

Structural and magnetic properties of nanocrystalline b.c.c. cobalt particles obtained by leaching of mechanically alloyed Co–Al

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Abstract

Nanocrystalline b.c.c. cobalt powder has been prepared using a combination technique of mechanical alloying and leaching aluminum in basic solution. The structure and magnetic properties of the as-milled and the leached alloys were examined by X-ray diffraction, transmission electron microscopy, differential scanning calorimetry and magnetization measurements. Even after removing most of the aluminum atoms by leaching, the specimen topotactically keeps the b.c.c. structure. The b.c.c. cobalt is ferromagnetic is stable below 430 K and transforms into the ferromagnetic f.c.c. cobalt at higher temperatures. The magnetic moment of the cobalt atom is smaller in the b.c.c. phase than in the f.c.c. phase.

1. Introduction

There has been considerable interest in producing and studying nanocrystalline materials because of the size sensitivity of their structure, physical and chemical properties [1]. In particular, nanoscale 3d transition metal (iron, cobalt and nickel) particles are expected to display unique magnetic and catalytic properties [2]. Recently mechanical alloying (MA) by simple ball milling has been utilized for preparing nanocrystalline powders with non-equilibrium structures in several metal and alloy systems [3]. In solid state chemistry a technology of topotactic reactions combined with MA opens up the possibility of making new materials with structures, magnetic and catalytic properties quite different from those of the original materials [4].

Since aluminum can be leached out of 3d metal aluminides by basic solution, we have used a combination technique of MA and leaching for topotactic transformation of mechanically alloyed Ni₃₅Al₆₅ of the B2 (CsCl) type of crystal structure into metastable nanocrystalline b.c.c. nickel. The lattice constant of the metastable b.c.c. nickel phase is almost the same as that of the initial Ni₃₅Al₆₅ alloy [5, 6]. The b.c.c. nickel exhibits a paramagnetic character in accordance with the recent band structure calculation of 3d transition metals [7]. Moreover, we have also produced nanoscale

quasi-amorphous nickel by leaching aluminum from sputter-deposited Ni₂₅Al₇₅ alloy [8].

The b.c.c. cobalt phase with a lattice constant $a = 0.2827$ nm has been stabilized by epitaxial growth on a GaAs crystal [9] and found to be ferromagnetic. This result has stimulated an energy band calculation, showing that the b.c.c. cobalt is ferromagnetic and the magnetic moment decreases with increasing unit-cell volume [10].

In this work therefore we use the idea of leaching aluminum from mechanically alloyed Co₄₀Al₆₀ in basic solution to obtain nanocrystalline b.c.c. cobalt and to study its structural and magnetic properties through X-ray diffraction, transmission electron microscopy (TEM), differential scanning calorimetry (DSC) and magnetization measurements.

2. Experimental details

A Co–Al crystalline alloy with 40 at.% Co of the B2-type structure has been obtained from pure elemental cobalt and aluminum powders using MA technique as described elsewhere [6]. The mechanically alloyed samples were leached in basic solution (20 wt.% KOH) to remove aluminum atoms, using the conventional method for obtaining Raney nickel catalysts [11]. X-ray diffraction measurements were carried out at 290 K using Cu K α radiation and a graphite monochromator. The microstructure characterization of the specimens was done by TEM (JEOL FX2000) operating at 200

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kV. The composition of the alloys was determined using energy-dispersive X-ray analysis with a detector installed in the microscope. The magnetization was measured between 77 and 800 K in magnetic fields up to 16 kOe using a conventional vibrating-sample magnetometer.

3. Results and discussion

3.1. Structure

Figure 1 shows the X-ray diffraction patterns of the as-milled and the leached Co–Al specimens. For the as-milled alloy all the elemental aluminum and cobalt peaks disappear and cobalt aluminide peaks of the B2-type order are detected. The X-ray diffraction pattern of the leached specimen does not display a considerable change from that of the as-milled specimen. The lattice constant of 0.286 ± 0.001 nm for the leached sample is almost the same as that of the as-milled sample. The apparent crystalline size has been estimated from the half-width of the diffraction peak using the Scherrer formula [12] to be about 6 nm in the diameter for the as-milled and the leached specimens. It should be emphasized that the lattice constant of the present b.c.c. cobalt phase is larger than the lattice constant of 0.282 nm for the epitaxially grown phase on the GaAs crystal. The larger lattice constant and the smaller crystal size are expected to affect the magnetic properties of the present b.c.c. cobalt phase.

