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A novel technique to extract Bi from mechanochemically prepared Bi–Fe_3O_4 nanocomposite

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Abstract

The solid-state reduction of Bi_2O_3 to bismuth (Bi) nanoparticles by high-energy ball milling of raw materials (Bi_2O_3 and Fe) in air and argon atmospheres has been described. XRD results show that in addition to bismuth, a second phase of nanocrystalline magnetite is also formed. This is due to the formation of Fe_2O_3 and the subsequent change to Fe_3O_4 in the course of ball milling. Mean particle sizes of the obtained Bi and Fe_3O_4 particles were 22 and 18 nm, respectively, using Scherrer's formula. A saturation magnetization of 80 emu/g is achieved for magnetic phase (Fe_3O_4). As both Bi and magnetite were nanosized particles, it was not possible to separate these two phases by the magnetic separation technique. A novel technique based on different thermal expansions of the Bi and Fe_3O_4 was then used to extract metallic Bi from the as-milled powders.

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1. Introduction

Mechanical alloying is basically a dry high-energy milling process, which has been primarily devoted to the production of composition metallic powders with a fine controlled microstructure [1–3]. This process has been used since 1960 and its field of application and scientific scope has been increased very rapidly [4]. In addition to alloys, various metallic materials, such as intermetallic compounds [5–7], magnets [8,9] and nanocomposite powders [10–12], etc., have been prepared by this method. The mechanochemistry of inorganic substances has also been widely studied in order to understand the change in the reactivity of solids by and after action of mechanical energy [13,14]. In this work, mechanical alloying was used to prepare Bi–Fe_3O_4 nanocomposite by reduction of Bi_2O_3 with Fe and then by a novel technique, metallic Bi component was extracted. This is due to the fact that Fe strongly reduces Bi_2O_3 with regards to a negative enthalpy ($\Delta H = -58.5\,\mathrm{kJ/mol}$) associated with the following oxido-reduction reaction:

$$Bi_2O_3 + 2Fe \rightarrow 2Bi + Fe_2O_3,$$

and can explain the self-sustained combustion of the reactants during mechanical alloying [3].

2. Experimental

The raw materials were powders of Bi_2O_3 and Fe both from E. Merck Co., with minimum purity of 99%. The powders were weighed in 1:2-mole ratio, respectively, with 10% Fe deficiency to compensate iron wear in the course of milling. A total of 30 g of the powders together with different sizes of hardened-steel balls were loaded into an air-filled hardened-steel vial (500 ml). The process was also repeated in an argon-filled vial, using a glove bag. The

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milling times in both processes were up to 240 min in a high-energy planetary mill (FRITSCH "Pulverisett6"). The number and size of the balls were chosen so that a ball to powder ratio of 10 was achieved. In order to maintain an equal powder to ball mass ratio in all experiments, the vial was cleaned and reloaded with 30 g of new raw materials. Phase formation of the as-milled composition was studied by a diffractometer (BRUKER, D8 model) using Cu K_α radiation ($\lambda = 1.5405$ Å). The mean particle sizes of the Bi and Fe_3O_4 in the composite were calculated from the XRD peak broadening, using the Scherrer's formula. Magnetic measurements were carried out on cold pressed as-milled samples, using a vibrating sample magnetometer (VSM). Magnetic separation was attempted to separate the magnetic phase (Fe_3O_4) from the nonmagnetic phase (Bi), but this was unsuccessful. A novel technique based on different thermal expansions of the Bi and Fe_3O_4 was then used to extract metallic Bi from the as-milled powder. In

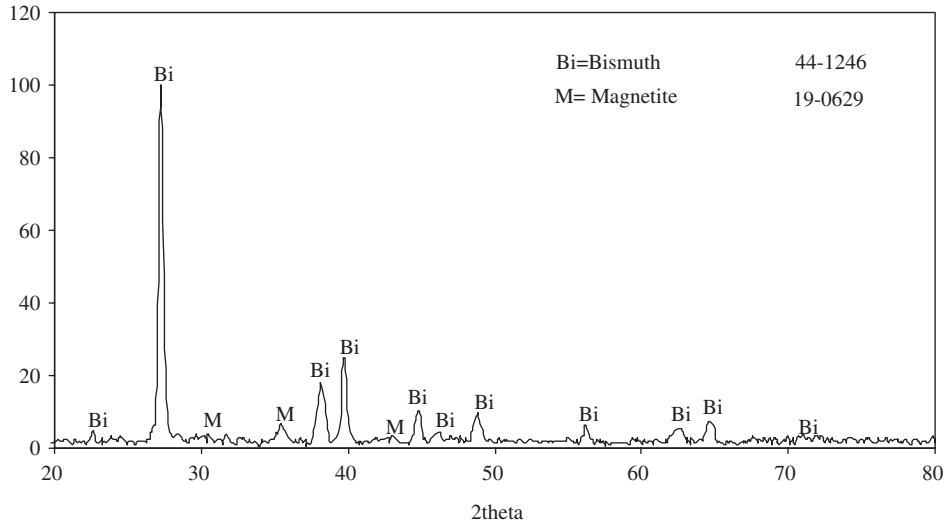

Fig. 1. XRD pattern of the as-milled product.

