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SPD-induced changes of structure and magnetic properties in the Cu–Co alloys

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ABSTRACT

The microstructure and magnetic properties of binary Cu–Co alloys are studied. The investigations have been carried out using samples in two structural states, i.e. as-cast and after severe plastic deformation by the high-pressure torsion (HPT) carried out at the ambient temperature and pressure of 6 GPa. The grain size after HPT is in the nanometer range. HPT allows one to control the ratio between ferromagnetic and superparamagnetic precipitates in the diamagnetic matrix.

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1. Introduction

At the moment, there is a lot of experimental works concerning the study of magnetic properties in nanocrystalline Cu-Co alloys. It is because these alloys have a pronounced giant magnetoresistance (GMR) effect. The nanocrystalline state of the alloys is manufactured by different techniques which can pronouncedly affect their structure and physical properties. The ball milling [1-5], electrodeposition [6-11], and melt-spinning techniques [12-16] were already used to control the microstructure and magnetic properties of nanocrystalline Cu-Co alloys. Very important method to produce bulk nanograined materials is the severe plastic deformation (SPD) [17-20]. SPD permits to control the grain size in one- and multiphase alloys on the very broad length scale. In particular, this feature allows reaching the unique combination of strength and plasticity [17-20]. SPD (in particular, high pressure torsion-HPT) forces the accelerated diffusion [21–24], despite of the fact that the high applied pressure (without deformation) always decreases the diffusivity and grain boundary mobility [25,26]. SPD also leads to the unusual phase transformations. Particularly, SPD drives the formation of the phases which are in the equilibrium at the certain effective temperature T_{eff} which is much higher than the temperature T_{SPD} of SPD treatment $T_{\text{eff}} > T_{\text{SPD}}$ [23,27,28]. However, the potential of SPD to control the magnetic properties is scarcely studied, in particular in the Cu–Co alloys. The goals of this work are to investigate for the first time: (1) the microstructure evolution of the Cu–Co alloys during SPD processing; (2) the interaction of nanostructures produced in the alloys and their magnetic properties; (3) the magnetization mechanisms providing the enhancement of magnetic characteristics in Cu–Co alloys.

2. Experimental

The Cu–Co alloys with 2.2 and 4.9 wt% Co were prepared from the high-purity 5N Cu and Co by a vacuum induction melting in a form of cylindrical ingots. For HPT processing the 0.4 mm thick discs 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 rotations of the anvil with the rate of 1 rpm). Samples for structural and magnetic investigations were cut from the HPT-processed discs at a distance of 3 mm from the sample center. A set of the as-cast samples with the same Co concentration were prepared for the investigations of structure and magnetic properties as well. Light microscopy (LM) was performed on a Zeiss Axiophot microscope. For the metallographic investigations the samples were ground by SiC grinding paper, polished with 6, 3, and 1 μ m diamond pastes and etched for 5–10 s in 1:1 solution of H₂O and HNO₃. X-ray diffraction (XRD)



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data were obtained on a Siemens diffractometer (Co K_{α} radiation). Magnetic measurements were fulfilled on SQUID (Quantum Design MPMS-7 and MPMS-XL). Magnetic field in the SQUID was applied parallel to the sample plane and was up to 7 T. The magnetisation of samples was measured at 290 K. Transmission electron microscopy (TEM) investigations were carried out on a JEM-4000FX microscope with an accelerating voltage of 400 kV and on a Tecnai G2 F20 microscope at an accelerating voltage of 200 kV.

