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Chemical Leaching of Non-Equilibrium Al(Fe-Co) Powder Produced by Rod Milling

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Abstract We report on the formation and chemical leaching of non-equilibrium $Al_{0.6}(Fe_{75}Co_{25})$ alloy produced by rod milling. X-ray diffractometry, transmission electron microscopy, differential scanning calorimetry, scanning electron microscopy, and vibrating sample magnetometry were used to characterize the as-milled and leached specimens. After 400 h, only the $Al_{0.4}Fe_{0.6}$ peak of the body-centered cubic type was present in the XRD pattern. The entire rod milling process could be divided into three different stages of milling: agglomeration, disintegration, and homogenization. The saturation magnetization, M_s decreased with increased milling time, the M_s of the powders before milling was about 113.8 emu/g, the M_s after milling for 400 h was about 11.55 emu/g. Leaching of the Al in KOH of the Al at room temperature from the as-milled powders did not induce any significant change in the diffraction pattern. After the leached specimen had been annealed at 600°C for 1 hour, the nanoscale crystalline phases were transformed into the bcc Fe, cubic Co, and $CoFe_2O_4$ phases. On cooling the specimen from 850°C, the degree of magnetization increased slightly, then increased sharply at approximately 364.8°C, indicating that the bcc $Al_{0.4}Fe_{0.6}$ phase had been transformed to the Fe and Co phases.

Keywords : Rod milling, Al(Fe-Co), Chemical leaching, Non-equilibrium

1. Introduction

Considerable interest exists in the production and study of nanocrystalline materials in anticipation of their having unique or improved properties compared with their conventional, coarse-grained, crystalline equivalents[1-5]. Recently, a technique of mechanically alloying pure elements has been shown to be one of the most effective methods of preparing nanocrystalline materials[6,7]. Nanometer order powders have found applications in catalysis, electromagnetic shielding, magnetic recording, refrigeration, and in the processing of advanced engineering materials.

A combination of rod milling and chemical leaching has been used to prepare nanometer-order metastable materials that have many interesting properties[8-16]. The leaching treatment of Al-Ni alloys with an alkaline solution leads to the removal of the major portion of the Al and the retention of a "skeleton Ni" catalyst. Similarly, a nanocrystalline body-centered cubic (bcc) Co phase has been obtained by leaching Al from mechanically alloyed bcc $Co_{40}Al_{60}$[12].

In this work, I further developed the idea of leaching Al from rod-milled $Al_{0.6}(Fe_{75}Co_{25})$ alloy in a basic solution to obtain a homogeneous, nanometer- order, Fe-Co alloy, and then I studied those structural and magnetic properties.

2. Experimental

Pure elemental powders of Al, Fe and Co were mixed in an argon-filled glove box to give a composition of $Al_{0.6}(Fe_{75}Co_{25})_{0.4}$. The rod-to-powder weight ratio was 28:1, and the vessel was rotated at an angular velocity of 100 rev/min. The vessel was opened after 100, 200, 300 and 400 h (milling time, t) of processing in an argon atmosphere.

The rod-milled powders were leached of Al in a 30-wt% KOH solution at 30°C. The process as described is the conventional way of obtaining Raney Ni catalysts[17]. The leached powders were then annealed in evacuated quartz tubes at 400°C, 500°C and 600°C for 1 h.

The specimens obtained were characterized by using X-ray diffractometry (XRD), scanning electron microscopy (SEM), differential scanning calorimetry

(DSC), and transmission electron microscopy (TEM). A conventional vibrating-sample magnetometer (VSM) was used to measure the magnetization from 20°C up to 850°C in an applied field of 5 kOe. The composition of the alloys was determined by inductively coupled plasma-emission spectrometry (ICP).

