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LETTERS

Arrays of Ferromagnetic Iron and Cobalt Nanocluster Wires

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We report a fabrication of arrays of ferromagnetic iron and cobalt nanocluster wires (NCWs), ranging from 8 to 10 nm in diameter and up to a few millimeters in length. The iron and the cobalt nanoclusters served as building blocks of the corresponding ferromagnetic NCWs. The iron and the cobalt nanoclusters were produced by thermally decomposing the corresponding metal carbonyl vapors with a resistive heater placed in the middle of a pair of permanent disk magnets. The NCWs were produced through pile-up of metallic nanoclusters along lines of magnetic flux, perpendicularly to the substrates attached to a pair of permanent disk magnet surfaces. We observed coercivities as large as 248 and 964 oersteds and remanences as high as 61 and 71% for the ferromagnetic iron and cobalt NCWs, respectively.

There is no doubt that the nanowires (NWs) have drawn a special attention from all of us because of their properties quite different from the bulk, resulting from nanometer-scale one-dimensional structure and their potential applicability to engineer a variety of state-of-the-art nanodevices.[1] For instance, the most spectacular of these may be arrays of ferromagnetic NWs which may be useful for a perpendicular magnetic recording.[2−4] In this work, we report a very easy fabrication of arrays of ferromagnetic nanocluster wires (NCWs), including characterization of their structures, physical dimensions, and magnetic properties. Here, the NCW is named because the NW consists of metallic nanoclusters.

The experimental setup used in the present experiment is quite simple, as represented in Figure 1. Here, the stainless steel reaction chamber is very similar to the one used to generate a variety of metallic nanoclusters by thermally decomposing metal carbonyl vapors with a resistive heater in the previous work.[5] The reaction chamber was evacuated with a 50 L/s mechanical pump down to 10^{-3} Torr. Even at this vacuum level, metallic

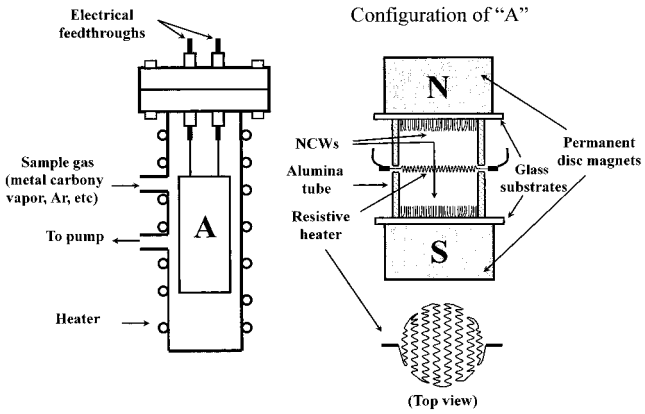

Figure 1. A schematic experimental setup.

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oxide production was minimal. The NCW production area is indicated as "A" in Figure 1 and the detailed configuration of "A" is represented to the right-hand of the reaction chamber. The "A", just hung by two electrical copper wires connected to the resistive heater and through which the alternating current (AC) flows, consists of a pair of permanent disk magnets, a tube spacer, a resistive heater, and the substrates. The electrical copper wires were electrically shielded with Teflon tubes. A pair of permanent disk magnets, separated from each other by a tube spacer provided magnetic field strength of 3000−4000 G at the center. To protect the permanent disk magnets from the ferromagnetic nanoclusters, etc., produced during experiment, they were wrapped with aluminum foils and the aluminum foils were removed after experiment. An alumina tube spacer with an inner diameter of 14 mm and a tube length of 15 mm was used but both dimension and material of the tube spacer can be changed. A resistive heater placed in the middle of the alumina tube spacer was used to decompose the metal carbonyl vapors into the metal atoms and the COs. A Nichrome alloy wire was used as a resistive heater in the present experiment but any kind of material can be used as a resistive heater. The glass substrates with 1 mm thickness were used in the present experiment but any kind of material can be used. The glass substrates were attached to the permanent disk magnet surfaces on which the NCWs grew. The metallic nanoclusters were produced near to the resistive heater environment through numerous collisions between the decomposed neutral metal atoms. To evenly decompose the metal carbonyl vapors and thus, to evenly produce the NCWs over the glass substrates, the resistive heater was shaped such as the top view represented in Figure 1. Here, the resistive heater temperature was kept at 300−400 °C in order to break only the metal atom−CO bond. Above this temperature, the CO was also dissociated into C + O, from which both undesirable metal carbides and oxides were also produced. The vapor pressures of both $Fe(CO)_5$ and $Co_2(CO)_8$ metal carbonyls used in the present experiment were 15−20 Torr, but can be changed. The $Fe(CO)_5$ metal carbonyl vapors were directly introduced from the lecture bottle into the vacuum chamber, whereas the $Co_2(CO)_8$ metal carbonyl vapors were obtained by heating the vacuum chamber up to ∼100 °C into which the solid $Co_2(CO)_8$ metal carbonyls were loaded. The iron or the cobalt nanoclusters produced near to the resistive heater environment were equally pulled in two opposite directions by the magnetic field applied by a pair of permanent disk magnets and piled up through aggregation perpendicularly to the glass substrates (see Figure 1). It took only a few minutes to complete the fabrication of arrays of NCWs. At the above conditions, arrays of NCWs, ranging 8 to 10 nm in diameter and up to a few millimeters in length were fabricated.