3. Results and discussion

In Fig. 1 the microstructure of as-cast alloys is shown. It contains the Cu-rich matrix with grain size about 20 μ m. This (Cu)-matrix contains primary (Co) particles [29] with Cu content around 13 wt% Co and size of 2 to 10 μ m (Fig. 1a) and rather small secondary (Co) precipitates with size between 5 and 20 nm (Fig. 1b and c). The ring-like contrast between small Co-particles and Cu-matrix as an artifact appeared due to the very low brightness difference between Co and Cu. It may be partly driven by the mechanical stresses around semicoherent spherical Co precipitates. In Fig. 2 the microstructure of the alloys after HPT is shown. Fig. 2c is the electron diffraction pattern from the sample after HPT. All observed rings are from Cu grains with the corresponding reflection indices. Absence of the rings from Co



Fig. 1. Microstructure of as-cast Cu-rich alloys. (a) SEM micrograph of the Cu-4.9 wt% Co alloy, primary (Co) particles appear dark and are visible in the (Cu) matrix. (b) Dark field TEM micrograph of the Cu-2.2 wt% Co alloys, fine (Co) precipitates are visible.

grains is due to their low quantity and also due to the vicinity of Co d-values to the Cu ones. It has been observed previously that HPT of Co-rich Co-Cu alloys leads to the $fcc \rightarrow hcp$ transition in Co-matrix [30]. Unfortunately, the small size and low quantity of Co-particles as well as the vicinity of Co *d*-values to the Cu ones does not allow us to judge, whether the similar HPT-driven phase transformation in Co takes place in the Cu-rich Cu-Co alloys. The grain size drastically decreases. It is about 100 nm for the Cugrains and 30 nm for the Co-grains. The last value was evaluated from the XRD data. All grains are equiaxial; the Co-particles are uniformly distributed among Cu grains. The HPT of pure copper also leads to the strong grain refinement [31-33]. However, the grains in copper after HPT treatment in similar conditions are somewhat larger (370 nm [31,33] or 400 nm [31,32]). Most probably, the cobalt atoms solved in copper matrix together with Co-precipitates retard the dynamic recrystallization and slow down the grain growth in comparison with pure copper. The physical mechanism of retarded grain growth could be the GB segregation of Co atoms and impurity drag of GB migration [34]. No tendency exists to the formation of uniform wetting layers of Co between Cu grains (like it has been observed in Zn–Al [35–37], Al-Mg [38] and Co-Cu [39] systems). However, this does not exclude the presence of a thin segregation layer of Co at the grain boundaries. This segregation in the case of varying grain size may be responsible for nucleation of nanometric Co precipitates [40]. Even the single-layer GB segregation [41,42] can lead in polycrystals with the low grain size to the measurable decrease of the amount of a second phase (it would be Co-precipitates in our Cu-Co alloys) in comparison with the coarce-grained polycrystals [43,44]. A certain tendency to the faceting of Co/Cu interphase boundaries is visible (Fig. 1a) [45,46].

The coercivity H_C of the Cu–2.2 wt% Co alloy both in the as-cast state and after HPT is rather small (Table 1). Its magnetization *J* does not reach saturation by increasing applied magnetic field both before and after HPT (Fig. 3a). There is a standard procedure to make a conclusion if a specimen saturates or the saturation is not reached [47,48]: the value of magnetization is plotted versus 1/H or $1/H^2$; the degree is structurally dependent. As far as the magnetization have been recalculated to the amount of Co contained in the material, in case of saturation the dependence will be extrapolated in the limit of infinite external field to the saturation magnetization of pure Co $J_s = 162 \text{ emu}/g_{Co}$. The dependences *J* vs. 1/H for these two alloys are shown in in the same figure (Fig. 3c and d). They are linear for all alloys in the region near zero point.

It is obvious from the plots that both alloys are not saturated: the magnetization values extrapolated to the infinite field are much lower than tabulated value for pure Co. For the as-cast alloy magnetization is only 79 emu/g_{Co} at the vanishing 1/*H*, which is about 50% of the saturation magnetization for Co. After HPT the Cu–2.2 wt% Co alloy demonstrates typical superparamagnetic behavior without any tendency to saturation, namely $J=18 \text{ emu/g}_{Co}$ at $1/H \rightarrow 0$, which is only about 11% of pure Co.