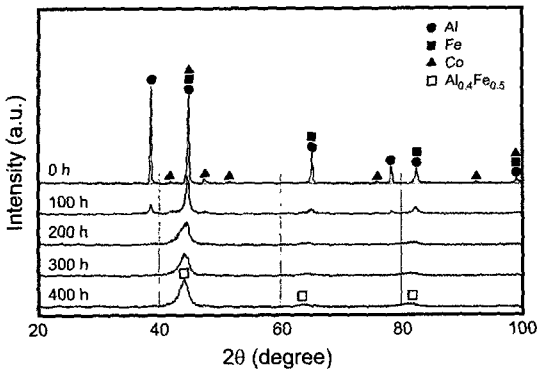

Fig. 1. X-ray diffraction patterns of rod-milled $Al_{0.6}(Fe_{75}Co_{25})$ powder for different milling times.

3. Results and Discussion

Fig. 1 shows the changes in the XRD patterns of the $Al_{0.6}(Fe_{75}Co_{25})$ powder at t's of 0, 100, 200, 300 and 400 h. After milling for 100 h, significant decreases in the relative intensities of the Al, Fe and the Co peaks were observed. Specially, the intensity of the Al peak decreased markedly, Co(101) peak disappears after milling of 200 h, only the bcc type $Al_{0.4}Fe_{0.6}$ peak was present in the XRD pattern.

SEM was used to follow the changes in the sizes and shapes of the rod-milled powder at different milling times and of leached specimen produced at 400 h (Fig. 2). The powders before milling were irregular, with a blocky or bar shapes (Fig. 2a). The initial powders produced at 100 h had agglomerated to form

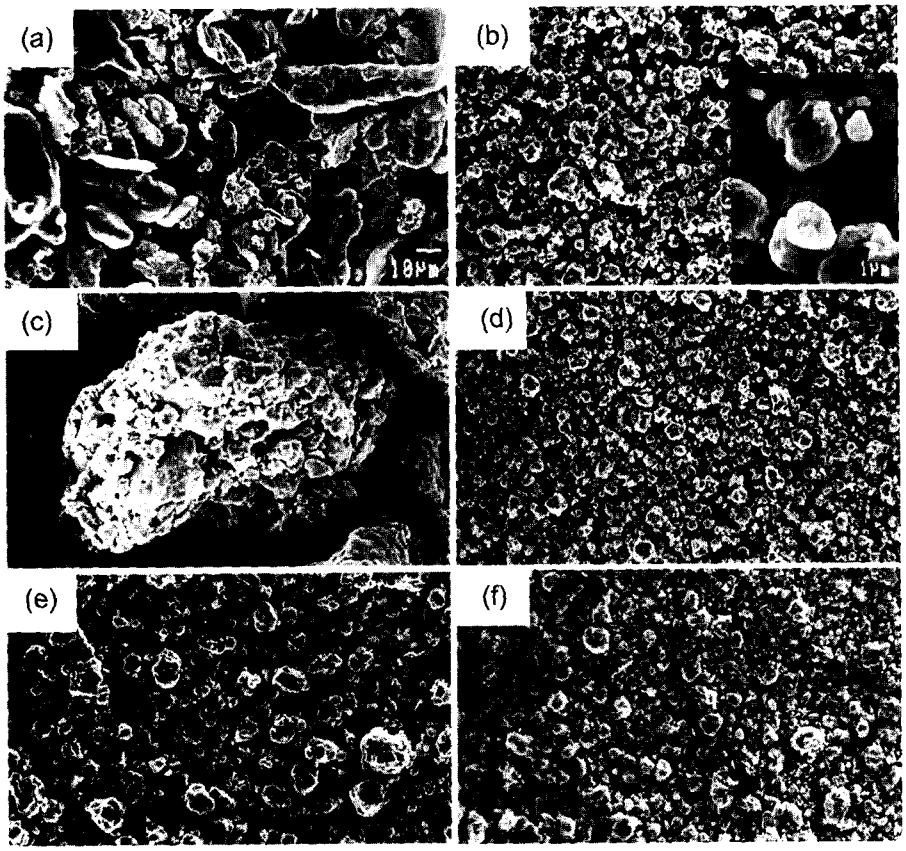

Fig. 2. SEM images of $Al_{0.6}(Fe_{75}Co_{25})$ after different milling times: (a) 0 h, (b) 100 h, (c) 200 h, (d) 300 h, (e) 400 h and (f) for the leached specimens at 400 h.