In order to understand the microstructure, TEM observations were carried out. The results of the as-milled $\text{Co}_{40}\text{Al}_{60}$ and leached specimens are shown in Figs. 2(a) and 2(b) respectively. The electron micrographs reveal nanometer-sized structures and the corresponding selected-area diffraction (SAD) patterns show the typical B2 structure for both alloys.

The aluminum content of the leached samples is much less than that of the as-milled samples; at least six sevenths of the aluminum atoms were removed during leaching process. The remaining aluminum was

found in the form of hydroxides and diluted aluminum in cobalt-rich primary solid solution. This indicates that the leached specimens topotactically keeps its b.c.c. structure even though most of the aluminum atoms were removed.

3.2. Thermal stability

In addition to the structural investigations, the thermal stability of the leached specimens was examined using DSC, X-ray diffraction and TEM observations. Figure 3 shows the DSC trace of the leached specimen obtained with a heating rate of 0.33 K s^{-1} . Two considerably broadened but distinct exothermic peaks are observed at around 425 and 630 K. In order to understand the origin of the observed peaks in the DSC trace, X-ray diffraction patterns have been observed at room temperature (RT) after heating the specimens to different temperatures as shown in Fig. 4. The X-ray pattern in Fig. 4(b) for the specimen heated to 425 K (at the first DSC peak) shows no considerable change from that of the as-leached specimen except for the broadening in the peak width. For the specimens heated to 670 and 800 K, after passing the second DCS peak, the f.c.c. Bragg peaks are observed as shown in Figs. 4(c) and 4(d). The X-ray diffraction pattern for a specimen annealed at 820 K for 3 h (Fig. 4(e)) indicates that the structural transformation has been completed; the f.c.c. cobalt phase has a lattice constant of 0.355 nm and an apparent crystalline size of 13 nm. Similar phenomena have been observed for the leached b.c.c. nickel specimens [6]; the low temperature peak does not correlate with any structural changes, whereas the high temperature peak is ascribed to the transformation from the b.c.c. to the f.c.c. nickel structure accompanied by a change in the magnetic properties.

The electron micrograph of the specimen annealed at 820 K, corresponding to Fig. 4(e), is shown in Fig. 5. The initial nanoscale crystallites shown in Fig. 2(b) grow into relatively large crystals. The corresponding SAD pattern shows several diffraction rings and spots, which is attributed to the f.c.c. cobalt structure in accordance with the result of X-ray diffraction.

3.3. Magnetic properties

Figure 6 shows the magnetization (σ vs. H) curves at RT and the temperature dependence of the magnetization σ for the as-milled and the leached alloys in an applied magnetic field H of 10 kOe. In Fig. 6(a), σ for both alloys technically saturates at a relatively low field and σ for the leached alloy is one order of magnitude higher than that of the as-milled alloy. In Fig. 6(b), σ for the leached alloy at RT is about 3 emu g^{-1} smaller than that at 77 K. Since the B2-type ordered CoAl alloy is paramagnetic, the σ value of about 8 emu g^{-1} for the as-milled specimen is mainly

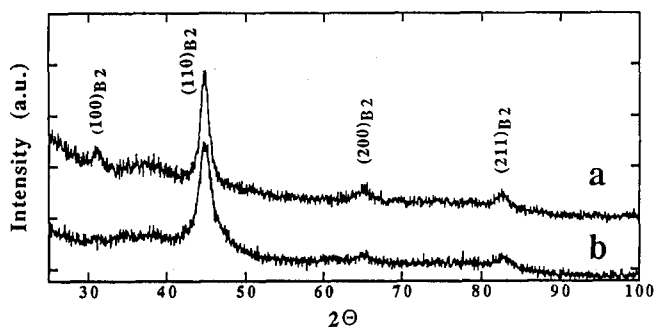


Fig. 1. X-ray diffraction patterns of the as-milled $\text{Co}_{40}\text{Al}_{60}$ (curve a) and the leached b.c.c. cobalt specimen (curve b) (a.u., arbitrary units)

