Effect of severe plastic deformation on the coercivity of Co-Cu alloys

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Cast Co–5.6 wt% Cu and Co–13.6 wt% Cu alloys were subjected to severe plastic deformation (SPD) by high-pressure torsion (HPT). The HPT treatment drastically decreases the size of the Co grains (from 20 μm to 100 nm) and the Cu precipitates (from 2 μm to 10 nm). As a result, the coercivity H_c of both the alloys radically increases. The saturation magnetization, M_s, remains almost unchanged. Thus, SPD of the bulk samples opens the way for drastic increase in the coercivity for the Co-based alloys.

Keywords: coercivity; Co-based alloys; high-pressure torsion; magnetic properties; plastic deformation

1. Introduction

Among ferromagnetics, Co possesses the maximal Curie temperature, T_c, and a large saturation magnetization, $M_s = 1.8$ T. Any increase in the coercivity, H_c, of Co-based and its alloys will make them attractive for many novel applications. The most general way to increase H_c is to decrease the grain size in the Co matrix and to tailor the shape and composition of second-phase precipitates. Such attempts were performed with Co-based nanograined materials obtained by ball milling [1–3] and electrodeposition [4–7]. These methods allow a moderate increase in the value of H_c in comparison with coarse-grained counterparts, namely a factor of two by ball milling [1] and a factor of three by electrodeposition [4]. The method of severe plastic deformation (SPD) is very promising for an increase in H_c since it produces a drastic decrease in the grain size in bulk materials [8–12]. It has been shown recently that SPD causes grain refinement and decomposition of a supersaturated solid solution [11,12]. The phase composition closely approaches the equilibrium state at SPD pressure and temperature. It has been concluded that SPD can be considered as a balance between deformation-induced grain refinement and deformation-accelerated formation of equilibrium phases. This work is devoted to the investigation of the possibility of increasing H_c in bulk Co-based alloys by SPD.

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The use of diamagnetic or paramagnetic particles or intergranular layers to increase H_c is also promising [13]. Diamagnetic Cu was chosen as an alloying element in this work. Our preliminary studies demonstrated that solid Cu not only forms isolated particles in the grain boundaries (GBs) in the Co matrix, but can also completely 'wet' the Co GBs, similar to the solid-phase wetting in Zn–Al alloys [14].

2. Experimental

Co–5.6 wt% Cu and Co–13.6 wt% Cu alloys were prepared from high-purity 5N Cu and Co by a vacuum induction melting in a form of 10 mm diameter cylindrical ingots. For the high-pressure torsion (HPT) treatment discs of 0.4 mm thickness were cut from the as-cast ingots, then ground and chemically etched. They were subjected to HPT at room temperature under a pressure of 6 GPa in a Bridgman anvil type unit (5 torsions; duration of process about 300 s; shear strain of about 6) [8]. Samples for structural and magnetic investigations were cut from the HPT-deformed discs at a distance of 3 mm from the sample center. The central (low-deformed) part of each disc (about 3 mm in diameter) was excluded from further investigations. A set of as-cast samples with the same Co concentration were prepared for investigations of structure and magnetic properties. Light microscopy (LM) was performed using a Neophot-32 microscope equipped with a 10 Mpix Canon Digital Rebel XT camera. For the metallographic investigations, the samples were ground by SiC grinding paper, polished with 6, 3 and 1 μm diamond pastes and etched for 5–10 s in a 1:1 solution of H_2O and HNO_3. Magnetic measurements were performed using a SQUID, with its magnetic field applied parallel to the sample plane. X-ray diffraction (XRD) data were obtained on Siemens diffractometer (Fe-Kα radiation). Transmission electron microscopy (TEM) investigations were carried out on a JEM–4000FX microscope with an accelerating voltage of 400 kV. The grain size was estimated by a modified Williamson–Hall approach for the XRD profile analysis [15].

