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Effects of Annealing Temperature on $Co_{30}Cu_{70}$ Mechanical Alloys

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ABSTRACT

Physical properties of $Co_{30}Cu_{70}$ mechanical alloys prepared by ball milling were investigated. After milling for 50 h, the powder contained Co-rich, Cu-rich clusters as well as Co-Cu solid solution. Annealing at 200 - 300 °C for 30 min modified thermal behaviors but only slightly affected magnetic properties. Higher temperature annealing (400 - 500 °C) led to substantial oxidation of Co and Cu and deteriorated magnetic properties. Pressed $Co_{30}Cu_{70}$ pellets exhibited 0.6 - 2 % giant magnetoresistance (GMR) but showed modest GMR after heat treatment. GMR disappeared by annealing at 500 °C as large fractions of Co and Cu were converted into oxides.

Keywords: Giant magnetoresistance, mechanical alloying, annealing

INTRODUCTION

Magnetoresistance (MR) is a change in electrical resistance when materials are subjected to a magnetic field. The applications of MR are in the sensing and recording industries. MR can be classified into several types according to their origin. The first known MR is due to the Lorentz force in metals and semiconductors [1]. In addition to this ordinary MR, ferromagnetic materials also possess anisotropic magnetoresistance (AMR) due to spin-orbit interactions [2]. The third type of MR, currently implemented in computer hard drives, is giant magnetoresistance (GMR) due to spin dependent scattering. After the discovery of GMR in multilayers [3], research has been extended to other structures. One example is Co-Cu mechanical alloys (MA) produced by milling fine ferromagnetic Co powder with non-ferromagnetic Cu powder. After the milling, the mixture becomes nanoscale Co granules embedded in a Cu matrix. These Co granules are in single-domain size ranges. Single-domain particles of different sizes have different blocking temperatures at which they are unblocked and become superparamagnetic. In a zero magnetic field, magnetic moments of superparamagnetic Co arrange randomly. As the magnetic field increases, the magnetic moments gradually align in the field direction. Since the electron scattering is spin dependent, the resistance decreases according to the orientation of magnetic moments and approaches saturation when most magnetic moments are aligned. According to Ikeda *et al* [4], Aizawa and Zhou [5], Zhang *et al* [6] and Champion *et al* [7], a maximum room temperature GMR of 4 - 6 % were observed in $Co_{30}Cu_{70}$ and $Co_{20}Cu_{80}$. In these studies, the alloying took place either in vacuum or argon atmosphere and oxide formation was therefore subdued. In our previous work, we showed that by milling $Co_{30}Cu_{70}$ powders in ethanol for 30, 60, 120 h, the powder exhibited GMR after compacting [8] and anomalous MR after encapsulating [9]. In this paper, structural, thermal, magnetic and magnetotransport properties of mechanically alloyed $Co_{30}Cu_{70}$ before and after heat treatment are studied.

MATERIALS AND METHODS

Mechanically alloyed $Co_{30}Cu_{70}$ were prepared by ball milling. Cobalt powder (of 99.8 % purity with average particle size less than 2 microns) and copper powder (of 99 % purity with average particle size less than 10 microns) with the atomic ratio 30:70 were mixed in a steel vial containing steel balls. In order to prevent the powder from sticking to the vial during the milling, ethanol was added to the mixture. The sealed vial was then spun on a milling machine for 50 h. After the milling, ethanol was removed by baking the mixture in an oven (150 °C for 18 h). The powders were characterized by scanning electron microscope (SEM), laser particle size analyzer, X-ray diffractometer (XRD), vibrating sample magnetometer (VSM) and differential scanning calorimeter (DSC). Measurements of MR were performed on bulk samples with a four-point probe technique. To produce bulk samples, the alloy powder was pressed into pellets under a high pressure of 15 MPa. The pellet was mounted on the end of a measurement probe where four pins made electrical contact with the sample. The probe was then installed between electromagnetic poles. A constant dc current was passed between a pair of outer contacts and the voltage drop across two inner contacts was measured by a nanovoltmeter. A computer-controlled power supply continuously swept the magnetic field up to 11 kOe and the voltage reading was transferred from the nanovoltmeter to a computer by a GPIB interface. The resistance was then deduced and plotted as a function of the magnetic field. The MR magnitude is defined as $100\times(R(H)-R(0))/R(0)$ where R(0) and R(H) are resistance in zero and 11 kOe fields, respectively. To study the effect of heat treatment, selected samples were annealed at 200, 300, 400 and 500 °C for 30 min.

