Synthesis and One-Dimensional Self-Assembly of Acicular Nickel Nanocrystallites under Magnetic Fields

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Received: July 20, 2003; In Final Form: November 5, 2003

Polycrystalline nickel wires with an average length of 10 μm and diameter of about 200 nm were prepared at 70 °C by a hydrothermal process with a 0.25 T magnetic field applied. Studies show that the magnetic field induced one-dimensional assembly of acicular Ni nanocrystallites with dimensions of 200 nm in length and 10−30 nm in diameter, leading to the formation of the polycrystalline nickel wires. Magnetic measurements show saturation magnetization (Ms) of the sample prepared in a 0.25 T external magnetic field is higher than that of the sample synthesized without an external magnetic field applied. It is suggested that the one-dimensional self-assembly of acicular nickel nanocrystallites with their magnetic easy axes [111] aligned along the magnetic line of force results in the improvement of the magnetic properties.

Introduction

Nanoscale magnetic materials have attracted intensive interest because of their potential applications including high-density magnetic recording, magnetic sensors, and addressing some basic issues about magnetic phenomena in low-dimensional systems.[1−4] Magnetic metal materials, such as Fe,[5,6] Co,[7−9] and Ni,[10,11] have been studied for many years. Various approaches have been developed to prepare nanoscale magnetic metal materials, including metal carbonyl pyrolysis,[12,13] water-in-oil microemulsion,[14] hydrogen arc plasma,[15] γ-ray irradiation,[16] borohydride reduction of metal salts,[17] and templated synthesis.[18] However, little attention has been paid to the effect of a magnetic field on the nucleation and growth process of magnetic materials and on the self-assembly behavior of magnetic nanocrystallites. It has been indeed found that the magnetic field can significantly influence the movement of magnetic particles.[19−21] It is, therefore, significant to study the growth and self-assembly behavior of magnetic nanocrystallites under an external magnetic field. In a recent letter, we reported the results of magnetic-field-induced self-assembly of spherical Co particles.[22] Co polycrystalline wires with an average length of 2 mm and diameter of 13 μm were formed by the self-assembly of Co nanocrystallites (15 nm in average size) under the induction of a 0.25 T external magnetic field. The wires were nearly parallel, likely due to their axes were all parallel to the magnetic line of force. Because of Co nanocrystallites without shape anisotropy, it is hard to understand whether a magnetic easy axis oriented to the magnetic line of force determines the assembly behavior of magnetic particles or not. In this paper, we further report the self-assembly behavior of acicular nickel nanocrystallites with great shape anisotropy under magnetic induction.

Experimental Section

In a typical experiment, all the reagents are analytical grade and are used as received. Quantities of 0.5 g of $Ni(CH_3CO_2)_2 \cdot H_2O$, 0.8 g of PEG ($M = 10000$), 0.3 g of CTAB, and 45 mL of distilled water were mixed in a flask at room temperature. A grass-green color was observed in the solution after strongly stirring for half an hour. A half-hour ultrasound treatment was carried out to ensure that Ni^{2+} ions were dispersed homogeneously in the solution. Then 5 mL of 80 wt % hydrazine hydrate solution was added dropwise into the solution, and the color changed from grass green to navy blue after strongly stirring for several minutes; the main possibility is the formation of a coordination compound of $Ni[N_2H_4]_6$. The solution was transferred into two Teflon-lined stainless steel autoclaves with 60 mL capacity (one without a magnet attached, and another with a magnet made of NdFeB under the Teflon vessel; the strength of the magnetic field on the inner surface of the Teflon vessel is 0.25 T at room temperature), respectively. Both of the autoclaves were closed tightly to perform hydrothermal processes at 70 °C for 3 h. After the reaction was completed, the resulting black precipitates were separated and washed with alcohol and distilled water several times, respectively, in order to remove the remaining PEG and CTAB. The as-synthesized products were dried in a vacuum oven at 40 °C. The samples obtained were characterized by X-ray powder diffraction (XRD) using an 18 kW advanced X-ray diffractometer with Cu Kα radiation ($\lambda = 1.54056$ nm) and high-resolution transmission electron microscopy (HRTEM) (JEOL-2010). The TEM images and selected area electron diffraction pattern (SAED) were taken with a HITICHAI H-800 microscope. The scanning electron microscopy (SEM) was also taken on a HITICHAI X-650 microscope. Magnetic hysteresis loops were measured using a vibrating sample magnetometer (VSM, BHV-55). For magnetization measurements, the powder was pressed strongly and fixed in a small cylindrical plastic box.