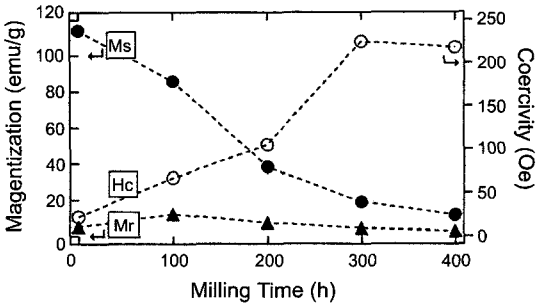

Fig. 3. The saturation magnetization, residual induction, and coercivity of the $Al_{0.6}(Fe_{75}Co_{25})$ as a function of the milling time.

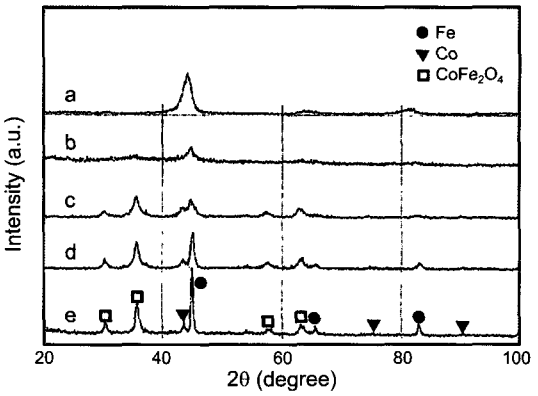

Fig. 4. X-ray diffraction patterns of, (a) the as-milled powder, (b) the leached specimen, (c) the leached specimen after annealing at 400°C for 1 h, (d) at 500°C for 1 h and (e) at 600°C for 1 h.

composite units of about 10~100 μm in diameter (Fig. 2b); they were blocky or plate-like. Upon increasing t, the agglomerated particles broke down, and from 300 h of milling (Fig. 2d), the particles were much finer and more uniform in shape, and with an average particle size of about 1.5 μm. The entire rod milling process could be divided into three different stages, i.e. agglomeration ($0<t\leq 100$ h), disintegration ($100\ h<t\leq 300$ h), and homogenization stages ($300\ h\leq t\leq 400$ h). Fig. 2f presents an SEM micrograph of a leached specimen originally produced at 400 h. The size and shape of the particles before (Fig. 2e) and after (Fig. 2f) leaching were almost unchanged, but the shapes of the leached powders were somewhat pressed because of the removal of Al by chemical leaching.

Fig. 3 shows the saturation magnetization M_s (emu/g), the residual induction M_r (emu/g) and the coercivity H_c (Oe) of variously milled powder samples. M_s decreased with increased t, and M_r decreased with increasing t from 100 h. M_s of the powders before milling was about 113.8 emu/g, which reduced to about 11.55 emu/g after milling of 400 h (as-milled powder). Therefore, M_s is reduced about 10 times. The magnetization M_s of the leached specimen (57.16 emu/g) was higher than that of the as-milled powder. However, the shapes of the hysteresis loop of the as-milled and leached specimens was unchanged. The M_s value of the leached specimen, smaller than that of the Fe-Co system, suggests the presence of non-magnetic impurities of either Al (9.86 wt%), oxygen (10.40 wt%), or hydrogen (0.32 wt%), as detected by ICP[18]. H_c generally increased with increased t. H_c after milling for 400 h (217.9 Oe) increased about 5.4 times over the as-received powder (40.43 Oe). This increased H_c resulted mainly from the internal stress.

