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$SmCo_5$/Cu particles elaboration using a supercritical fluid process

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Abstract

Supercritical fluids exhibit a range of unusual properties that can be exploited for developing new processes. Thus, a new way for particles coating is presented. It consists of depositing on a core particle a thin layer of copper. The core particles are made of ground $SmCo_5$. The evolution of the magnetic properties of $SmCo_5$ is studied as a function of the milling time. The copper source is the copper hexafluoroacetylacetonate ($Cu(hfa)_2.H_2O$), which is thermally decomposed in a supercritical medium. Then, the influence of the copper layer is evaluated. This process obtains new 'core-shell structures' as $SmCo_5$/Cu. New interesting properties are expected for these structures more particularly in the magnetic recording field.

Keywords: Intermetallics; Supercritical fluid; Mechanical alloying; Permanent magnets

1. Introduction

The elaboration of new core-shell structures as $SmCo_5$/Cu presents a strong interest in the magnetic recording field. For such applications, there is a double challenge: (i) to elaborate small magnetic particles; (ii) to coat these particles in order to get them magnetically independent.

The mechanical grinding seems to be an effective technique to synthesize various magnetic materials. Recently, mechanical alloying has found interests in the elaboration of hard magnets and spin-glasses [1,2]. In this paper, we report, in a first part, the evolution of the magnetic properties of $SmCo_5$ as a function of the milling time.

Today's CVD process and its derivatives are well-known to deposit a thin metallic layer on plane surfaces [3–5]. The nature and quality of these layers are now under control. Concerning particles coating, numerous papers present results about the encapsulation by a polymer. In such processes the polymer is dissolved in a supercritical fluid containing the solid particles to be coated. A rapid expansion of the solution causes the precipitation of the polymer on the solid particles [6,7]. However, there are few examples quoted in the literature concerning the particle coating with metal or oxide [8]. The development of processes which permit to deposit a metallic layer is very interesting since new properties can be achieved in such core-shell structure. For instance, the deposit of a thin metallic protects the particles against atmospheric aggression and may favor the use of ultra-fine powder in metallurgical and ceramic processing or in electronics application. In the magnetic recording field, there has been an ongoing effort to improve the information-storage capacity [9,10]. Since the elementary particles need to be physically small and magnetically independent, the powder coating process may be a solution to obtain isolated magnetic particles. The second part of this work consists in the presentation of a new original coating process using a supercritical medium [11]. Precursor solubility in supercritical fluids is higher than in gases. Thus, in comparison with the CVD process, the mass transport is enhanced in the supercritical media. Moreover, the tunable properties of supercritical fluids with P and T allow a better control of the process. In this second part, we present the modification of the properties of $SmCo_5$ induced by the copper deposition technique.

2. Milling process

2.1. Experimental procedure

The initial $SmCo_5$ powder is prepared by melting of stoichiometric amounts of the constituent elements under a purified argon atmosphere in an induction levitation fur-

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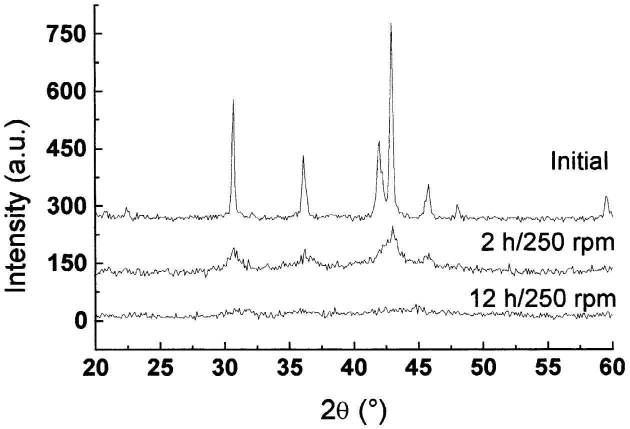

Fig. 1. X-ray diffraction pattern of mechanically milled $SmCo_5$ powders at 250 rpm for 0, 2 and 12 h.

nace. The purity of the starting materials was: Sm 99.9% and Co 99.99%. Before milling, the powder is screened at 100 μm. The different $SmCo_5$ samples were obtained by mechanical grinding under a purified argon atmosphere, using a Fritsch P5 high-energy instrument. In each case the ratio weight ball over weight sample is close to 15. The rotation speed of the turn disc was fixed at 250 rpm.