RESULTS AND DISCUSSION

According to SEM micrographs in **Figure 1**, submicron granules tend to agglomerate as micron-sized clusters. Size distribution of the clusters, measured by laser particle size analysis, is shown in **Figure 2**. As-milled $Co_{30}Cu_{70}$ powder shows bimodal distribution with an average diameter around 20 μm and 100 μm. The cluster size is modified by the ball milling via two competing mechanisms. Fracturing breaks clusters into smaller pieces whereas cold welding tends to increase size of clusters. From our measurements, the precise composition and distribution of Co and Cu granules in these clusters cannot be obtained but we expect both clusters of fcc Co-Cu solid solution and inhomogeneous clusters due to the decomposition between Co and Cu.

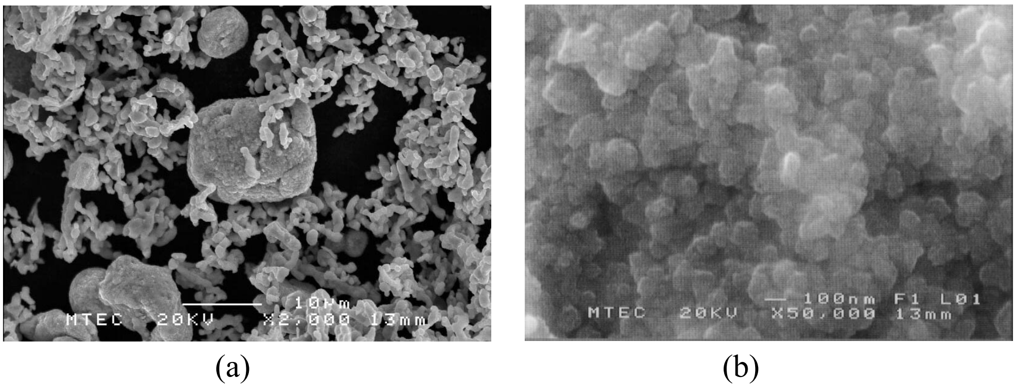

Figure 1 SEM micrographs of as-milled $Co_{30}Cu_{70}$ alloys taken with a magnification of (a) 2,000 and (b) 50,000.