Fig. 4 shows the XRD patterns of the as-milled powders (curve a), the leached specimen (curves b), the leached specimen annealed at 400°C for 1 h (curve c), the leached specimen annealed at 500°C for 1 h (curve d), and the leached specimen annealed at 600°C for 1 h (curve e). Leaching of the Al from the as-milled powder did not induce any significant change in the diffraction pattern, even though the Al had been removed. After annealing the leached specimen at 400°C for 1 h, the as-milled nanoscale crystalline phase was transformed in the cubic Co and bcc type Fe, and $CoFe_2O_4$ phases, which were accompanied by a change in the magnetic properties. Specially, the structure of Co was changed from the hexagonal structure of the as-milled powder to a cubic one.

The DSC traces of the as-milled and leached specimens obtained at a heating rate of 10 °C/min are shown in Fig. 5. The peak temperatures of the leached specimen, T_{p1} and T_{p2}, were 280.1°C and 470.8°C, respectively. The peak temperature of the as-milled powder, T_p, was 506.5°C. In the DSC curves of the leached specimen, the low-temperature peaks observed at 98.0°C and 135.0°C was not found to correlate with any structural changes.

To determine the corresponding microstructures, TEM observations were carried out. Fig. 6a shows a bright field image (BFI), dark field images (DFI), and the corresponding selected-area diffraction (SAD) pattern of the as-milled powder. The structure was fine with a crystallite size of about 7.0~15.0 nm, as calculated from the XRD patterns of the as-milled powder (about 15.0 nm)[19]. In addition, the SAD pattern indi-

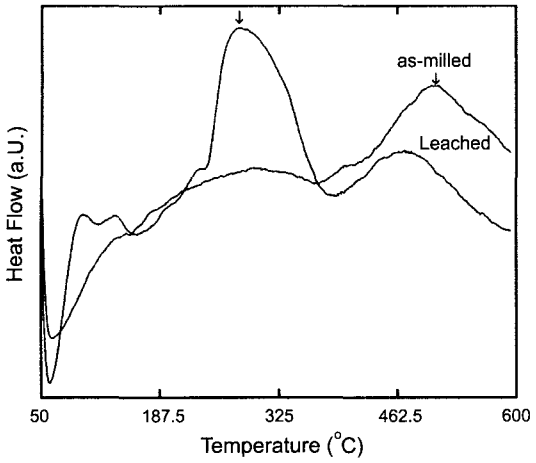

Fig. 5. DSC curves of as-milled and leached specimens.

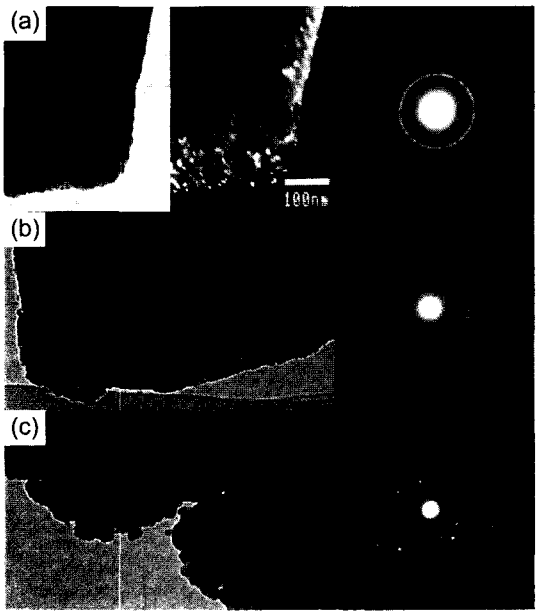

Fig. 6. TEM images and SAD patterns of (a) bright-field and dark-field TEM images, together with the corresponding diffraction patterns for as-milled powder, (b) the leached specimen and (c) the leached specimen after annealing at 600°C for 1 h.