The behavior of the Cu–4.9 wt% Co alloy is different (Fig. 3b). Its coercivity both in the as-cast and HPT state is much higher than that of Cu–2.2 wt% Co and even higher than that of Co-rich alloys (Table 1). The magnetization of the as-cast alloy reaches the saturation at J_s = 135 emu/g_{Co}. It is somewhat lower than the J_s for Co. However, if we did not take into the consideration the amount of Co remained in the (Cu) solid solution, the recalculated J_s value for the as cast Cu–4.9 wt% Co alloy would almost coincide with J_s for pure Co. The magnetization of the HPT-treated alloy does not saturate, although it is about three times higher at $1/H \rightarrow 0$ in comparison with the Cu–2.2 wt% Co alloy.

Possible origin of such magnetic behavior is the superparamagnetism of tiny Co particles which are precipitated in Cu-grains of



Fig. 2. TEM micrographs the Cu-2.2 wt% Co alloy after HPT (a) bright-field, (b) dark field and (c) electron diffraction pattern.

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oercivity H_C for the Cu–Co alloys versus Co concentration and treatment	t.

Co content, wt %	<i>H_C</i> , as-cast alloys, Oe	H_{C} , alloys after HPT, Oe
2.2	3.8	7.5
4.9	53	225

the as-cast alloys. Such a behavior of the Cu-Co alloys (with a low Co content) after melt spinning and ion-beam sputtering treatments was also observed earlier [12,15,16,49]. The absence of the saturation and low J values in the Cu-2.2 wt% Co alloy mean that after HPT the size of all Co particles is below the ferromagnetic limit for Co which is between 4 and 10 nm [12,15,16,49]. In Fig. 1c Co particles of a size lower than 10 nm are visible to precipitate within the Cu grains for as-cast alloys. Only small fraction of larger $(\sim 1-2 \,\mu\text{m})$ Co grains presents in the specimen's structure (Fig. 1a). Just these coarse Co grains yield the ferromagnetic input into the hysteresis loop. These coarse Co grains were strongly refined during the HPT deformation, which resulted in a higher paramagnetic fraction in the hysteresis shape. It is possible to estimate amount of Co paramagnetic components in Cu-Co alloys using the obtained hysteresis data. For as-cast alloys with 2.2 wt% Co it is about 50% and about 90% for alloys after HPT.

The behavior of the Cu-4.9 wt% Co alloy is different. According to the phase diagram and from the structural investigations, the amount of coarse Co grains (grain size $\sim 2 \mu$ m) is higher (Fig. 1b), and correspondingly higher their ferromagnetic contribution to the

hysteresis behavior (Fig. 3b). Saturation magnetization is reached, although its value is lower (135 emu/g_{Co}) than that for bulk Co (162 emu/g_{Co}). The amount of small Co nanograined precipitations is less than in the alloy with 2.2 wt% Co. It is about 16% for as-cast state. For the HPT samples, the amount of fine particles is sufficiently large, namely about 70%. Structural state of the material determines also the coercivity value which is four times larger in the deformed specimens than in the initial as-cast state. The structure of nanograined Co–Cu alloys obtained by other methods differs from that produced by HPT. Normally Co is prepared as a mixture of fcc and hcp phases, and it is difficult to obtain single hcp phase which is thermodynamically equilibrium at room temperature.

As we can see, the magnetic properties of an alloy with minor ferromagnetic phase (Co precipitates in Cu matrix) is quite different after HPT from the HPT-treated ferromagnetic alloys like Co–Cu [30] of pure nickel [50]. In latter case HPT always leads to the strong coercivity increase, but saturation magnetization remains unchanged. It is because the input of superparamagnetism of small particles in such alloys is negligible.

4. Conclusions

The grain size in the Cu–Co alloys strongly decreased after HPT and is in the nanometer range. HPT allows one to control the ratio between ferromagnetic and superparamagnetic precipitates in



Fig. 3. ((a), (b)) Magnetization J vs. external field H. The insets show the central parts of the J(H) curves for low H. ((c), (d)) J vs. 1/H dependences extrapolated to 1/H→0.

the diamagnetic matrix. Therefore, SPD can be used to successful control of magnetic properties of the dense bulk materials.

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