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Structure and magnetic properties of nickel nanoparticles prepared by selective leaching

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ABSTRACT

In this study, we propose a novel method for preparation of nanocrystalline powder precursors for powder metallurgy processing. Nickel nanocrystalline powders were prepared by selective leaching of the Al-20Ni alloys in NaOH solution. The powders were studied by SEM, TEM, XRD, magnetometry and by small angle neutron scattering. The prepared powders had internal structure formed by grains of 5–50 nm in size depending on the leaching temperature. It was also proven that slight grain coarsening occurred during heating of particles at 40–80 °C for one hour. Magnetometry testing revealed significantly reduced magnetization of nanocrystalline nickel which is related to the internal structure. The results indicate that nickel powders prepared by selective leaching are suitable precursor for powder metallurgical preparation of bulk products with interesting physical and possible also mechanical properties.

1. Introduction

Much attention has been paid to preparation of magnetic nanoparticles in last decade [1]. Many papers describe preparation of Ni nanoparticles by reduction of aqueous solution of nickel salts alternatively with or without addition of alcohol or oil [2–7]. Some other paper describe production of nickel nanoparticles by micelles route [2,9], by utilization of plant extracts as reduction agent [3,8], by gamma irradiation [1] or laser ablation of solids in organic solutions [10]. This paper is focused on preparation of nickel nanoparticles by a selective leaching method. This process is based on preparation of binary alloy, its appropriate heat treatment to obtain supersaturated solid solution followed by possible tempering to grow nanoparticles from minor element and leaching of matrix element [11,12]. The advantage of this method is the ability to produce industrially significant amount of nanoparticles suitable for consequent processing by powder metallurgy to produce bulk nanocrystalline material. It was proven that by selective leaching of Al–20Ni alloy, Ni submicrometer nanoparticles with internal nanocrystalline structure are produced [11]. For further compaction, this is even more suitable than individual nanoparticles, while it suppresses the surface oxidation of particles and improves the homogeneity of a compact product.

2. Experimental

The master alloy with compositions of Al–20 wt% Ni (34 at% Ni) was prepared by melting of appropriate amount of pure metals in induction furnace followed by melt spinning process with circumferial speed of cooling wheel of 20 m/s. The rapidly solidified alloy was leached in 20% (wt.) solution of NaOH, following this reaction (1)

$$3.03AlNi_{34}+2NaOH+6H_2O\rightarrow 2Na[Al(OH)_4]+3H_2+1.03Ni \qquad (1)$$

The nickel nanoparticles were prepared by selective leaching at different temperatures - −20, 0, 40, 60 and 80 °C. Leaching at 0–80 °C was performed using magnetic stirring and heating device, while leaching at −20 °C took place in cryostat cell with mechanical stirring. The leaching was performed for 3 h at high temperatures (40–80 °C), 2 days at middle temperatures (0–20 °C) and 14 days at the lowest temperature (−20 °C). Phase composition of initial materials and prepared nanoparticles was determined by X-ray diffraction (PAN analytical X'Pert PRO+High Score Plus, Cu anode). The structure of nanoparticles was observed by scanning electron microscope TESCAN VEGA 3 LMU equipped by EDS

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detector (Oxford Instruments) and by transmission electron microscope Jeol JEM 3010. As the nickel nanoparticles are magnetic, the quality of images is not very good and it is necessary to measure them by some other method. For this purpose, neutron small angle scattering was chosen assuming that the radius of gyration corresponds to the grain size of nickel powder. SANS was performed in Budapest Neutron Centre. The samples were measured in glass cuvettes in water environment. Magnetic properties of the samples in form of dry powder were measured by vibrational magnetometer PAR 4500 at room temperature.

3. Results and discussion

The nickel nanoparticles were prepared by selective leaching at different temperatures - −20, 0, 40, 60 and 80 °C. The size of prepared nickel particles is almost the same with differing temperature (about 200 nm, as illustrated in Fig. 1(a). Fig. 1 (b) shows that Ni particles are composed of several crystalline grains separated by high angle grain boundaries. Detailed analysis of HRTEM images revealed different sizes of nickel grains forming the particles. At the lowest leaching temperature of −20 °C, smallest grains of approximately 2 nm are formed. At higher