Results and Discussion

A controlled hydrothermal synthesis route was developed to prepare acicular nickel nanocrystallites at low temperatures. The chemical reaction for the synthesis can be expressed as Scheme 1. The standard Gibbs free energy change $\Delta G°$ of reaction 2 implies a very strong tendency to progress toward the right side.

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10.1021/jp0361172 CCC: $27.50
Published on Web 03/05/2004

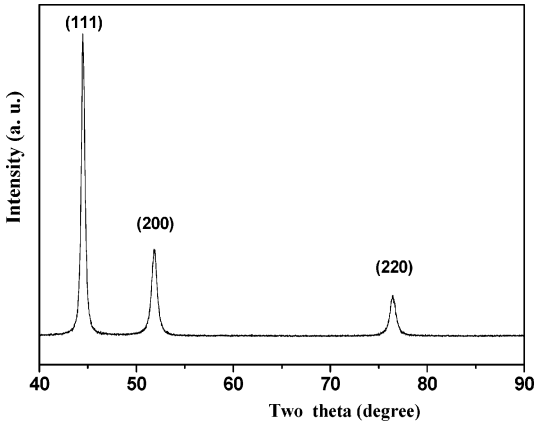

Figure 1. XRD pattern of nickel nanocrystallites prepared with a 0.25 T magnetic field applied.

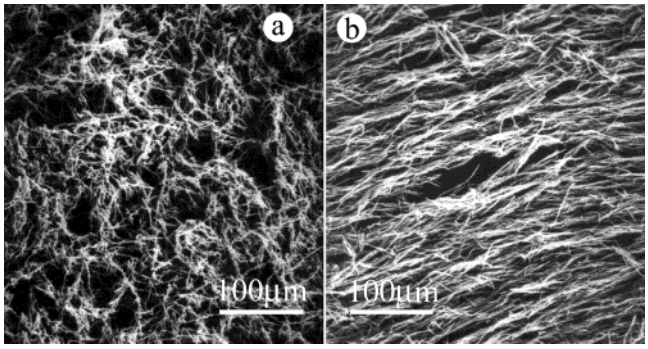

Figure 2. SEM micrographs of products prepared at 70 °C for 3 h (a) without and (b) with a 0.25 T magnetic field applied.

SCHEME 1: The Chemical Reaction for the Synthesis of Nickel Nanocrystallites

$$Ni(AC^-)_2+2en \longrightarrow Ni(en)_2^{2+}+2AC^- \quad (1)$$

$$2Ni(en)_2^{2+}+N_2H_4+4OH^- \longrightarrow 2Ni+N_2+4en+4H_2O \quad (2)$$

$$AC = CH_3COO\ ,\ en = NH_2CH_2CH_2NH_2$$

The XRD patterns of the products prepared with and without an external magnetic field applied are similar. Figure 1 shows an XRD pattern of the obtained product with a 0.25 T external magnetic field applied. It can be well indexed with the reflections of face-centered cubic Ni (PDF standard cards, JCPDS 01-1260, space group *Fm*3*m*), without impurity peaks. Furthermore, the broadening of the peaks is obvious, and the crystalline size is about 25 nm, calculated by the Scherrer's equation from the full width at half-maximum (fwhm) of (111), (200), and (220) reflections. The size distribution could fall into the stable single domain range of magnetic particles; hence, each crystallite might contain a single magnetic domain.[19] As we know, single-domain magnetic particles with uniaxial anisotropy are fascinating for magnetic recording media.