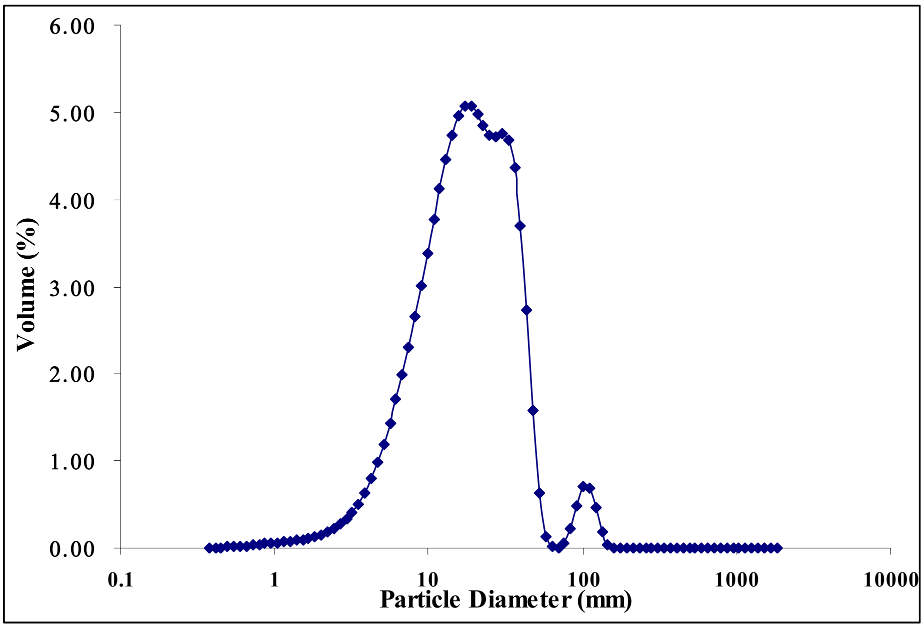

Figure 2 Particle size analysis of as-milled $Co_{30}Cu_{70}$ powder.

From XRD analysis of starting powders, the Co powder consists of fcc and hcp phases and the Cu is fcc. After the milling (**Figure 3**), the alloy is mainly composed of hcp Co and fcc Cu but the fcc Co peaks are not clearly identified. Gente [10], Yoo [11], Elkalkouli [12] and their co-workers similarly showed that fcc Co XRD peaks disappear after a few hours of Co-Cu milling. Gente *et al* [10] also analyzed the thermodynamics of the Co-Cu system and suggested that the formation of a solid solution was preferred to the amorphous phase. The formation of a supersaturated fcc solid solution was confirmed by X-ray absorption fine structure (EXAFS) [11]. After heat treatment, oxide peaks are observed and their intensity increases with annealing temperatures. By annealing at 400 and 500 °C, both Cu and Co are largely oxidized and oxide peaks clearly grow at the expense of Co and Cu peaks. Annealing temperature is therefore divided into 2 regimes; 200 - 300 °C for the low temperature regime and 400 - 500 °C for the high temperature regime. It is also noted that the heat treatment affects the lattice constants of Co and Cu (measured by XRD) because of the lattice recovery process. Thermal treatments at 200 and 300 °C decrease the lattice constant of Cu (from 2.087 to 2.082) but increase that of Co (from 1.913 to 1.922). This can be attributed to the decomposition of Co and Cu. By annealing at 400 and 500 °C, lattice constants of both Co and Cu are reduced to 1.911 and 2.079 respectively as both metals are largely oxidized.