The NCWs grew through aggregation of metallic nanoclusters along lines of magnetic flux. Without a magnetic field, however, only the metallic nanoclusters had been produced.[5] Thus, the size and the structure of individual nanoclusters are conserved in the NCWs, as confirmed from the high-resolution transmission electron microscope (HRTEM) micrographs and the X-ray diffraction (XRD) patterns, respectively, which will be discussed later.

Figure 2a−h represents the scanning electron microscope (SEM) micrographs of arrays of the ferromagnetic iron and cobalt NCWs. It is interesting to note that the NCWs exist as a bundle of NCWs somewhat like woolen yarn, as can be seen in Figure 2c,g for the ferromagnetic iron and cobalt NCWs, respectively, which likely originates from the fact that the NCWs are so long (∼ a few millimeters) that they cannot maintain straightness and thus, are tangled together with neighboring NCWs to form bundles of NCWs. Each magnified picture of one bundle of NCWs is represented in Figure 2d,h for the ferromagnetic iron and cobalt NCWs, respectively.

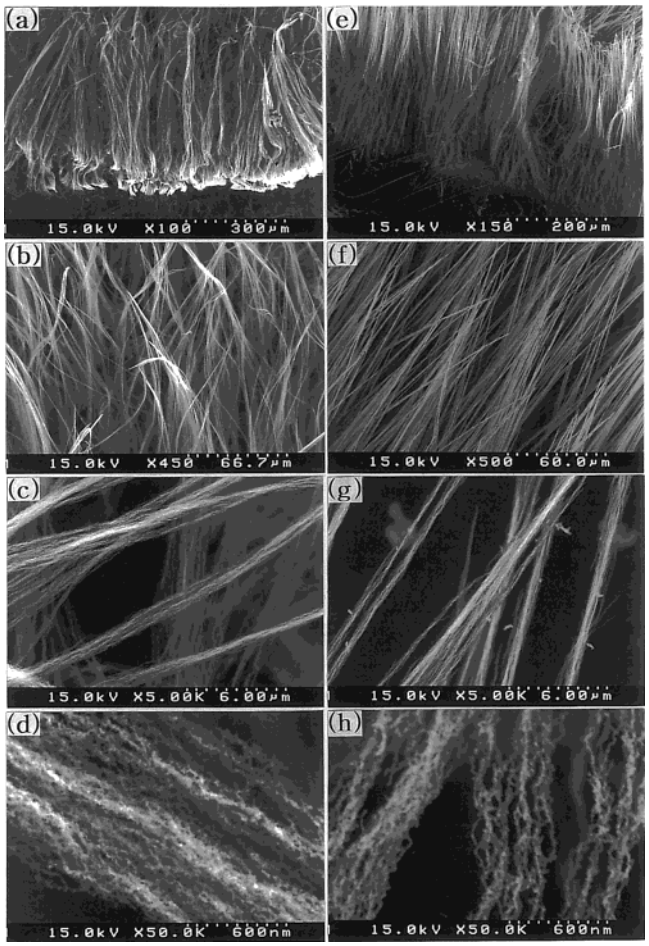

Figure 2. The SEM micrographs of arrays of (a) − (d) the iron NCWs and (e) − (h) the cobalt NCWs.

