CoCr Binary Nanocluster Wires: Enhanced Magnetic Properties of the Co-rich Phase

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We report fabrication of CoCr binary nanocluster wires (NCWs) by thermally decomposing $Co_2(CO)_8/Cr(CO)_6$ metal carbonyl vapors by using a resistive heater placed in the middle of a pair of permanent disk magnets. In general, NCWs grow through the pile-up of binary CoCr nanoclusters perpendicularly to the substrates attached to the magnet surfaces. NCWs, ranging from 10 to 20 nm in diameter and also branching out while they grow, exist as a bundle. The bundles with lengths up to 2−3 mm form a three-dimensional array. We observed much higher coercivities and larger remanences for arrays with magnetic field applied parallel to the NCWs than those with magnetic field applied perpendicular to the NCWs. Importantly, we observed that arrays of CoCr NCWs with a 0.8−2.2 mol % Cr in which only Co-rich phase exists showed enhanced magnetic properties, that is, nearly doubled coercivities compared to that of the array of pure Co NCWs. When the Cr mole percentage is above 2.2, however, coercivities decreased because the amount of nonmagnetic Cr-rich phase increased accordingly.

Introduction

Ferromagnetic nanowires (NWs) are scientifically important because they have unique magnetic properties originating from their one-dimensional structure[1−7] and are also technologically important because they may be applied to a high-density perpendicular magnetic recording with their excellent magnetic properties.[1] That is, ferromagnetic NWs possess high coercivities and ratio of remanences to saturation magnetizations close to 1, which arise from a zero demagnetization factor parallel to NWs.[8] Because of this, a variety of methods to fabricate arrays of ferromagnetic NWs have been reported by many researchers. These include electrochemical deposition of metals into the well-defined arrays of nanopore templates made of either aluminum oxides[1−4] or polymer membranes.[5−7] These methods may be used in fabricating a variety of arrays of ferromagnetic NWs by controlling nanopore sizes, lengths, and the separation between nanopores in the templates.

The CoCr thin films have been intensively studied because their magnetic properties are suitable for a high-density perpendicular magnetic recording.[9−13] It has been found that CoCr films made of a 5−30 at. % Cr consist of ferromagnetic Co-rich and nonmagnetic Cr-rich hexagonal close-packed (hcp) phases.[14−21] This magnetic phase separation, originating from surface segregation in the CoCr alloy, together with columnar growth of a ferromagnetic Co-rich phase makes CoCr thin films valuable for a high-density perpendicular magnetic recording. Recently, it was reported that

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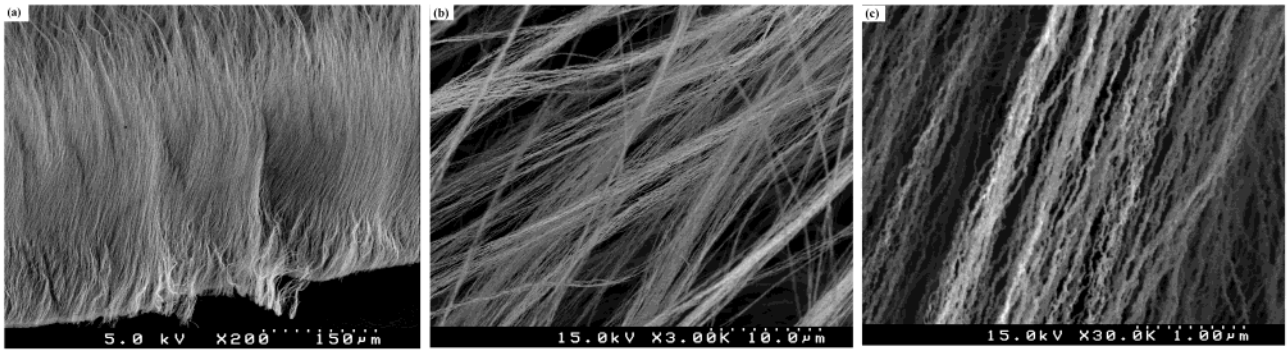

Figure 1. SEM micrographs of arrays of $Co_{99.2}Cr_{0.8}$ binary NCWs at various magnifications.

ferromagnetic Co-rich phase contained about 2 at. % Cr from NMR study[22−24] and 0.5−1.0 at. % Cr from an empirical calculation based on high-temperature experimental data,[15] implying that solubility of Cr in Co is ∼2 mol % Cr. However, magnetic properties of the Co-rich phase itself have not been studied at all due to difficulty in preparation.

