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METALLURGICAL TWO-STEP PRODUCING METHOD OF FE NANOPARTICLES

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ABSTRACT: Submitted paper is dealt with preparation of iron based nanoparticles and marginally also cobalt nanoparticles through precipitation from solid solution of age-hardenable alloys and their subsequent insulation by electrochemical or chemical resolution of matrix. The simpliest system is Cu-matrix in which Fe resp. Co as elements are precipitated in form of coherent particles γ-Fe,Co. These particles are changed at plastic deformation or at extraction and insulation by martensitic transformation on α-Fe, Co. For purposes of nanoparticles precipitation from solid solution there is performed the targeted heat treatment consisting of solution annealing, quenching and precipitation annealing. The size of nanoparticles is regulated by heat treatment of chosen material according to the required procedure. The volume of separated nanoparticles is proportional to the time of dissolution and to the potentiostatic mode according to applied potential-dynamic curves. The quality and material characteristics of nanoparticles was controlled by the methods of TEM, x - ray analysis and measurement of magnetic properties.
KEYWORDS: Fe nanoparticles, precipitation, electrochemical dissolution, chracteristics

❖ INTRODUCTION

At present time the nanoparticles are produced by intricate sophisticated techniques e.g. laser-induced pyrolysis, laser evaporation and condensation, plasma torch synthesis, deposition from colloidal solutions, reduction from aqueous solutions, crystallization from amorphous solid phase, etc. from which neither one reckons with precipitation of nanoparticles from crystallic solid phase. At the same time almost each of the appointed technologies is complicated and from views of investment and also operating cost is considerably demanding. When techniques producing free metallic nanoparticles are used, the particles are usually covered by oxides with thickness depending on technique [1,2].

Method for nanoparticles preparation presented in this work consists of the aimed heat treatment of basic material where nanoparticles are formed by controlling precipitation from solid solution and the production is reposed on insulation or extraction of nanoparticles by electrochemical eventually chemical way. So, the largeness of nanoparticles in the range 3 – 1000 nm is intentionally regulated by metallurgical heat treatment of chosen material according to the required procedure. Quantity of separated nanoparticles is straight-proportioned to the time of solution and to the potentiostatic mode. According to [3] the amount of Fe nanoparticles electrochemically separated from Cu matrix is 0,024μg from the plane 0,5 cm^2 within 30 min and are stored in n-hexane. Besides, preliminary experiments with Cu-Fe material system show that extracted Fe particles are either oxidless or only with small not dangerous oxide layer.

It is a matter-of-course, the supposed method allow to production also of nanowires by creating their shape through the thermo-mechanical treatment or through the separation of regular rod-shaped Fe particles from eutectoid or eutectic alloys. The idea as well as the procedure of nanoparticles separation are safekeeping by two patents [4,5]. As a very significant factor from the point of view of exploitability of nanoparticles prepared by „metallurgical“ method there is high quality of particles appreciated by size and shape homogeneity as well as their structure. It‘s utilizable in the medical applications [6-7]. Electrochemical isolation consists of the matrix solution in the selected solvent during which the nanoparticles are at least ~100 mV more ingenuous and their corrosion potential is more positive towards the metal potential of the basal matrix. During the solution process of the matrix, the particles hold their stability and keep their consistency in solution. In some alloyed systems it is sufficient to use a chemical solution of the matrix for favorable insulation of particles, so as not to come to attacking of the particles [3].

❖ EXPERIMENTAL METHODS

For the operation of presented method of nanoparticles preparation the model alloy system Cu-Fe was chosen, which marks out max solubility of Fe in Cu solid solution ε 4 % at 1096°C. With decreasing temperature the solubility of iron in solid solution is falling down to zero at room temperature.

Copper wire with diameter 10 mm and chemical composition 1,88 % Fe, 0,015 % P, 0,08 % Zn a 0,05 % B was submitted to the dissolving annealing at 1000 °C / 12hod and was quenched into cold water. In order to precipitate the spheroid Fe nanoparticles, the samples were annealed at the temperature of 600 °C / 30 min, 1, 12 and 24 hours, and quenched into cold water.

Producing of Fe nanoparticles was design by electrochemical dissolution of copper matrix in aqueous solution as well as etching solution by potentiostatic mode. Labor technique was followed: Pt electrode as auxiliary; SCE (saturated calomel electrode) as reference; specimen as anode. Computer controls the potentiostat fixed on a defined value. The dissolving conditions are appropriate at the potentiostatic mode of – 250 mV (SCE) in ammonia solution.