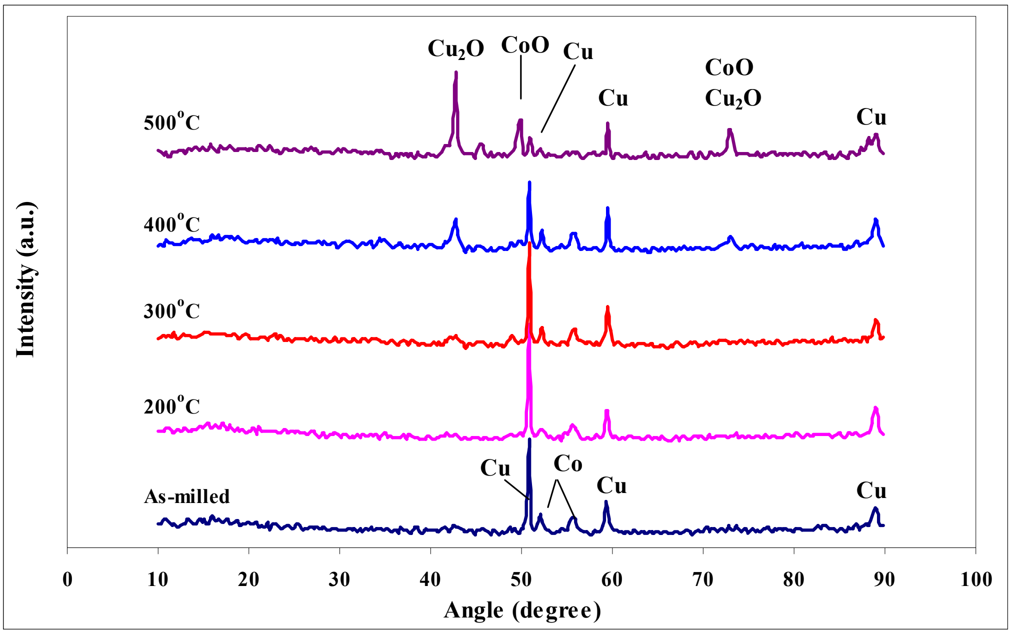

Figure 3 X-ray diffraction patterns of as-milled and annealed $Co_{30}Cu_{70}$ alloys.

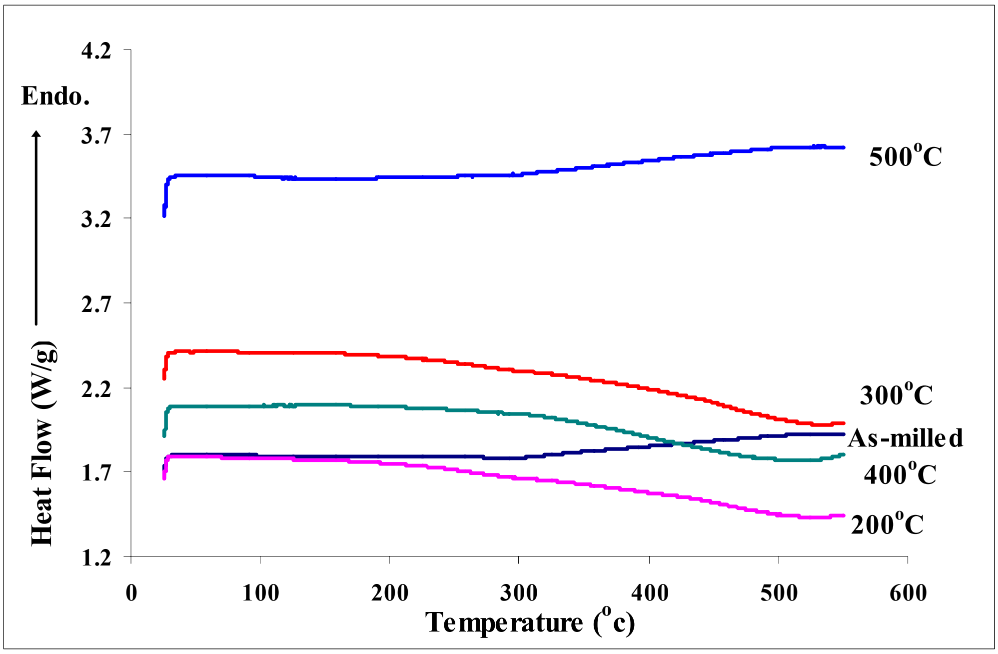

Figure 4 DSC curves of as-milled and annealed $Co_{30}Cu_{70}$ alloys.

In **Figure 4**, the as-milled sample is characterized as endothermic due to its heat absorption in a lattice recovery process. Thermal energy gained by annealing at 200 - 400 °C leads to decomposition and the samples become exothermic. The sample reverts to endothermic after large amounts of Co and Cu are oxidized by annealing at 500 °C. These thermal behaviors are different from the broad exothermic double peak observed by Gente and co-workers [10]. They also proposed that, unlike Cu-Ta and Cu-W, Co-Cu did not absorb large quantities of nitrogen and oxygen. Moderate oxygen content did not influence phase formation and heat of mixing. However, large oxygen content is involved in our samples and is able to modify thermal behaviors.