Spherical particles are common due to the low surface energy associated with the morphology.[23] It is reported that CTAB associated with the polymer chains could facilitate the formation of rod-shaped micelles;[24,25] in our experiments polymer (PEG) and surfactant (CTAB) complexes were employed for controlled-synthesis nickel nanocrystallites with shape anisotropy. Figure 2 shows the difference in morphology between the products prepared with (AF sample) and without (ZF sample) an external magnetic field applied during particle growth. The morphology of the ZF sample appears disorderly, consisting of zigzag wires, while the AF sample contains highly oriented straight wires; this indicates that a magnetic field can effectively affect the aggregation of nickel nanocrystallites.

To further reveal the fine structure of the wires shown in Figure 2b, TEM analysis was also carried out. Figure 3, parts a and b, depict straight wires with an average length of 10 μm and diameter of about 200 nm forming in the AF sample, while zigzag wires formed in the ZF sample. To understand well the effect of magnetic field on the linear alignment feature of acicular nanoparticles, a postsynthesis magnetic induction experiment was carried out on the ZF sample. It is observed that after postsynthesis induction by a 0.25 T magnetic field, the morphology of the particles in the ZF sample is still zigzag wires (a1, inset of Figure 3a); no straight wires such as those that appeared in the AF sample were observed, which further reveals that the magnetic structure of acicular nanoparticles could be strongly modified by a magnetic field during particle formation. These acicular nanoparticles can be aligned to form straight wires under a magnetic field. It is found the dipole magnetic interactions of these nanoparticles in the wires are quite strong. As a rule, samples must be sonicated continuously for more than half an hour to prepare a sample for TEM observation; however, straight wires have not been destroyed, indicating that the polycrystalline wires are rather stable as a result of strong magnetic interactions. Figure 3c shows a magnified image of an individual polycrystalline wire. The acicular nanoparticles are about 200 nm in length and 10−30 nm in diameter. The SAED pattern (c1, inset of Figure 3c) for one typical wire also shows that it is polycrystalline. The diffraction pattern can readily be indexed as (111), (200), (220), (331) of the face-centered cubic Ni with $a = 3.517$ Å. An individual acicular nanocrystallite was characterized by HRTEM analysis. The SAED pattern (Figure 3C (c2)) reveals the acicular nanocrystallite to be single crystalline. An HRTEM image of a nanocrystallite is shown in the inset of Figure 3C (c3). The nanocrystallite is imaged to have nearly parallel lines, which are nickel atomic planes separated by about 2.03 Å, corresponding to the {111} planes of a face-centered cubic nickel crystal. The growth orientation of an acicular nanocrystallite is along the {111} planes, namely, the long axis of the nanocrystallite is perpendicular to the [111] axis. It is known that [111] is the magnetic easy axis of a cubic nickel crystal.[26] The nanocrystallites are not oriented growing along the magnetic easy axis under magnetic induction, which indicates that the magnetic field could not have an influence on the growth direction of Ni nanocrystallites although a significant effect on their assembly was observed.

Regardless of whether or not an external magnetic field was applied, the acicular nickel nanocrystallites were formed by addition of PEG and CTAB. The acicular nickel nanocrystallites will aggregate due to dipolar interaction, which is affected by several factors such as velocity of nucleation, spacial hindrance, dipolar interaction, and magnetic field alignment as well. It is known that the magnetic anisotropy energy (MAE) is the lowest when magnetizing along the magnetic easy axis. [111] is the magnetic easy axis of a cubic nickel crystal. When an external magnetic field is applied, magnetization makes the magnetic easy [111] axes of all particles orientate along the magnetic line of force, leading to acicular nanocrystallites to be arranged regularly and finally the formation of straight wires. Because nanocrystallites did not aggregate along other directions such as long axes of acicular nanocrystallites, but the magnetic easy axes, it is, therefore, suggested that the alignment of the magnetic easy axis along the magnetic line of force determined