The morphology and distribution of particles and the state of substructure and interphase boundary were monitored by optical and transmission electron microscopy TEM by electronic microscope JEM 2000 FX and JSM 35 CF with microanalytical Link 860. Results of electron-microscopic observation will be evaluated by statistical methods.

❖ RESULTS AND DISCUSSION

Morphology and distribution of the Fe particles were studied by means of carbon replica technique by TEM. After precipitation annealing, soft precipitate consisting of regular globular particles was found within the samples. The information about its control is very important for obtaining the specific dimension of particles by consumer order especially for medical applications. The distribution function is time invariant during the steady-state precipitation annealing. This reason is a good condition for preparing the smaller (one domain) particles, because the smaller precipitates are assigned the smaller dispersion.

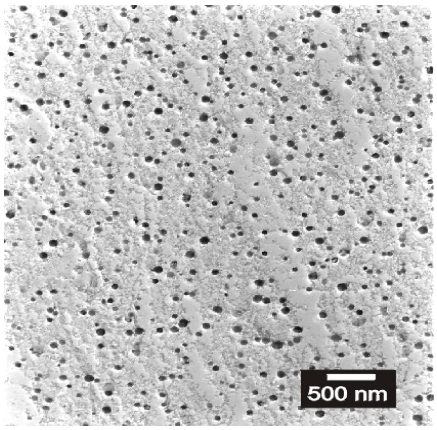

Fig. 1 Extracted Fe precipitates from Cu matrix

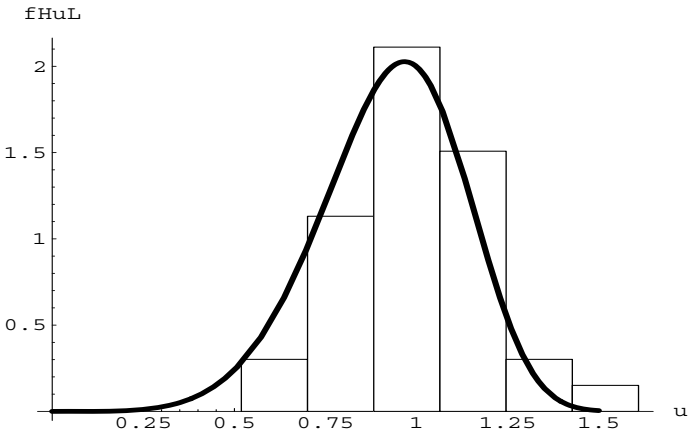

Fig. 2 The size distribution of Fe precipitates aged at 973 K for 86.4 ks

The regular spherical particles with extraordinary homogeneous distribution can be observed in the Fig. 1. According to the expectation, the increase of annealing time resulted in growth of particles. The range size of particles after annealing 12 hours moves between 18 – 22 nm. Fe particles after 24 hrs of annealing had the dimension ≅ 26 – 32 nm. In all cases, the distribution of particles was statistically equable in whole volume of samples and the particles had globular shape [8].

Quantity of isolated nanoparticles is directly proportional to time of dissolution in potentiostatic mode. The amount of 0,024 mg Fe spherical nanoparticles were separated from the surface 0,5 cm^2 in 20 ml electrolyte at potentiostatic mode –250 mV (SCE) for 30 min.

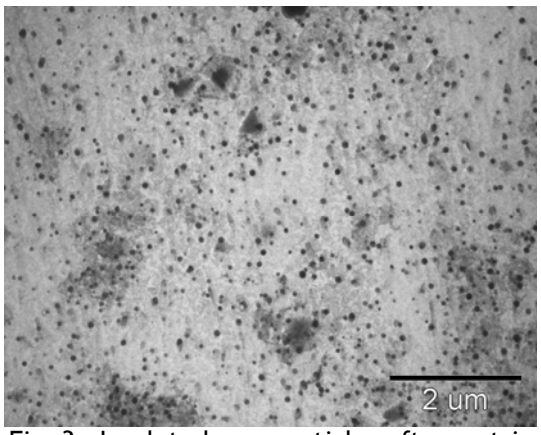

Fig. 3 Insulated nanoparticles after matrix dissolution

Characterization of Fe nanoparticles after their insulation from Cu matrix is documented in Fig. 3. Measuring of the nanoparticles radiuses was shown a good agreement with the mean precipitate radius after precipitation annealing. This confirms that precipitates are not dissolution in the electrolyte.

