelength, β is the half-height width of the XRD peak, and θ is the Bragg angle.

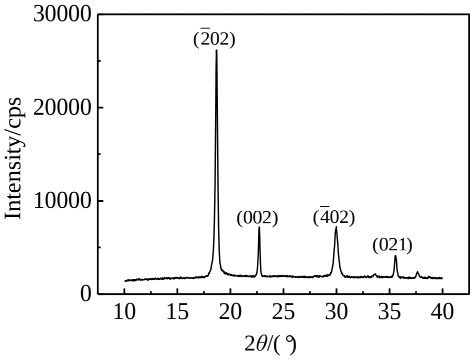

Fig. 1 XRD pattern of nickel oxalate nano-fibers

Fig.2 shows SEM and TEM images of nickel oxalate fibers as-prepared. SEM image shows that the powders consist of a large quantity of well-separated, uniform and nano-sized fibers (Fig.2a), and the surface of fiber is a little rough. SEM and TEM images show that the fibers are very fine and thin, which are 100~200 nm in diameter, and 1.0~5.0 μm in length. The clear electron diffraction ring set in Fig. 2b indicates that the nickel oxalate nano-fibers are of good polycrystalline.

2.2 Characteristics of nickel nano-fibers

XRD pattern show three significant diffraction peaks located at 44.59 °, 51.99 °, and 76.52 °, which correspond to the (111), (200), and (220) crystal planes of nickel, respectively (Fig. 3), indicating the formation of nickel crystal with face-centered cubic geometry (JCPDS:04-0850). The strongest diffraction peak (111) implies that the crystal growth direction of nickel seed is favorably oriented parallel to the [111] direction. According to the β values of the (111) and (200) peaks, the average crystal size of nickel nano-fibers calculated with Scherrer formula $D = 0.89\lambda/(\beta\cos\theta)$, D is about 25 nm.

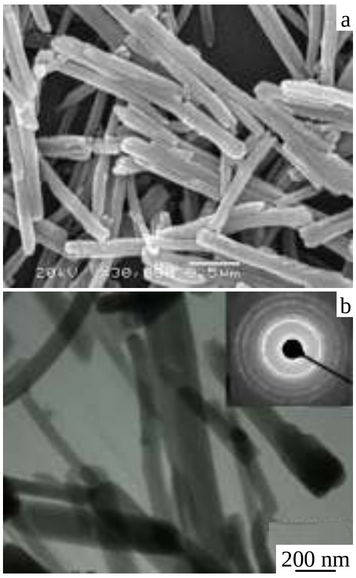

Fig. 2 SEM (a) and TEM (b) images of nickel oxalate fibers

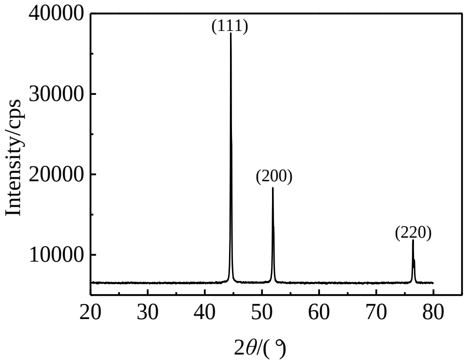

Fig.3 XRD pattern of nickel nano-fibers

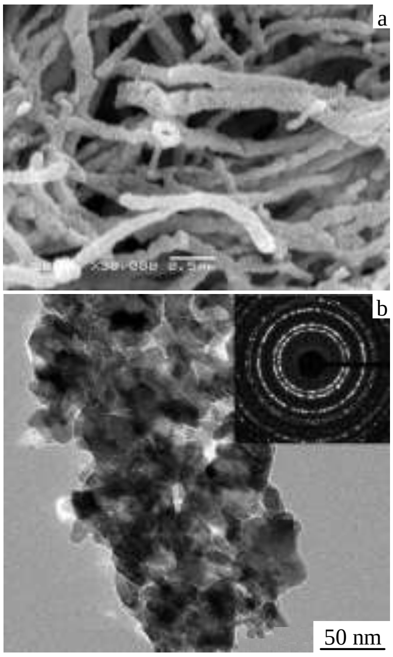

Fig.4 SEM (a) and TEM (b) images of nickel nano-fibers

Fig.4a shows that the powders consist of a large quantity of well-separated, and uniform nickel nano-fibers, which surface is very rough. The nickel nano-fiber is 100~200 nm in diameter and 1~5 μm in length. TEM provides further insight into the morphologies and structure details of this nickel product. Fig.4b indicates that the fibers are made of much small nickel monocrystalline connecting together into fibers structure. The single crystal size is less than 25 nm in diameter, which is nearly the size of calculated value of 25 nm. TEM image also shows the appearance of black alternating with white, the black area is crystal grain, and the white area is crystal boundary. So the inner structure of nickel nano-fibers as-prepared is not continuous. The electron diffraction ring set in Fig.4b indicates that the nickel nano-fibers are of good polycrystalline.