The samples were characterized by conventional X-ray powder diffraction using Cu-Kα radiation. The particle size and morphology were investigated using a Jeol 840 microscope. Magnetization measurements were carried out at 270 K using a SQUID (Superconducting Quantum Interference Device) magnetometer. The sample was loaded in a paraffin resin in order to immobilize the randomly oriented particles during measurement. The coercitivity H_C and remanence ratio ($R=M_R/M_S$) were extracted from the hysteresis loop. In some case, the saturation was not obtained even at 4 T, so the value of the magnetization at 4 T is considered to be the value of M_S.

2.2. Results

The first part of this work consists in the evaluation of the milling time influence on the $SmCo_5$ particles properties.

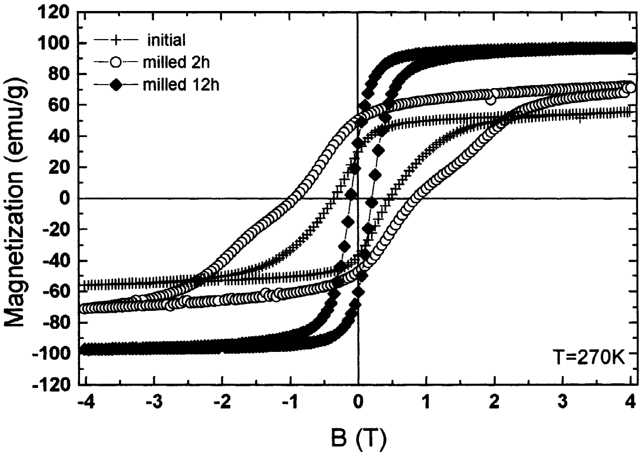

Fig. 3. Representative hysteresis loops for $SmCo_5$ samples milled for 0, 2 and 12 h.

2.2.1. Influence of the milling time

Fig. 1 shows the X-ray diffraction pattern of the $SmCo_5$ as a function of the milling time. The crystallinity of the powder decreases with the milling time. After a milling period of 2 h, the characteristic lines of $SmCo_5$ broaden. After 12 h, $SmCo_5$ presents a nearly amorphous structure. Moreover, no pollution due to the milling process is detected by X-ray diffraction analysis.

The milling time increase has a significant influence on the particles morphology (Fig. 2). The initial particles are facetted. After grinding, they are basically spherical in shape and appear to be made up of layers of materials in agreement with previous observations for mechanically alloyed materials [12]. Secondly, the particles size increases with the milling time. After 2 h, the particles are in the range 1–10 μm. After 12 h most of them falls within the range 20–30 μm.

Fig. 3 presents the evolution of the magnetization of these different samples. In each case, the hysteresis loop is characteristic of a magnetic isotropic sample due to the milling process, which leads to random crystallite orientation. The coercive field increases for the short milling time (0.4 T for the initial sample, 0.9 T after 2 h) and decreases drastically after a long milling period (0.2 T for 12 h).

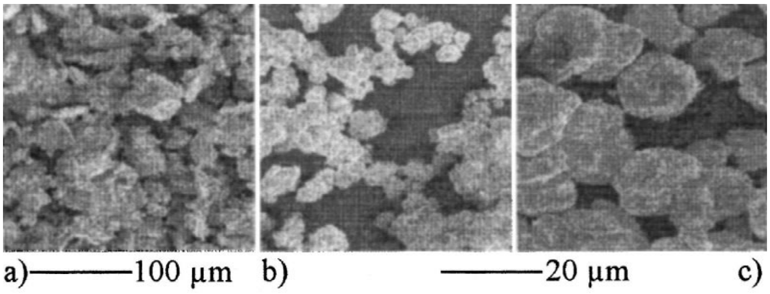

Fig. 2. SEM images of mechanically milled $SmCo_5$ powders at 250 rpm for 0 (a), 2 (b) and 12 h (c).

Moreover, only the 2 h sample presents a step in the hysteresis loop. The magnetization at 4 T increases with the milling time: 56 emu/g (initial sample), 70 emu/g (2 h) and 96 emu/g (12 h). Moreover, there is an important decrease in the remanence ratio (from 0.7 (2 h) to 0.4 (12 h)).

