

Using High-Temperature Chemical Synthesis To Produce Metastable Nanostructured Cobalt

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Chemical synthesis at elevated temperature (200 °C) produces a highly disordered form of cobalt similar to that produced by mechanical milling. Annealing of the disordered phase produces material with different face-centered cubic (fcc) to hexagonal close-packed (hcp) ratios, depending on the particular thermal treatment and the amount of disorder prior to annealing. The fcc-to-hcp ratio changes with the molecular weight (or boiling point) of the solvent, but this correlation does not appear to be linear. The coercivity and remanence ratio of chemically synthesized cobalt depend on the crystallite size, phases present, and amount of disorder.

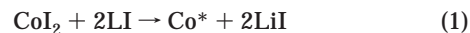
I. Introduction

Elemental cobalt has two phases. The hcp (hexagonal close-packed) phase is stable in the bulk at temperatures below 450 °C. The fcc (face-centered cubic) phase is stable above 450 °C and at room temperature for small particles (<20 nm diameter for sputtered particles).¹ The relationship between size and phase can be explained by energy considerations.² Dmitriev et al.³ showed theoretically that the hcp and fcc phases are ordered phases deriving from a common disordered "parent" phase. Mechanical milling has been used to produce the disordered parent phase and different annealing protocols utilized to produce hcp, fcc, and mixed hcp–fcc phases.^{4,5} We demonstrate that chemical synthesis at elevated temperatures (200 °C) produces a disordered cobalt phase similar to that produced by mechanical milling. The coercivity and remanence ratio of chemically synthesized cobalt depend sensitively on crystallite size, phases present, and the amount of disorder.

II. Experimental Procedure

A. Synthesis. Chemical synthesis is an attractive fabrication technique due to the lack of specialized equipment

required, the ready availability of starting materials, and the ability to easily scale-up the quantity of material produced. Rieke and co-workers have developed a general approach for preparing highly reactive metal powders by reducing metal salts in ethereal or hydrocarbon solvents using alkali metals.^{6–8} We have previously used this technique to make and study nanostructured nickel and Ni₃C:Ni nanocomposites.⁹ Nanostructured cobalt is produced using reductions of the form



All manipulations were carried out under an argon atmosphere on a dual manifold vacuum/argon system. The Linde prepurified-grade argon was further purified by passage over a BASF R3–11 catalyst column at 150 °C, a phosphorus pentoxide column, and a column of granular potassium hydroxide. Lithium and anhydrous cobalt iodide were weighed and charged into reaction flasks in a Vacuum Atmospheres Company drybox. Tetrahydrofuran was distilled immediately before use using Na/K alloy under an argon atmosphere.

In a typical preparation, lithium (9.68 mmol) and anhydrous cobalt iodide (4.71 mmol) were stirred in the refluxing solvent (15 mL). Undecane and pentadecane were used as solvents. Undecane (CH₃(CH₂)₉CH₃) has a boiling point of 196 °C and pentadecane (CH₃(CH₂)₁₃CH₃) has a boiling point of 271 °C. After stirring, the mixture was allowed to settle and the supernatant was drawn off via cannula. The precipitate was washed with THF (15 mL × 3) to remove LiI. The resulting active cobalt (Co*) was dried under vacuum. The limited solubility of anhydrous cobalt iodide in decanes prohibits synthesis at room temperature. The yield ratios (ratio of mass produced to the mass expected if all reactants are completely reacted) are approximately 1 for both solvents.

High-temperature synthesis has several advantages over the standard room-temperature technique. First, an electron

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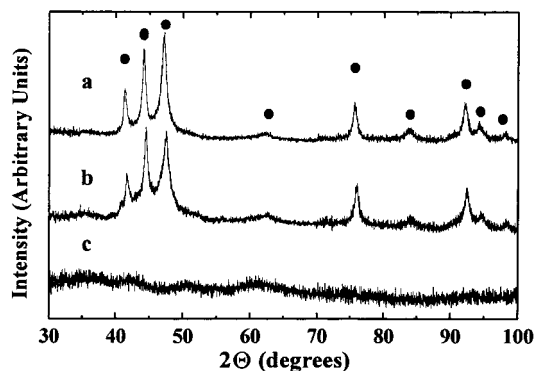


Figure 1. XRD patterns for samples synthesized in (a) undecane and (b) pentadecane at high temperature and (c) at room temperature in THF.

carrier is necessary at room temperature to facilitate the reduction; high-temperature synthesis eliminates the need for an electron carrier, as the high-temperature promotes thermal ionization of the lithium. Second, variation of synthesis temperature allows direct control of the as-synthesized crystallite size, which can eliminate the need for postsynthesis annealing. Finally, high-temperature synthesis decreases the reactivity of the materials and thus reduces the propensity for oxidation.