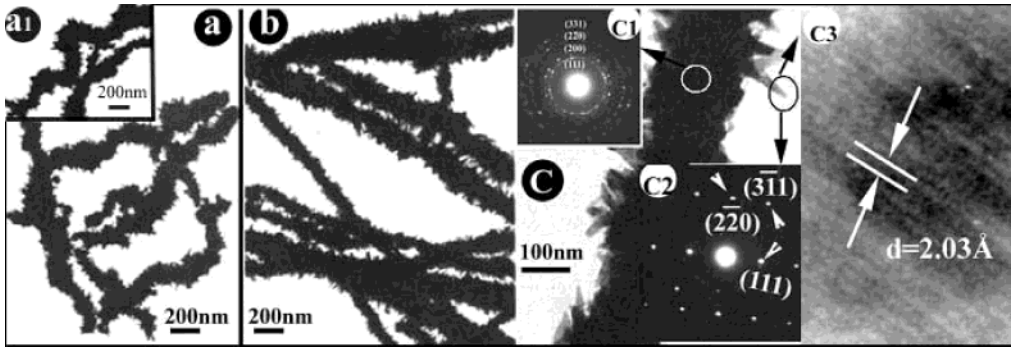

Figure 3. Representative TEM images of two samples obtained(a) without and (b) with a 0.25 T external magnetic field applied. Inset in (a) shows an image of a sample postsynthesis magnetic alignment of the ZF sample under a 0.25 T magnetic field a_1. (c) A magnified image of a wire within (b), of which c1 and c2 are two SAED patterns taken on the surface of a wire and an acicular nanocrystallite, respectively, and c3 is its HRTEM image.

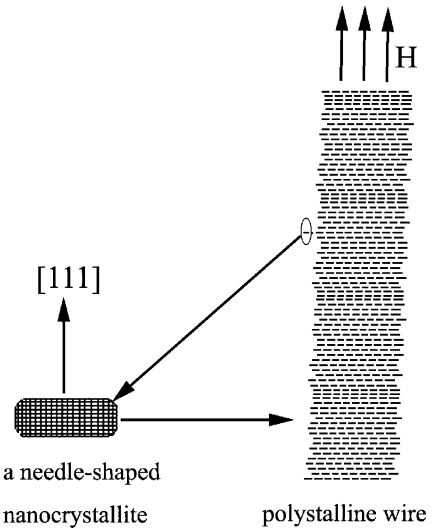

Figure 4. Sketch of the ideal process of assembly of acicular Ni particles induced by an external magnetic field.

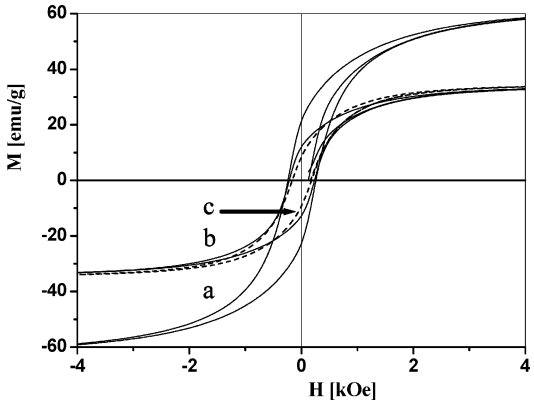

Figure 5. The hysteresis loops measured at room temperature for three samples obtained (a) with a 0.25 T and (b) without an external magnetic field applied, (c) the hysteresis loop (line of dashes) of the nanorods postsynthesis magnetic alignment under a 0.25 T magnetic field.

their self-assembly behavior and the morphology of aggregates formed. The formation of straight wires through magnetic field alignment is schematically shown in Figure 4. The morphology of the particles formed under magnetic induction is straight wires with acicular Ni nanocrystallites homogeneously distributed. However, the actual aggregating process is very complicated, determined by nucleation, spacial hindrance, magnetic attraction of excessive finer particles, and other kinetic factors. When no external magnetic field is applied, the orientation of each magnetic domain is spontaneously random. The acicular nanocrystallines may magnetize one another by dipolar interaction in an arbitrary direction, which finally results in formation of zigzag wires.