In this work, we fabricated, for the first time, arrays of ferromagnetic Co_xCr_{100-x} binary nanocluster wires (NCWs) with a Cr mole percentage between 0 and 17.9% (or $x = 100-82.1$ mol % Co) by using a novel method developed by our group[25] and investigated magnetic properties of the Co-rich phase. We observed unexpected excellent magnetic properties that include nearly doubled coercivities compared to those of arrays of pure Co NCWs when the Cr mole percentage is <2.2, which might explain the excellent magnetic properties of CoCr thin films. However, coercivities decreased with increasing Cr mole percentage above 2.2 are likely due to the increase in the amount of nonmagnetic Cr-rich phase, as in the case of both CoCr films and bulk alloys.[23,26−29] We discussed these enhanced coercivities by using particle size effects because coercivity can increase with decreasing particle size for single-domain nanoclusters.[30]

Experimental Section

Fabrication. The experimental setup used to fabricate arrays of ferromagnetic CoCr binary NCWs has been described elsewhere.[25] Briefly, the experimental setup is a reaction chamber that houses a pair of permanent disk magnets, a tube spacer, a resistive heater, and two substrates. 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. A glass tube spacer with an inner diameter and a tube length of 14 and 15 mm, respectively, was used but both dimension and material of the tube spacer can be changed. A resistive heater placed in the middle of the glass tube spacer was used to decompose metal carbonyl vapors into metal atoms and the COs. A Nichrome alloy wire was used as a resistive heater. The glass plates with 1-mm thickness were used for substrates. The glass substrates were attached to the permanent disk magnet surfaces onto which NCWs grew vertically. The nanoclusters were produced near the resistive heater environment through numerous collisions between the decomposed neutral Co and Cr atoms. These nanoclusters were then equally pulled into opposite directions by the magnetic field produced by a pair of permanent disk magnets and piled up vertically to the substrates to become NCWs. It took only a few minutes to complete this fabrication of arrays of NCWs. The metal carbonyl vapor pressures (i.e., $Co_2(CO)_8$ and $Cr(CO)_6$) used in the present experiment were 1−20 Torr. To vary x (i.e., the Co mole percentage) in Co_xCr_{100-x} nanoclusters, different mole ratios of two metal carbonyls were used for production and then exact values of x's were determined by using an inductively coupled plasma atomic emission spectrometer (ICPAES) after the experiment. When the Cr mole percentage was larger than 10, a few arrays of CoCr NCWs were produced as CoCr binary nanoclusters were not easily drawn by magnetic fields because of a large amount of nonmagnetic Cr-rich phase in CoCr binary nanoclusters.

Characterization. To characterize structure, the Philips X-ray diffraction spectrometer (model: X-PERT) was used. The X-ray diffraction (XRD) patterns were recorded between $2\theta = 20°$ and $2\theta = 80°$. Both 1.54056 and 1.54439 Å of the Cu Kα radiation with an intensity ratio of 2 to 1 were used without filtering to increase the signal-to-noise ratio. A scanning electron microscope (SEM) (Hitachi, model: S-4200) operated at 5−15 kV was used to characterize arrays of CoCr NCWs. A high-resolution transmission electron microscope (HRTEM) (model: JEOL, JEM 3010) operated at 300 kV was used to measure diameters of both CoCr nanoparticles and NCWs. Samples for a HRTEM measurement were placed onto a carbon-coated copper grid, which was dipped into a methanol solution in which NCWs were suspended. A magnetic property measurement system (MPMS) (Quantum Design, model: MPMS7) was used to record hysteresis loops at 300 K from which magnetic properties such as coercivities and remanences were obtained.