B. Structural and Magnetic Analysis. X-ray diffraction (XRD) measurements were performed with a Rigaku D-Max B diffractometer using Cu K α radiation. The diffracting crystallite size (DCS) is obtained using the Scherrer equation, in which the breadth, B , of a diffraction peak located at 2θ is related to the DCS by

$$\text{DCS} = \frac{0.9\lambda}{B \cos(\theta)} \quad (2)$$

where λ is the X-ray wavelength. We have specifically adopted the terminology of diffracting crystallite size to distinguish the quantity obtained from eq 2 from overall particle size, which can be larger.

Magnetic properties are measured using an alternating gradient force magnetometer. Powder is placed in a paraffin-filled polyethylene bag and sealed under an inert atmosphere. The polyethylene bag prevents oxidation during the measurements and the paraffin immobilizes the particles to prevent whole-particle rotation.

III. Results and Discussion

A. Structural Properties. Figure 1 compares the X-ray diffraction patterns from a sample synthesized at room temperature in THF (requiring an electron carrier)¹⁰ to the XRD patterns from samples synthesized in undecane and pentadecane. The XRD pattern of the room-temperature-synthesized cobalt is relatively featureless. Although the high-temperature syntheses exhibit well-defined peaks at the positions corresponding to hexagonal cobalt, there are some anomalous features in the XRD patterns. First, the ratios of peak intensities do not match those predicted for hcp cobalt. The (101) peak should be the most intense peak, the intensity of the (002) peak should be 60% of the (101) peak, and the intensity of the (100) peak should be 20% of the (101) peak. The intensities of the high-temperature synthesized cobalt are clearly different from these

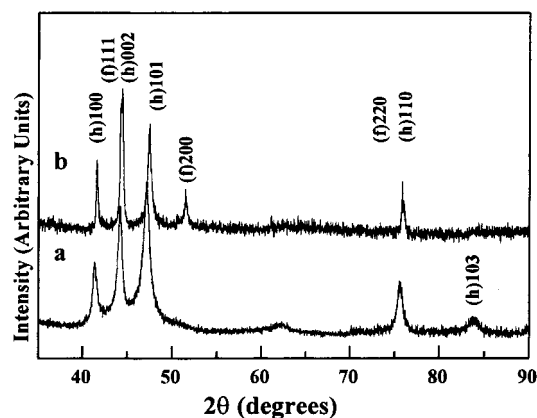


Figure 2. Comparison of XRD patterns from the undecane-synthesized sample. Pattern a is the as-synthesized sample and pattern b is from a sample annealed for 8 h at 500 °C. The peak identifications are preceded by "h" if the peak corresponds to hcp cobalt and by a "f" if the peak corresponds to fcc cobalt.

values. Another difference is that the (110) peak and (103) peaks should be of equal intensity, but are not. The small peak near 62° may correspond to a low-intensity peak in hcp cobalt; however, CoO could also produce such a peak. XRD measurements are made in air and oxidation may occur during the measurement.

The XRD peaks of both the high-temperature-synthesized materials show differential broadening. The reflections for which $h - k \neq 3n$ are much broader than those for which $h - k = 3n$. For example, compare the breadth of the (103) peak at 84.2° to that of the (112) peak at 92.5°. This type of differential broadening indicates defects within individual close-packed layers and faults in their stacking sequence.¹¹

DCS values were obtained from the (100) and (101) peaks using eq 2. The peak at 44.8° is not used, as there is a possible overlap with a fcc cobalt peak. As-synthesized samples made with different solvents have similar DCS values and similar differential broadening, with the (101) peaks having DCS values of 10 nm/13 nm and the (100) peaks having DCS values of 16 nm/17 nm for the undecane/pentadecane-synthesized samples, respectively. In addition to the differential broadening, the peak positions of the high-temperature-synthesized samples are shifted to lower values than expected, with the greatest shift in the undecane-synthesized sample.