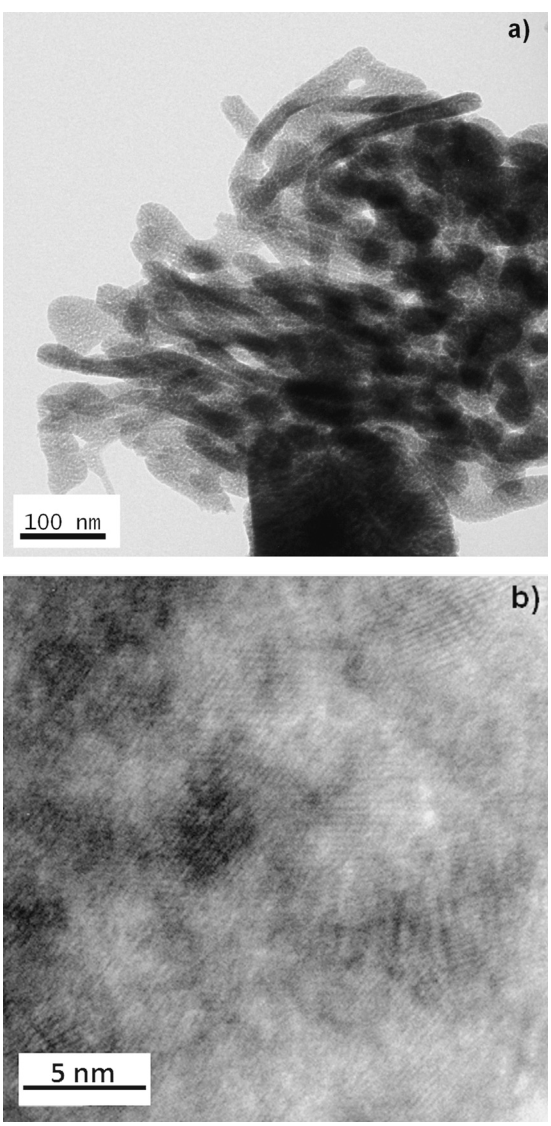

Fig. 1. Microstructure of nickel powder prepared by selective leaching at −20 °C a) overview, b) detailed HRTEM image.

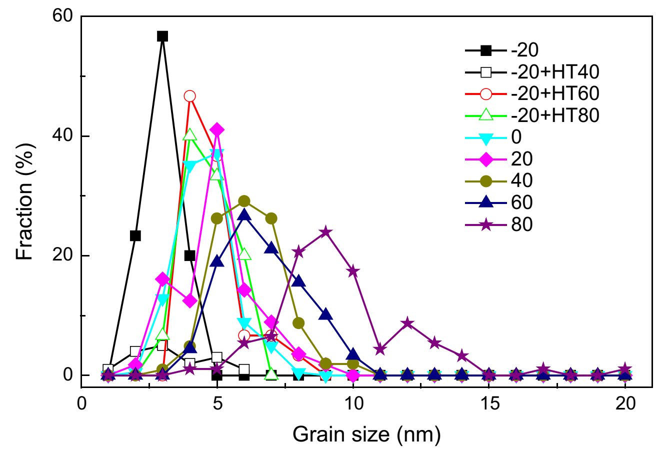

Fig. 2. Grain size of nickel nanoparticles (measured from HRTEM images) prepared by selective leaching at various temperatures and prepared at −20 °C with consequent heat treatment (HT) at 40, 60 and 80 °C for 1 h.

leaching temperatures, the size increases and after leaching at 80 °C it reaches 10–15 nm. The grain size of the sample prepared at 20 °C was verified by SANS measurement. The radius of gyration was 22.78 ± 0.06 Å, which is in good agreement with TEM observation. The observed difference can be attributed to accelerated diffusion of Ni atoms during selective leaching. The differences between size of grains leached at −20 °C and 0 °C can be also partially explained by the change of experimental conditions. While the nanoparticles prepared at 0–80 °C were leached using magnetic mixing device, the experimental setup did not allow to use magnetic mixing at −20 °C (leaching in cryostat). The presence of magnetic field during nickel nanoparticle formation has crucial effect to its size and shape [1].

As stated before, the sample prepared at −20 °C exhibits the finest grain size. When the powder is heated the grains start to grow (Fig. 2), but the changes are not so significant compared to samples prepared at different temperatures. It is obvious from Fig. 2 that a slight grain coarsening from approximately 3 nm to 5 nm takes place during heating at 80 °C/1 h. The change is small because it is controlled by solid state diffusion of Ni atoms which is much slower than diffusion in the liquid state during leaching. The grain size coarsening of nanoparticles heated for 1 h was confirmed also by X-ray diffraction shown in Fig. 3. The diffraction pattern of nickel nanoparticles leached at −20° exhibit broad diffraction maxima of nickel. After heating the peaks of nickel become narrower, which indicates crystallites (grains) coarsening. The crystallite size marked in Fig. 3 is estimated from Scherrer equation. To grain size values obtained in this study are slightly different than in our previous work, which can be caused by changes in experimental set-up. In [11], the AlNi20 alloy was prepared at higher cooling rate leading to finer structure. It can explain the change in shape of forming particles a partially also the change in grain size. Moreover the leaching process [11] was performed with mechanical stirring and as it was discussed above, the presence of magnetic field during selective leaching may have influence on grain size of formed particles [1].

To characterize the change in properties with grains coarsening, magnetization curves were measured. Fig. 4 shows magnetization curves of as-prepared nanopowder leached at −20 °C and nanopowders consequently heated at 40, 60 and 80 °C for 1 h. These curves are compared to the curve of electrolytic nickel taken as standard material. All studied material had significantly lower saturated magnetization than standard material. It indicates very fine structure of particles formed by grains with size of few nanometers. The suppression of saturated magnetization is due