2.3 Mechanism of formation of nickel oxalate and nickel fibers

In the present paper, the mechanism of formation of nickel nano-fibers consists of two main steps: growth of polycrystalline nickel oxalate nano-fibers via ionic liquid precipitation process (Fig.5a~5c) and formation of polycrystalline nickel nano-fibers via thermal decomposition process in inert gas atmosphere (Fig.5d~5g).

In the process of growth of polycrystalline nickel oxalate nano-fibers, when ammonium oxalate solution is sprayed into nickel dichloride solution under continuous stirring, the pH value increases, at the same time nano-sized primary particles are nucleated in a supersaturated solution via the reaction process between Ni^{2+} and $C_2O_4^{2+}$, and grow to the crystal grains, which are shown as Fig.5a and 5b. When ammonia water is dropped into the mixed turbid liquid quickly, the pH value becomes high and there are a lot of NH_3 molecules in the mixed precipitation system. As a result, the growth behavior changes from free mode to restricted one, owing to the existence of ammonia water in precipitation system, so the nickel oxalate nano-fibers were formed (Fig.5c).

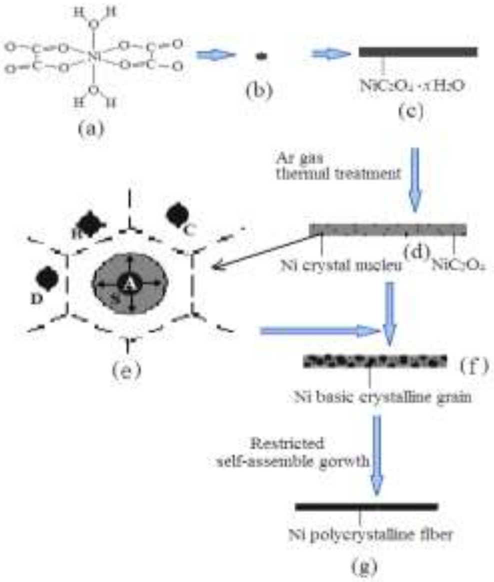

Fig. 5 Schematic illustration of the formation process of nickel oxalate and nickel nano-fibers

In the other process of preparation of polycrystalline nickel nano-fibers, nickel oxalate nano-fibers dehydrate the crystal water firstly, when thermal treating in Ar gas. Then, nickel oxalate decomposed, and the nickel crystal nuclei are formed via the aggregate process of nickel atoms, and dispersed irregularly in the volume space formed by nano-fibers (Fig.5d). In the growth process of nickel nuclei, many gravitation areas, for example marked with letter S, are formed around nickel nuclei marked with letter A (Fig.5e). A great deal of nickel nuclei grow in the gravitation areas, by capturing the nickel atoms created newly. As a result, a large quantity of nickel basic crystal grain is formed and dispersed irregularly in the volume space of nano-fibers (Fig.5f). Finally, along with the action of restricted growth and aggregation of a large quantity of nickel crystals in the volume space formed by the nickel oxalate precursor nano-fibers, also with the shrinkage of fiber space, the well crystallized polycrystalline nickel nano-fibers was obtained (Fig.5g).

3 Conclusions

1) Polycrystalline nickel nano-fibers with face-centered cubic geometry, 100~200 nm in diameter, and 1~5 μm in length, are obtained via thermal decomposition process using nickel oxalate nano-fibers as precursor, at 350 ℃ for 40 min, in the atmosphere of Ar gas.

2) In the synthesis process of nickel oxalate nano-fiber precursor, it self-assembly grow with quasi one- dimensional mode, under the restriction and guidance of the space structure formed by ammonia molecules which are adsorbed on the surface of nickel oxalate crystal.

3) In the formation process of polycrystalline nickel nano-fibers, the nickel crystal nuclei are created by decomposition of nickel oxalate. Then the nickel crystal nuclei grow and aggregate under the conditions of restriction and guidance, in the long and narrow space structure created by nickel oxalate nano-fibers. As a result, a large quantity of polycrystalline nickel nano-fibers are formed.

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草酸镍前驱体纤维微结构诱导制备多晶态纳米镍纤维的演化机理

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摘 要：在离子液相沉淀体系中，通过受限自组装生长可控制备草酸镍纳米纤维。在氩气环境中，在纤维微结构诱导下，通过热分解草酸镍纤维制备出镍纳米纤维。通过 X 射线衍射 (XRD)、扫描电镜 (SEM) 和透射电镜 (TEM) 等技术检测所得样品的性质。结果表明，氨的存在使草酸镍的生长习性从自由自组装模式转变为了受限自组装模式，制备的草酸镍纤维具有单斜晶体结构，直径 100~200 nm，长度为 1~5 μm。 热分解制备的镍纤维表面粗糙，具有面心立方晶体结构，直径 100~200 nm，长度为 1~5 μm。在草酸镍纤维形成的细而长空间的诱导作用下，镍原子经过成核、生长和聚合过程，从而形成纤维状纳米镍。

关键词：镍；纤维；结构诱导；化学合成；热分解

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