Samples were annealed under a vacuum of 10^{-6} Torr at temperatures from 150 to 700 °C to study phase formation and DCS growth. Figure 2 shows the XRD pattern from the undecane-synthesized sample in the unannealed state (a) and annealed at 500 °C for 8 h (b). The annealed sample shows a change in the relative intensities of the (100) and (002) peaks, as well as the appearance of a peak at 51.8° that can be indexed to the (200) peak of fcc cobalt. The shift in the peak positions disappears with annealing, suggesting that lattice distortions in the as-synthesized material are removed.

The differential broadening of the XRD peaks increases as the samples are annealed. In the undecane-synthesized sample, the DCS obtained from the (101)

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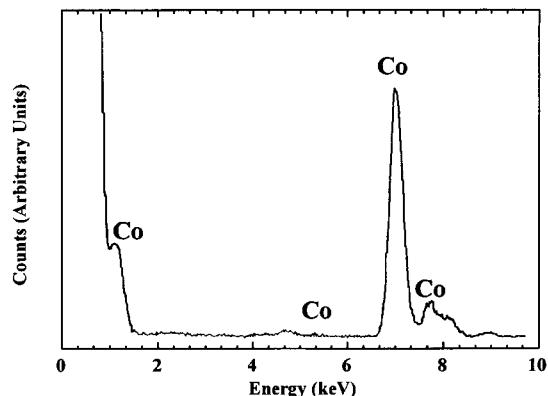


Figure 3. An energy-dispersive X-ray analysis spectrum from an undecane-synthesized sample annealed at 200 °C for 2 h.

peak changes from 10 nm to a maximum value of 19 nm when annealed at 700 °C. The DCS obtained from the (100) peak, however, changes from 16 to 50 nm over the same range of annealing temperatures. Similar behavior is observed in all high-temperature synthesized cobalt, regardless of solvent.

Figure 3 shows an energy-dispersive X-ray (EDX) spectrum for an undecane-synthesized sample annealed for 1 h at 200 °C. EDX confirms the presence of cobalt and shows no significant impurities. Figure 4 shows dark-field transmission electron micrographs of the same undecane-synthesized sample. Two different types of crystallites are observed. The most frequently observed crystallites, shown in Figure 4a, are of average size 10–20 nm and show some evidence of faceting. The second type of crystallites, shown in Figure 4b, are observed less frequently, are larger, and are distinctly faceted. Crystallites of both types exhibit stacking faults, as indicated by the striations in the micrographs. Electron diffraction indicates that, although each particle is formed from multiple crystallites, the crystallites within a particle often share a common crystallographic orientation. The sizes of the smaller crystallites are consistent with the DCS values obtained by XRD. The overall size of the larger crystallites is greater than the XRD values, which are 13 nm for the (100) peak and 11 nm for the (101) peak. The DCS obtained from X-ray diffraction is an average value dependent on dislocations and other defects that cause a loss of coherence in X-ray scattering; thus, the DCS often does not reflect overall particle size.

Analysis of the structure of the chemically synthesized material shows significant similarities to cobalt produced by mechanical milling.^{4,5,12–15} Mechanical milling introduces defects and vacancies to produce highly faulted phases. The material to be milled is initially a mix of hcp and fcc phases. As the milling time increases, the hcp phase grows at the expense of the fcc phase. Differential broadening, with the (10 \bar{l}) peaks being significantly more broadened than other peaks, is also observed. The nature of the disordered