3. Results and discussion

In Figure 1, bright-field TEM micrographs of Co–5.6 wt% Cu alloy in the as-cast state (a) and after HPT deformation (b) are shown. In the as-cast state, the microstructure consists of large grains (20 μm) of supersaturated solid solution of Cu in Co and Cu precipitates with a mean size of 2 μm. According to XRD measurements and reference data of Cu solubility in a Co matrix [16], the supersaturated solid solution (Co) contains from 2 to 5 at% Cu. Cu particles in the as-cast Co-based alloys also contain some Co (the shift of XRD peaks is visible, but their intensity is low owing to the low number of Cu-particles). The (Co) matrix consists of a mixture of Co grains with face-centered cubic (fcc) structure and grains with hexagonal close-packed (hcp) structure. In the as-cast state, the grains of fcc Co contain numerous fine twins (Figure 1a). Below 722 K, the hcp Co is stable. Fcc Co is an equilibrium phase above 722 K; however, it can be easily supercooled. Usually, fcc Co, formed during solidification, remains in the cast samples even at moderate
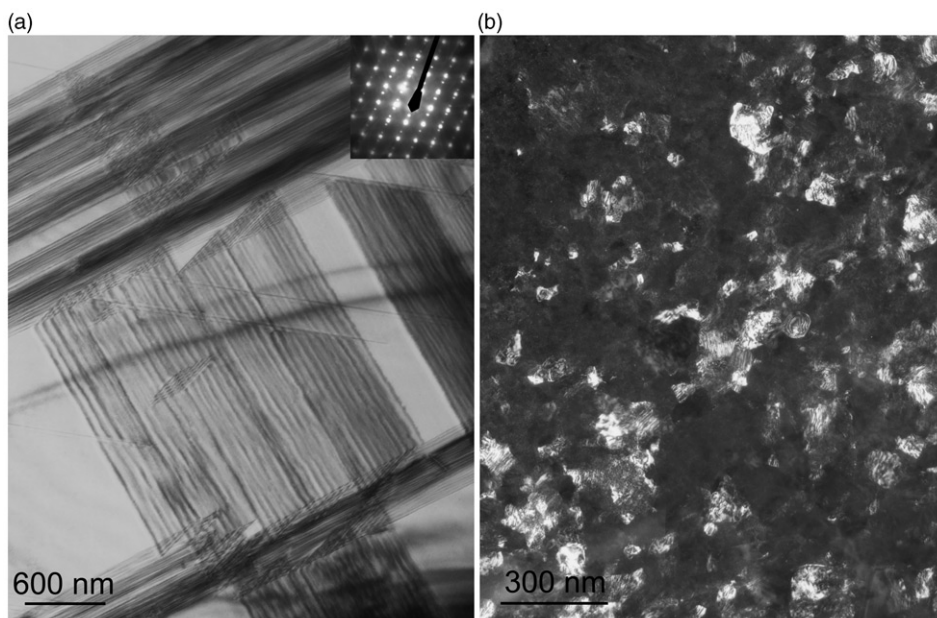
Figure 1. TEM micrographs of Co–5.6 wt% Cu alloy (a) in the as-cast state (bright-field) and (b) after HPT deformation (dark-field).

cooling rates [17–20]. However, the Co films grown on the cold substrates from the Co-based plasma can have hcp structure [20].

The HPT treatment drastically decreased the size of the Co grains (to 100 nm). Owing to the small Cu concentration and hence low peak intensity, the size of Cu precipitates was only roughly estimated to be about 10 nm. The samples remained dense and free from pores after HPT. The supersaturated solid solution (Co) completely decomposed and formed almost pure Co grains and Cu precipitates. The 'primary' Cu particles, which were also supersaturated by Co in the as-cast state, decomposed and transformed into practically pure Cu precipitates. The fcc Co also disappeared, and only hcp Co remained in the HPT-treated alloys. In other words, similar to our previous work on Al–Zn and Fe–C alloys [11,12,21], HPT led to the formation of phases which are stable at the temperature of the HPT treatment (ambient temperature). Numerous twins also disappeared from the microstructure. The Co grains after HPT are small, equiaxial, free from twins and mainly contain low-angle dislocation sub-boundaries.

The magnetization curves are shown for both Co alloys (with 5.6 and 13.6 wt% Cu) before and after HPT in Figure 2. The saturation magnetization M_s remains almost unchanged after HPT and is equal to 155 emu/g for the Co–5.6 wt% Cu and 140 emu/g for the Co–13.6 wt% Cu alloy. The coercivity H_c of both alloys radically increases, namely from 13 ± 1 Oe to 120 ± 3 Oe for the Co–5.6 wt% Cu alloy and from 1.7 ± 0.2 Oe to 104 ± 3 Oe for the Co–13.6 wt% Cu alloy. In other words, HPT increases H_c by about 10–60 times. HPT formed fine (about 100 nm) and equiaxial Co grains randomly mixed with extremely small ($\sim$10 nm) Cu grains. Such refinement
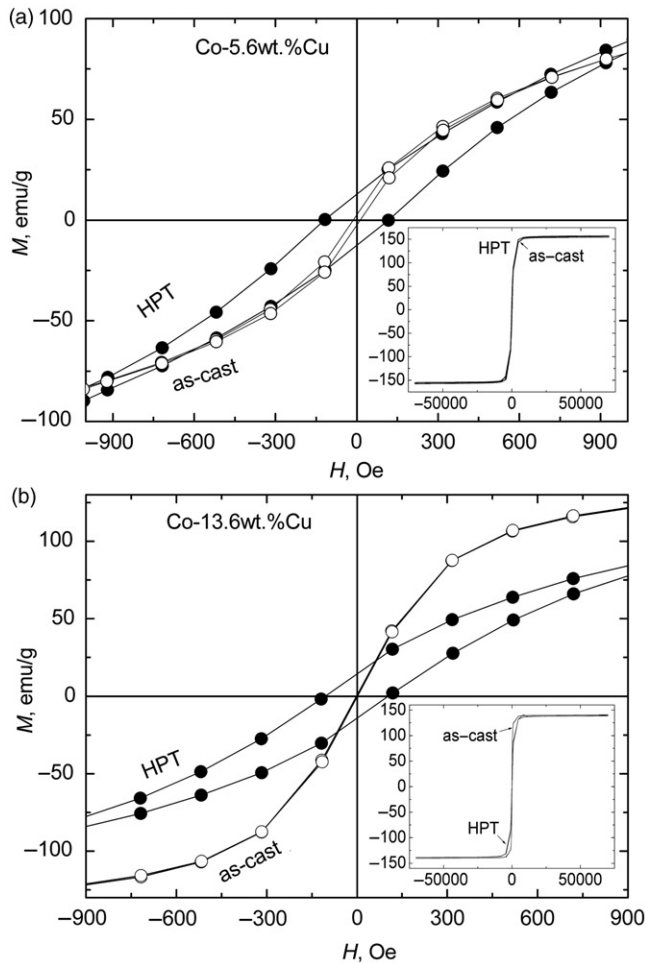
Figure 2. Dependences of magnetization M on the applied field H for the Co–5.6 wt% Cu (a) and Co–13.6 wt% Cu (b) alloys in the as-cast state (open circles) and after HPT (full circles). Full $M(H)$ curves are shown in the insets.