The evolution of the microstructure of this sample as a function of the milling time is currently under study in order to explain the different observed magnetic behaviors.

3. Coating process

The second part of this work consists in the presentation of a new original coating process. This study concerns the coating of $SmCo_5$ obtained after grinding of 2 h.

3.1. Experimental procedure

The general principle of the process is to realize a suspension of micronic particles in a supercritical medium. The decomposition of a metallic precursor in this suspension may lead to a coating of the micronic particles.

The used apparatus is shown in Fig. 4. The high-pressure reactor is made of 316 stainless steel (diameter=1.8 cm, volume=20 cm^3). An external heating resistor allows to reach the precursor decomposition temperature. This resistor is placed at the top of the reactor in order to generate an important natural convective movement. It permits to avoid the sedimentation of the particles in suspension. A polytetrafluoroethylene film (PTFE, thickness=0.25 mm) is rolled up inside the reactor to avoid contamination of the cell's wall. The system itself is placed in a hot-air oven. Two thermocouples measure the temperature, one inside the hot-air oven and the other inside the reactor.

The high-pressure generator is a fluid metering pump (CM 3200 P/F), which permits to introduce the initial quantity of CO_2. The pressure is maintained constant at 19 MPa.

A known amount of a metallic precursor and of $SmCo_5$ particles is placed in the reactor. The system is filled up with a mixture of CO_2/ethanol in the molar proportion 80/20. The hot-air oven is heated at T_A. In this configuration, the temperature of the cell's bottom is T_A too. Thanks to the resistive heater, the temperature of the cell's top is maintained constant at T_B with $T_B > (T_A$ and $T_{dec})$ where T_{dec} is the precursor decomposition temperature. The increase of the temperature from ambient to T_B leads to an increase of the pressure to the working pressure P that is then maintained constant. In the same time, the precursor is solubilized.

In the reactor, the convective movement created by the temperature gradient $(T_B - T_A)$ sets the particles going. In the volume where $T > T_{dec}$, the precursor decomposition occurs and releases atomic copper which coats the in-movement particles. A strong point of this process is that after the decomposition stage the organic part of the precursor is still soluble in the supercritical fluid and is trapped at the outlet of the installation. After going back to ambient conditions, the coated particles are directly obtained free of solvent and organic contamination. In each experiment, the conditions are $T_A=403$ K; $T_B=473$ K and $P=19$ MPa.

The copper hexafluoroacetylacetonate $\{CF_3COCH{=}C(O\text{-})CF_3]_2Cu.xH_2O,\ x \leq 1\}$, $(Cu(hfa)_2.H_2O)$, provided by Sigma–Aldrich, was used as copper source in the deposit experiments.

3.2. Results and discussion

3.2.1. Supercritical treatment

Before coating, the influence of the supercritical treatment on the sample must be checked. A known amount of