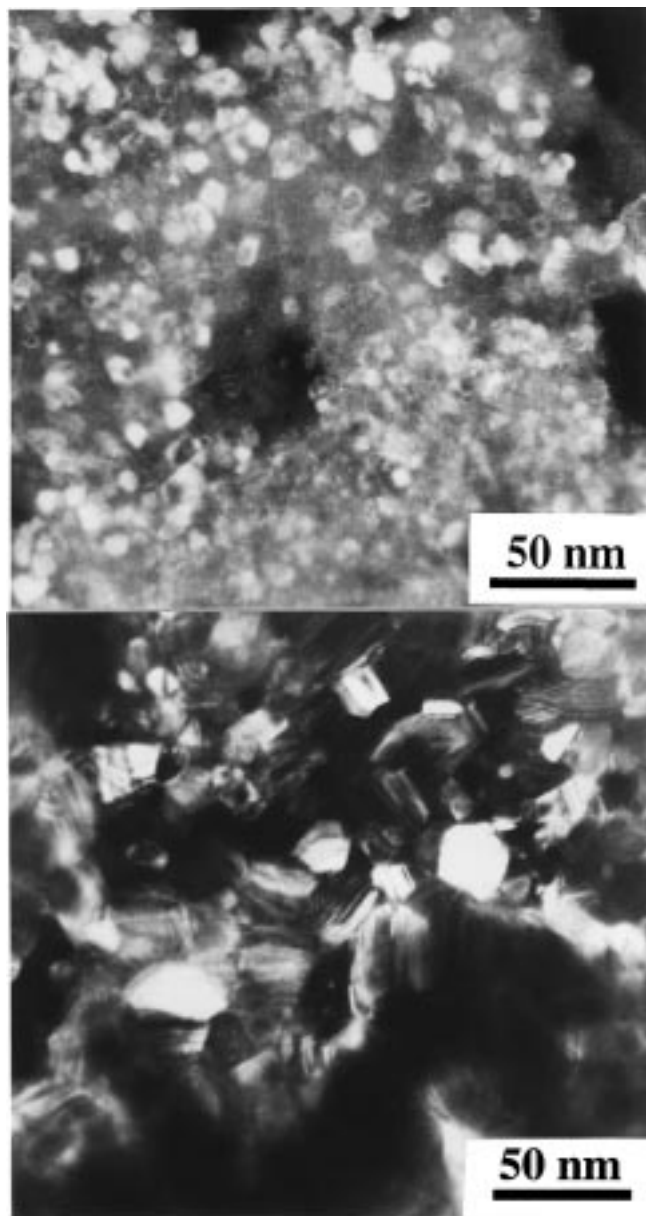


Figure 4. Dark-field electron microscopy showing the two types of crystallites observed in annealed samples from the undecane-synthesized run. Part a (top) shows the more frequently observed, smaller crystallites, while part b (bottom) shows less frequently observed larger crystallites with distinct faceting. The striations in the micrographs indicate stacking faults.

phase determines the fcc-to-hcp ratio obtained on annealing. Unlike the chemically synthesized cobalt, mechanically milled cobalt can be annealed to produce primarily fcc Co; however, the experiments reported were performed in a stainless steel vial and the resulting Fe contamination can stabilize the fcc phase.^{4,12} There remains some disagreement about whether the fcc phase can be stabilized through increased mill intensity without Fe.^{4,5,13} The lack of a pure fcc phase (as evidenced by XRD) in the chemically synthesized material thus may not indicate a significant difference between the materials produced by the two processes. The amount of disorder in the mechanically milled cobalt is much greater than that of the chemically synthesized cobalt. Further understanding of the role of the different synthesis parameters is necessary to

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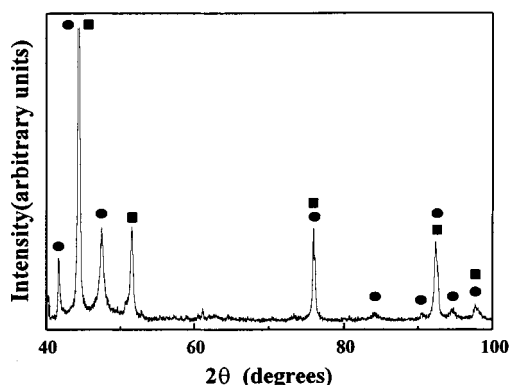


Figure 5. X-ray diffraction pattern for cobalt from the pentadecane-synthesized run, annealed at 500 °C for 2 h.

determine if the same degree of disorder can be produced by chemical synthesis.

Varying the solvent changes the disorder of the as-synthesized material, which allows investigation of the effect of disorder on subsequent phase formation. Pentadecane synthesis produces a much larger fraction of fcc cobalt than undecane synthesis. Figure 5 shows the XRD pattern of a sample from pentadecane-synthesized cobalt annealed at 500 °C for 2 h. This sample has the maximum amount of fcc phase produced of any of the samples in this study. Note that the peak at 44.8° is significantly more intense than the other peaks, and that the (200) fcc peak at 51.5° is larger than the (100) and (101) hcp peaks. Observation of the fcc phase requires annealing at or above 350 °C regardless of which solvent is used. The relationship between solvent, synthesis temperature, and the nature of the as-synthesized disordered phase requires additional study to reveal the mechanism responsible for producing disorder in these materials. We will extend this investigation to determine whether solvents with even higher boiling points can be used to produce a pure fcc phase in the future.