Figure 3a−c represents the HRTEM micrographs of the ferromagnetic iron (Figure 3a) and cobalt (Figure 3b,c) NCWs. Here, the diameter of NCW ranging from 8 to 10 nanometers can be observed for both ferromagnetic iron and cobalt NCWs. Figure 3c represents two cobalt NCWs connected to each other (the connected area is indicated as an arrow), which is produced while the NCWs are tangled together with neighboring NCWs because the NCWs cannot maintain straightness due to their long length as mentioned before. Examples of individual nanoclusters are represented as arrows in Figure 3a,b for the iron and the cobalt nanoclusters, respectively, which are barely visible due to a tight aggregation between nanoclusters.

The structures of the ferromagnetic iron and cobalt NCWs were characterized by using the XRD patterns, as represented in Figure 4a,b, respectively. Since the ferromagnetic NCWs consist of metallic nanoclusters as roughly observed in the HRTEM micrographs (Figure 3a−c), the structures of NCWs should correspond to those of metallic nanoclusters. The XRD patterns indicate that the iron nanoclusters consist of a body-centered-cubic (bcc) structure whereas the cobalt nanoclusters consist of a fcc structure with some contribution from a hexagonal close packing (hcp) structure because the broad feature below the fcc (111) peak fits well to the three hcp peaks. The cell constants are estimated to be 2.8697 ± 0.0011 and 3.5413 ± 0.0068 Å for the iron and the cobalt nanoclusters,

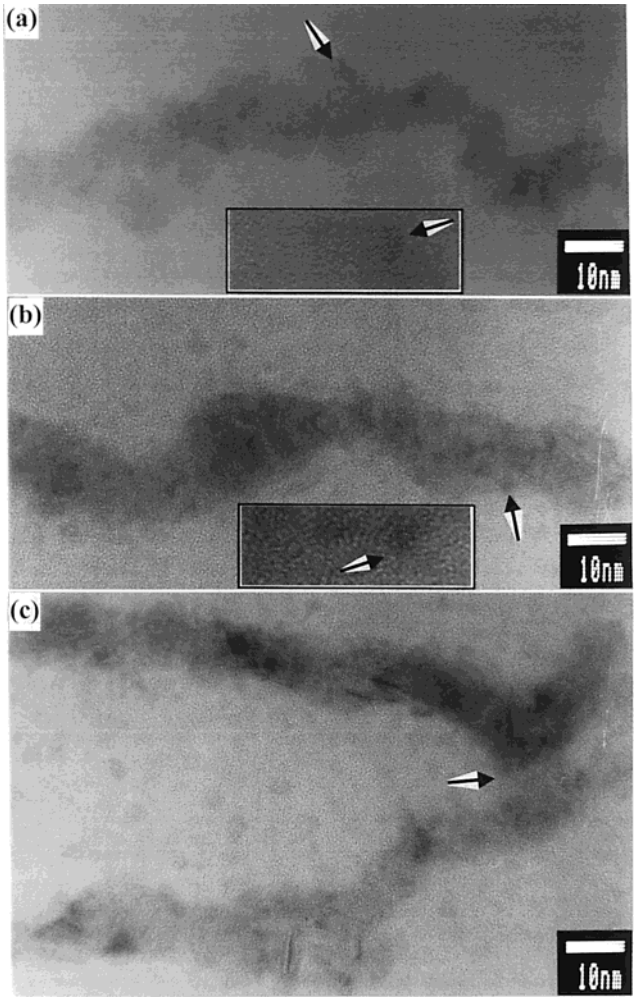

Figure 3. The HRTEM micrographs of (a) an iron NCW, (b) a cobalt NCW, and (c) two cobalt NCWs connected to each other. Examples of individual nanoclusters are represented as arrows in both original (10 nm scale) and further magnified (shown in a box, 3.8 nm scale) micrographs for the same nanoclusters, which are barely visible due to a tight aggregation between nanoclusters. The arrow in (c) indicates a connected area between two cobalt NCWs.