Results and Discussion

Arrays of ferromagnetic CoCr binary NCWs at various magnifications are presented in Figure 1a−c. Figure 1a shows an overall image of arrays of CoCr NCWs. As can be seen in Figure 1b,c, NCWs form bundles (Figure 1b) and also branch out while they grow. The reasons for forming bundles and branches likely originate from long lengths of NCWs because either thermal fluctuation or mechanical vibration will make them interact with one another. The bundles with lengths up to a few millimeters formed a three-dimensional array (Figure 1a). An HRTEM micrograph of a single CoCr NCW is presented in Figure 2a. As shown in Figure 2a, the

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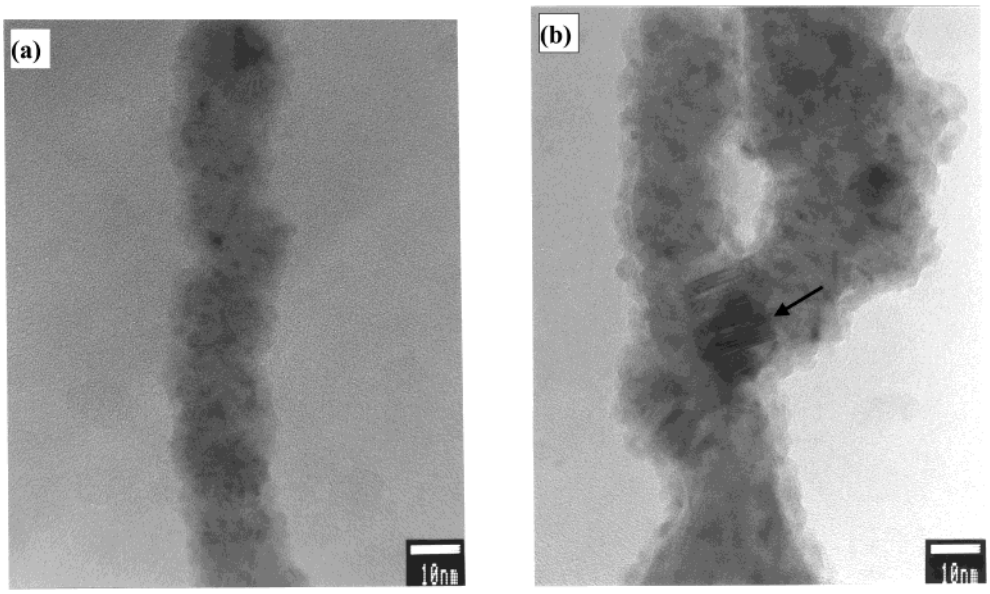

Figure 2. HRTEM micrographs of (a) a single $Co_{99.2}Cr_{0.8}$ binary NCW and (b) branched $Co_{97.8}Cr_{2.2}$ binary NCW. An arrow in (b) indicates one large CoCr binary nanocluster with a particle diameter of ~20 nm.