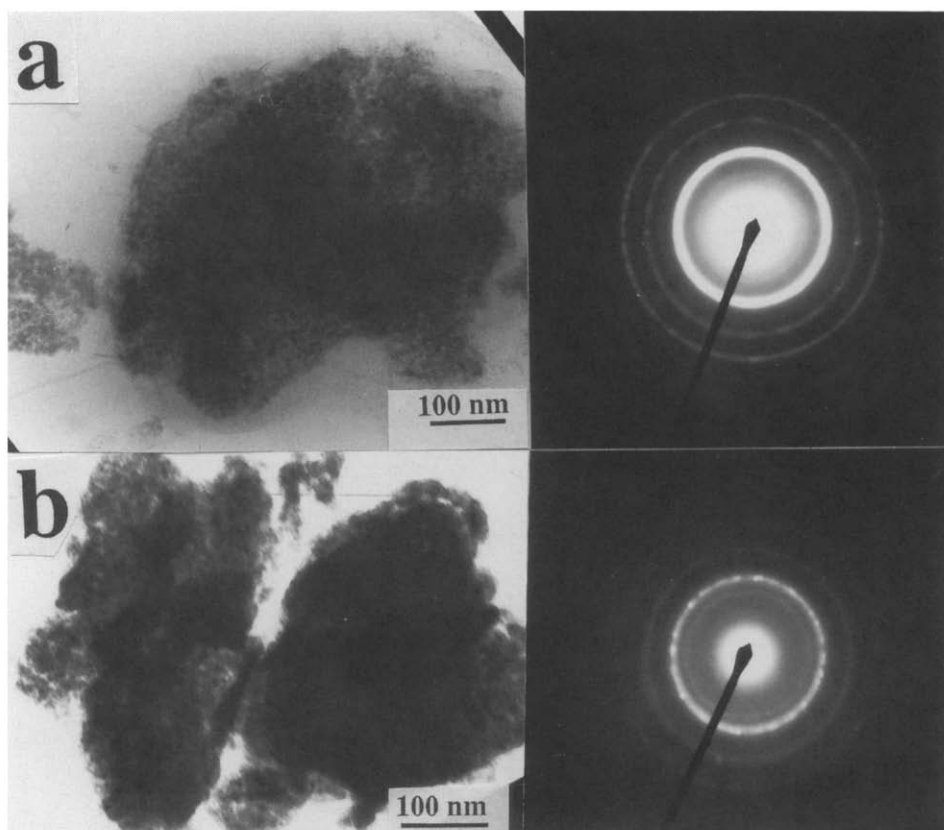


Fig. 2. TEM micrographs and SAD patterns of (a) the as-milled $\text{Co}_{40}\text{Al}_{60}$ and (b) the leached b.c.c. cobalt specimen.

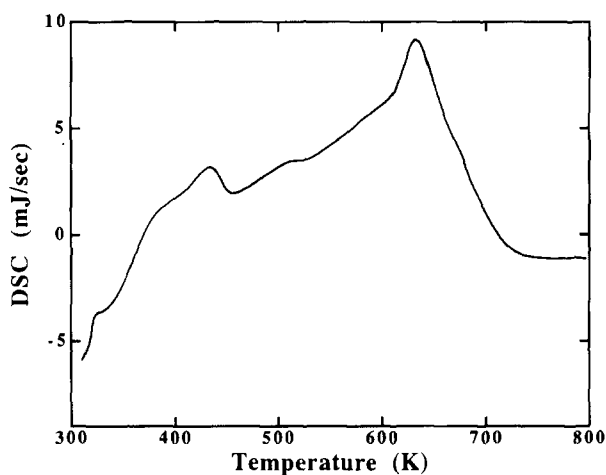


Fig. 3. DSC trace of the leached b.c.c. cobalt specimen.

due to the coexistence of ferromagnetic cobalt impurities in the specimen. Leaching aluminum atoms from the specimen leads to the formation of a non-equilibrium ferromagnetic b.c.c. cobalt phase consistent with the recent band structure calculation [10]. Figure 6(b) suggests that the Curie temperature of this b.c.c. phase is much higher than room temperature.