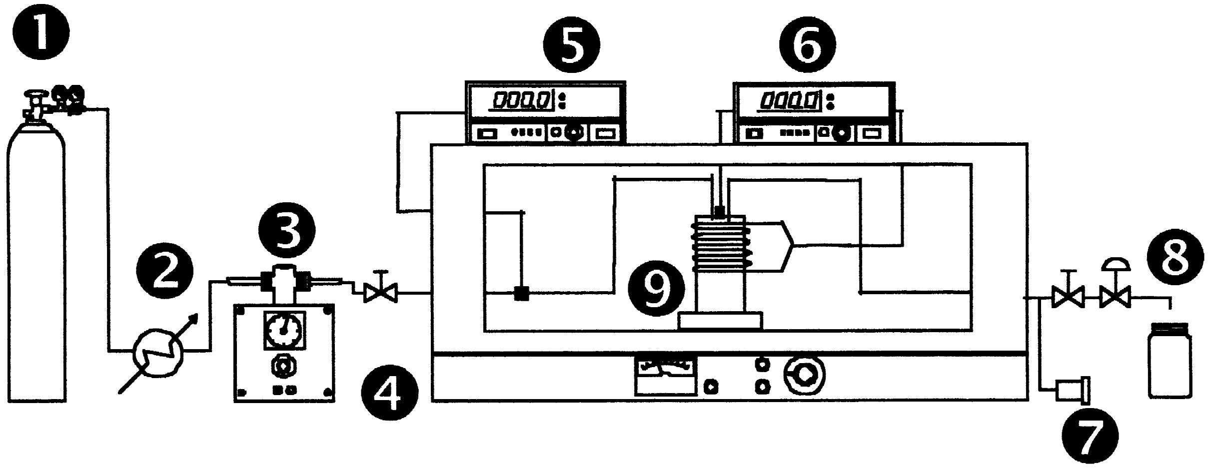

Fig. 4. Apparatus for coating process: (1) CO_2; (2) cooler; (3) pump; (4) hot-air oven; (5) pressure sensor; (6) temperature regulator; (7) contact breaker; (8) solvent trap; (9) reactor fitted with an external heater.

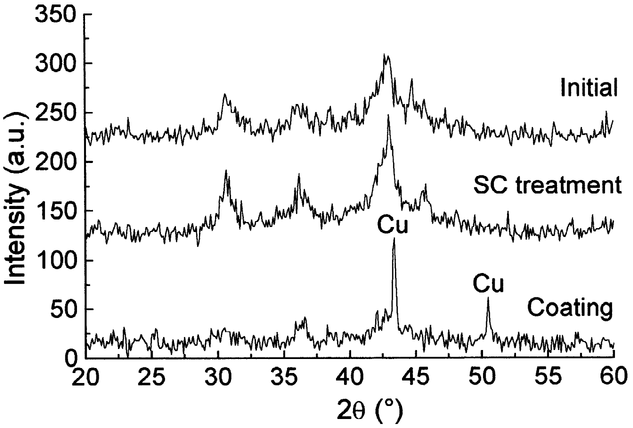

Fig. 5. X-ray diffraction pattern of different $SmCo_5$ samples: initial= $SmCo_5$ milled 2 h; supercritical treatment=$SmCo_5$ (initial) treated in a supercritical mixture of CO_2/EtOH (1 h at 473 K and 19 MPa) and coating=$SmCo_5$ (initial) coated by copper.

$SmCo_5$ particles was placed in the reactor. No precursor was added. The particles were maintained in the supercritical mixture of CO_2/ethanol for 1 h (473 K, 19 MPa).

The comparison of both X-ray diffraction patterns (Fig. 5) and the SEM observations (Fig. 6) of the initial and treated particles do not reveal any significant changes both in the nature and the morphology of these particles. Moreover, we verify that the magnetic properties of the $SmCo_5$ particles are not affected by the supercritical treatment (Fig. 7).

It can be inferred from these results that no reaction occurs between the supercritical mixture and $SmCo_5$ milled sample.

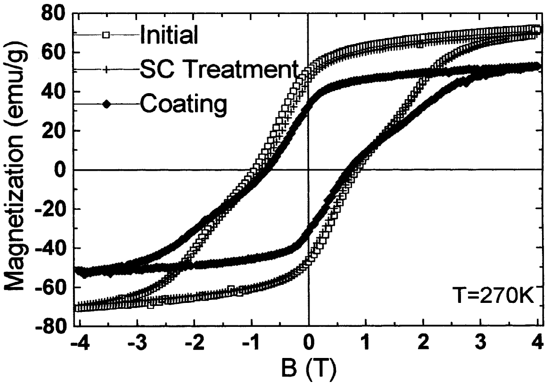

Fig. 7. Representative hysteresis loops for $SmCo_5$ sample milled 2 h=initial; supercritical treatment=$SmCo_5$ (initial) treated in a supercritical mixture of CO_2/EtOH (1 h at 473 K and 19 MPa) and coating= $SmCo_5$ (initial) coated by copper.

3.2.2. Coating process

In this experiment 0.9 g of $Cu(hfa)_2.H_2O$ was added to 0.1 g of $SmCo_5$ particles in the mixture of CO_2/ethanol in the molar proportion 80/20. The treatment lasted 30 min at 473 K. X-ray diffraction pattern reveal the presence of metallic copper (Fig. 5).