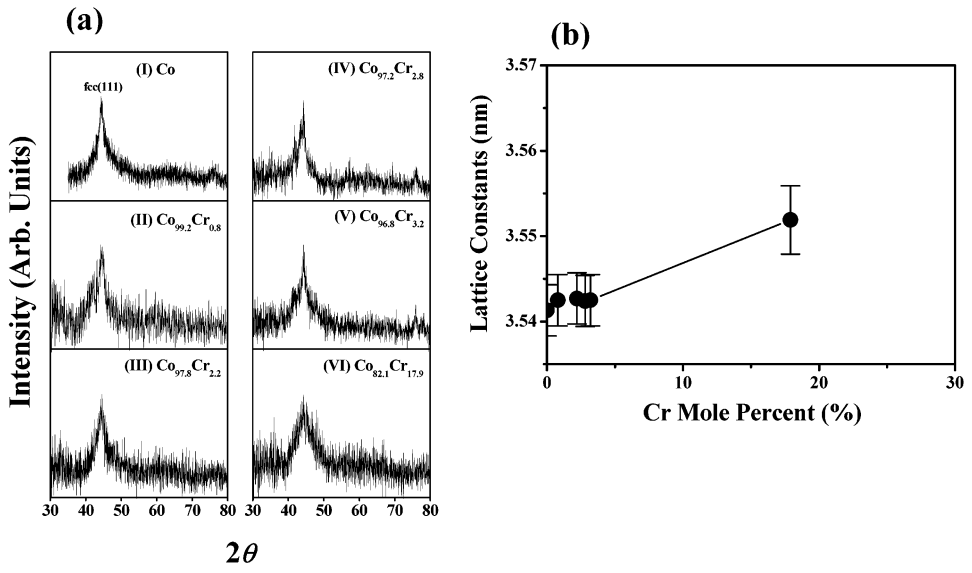

Figure 3. (a) XRD patterns of arrays of ferromagnetic CoCr NCWs and (b) plot of lattice constants versus Cr mole percentage.

diameter of a NCW is ~15 nm. In general, the diameter of NCWs ranges from 10 to 20 nm. Individual CoCr nanoclusters that make up NCWs are barely visible because of severe aggregations between CoCr binary nanoclusters, probably because they were piled up by a strong magnetic field of 3000−4000 G and thus are roughly estimated to be 3−5 nm in diameter. There also exist large CoCr nanoclusters with a diameter larger than 10 nm, as indicated by an arrow in Figure 2b in which a branched NCW is presented. Thus, there exist two size distributions in CoCr nanoclusters that make up NCWs, although we do not know the exact ratio in the amount of small nanoclusters (3−5 nm) to that of large nanoclusters (>10 nm).

The XRD patterns of arrays of CoCr NCWs are presented in Figure 3a. Since solubility of Cr in Co is ~2 mol % as found in the NMR study,[22−24] phase separation should occur when the Cr mole percentage is more than ~2. Unless the Cr mole percentage is sufficiently large, however, only the fcc structure will be observed in the XRD patterns. In fact, only the fcc structure was observed up to 3.2 mol % Cr. However, the XRD pattern (VI) with a large Cr mole percentage is different from (i.e., broader than) the others (I)−(V). It is likely that the broad peak in (VI) is due to the overlap between the two peaks, originating from phase separation, i.e., one from the fcc Co-rich phase (majority) and the other from the bcc Cr-rich phase (minority) because fcc Co (111) and bcc Cr (110) peaks closely occur at 44.26° and 43.51°, respectively.[31,32] Lattice constants (Figure 3b) slightly increase up to 0.8 mol % Cr and then become nearly constant up to 3.2 mol % Cr within an experimental limit, implying that solubility of Cr in Co nanoclusters is 2−3 mol % Cr, as consistent with the NMR study.[22−24] The slight increase of the lattice constant with increasing Cr mole percentage is because the Cr atom has a slightly larger atomic radius than

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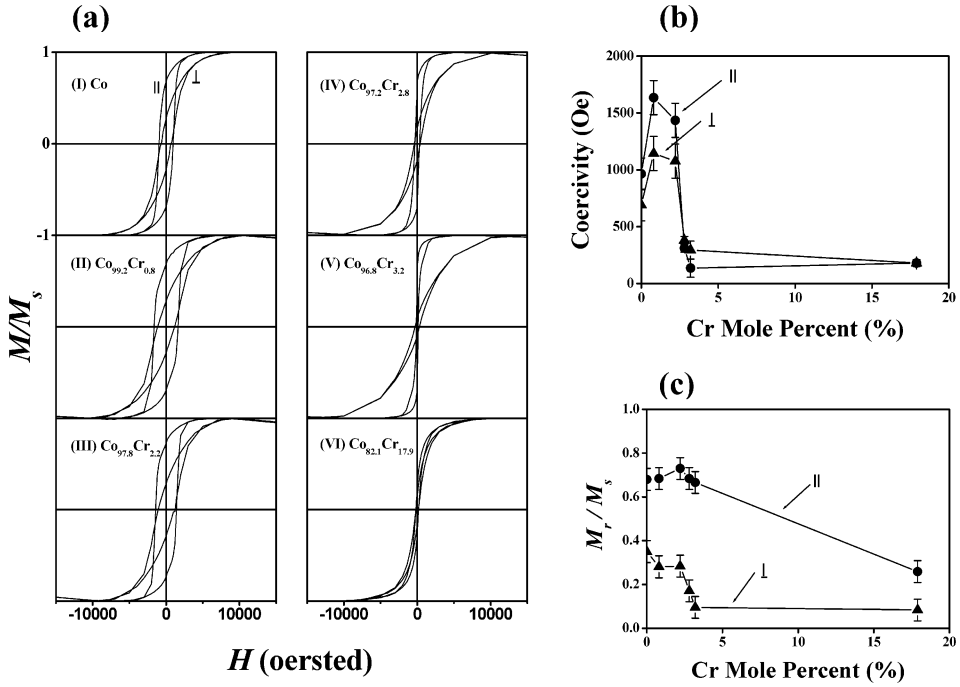