Figure 7 shows the variation in σ at $H=10$ kOe in the temperature cycle (RT \rightarrow 800 K \rightarrow RT) for the leached b.c.c. cobalt phase. σ at 290 K is about 65

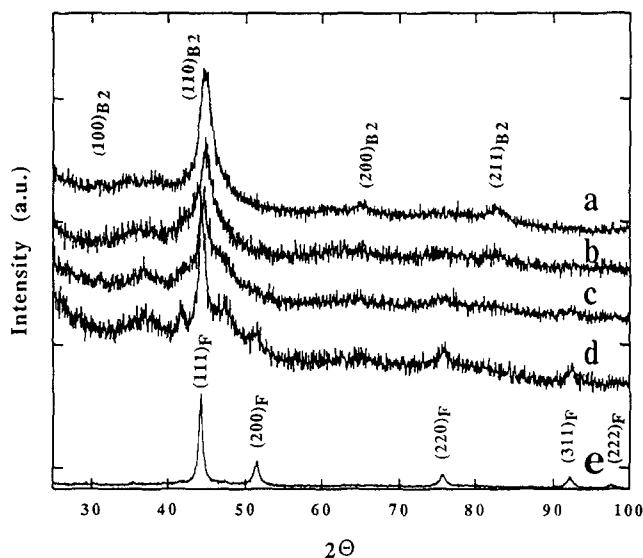


Fig. 4. X-ray diffraction patterns measured at RT for leached b.c.c. cobalt specimens (a.u., arbitrary units): curve a, as-prepared specimen; curve b, specimen heated to 425 K; curve c, specimen heated to 670 K; curve d, specimen heated to 800 K; curve e, specimen annealed at 820 K for 3 h.

emu g^{-1} and slightly decreases with increasing temperature up to 430 K. With increasing temperature above 430 K, σ slightly increases up to 600 K and

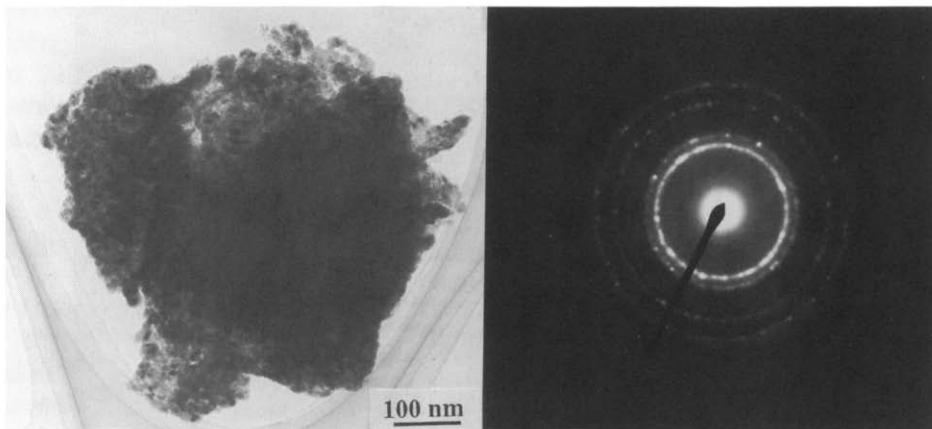


Fig. 5. TEM micrograph and SAD pattern of the leached cobalt specimen annealed at 820 K for 3 h.