Room temperature magnetization curves of as-milled and annealed $Co_{30}Cu_{70}$ samples are shown in **Figure 5**. Wide hysteresis loops indicate the existence of non-superparamagnetic Co-rich clusters even after the 50-h milling. This result, agrees with that of Elkalkouli *et al* [12], confirming that decomposition of Co and Cu can occur even without annealing. The as-milled sample has a coercivity of about 250 Oe, remanence about 4 emu/g and magnetization about 40 emu/g in a 10-kOe magnetic field. Magnetization can be as high as 162 emu/g in bulk Co but complete saturation may not be obtained in granular structures because of their large anisotropy [12]. By annealing at low temperatures (200 - 300 °C), the saturation magnetization, remanence and permeability are only slightly modified but these parameters significantly decrease after annealing at high temperatures (400 - 500 °C). This can be understood in terms of the reduction of the ferromagnetic Co phase under high temperature annealing.

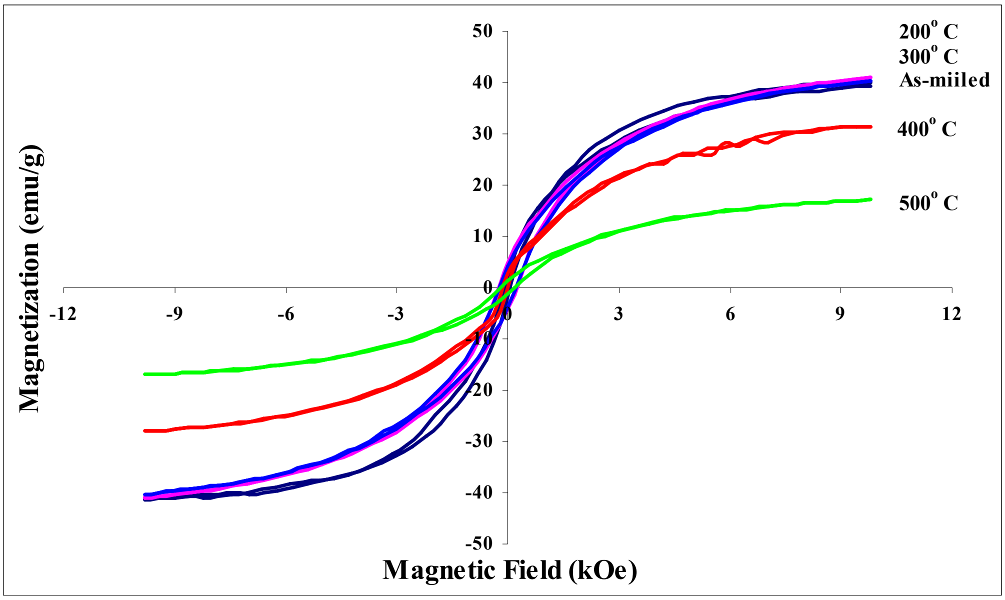

Figure 5 Magnetization curves of as-milled and annealed $Co_{30}Cu_{70}$ alloys.

The pressed $Co_{30}Cu_{70}$ pellets have an electrical resistance of the order of 10 kOhm. The resistance decreases with increasing annealing temperatures because of the lattice recovery by the thermal treatment. Before annealing, the pressed pellets exhibit 0.6 - 2 % GMR in a 11-kOe magnetic field. In **Figure 6**, a sharp drop in the MR curve corresponds to magnetization reversal of a large number of Co-rich clusters. Thus, thermal treatment reduces GMR. The samples annealed at 200 - 400 °C exhibit only 0.06 - 0.41 % GMR and GMR is not observable in any samples annealed at 500 °C. The disappearance of GMR coincides with the growth of oxide phases as previously shown by XRD and VSM.