of ferromagnetic matrix grains and diamagnetic precipitates drastically increased the coercivity in comparison with the coarse-grained alloys [13,22]. Although the value $H_c = 120 \pm 3$ Oe for the Co–5.6 wt% Cu alloy after HPT is low in comparison with existing hard magnetic alloys, the large relative increase in H_c allows the conclusion that SPD is a very promising method for increasing coercivity. It is especially important that after HPT the alloys contain phases which are equilibrium at room temperature. This property is necessary to ensure the stability of the structure during the lifetime of the material.

It is important to ask why HPT leads to better results in increasing coercivity than other methods used for the synthesis of nanograined materials. Electrodeposition also allows one to obtain the grain size of a few nanometres [4–7]. Electrodeposited Co films also contain only hcp-Co, and no fcc-phase. This is

favorable for high H_c since fcc structured Co is more magnetically reversible than hcp-structured Co [6,7]. However, electrodeposition allows one to obtain rather thin films. These films are usually not completely dense, contain holes and are frequently contaminated by impurities and oxides. SPD methods allow the production of poreless bulk nanograined materials and impose no chemical restrictions for alloying by second (third, etc.) components [23]. Up to now, electrodeposition has allowed an increase in H_c by a factor of three in comparison with coarse-grained counterparts [4]. This is easy to understand, since electrodeposited films are not completely dense and the slots between the grains drag the magnetic domain walls. Our method increases H_c by about 10–60 times (Figure 2) without any internal cracks.

Another important method for the production of nanograined Co is ball milling (or mechanical alloying) [1–3]. In this method, the individual particles are subjected to external action from the other particles, the milling bodies and the walls of the mill. Therefore, the results of the ball milling are similar to those of ion implantation. In a sense, the second components are 'implanted' into the surface of the particles during the milling. These lead to the formation of supersaturated solid solutions, metastable phases, etc. [1–3]. In the case of Co and Co-based alloys, ball milling produces nanograins (10 nm), but leads to the formation of supersaturated solid solutions (for example to the dissolution of 9 wt% Co in Cu) [2]. Ball milling also forms metastable fcc-Co and introduces stacking faults, reducing H_c [1]. Ball-milled materials need additional isothermal annealing at increased temperature for the precipitation of non-ferromagnetic particles. The mechanism of SPD (including HPT) is in principle different from ball milling. It also leads to grain refinement, but the intensive lattice shear leads to the formation of the phases, which are stable at the temperature and the pressure of SPD. All metastable phases disappear [11,12,21], most probably because the shear deformation shuffles the atoms in the lattice and also produces many additional vacancies. The diffusion of these to sinks (dislocations, GBs, interfaces) ensures the formation of stable phases and destroys the metastable phases even at room temperature. From this point of view, one can compare SPD with neutron bombardment, just as ball milling is comparable to ion implantation. As a result, SPD produces a uniform distribution of very fine Cu particles and a low-temperature hcp Co phase, at the same time destroying the stacking faults which were present in as-cast alloys. According to [22], the coercivity can be described by the equation $H_c(T) = 2\mu_0 K_1 / M_s$, where K_1 is the constant of magnetic anisotropy and μ_0 is the magnetic permeability of free space. The magnetic anisotropy is much higher for hcp Co than for the fcc phase. Therefore, the complete exclusion of the fcc Co after HPT also contributes to the coercivity increase. SPD-treated materials have no free surface that can oxidize as is the case with ball milling, and contaminations usually present in ball-milled materials are excluded [3]. Up to now, ball milling has allowed an increase in H_c by a factor of two in comparison with coarse-grained counterparts [1]. Our method has increased H_c by about 10–60 times (Figure 2).

Thus, SPD of bulk samples opens a novel way for the drastic increase in coercivity H_c for the Co-based alloys and possesses great advantages for the synthesis of advanced magnetic materials. Further increase in coercivity in Co-based alloys may be reached by the combination of SPD and smart alloying of Co. In particular, experimentation with the composition of the ferromagnetic matrix

(for example, with Fe, Ni, etc.) and the precipitates (additions of Nd, Pr, etc.) bear considerable potential for the development of Co-based magnetic materials.

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