Figure 4. (a) Hysteresis loops, (b) coercivities, and (c) remanences (M_r)/saturation magnetizations (M_s).

the Co atom. A large deviation of the last point from the others is likely due to the overlap between the fcc Co and bcc Cr peaks, as mentioned before.

To measure magnetic properties for arrays of ferromagnetic CoCr binary NCWs, hysteresis loops were recorded at 300 K (Figure 4a). From hysteresis loops, both coercivities (H_c) and ratios of remanence (M_r)/saturation magnetization (M_s) were extracted, as represented in parts b and c, respectively, of Figure 4. In general, both H_c and M_r/M_s with magnetic field applied parallel to NCWs (||, so-called easy axis) are larger than those with magnetic field applied perpendicular to NCWs (⊥). This originates from the 2π demagnetization factor perpendicular to NCWs, although there is no demagnetization factor parallel to NCWs.[8] Importantly, for 0.8−2.2 mol % Cr, H_c's are much larger than that of the array of pure Co NCWs and M_r/M_s's are larger than 0.7. As the Cr mole percentage increases, however, both H_c and M_r/M_s decrease, likely because of the increase in the amount of nonmagnetic Cr-rich phase, consistent with both CoCr films and bulk alloys.[23,26−29]

The enhanced coercivities of arrays of CoCr NCWs when the Cr mole percentage is <2.2 are unexpected results. Since Cr antiferromagnetically couples with Co,[33] these enhanced coercivities may result from other factors. Note that the particle size of binary nanoclusters generally decreases with increasing concentration of impurity atoms[34] and that the coercivity can increase with decreasing particle size for single-domain nanoclusters.[30] In both CoCr films and bulk alloys, the coercivities are found to increase with decreasing grain size,[28,35,36] implying that the enhanced coercivities in CoCr NCWs may be related to the cluster size decrease due to alloying with Cr. Note that CoCr nanoclusters consist of small (3−5 nm) and large CoCr nanoclusters (10 nm), as observed in HRTEM micrographs. Since Co nanoparticles with cluster diameter <8 nm are superparamagnetic,[37,38] however, the enhanced coercivities of arrays of CoCr NCWs may be related to the particle size decrease of large CoCr nanoclusters because of alloying with Cr atoms if they arise from the particle size effects. To clearly understand these enhanced coercivities, however, a more thorough study through both experiment and theory will be necessary. For example, measurement of coercivities for arrays of CoCr NCWs at several CoCr nanocluster diameters will be helpful, which is beyond our present experimental capability.

Conclusion

We fabricated arrays of CoCr binary NCWs by thermally decomposing $Co_2(CO)_8/Cr(CO)_6$ metal carbonyl vapors by using a resistive heater placed in the middle of a pair of permanent disk magnets. The NCWs, ranging from 10 to 20 nm in diameter, exist as bundles with lengths up to 2−3 mm. These bundles form a three-dimensional array. We observed that arrays of CoCr NCWs with 0.8−2.2 mol % Cr, in which only Co-rich phase exists, showed enhanced magnetic properties, that is, nearly doubled coercivities compared to that of an array of pure Co NCWs and high M_r/M_s larger than 0.7. These unexpected excellent magnetic properties of the Co-rich phase, which can be magnetically isolated from one another by a nonmagnetic Cr-rich phase when the Cr mole percentage is more than ∼3, may make these arrays useful for a high-density perpendicular magnetic recording if further technical improvements are properly made to the present arrays.

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