Fig. 6 presents SEM observations of the coated powders. An original behavior can be detected during the coating process. It seems that the initial aggregates are transformed into small particles as if the precursor decomposition was led to the division of the initial particles. In fact, after coating, the obtained powders are composed of two different populations. The first one is made of small spherical particles constituted of both $SmCo_5$ and Cu. The size of these particles is in the range of 1–5 μm (before

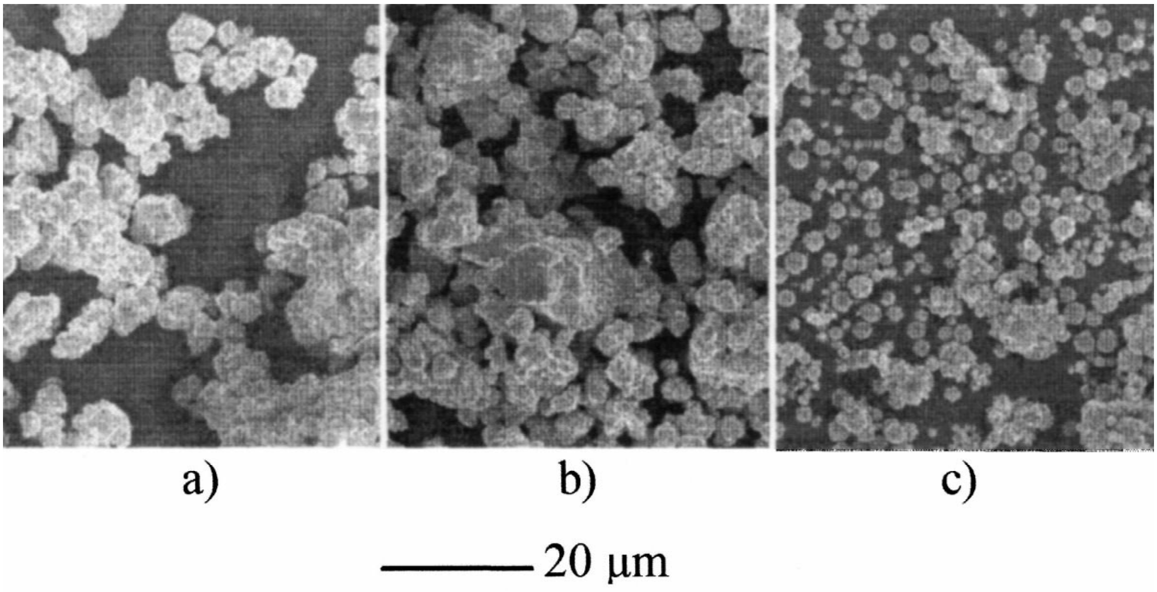

Fig. 6. SEM images of the $SmCo_5$ powder milled 2 h: (a) initial, (b) treated in supercritical fluid and (c) coated by a metallic copper layer.

coating, the particles are in the range 1–10 μm). The second one is composed by the initial $SmCo_5$ particles whose morphology has not been changed. It can be noticed that small spherical Cu particles are deposited on their surface. As presented in the first part of this work, the long milled time samples ($\geq$2 h) appear to be constituted by layers of materials. Two of the interesting properties of the supercritical fluid are both its high diffusivity and its low viscosity. It can be considered that before the decomposition stage of the copper precursor, $SmCo_5$ particles are filled with the supercritical mixture CO_2+ethanol+$Cu(hfa)_2.H_2O$. The $Cu(hfa)_2.H_2O$ decomposition releases different molecules (metallic and organic). This volume variation breaks the $SmCo_5$ particles into smaller ones, which are coated, in the same time.

Fig. 7 presents the evolution of the magnetic properties of the coated samples. A slight decrease in the coercive field can be noticed (from 0.88 T to 0.74 T). It could be due to the fact that during the process, different randomly magnetically oriented particles can be coated together. The magnetization at 4 T decreases after coating (from 70.5 emu/g to 53 emu/g) due to the presence of Cu. The remanence ratio is slightly diminished (from R=0.71 to R=0.69).

4. Conclusion

This study presents the influence of the milling time on the properties of $SmCo_5$ powders. The sample grinded 2 h at 250 rpm presents both the classical morphology of milled materials and the best magnetic properties.

In a second part, we present a new original process to deposit a thin layer of Cu on $SmCo_5$ particles. It consists of the copper precursor decomposition in a supercritical fluid. The strong point of our process is its capability to reduce the particle size during the process. It could be due to both the properties of supercritical fluids and the precursor decomposition reaction. This coating process would permit the compatibility of the core material for its further processability and more particularly in the development of new improved materials for magnetic recording systems.

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