cated a typical bcc type structure. As shown in Fig. 6b, the crystallite sizes of the leached specimen were finer and more homogeneous than those of the as-milled powder and had topotactically kept their nanometer order crystalline structure even though most of the Al atoms had been removed. The electron micrograph and the SAD pattern of the leached specimen annealed at 600°C for 1 h are shown in Fig. 6c. The

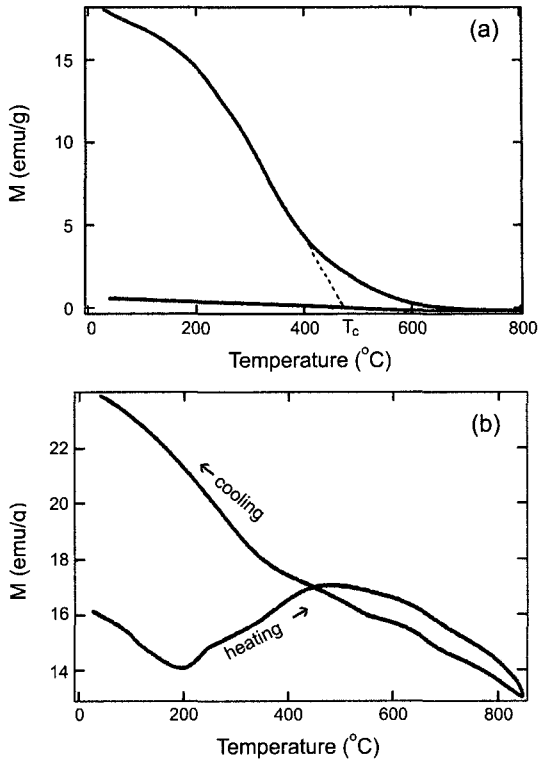

Fig. 7. Temperature dependence of the magnetization of leached specimen subjected to the temperature cycle RT↔ 850°C.

initial nanometer-order crystalline phases had a relatively larger crystalline phase with increasing annealing temperature. The corresponding SAD pattern showed several diffraction rings and spots, which were attributed to the nanocrystalline structure in accordance with the XRD results.

Fig. 7 shows the temperature dependence of the magnetization, M, for the leached specimen in an applied magnetic field of 5 kOe. M decreased gently at first to 215.4°C with heating, then increased gently to 474.1°C, and finally decreased gently to 850.0°C, as the Fe and Co atoms were rearranged. On cooling the specimen from 850°C, M increased slightly, then increased sharply at approximately 364.8°C, indicating that the bcc $Al_{0.4}Fe_{0.6}$ phase had been transformed to the Fe and Co phases. M_s and the Curie temperature, T_c, are the magnetic properties most frequently used for phase analyses. T_c is the temperature at which the spontaneous magnetization vanishes for zero magnetic field. T_c wase about 464.0°C for as-milled powder.

4. Conclusions

This study shows that as-milled, non-equilibrium, nanocrystalline, $Al_{0.6}(Fe_{75}Co_{25})$ alloy and leached specimen can be prepared using a combination of rod milling and chemical leaching in basic solution. After 400 h, only the $Al_{0.4}Fe_{0.6}$ peak of the bcc type was present in the XRD pattern. The entire rod milling process could be divided into three different stages,: agglomeration, disintegration, and homogenization. The saturation magnetization, M_s decreased with increased milling time, M_s of the powders before milling was about 113.8 emu/g, M_s after milling for 400 h was about 11.55 emu/g. Leaching of the Al from the as-milled powders did not induce any significant change in the diffraction pattern. After annealing at 600°C for 1 h, the nanoscale crystalline phase was transformed into the bcc Fe and cubic Co, and $CoFe_2O_4$ phases. On cooling the specimen from 850°C, the magnetization increased slightly, then increased sharply at approximately 364.8°C, indicating that the bcc $Al_{0.4}Fe_{0.6}$ phase had been transformed to the Fe and Co phases.

Acknowledgments

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