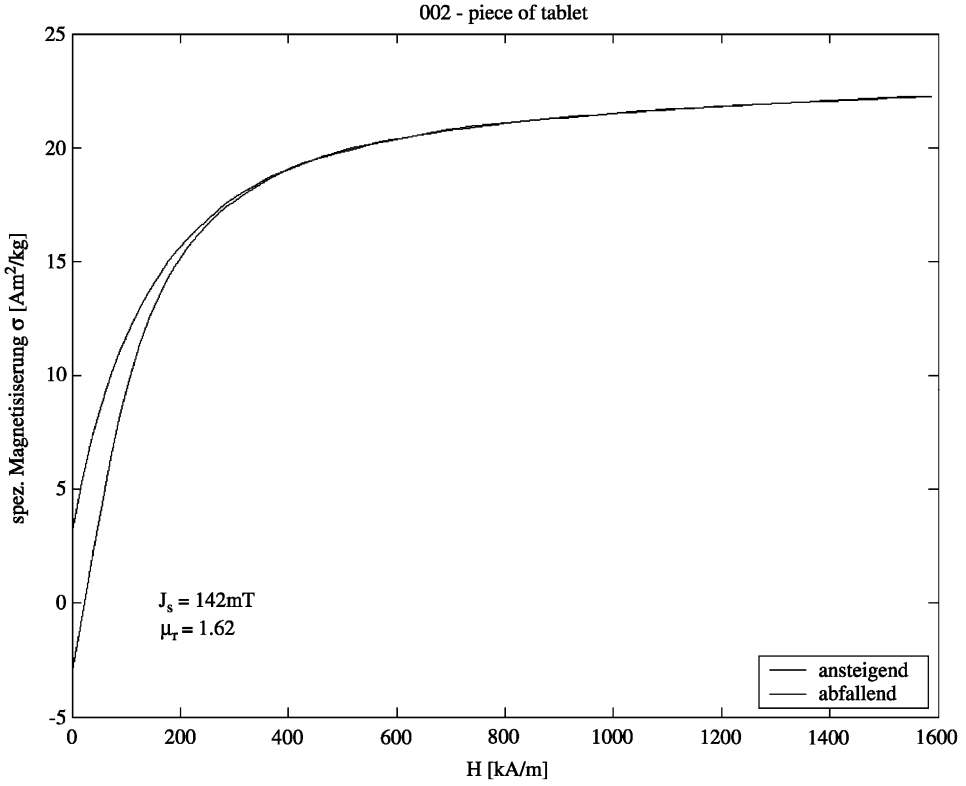

Fig. 2. Magnetization curve of the as-milled composite.

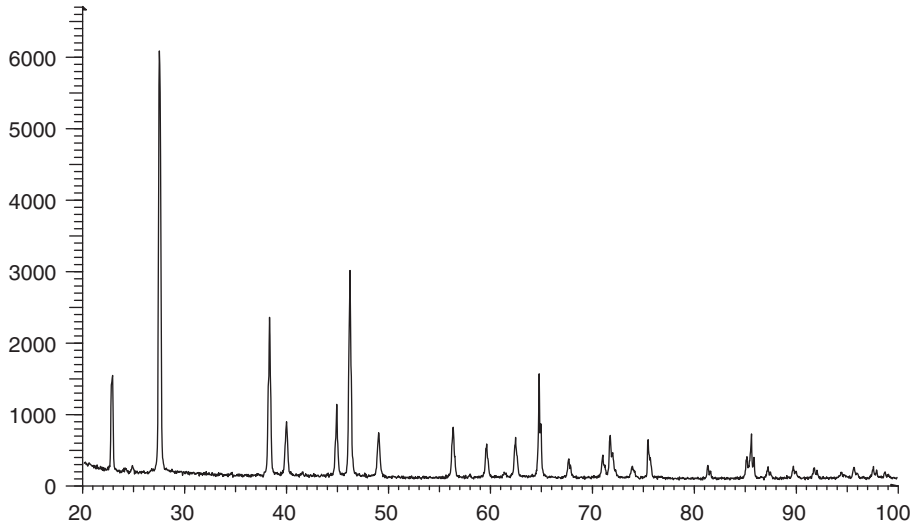

Fig. 3. XRD pattern of the extracted Bi. All peaks belong to a pure metallic Bi.

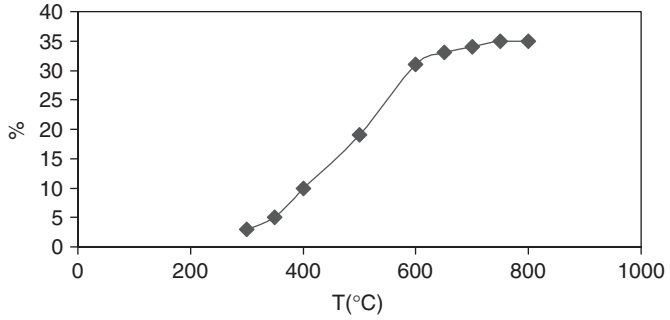

Fig. 4. Variation of extraction percentage of the metallic Bi with temperature for constant soaking time (1 h) and constant shaping pressure (7 kbar).