TEM micrograph of nanoparticles diffraction is shown in Fig. 4. The core-shell structure can be shown with the dark core end the light shell. Shel thickness is around 3 – 4 nm at mean diameter of nanoparticles 10 – 21 nm. Fig. 5 presents the selection electron diffraction. The straight pattern of α – Fe phase and two diffusive rings corresponding to 2 line ferrihydrite.

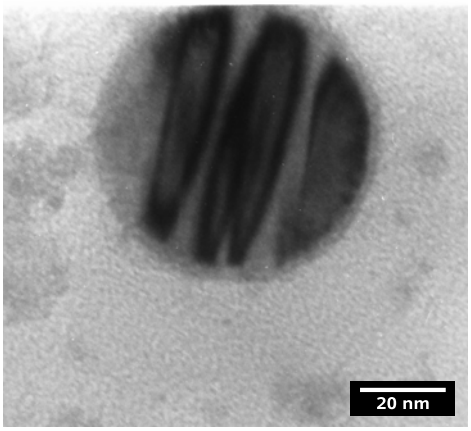

Fig. 4 TEM micrograph of insulated Fe nanoparticles

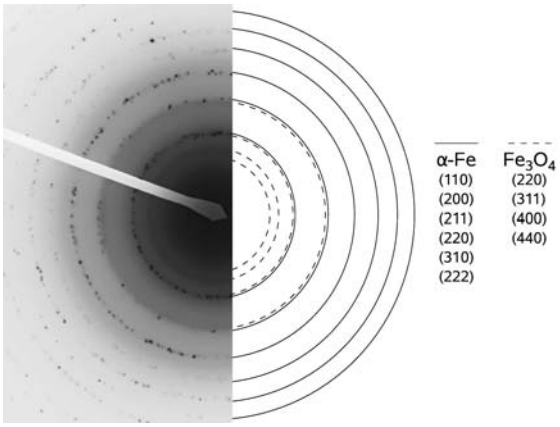

Fig. 5 Selection electron diffraction of nanoparticles

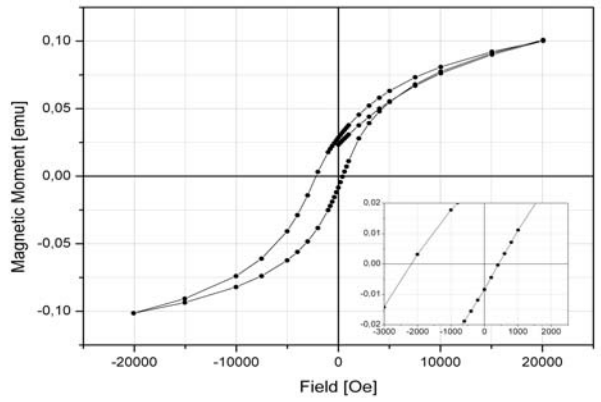

Fig. 5 Magnetic hysteresis loop at 2 K

Characteristics of the magnetic properties of nanoparticles was determined by measuring the temperature dependence of magnetization in the magnetic field (FC) and without magnetic field (ZFC) and also from measurements of magnetic hysteresis loops at different temperatures.

Measurements of magnetic properties of Fe nanoparticles with a mean radius of 27.7 nm from the dependence of magnetic moment on the temperature not confirmed the superparamagnetic behavior of these particles. At produced nanoparticles with mean radius of 10 nm was found the blocking temperature (Tb = 65 K), which characterizes the behavior of superparamagnetic particles above this temperature. This justifies the fact that the presented method of nanoparticles production can be used for applications which require phenomenon of superparamagnetism (medicine: magnetic resonance imaging, medicament carrier).

❖ CONCLUSION

- After choosing experimental treatment of precipitation annealing at 600 °C/0,5, 1, 12, 24 hours, the statistically regular distribution of precipitate was obtained in the volume of samples. There were the particles with globular shape, which dimensions grew by annealing time from 4,5 to 32 nm.
- The advantages of this method consists of possibilities to control the size and shape of nanoparticles in a narrow range tolerance with relative accuracy 5 nm by heat treatment at min financial costs of the production facilities.
- The amount of Fe nanoparticles separated from the surface of 0,5 cm^2 for 30 min is 0,024 mg. The particles are not dissolved during the dissolution process of the matrix and the particles don't change their chemical composition.
- Nanoparticles with mean radius of 10 nm have the blocking temperature (Tb = 65 K), which characterizes the behavior of superparamagnetic properties above this temperature, what can be used for applications in medicine.

❖ ACKNOWLEDGEMENTS

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