respectively, which are in good agreement with those of the corresponding bulk metals, respectively.[6,7] The cluster diameters of the iron and the cobalt nanoclusters estimated by using the full width at half-maximums (fwhms) of 1.483 ± 0.010 and 2.027 ± 0.137°, for the iron and the cobalt nanoclusters, respectively, and the peak centers of 44.657 ± 0.019 and 44.303 ± 0.090° for the iron and the cobalt nanoclusters, respectively, and by using the Scherrer's formula[8] are 5.82 ± 0.34 and 4.26 ± 0.29 nm, for the iron and the cobalt nanoclusters, respectively, which are consistent with those roughly estimated from the HRTEM micrographs, respectively. Here, both fwhms and peak centers were obtained by fitting the (110) peak of the iron nanoclusters and the (111) peak of the cobalt nanoclusters to the Lorentzian function. It is likely that both metallic atoms and metallic molecules were also drawn by the magnetic field along lines of magnetic flux and deposited together with the metallic nanoclusters to become the part of NCWs. The NCWs, however, mostly consist of metallic nanoclusters because amorphous peaks which originate from both metallic atoms and metallic molecules are negligible in the XRD patterns (see Figure 4a,b).

To characterize the magnetic properties, we measured the hysteresis loops by using the Magnetic Property Measurement

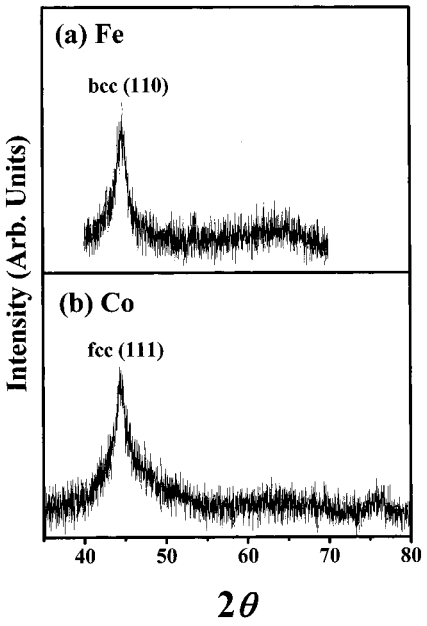

Figure 4. The XRD patterns of (a) the iron NCWs and (b) the cobalt NCWs. The assignments are the Miller indices (*hkl*).

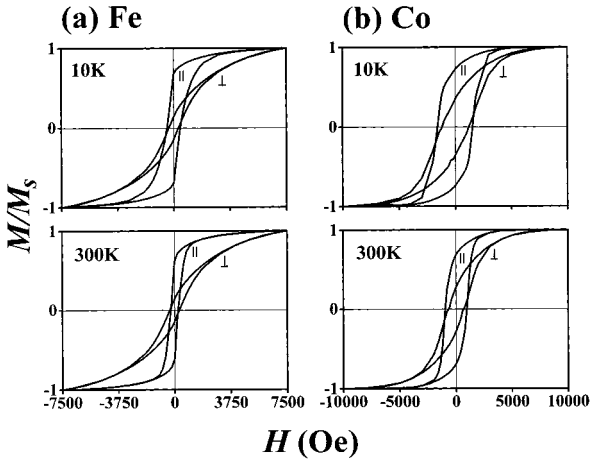

Figure 5. The hysteresis loops of (a) the iron NCWs and (b) the cobalt NCWs with the magnetic field applied parallel (||) and perpendicular (⊥) to the NCWs at 10 and 300 K. M/M_s indicates the magnetization (M) normalized by the saturated magnetization (M_s).