B. Magnetic Properties. The DCSs obtained from the (100) X-ray diffraction peaks are comparable for identical annealing conditions, regardless of the solvent used. The primary difference between samples made with different solvents is the fcc-to-hcp ratio and the degree of differential broadening, which allows us to investigate the effect of the different phases on overall magnetic properties. Unannealed pentadecane-synthesized cobalt has a coercivity of 195 Oe and a remanence ratio of 0.12. The undecane-synthesized cobalt, which has a DCS comparable to that of the pentadecane-synthesized sample, has an as-synthesized coercivity of 534 Oe and a remanence ratio of 0.33.

The dependence of the coercivity and remanence ratio on DCS can be explored within a set of samples synthesized using the same solvent; however, differential broadening complicates interpretation. Figure 6 shows the dependence of the remanence ratio and coercivity on the DCS values obtained from the (100) and (101) hcp cobalt peaks. Open symbols represent samples in which fcc cobalt is observed, while no significant amounts of fcc cobalt are found in the samples represented by solid symbols. Figure 6 shows that the coercivity and remanence generally increase with decreasing DCS. Regardless of which peak is used,

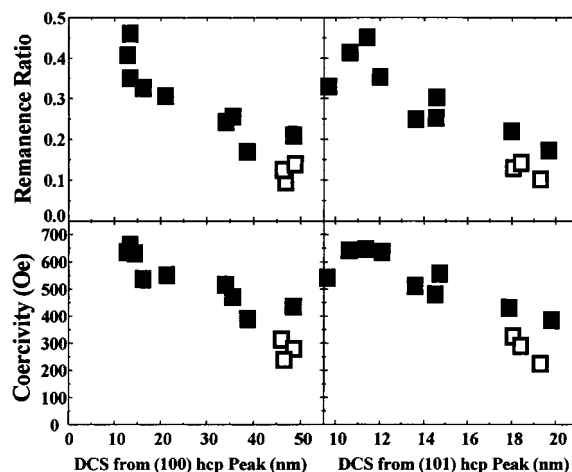


Figure 6. Dependence of coercivity and remanence ratio on the DCS values obtained from the (101) and (100) cobalt peaks for the undecane-synthesized samples.

the coercivities and remanence ratios are higher for samples without evidence of fcc cobalt than for samples with comparable DCS values but with fcc cobalt. The pentadecane-synthesized samples have consistently lower coercivities, with a maximum coercivity of only 240 Oe. The maximum coercivity in the series of undecane-synthesized samples is 634 Oe. The primary difference between the two series of samples is the fcc-to-hcp ratio. The magnetic measurements are consistent with the decreased anisotropy of fcc cobalt compared to hcp cobalt.

Cobalt was also synthesized at high temperature using dodecane ($\text{CH}_3(\text{CH}_2)_{10}\text{CH}_3$, boiling point 216 °C) as a solvent.¹⁰ The structural and magnetic properties are very close to those of pentadecane-synthesized cobalt. The coercivity of the unannealed dodecane-synthesized cobalt is 195 Oe, which is between the 162 Oe of the pentadecane-synthesized cobalt and the 534 Oe of the undecane-synthesized cobalt. Fcc-to-hcp ratios in the dodecane-synthesized cobalt are comparable to those in the pentadecane-synthesized cobalt. The appearance of fcc cobalt occurs at the same annealing temperature (350 °C) as in the pentadecane-synthesized material. The similarity of the dodecane- and pentadecane-synthesized cobalt is important, as dodecane is much more similar to undecane than to pentadecane; however, the structural and magnetic properties of the dodecane-synthesized cobalt are much closer to the properties of the pentadecane-synthesized cobalt. The dependence of structural and magnetic properties on solvent molecular weight or solvent boiling point does not appear to be linear, suggesting that there is a threshold for producing the predominantly hcp cobalt particles. Further investigation is necessary to determine whether the fact that the synthesis temperature was approximately equal to the solvent boiling point in the sample with the highest proportion of hcp cobalt is a coincidence or a necessary requirement.

V. Conclusions

High-temperature chemical synthesis produces disordered cobalt similar to that produced by mechanical milling. The molecular weight (or boiling point) of the

solvent determines the degree of disorder, which in turn affects the formation of fcc and hcp cobalt after subsequent annealing. Higher molecular weight solvents produce materials with a larger fraction of fcc cobalt and correspondingly lower coercivities and remanence ratios; however, the relationship between solvent molecular weight (or boiling point) does not appear to be linear. Chemical synthesis offers the ability to vary the solvent and the synthesis temperature, suggesting that this

technique may be useful for investigating the polymorphism of cobalt and other metastable phases.

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