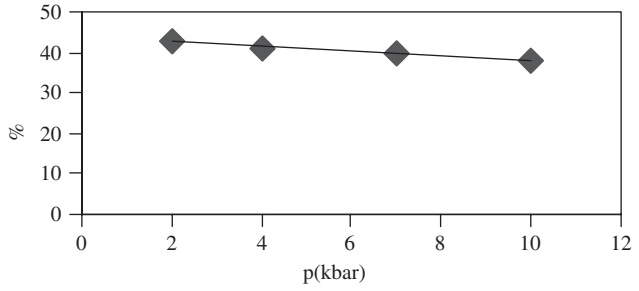

Fig. 5. Extraction percentage of metallic Bi as a function of pressure heated at 700 °C.

this technique, the as-milled powder was shaped into pellets of about 10 mm in diameter and about 6 mm in height under different pressures (1–10 kbar). The pressed samples were then heated at different temperatures up to 800 °C with different soaking times of 15, 60, 120 and 180 min in a vacuum-sealed quartz tube in order to avoid any oxidization of the metallic Bi. In the course of the heating process, the molten Bi was squeezed out of the samples and then removed and characterized carefully.

3. Results and discussion

The XRD pattern of the as-milled powder, Fig. 1, shows that a nanocomposite of only two phases, bismuth (Bi) and magnetite (Fe_3O_4), has been formed. The mean particle sizes of the Bi and Fe_3O_4 were 22 and 18 nm, respectively, using Scherrer's formula. Fig. 2 shows the magnetization curve of the as-milled composite. A saturation magnetization of 142 mT was obtained, which is related to the magnetic portion of the nanocomposite. Using Fig. 2 and calculations based on the weight percent of each phase, a saturation magnetization of 80 emu/g is achieved for magnetic phase (Fe_3O_4). This of course is smaller than the value of 90 emu/g, related to bulk Fe_3O_4. This is due to the fact that as the particle size is inclined, the value of magnetization decreases [15].

Magnetic separation was attempted to separate the magnetic phase (Fe_3O_4) from the nonmagnetic Bi phase. This was not successful, because both phases were agglomerated together and precipitated simultaneously by the magnetic driving force of a strong magnet located beneath the beaker containing the mixture of distilled water and the nanocomposite. The cause of the simultaneous precipitation is that during attraction of the magnetite particles, they will collide with Bi nanoparticles and push them towards the bottom of the beaker. In order to obtain Bi metallic phase, the nanocomposite was pressed into pellets, and heated in a vacuum-sealed quartz tube. It was observed that a pure metallic Bi phase had been squeezed out of the body of the pellets, which was carefully separated from the samples. The reason for the squeezing was that thermal expansion coefficients of Bi and Fe_3O_4 are different and is higher for metallic Bi. The XRD pattern of the squeezed Bi has been shown in Fig. 3. As it can be seen from this pattern, all the peaks belong to a pure Bi phase. Fig. 4 shows the variation of extraction percentage of the metallic Bi as a function of temperature for a constant

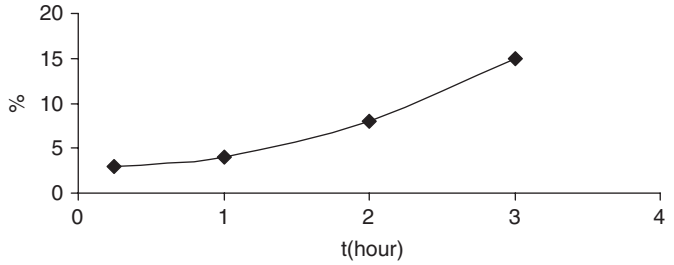

Fig. 6. Evaporation percentage of Bi as a function of soaking time (with a constant annealing temperature of 700 °C).

soaking time (1 h) and a constant shaping pressure (7 kbar). This shows that the driving force to push the Bi out of the nanocomposite is stronger at higher temperatures up to 700 °C. At higher temperatures, as can be seen in Fig. 4, the extraction percentage reaches a nearly constant value and it is not necessary to heat the samples above 700 °C. Fig. 5 shows the variation of extraction percentage of Bi at different shaping pressures. As can be seen, the extraction of the Bi is more or less independent of the applied pressure. It was also found that the shorter soaking times are much better than longer ones, because the latter will increase the evaporation percentage of the Bi phase, Fig. 6.

4. Conclusion

Bi–Fe_3O_4 nanocomposite has been formed during mechanochemical processing of Fe and Bi_2O_3 powders as the starting materials. The phase formation was checked by XRD. VSM measurements also show that there is a magnetic phase in the nanocomposite. A novel technique has been established to extract metallic Bi from the nanocomposite. In order to maximize the amount of Bi extracted from the nanocomposite, the parameters such as temperature, pressure and soaking time were optimized. The results show that the optimum temperature is 700 °C, but the values for pressure and soaking time should be chosen as low as possible.

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