System (MPMS). Figure 5a,b represents the hysteresis loops of the ferromagnetic iron and cobalt NCWs with magnetic fields applied parallel ($H_{||}$) and perpendicular ($H_{\perp}$) to the NCWs, respectively. As expected, the remanences of the $H_{||}$ (i.e., the "easy axis") are much higher than those of the $H_{\perp}$ for both ferromagnetic iron and cobalt NCWs due to the demagnetizing field in the $H_{\perp}$.[9] Here, the magnetic properties of the $H_{||}$ are important for the perpendicular magnetic recording. The coercivities as large as 248 and 964 oersteds and the remanences up to 61 and 71% for the $H_{||}$ have been observed at 300 K for the ferromagnetic iron and cobalt NCWs, respectively. We noticed that both coercivities and remanences for the $H_{||}$ could be improved by improving the collection technique of the NCWs because the number of the NCWs which possessed the original straight direction could be maximized.[10] Thus, the actual coercivities and remanences for the $H_{||}$ will be higher than the measured values given above. At 10 K, the coercivities as large as 439 and 1576 oersteds and the remanences up to 69 and 72% for the $H_{||}$ have been observed for the ferromagnetic iron and

cobalt NCWs, respectively, and are all higher than those measured at 300 K, simply because of lower temperature. All of these values are much higher than the corresponding bulk values.

The possible application area of arrays of ferromagnetic NCWs may be a high density perpendicular magnetic recording.[3,4] The high remanences and the large coercivities, resulting from the single domain nature of the small iron and cobalt nanoclusters which are the components of the corresponding NCWs, together with a dense population of NCWs in the arrays, may make these arrays extremely useful for a high density perpendicular magnetic recording. In addition, fabrication of arrays of NCWs is quite simple as described previously and more importantly is suitable for a large scale production and costs low, and dimension of arrays of and length of NCWs can be easily modified by using a pair of permanent disk magnets with a different disk area and a different metal carbonyl vapor pressure, respectively, as described before, which are certainly the great advantages over the other fabrication methods used to produce arrays of NWs.[1,2] There is, however, no doubt that a further technical improvement should be made to the present arrays in order to make these arrays useful for a high density perpendicular magnetic recording.

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References and Notes

(1) See, for example, Komarneni, S.; Parker, J. C.; Hahn, H. *Nanophase and Nanocomposite Materials III*; Material Research Society: Warrendale, 2000; Vol. 581, pp 213−250.

(2) Whitney, T. M.; Jiang, J. S.; Searson, P. C.; Chien, C. L. *Science* **1993**, *261*, 1316.

(3) Speliotis, D. E. *J. Magn. Magn. Mater*. **1999**, *193*, 29.

(4) White, R. L. *J. Magn. Magn. Mater*. **2000**, *209*, 1.

(5) Huh, S. H.; Oh, S. J.; Kim, Y. N.; Lee, G. H. *Rev. Sci. Instrum*. **1999**, *70*, 4366.

(6) Villars, P.; Calvert, L. D. *Pearson's Handbook of Crystallographic Data for Intermetallic Phases*; American Society for Metals: Metal Park, 1985; Vol. 3, p 2162.

(7) Villars, P.; Calvert, L. D. *Pearson's Handbook of Crystallographic Data for Intermetallic Phases*; American Society for Metals: Metal Park, 1985; Vol. 2, p 1736.

(8) Cullity, B. D. *Elements of X-ray Diffraction*; Addison-Wesley: Reading, 1978; p 102.

(9) Chikazumi, S. *Physics of Ferromagnetism*, 2nd ed.; Clarendon Press: Oxford, 1997; pp 11−17.

(10) To measure both $H_{||}$ and $H_{\perp}$ hysteresis loops, the NCWs were collected simply by using a tape while a pair of permanent disc magnets were applied in order to maintain the original straightness of NCWs as much as possible. It is important to note that both actual coercivities and remanences should be all higher than the measured values because it is impossible to collect all of NCWs with their original straightness maintained. At 300 K, the coercivities and the remanences of the iron NCWs were in the range from 70 to 248 oersteds and from 34 to 61%, respectively, for the $H_{||}$ and from 170 to 318 oersteds and from 10 to 13%, respectively, for the $H_{\perp}$, and the coercivities and the remanences of the cobalt NCWs were in the range from 578 to 964 oersteds and from 68 to 71%, respectively, for the $H_{||}$ and from 673 to 690 oersteds and from 20 to 28%, respectively, for the $H_{\perp}$.