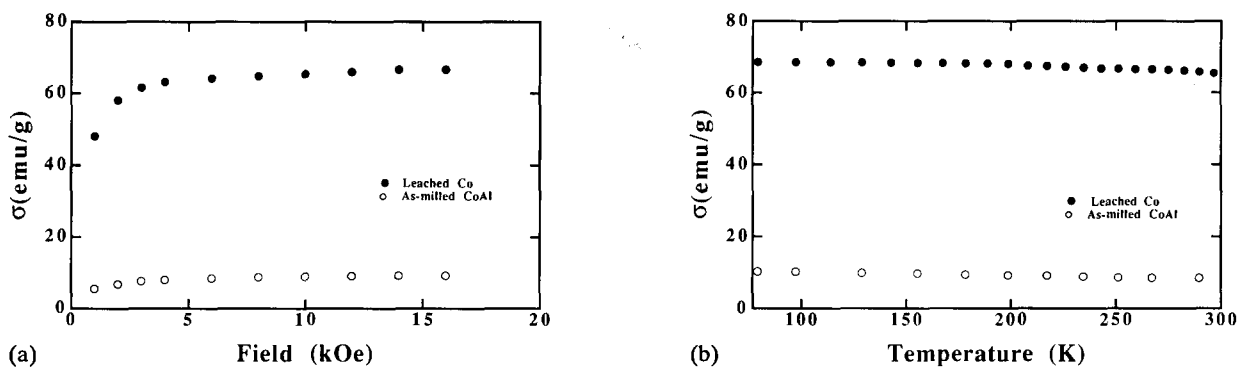


Fig. 6. (a) Magnetization (σ vs. H) curves at RT; (b) thermomagnetic curve (σ vs. T) at an applied field of 10 kOe for the as-milled $\text{Co}_{40}\text{Al}_{60}$ and the leached b.c.c. cobalt alloys.

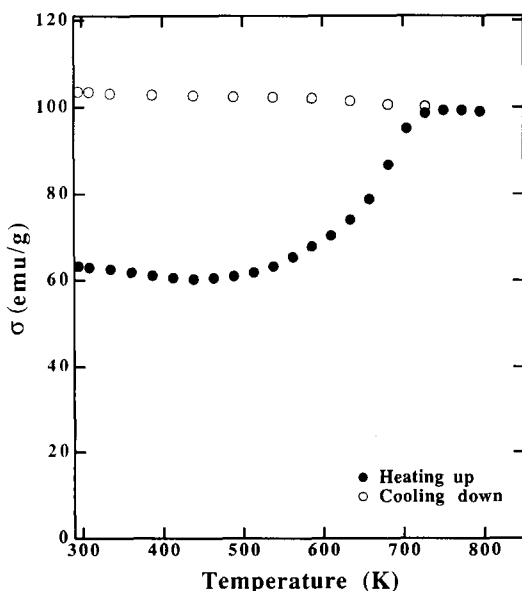


Fig. 7. Temperature dependence of the magnetization σ for the leached b.c.c. cobalt in the temperature cycle (RT \rightarrow 800 K \rightarrow RT).

sharply increases between 600 and 700 K. When the specimen is cooled from 800 K, σ slightly increases and attains a value of about 105 emu g^{-1} at 290 K.

The increase in magnetization at the first heating stage is mainly due to the structural change as detected by X-ray diffraction and TEM observations for the specimen heated above 430 K. Here, we could not discuss the magnetic moment per cobalt atom and its correlation with the lattice constant in the present b.c.c. cobalt phase because of the heterogeneity of the mechanically alloyed $\text{Co}_{40}\text{Al}_{60}$ and leached specimens, the formation of some non-magnetic aluminum oxides in the leaching process and the effect of retaining aluminum atoms on the b.c.c. and f.c.c. cobalt phases. The relatively small size of the b.c.c. cobalt crystals may partly contribute to a reduction in the saturation magnetization M_S because M_S for nanocrystalline iron is about 40% smaller than that of $\alpha\text{-Fe}$ [13]. The smaller values for the b.c.c. phase in comparison with that of the f.c.c. phase is qualitatively consistent with the theoretical calculation [10].

4. Conclusion

Nanocrystalline b.c.c. cobalt phase has been prepared using a combination technique of mechanical alloying and leaching of aluminum in basic solution. X-ray

diffraction, TEM, DSC and magnetization measurements have been carried out for the as-milled and the leached specimens. The crystal structure of the leached cobalt specimens is b.c.c. and their crystalline sizes are about 6 nm. After annealing above 430 K, a sharp increase in the magnetization is observed owing to the transformation of the b.c.c. cobalt phase to the f.c.c. phase and the growth of the crystalline size. In accordance with the theoretical prediction, the b.c.c. cobalt phase is ferromagnetic. Its magnetic moment is smaller than that of the f.c.c. cobalt.

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