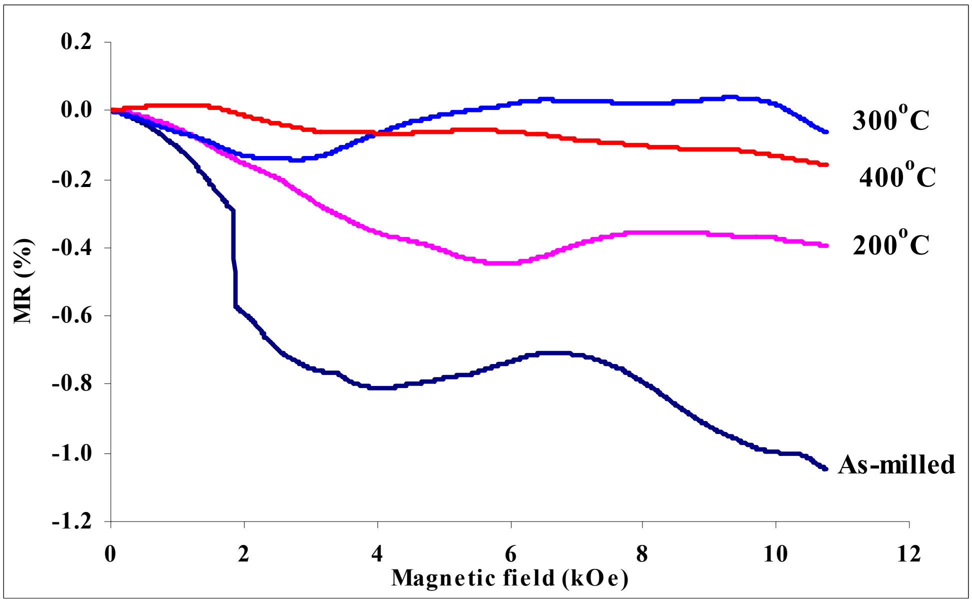

Figure 6 Room temperature MR curves of as-milled and annealed $Co_{30}Cu_{70}$ pressed pellets.

CONCLUSIONS

Thermal treatment affects the structural, thermal, magnetic and magnetotransport properties of $Co_{30}Cu_{70}$ alloys. Thermal treatments at 200 and 300 °C only slightly modify magnetic properties but higher temperature annealing has adverse effects on magnetic properties and GMR because of the replacement of ferromagnetic phase by oxides. It is therefore necessary to control oxygen during the annealing process.

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บทคัดย่อ

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ผลของการให้ความร้อนต่ออัลลอยด์เชิงกล $Co_{30}Cu_{70}$

งานวิจัยนี้ศึกษาสมบัติกายภาพของอัลลอยด์เชิงกล $Co_{30}Cu_{70}$ ที่เตรียมจากวิธีบดผงด้วยลูกบดโลหะ ภายหลังการหมุนบด 50 ชั่วโมง ตัวอย่างประกอบด้วยกลุ่มผงที่มีโคบอลท์สูง กลุ่มผงที่มีทองแดงสูง และส่วนที่เป็นสารละลายของแข็งโคบอลท์-ทองแดง การให้ความร้อนที่อุณหภูมิ 200 - 300 องศาเซลเซียส เป็นเวลา 30 นาที เปลี่ยนพฤติกรรมเชิงความร้อนของตัวอย่าง แต่ส่งผลต่อสมบัติแม่เหล็กเพียงเล็กน้อย การให้ความร้อนที่อุณหภูมิสูงขึ้น (400 - 500 องศาเซลเซียส) นำไปสู่การเกิดออกไซด์ของทองแดงและโคบอลท์ และทำลายคุณสมบัติทางแม่เหล็ก ผง $Co_{30}Cu_{70}$ ที่อัดขึ้นรูปแสดง GMR 0.6 - 2 % แต่ GMR ลดลงภายหลังการให้ความร้อน ตัวอย่างที่ผ่านอุณหภูมิ 500 องศาเซลเซียส ไม่แสดง GMR เลย เนื่องจากโคบอลท์และทองแดงส่วนใหญ่ถูกเปลี่ยนเป็นออกไซด์

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