Figure 5 shows M−H hysteresis loops of the products prepared with (a) and without (b) an external magnetic field applied. The Ms for the sample formed with a 0.25 T and without an external magnetic field applied are 59 and 33 emu/g, respectively. The saturation value of bulk nickel is 55 emu/g.[27] Generally, the Ms for nanoscale magnetic materials is lower than that for corresponding bulk material because the spin disorder on the surface and surface oxidation would significantly reduce the total magnetic moment.[28] Accordingly, it is reasonable to explain the decrease of Ms for the ZF sample prepared without a magnetic field applied, but it is hard to understand that the Ms for the AF sample prepared under a magnetic field is higher than that of the ZF sample, even the corresponding bulk Ni (7%). It is hard to understand the 7% difference of the Ms for the AF sample compared to that of the bulk Ni. It might arise from the systematic and accidental error due to the nature of the nanowires being measured, inconstant environmental conditions, limitations in instruments et al., but it is worth emphasizing that the increase tendency of Ms for the AF sample is obvious, when compared to that for both the AF sample and nanoparticles fabricated by other group. The Ms value of ZF sample prepared without an external magnetic field applied is very consistent with that of the nanoscale Ni particles reported in the literature (32 emu/g, ref 29). Moreover, the Ms value of AF sample is almost two times as large as that of ZF sample with the measurements for the two samples being carried out in the same manner. We, therefore, suggest that the self-assembly structure of acicular Ni nanocrystallites formed under a magnetic field could significantly improve the magnetic properties. The magnetic easy axis [111] of acicular Ni nanocrystallites is aligned along the long axis of the polycrystalline wires oriented parallel to the magnetic force line of the external magnetic field, which would improve the Ms. Therefore, it is suggested that Ms for acicular Ni nanoparticles is largely dependent on alignment of the easy axis, not only dependent on some above-mentioned factors such as size of crystallites and degree of surface oxidation. The coercivity Hc for the two samples with and without magnetic induction is 51 and 45 Oe, respectively. Although the value for the AF sample is higher than the corresponding value for the ZF sample, both are much lower than that of the corresponding bulk material (Hc = 100 Oe),[27] which indicates that magnetic nanocrystallites have a tendency to be in a superparamagnetic state. As shown in Figure 5, parts b and c, the Ms and Hc of the ZF sample

after postsynthesis magnetic alignment under a 0.25 T magnetic field are still much lower than that of the AF sample, which also reveals that the magnetic structure of Ni nanoparticles can be modified during their formation under a magnetic field, which would affect the magnetic-field-induced alignment behavior and finally the magnetic properties of Ni nanoparticles.

Conclusions

In conclusion, polycrystalline nickel nanowires with an average length of 10 μm and diameter of about 200 nm were formed through a low-temperature hydrothermal process by magnetic induction. It is found that an external magnetic field can make acicular Ni nanocrystallites one-dimensionally self-assemble with their magnetic easy axes aligned along magnetic line of force, leading to the formation of polycrystalline wires. The as-prepared Ni wires possess higher Ms than that of the Ni nanocrystallites formed without a magnetic field applied. The magnetic easy axis [111] is aligned along the long axis of the polycrystalline wires, which would improve Ms as the wires oriented parallel to the line of the external magnetic field during the magnetic measurements. It is suggested that this process could be a promising approach to improving the magnetic properties and forming arrays of uniform wires of magnetic materials.

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