



Macromolecular Nanotechnology

Effect of molecular weight of sodium polyacrylates on the size and morphology of nickel nanoparticles synthesized by the modified polyol method and their magnetic properties

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ABSTRACT

Nickel nanoparticles were synthesized by the reduction of nickel chloride with hydrazine hydrate in a polyol medium in the presence of sodium polyacrylates (Na-PA) having molecular weights (M_w) of 1200, 5100 and 8000. The size and morphology of the resulting nickel nanoparticles were characterized by X-ray diffraction, scanning and transmission electron microscopy. Polymers having lower M_w values were found to be more efficient in reducing the nickel particle size. A decrease in the polymer concentrations yielded the smaller particles. Magnetic measurements showed that the as-prepared powders are ferromagnetic and their saturation magnetization and coercivity are size-dependent. Compared with bulk nickel, the nanoparticles exhibit an enhanced coercivity which is due to their small size and a decreased saturation magnetization resulted from the surface oxidation of the powder. The synthesis procedure offers a simple approach to preparing nickel nanoparticles on a large scale which could be used as magnetic recording materials, including high-density memory storage devices.

1. Introduction

Materials based on nanoparticles represent a new class of functional materials with unique properties that are currently of great interest and are widely studied. In recent years, interest in the preparation of nickel nanoparticles has increased substantially, which is caused by the possibility of their application in catalysis and medical diagnostics, as well as in magnetic devices, batteries, superconducting devices, etc. Nickel nanoparticles were shown to be efficient catalysts for the hydrogenation of nitrobenzene and nitrophenol, for the reduction of oxygen and oxidation of olefins [1]. They are also used as biosensors, composites and materials for solar energy usage and as magnetic nanofluids [2,3]. In addition, nickel, being a cheaper alternative to silver, platinum and palladium, is more attractive from a commercial point of view.

To produce nickel nanoparticles, various chemical and physical approaches have been developed. Among them, the chemical reduction of various nickel salts in organic or aqueous solutions with hydrazine hydrate or sodium borohydride is most commonly used. The methods for the synthesis of nanoparticles based on this approach are easy to use, since they do not require special equipment or conditions for their

implementation. In addition, they allow control of the size of the resulting particles, their morphology, composition and other properties by changing the reaction conditions, such as temperature and concentration of all the reagents, the nature of the stabilizer and the type of solvent.

When preparing metal nanoparticles in solutions, preventing their aggregation is one of the challenges [4]. Aggregation can be eliminated by coating the particles with a surfactant layer. This is widely used in practice. In the case of nickel, such a surface coating protects the particles from both aggregation and oxidation and it can also affect their size and shape. Polyelectrolytes are one of the most effective and promising nanoparticle stabilizers due to the interaction of the functional groups of the organic macromolecules with the nanoparticle surface. Water-soluble polymers such as polyvinylpyrrolidone (PVP) and polyvinyl alcohol (PVA) were shown to be very good candidates for the stabilization of nanoparticles [5–7]. Using PVP as a surfactant, Singh et al. [8] synthesized nickel nanoparticles in ethylene glycol with an average size of ~3 nm. Roy and Battacharya [9] prepared polymer-protected stable nickel nanoparticles by reducing nickel chloride with sodium borohydride in the presence of both polyvinylpyrrolidone and

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polyacrylic acid. The authors found that the size of the resulting nanoparticles can be easily controlled by changing the type of polymer, as well as its concentration. Thus, a decrease in the nickel to polymer ratio was reported to result in a decrease in the average particle diameter and smaller nanoparticles are formed in the presence of PVP. A comparative study of the effect of molecular weight of polyethylene glycol and polyvinyl alcohol on the size, shape and dispersity of silver nanoparticles was carried out by Diaz-Cruz et al. [10]. The authors showed that the molecular weight of the polymers has no influence on the nanoparticle shape but is directly proportional to their size which decreases as the polymer molecular weight decreases too.

A review of the literature revealed only a limited number of studies on the stabilization of metal nanoparticles with polyacrylic acid and its salts, particularly with regard to nickel nanoparticles. However, there are a number of studies reporting the effect of the concentration of sodium polyacrylate on the size and morphology of platinum nanoparticles and the mechanism of their growth in the presence of this polymer [11,12]. Prucek et al. studied the stabilization of copper and silver nanoparticles using sodium polyacrylates with different molecular weights (1200, 8000 and 15,000) [13–15]. Nano-copper particles, with a size of 20–100 nm, were prepared in an aqueous medium in the presence of sodium polyacrylate with a molecular weight of 1200 by reduction of copper sulfate with sodium borohydride [14]. It was shown that, the growth of the copper nanoparticles is hindered at a higher concentration of sodium polyacrylate. The authors explain this by electrostatic repulsion of the negatively charged anions of sodium polyacrylate adsorbed on the nanoparticle surface.

Thus, using polyacrylic acid and its salts, it is possible to efficiently control the size and morphology of nanoparticles, as well as the degree of their aggregation. However, to our knowledge, no such systematic studies concerning the stabilization of nickel nanoparticles with polyacrylates of different molecular weights have been reported so far. Therefore, the objective of the present study was to investigate the process of the reduction of nickel chloride with hydrazine hydrate in a polyol medium in the presence of the sodium salt of polyacrylic acid as the stabilizing agent. The novelty of this work is that it is the first systematic study on the effect of the polyacrylate-to-nickel ratio and sodium polyacrylate molecular weight on the size and morphology of nickel nanoparticles formed in a polyol medium. The effect of temperature and the type of polyol was also studied which allowed us to determine the optimum reaction conditions under which uniform nickel nanoparticles of less than 20 nm in size were obtained.

2. Experimental

2.1. Materials

Nickel(II) chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) of $\geq 97.0\%$ purity grade, and ethylene glycol ($\text{HO}(\text{CH}_2)_2\text{OH}$) of 99.8% purity grade, $\geq 99.7\%$ pure propylene glycol ($\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{OH}$), 95% pure ethanol, and hydrazine monohydrate of 100% purity, supplied by Sigma Aldrich, were used in the experiments without further purification. Sodium polyacrylates $[-\text{CH}_2-\text{CH}(\text{CO}_2\text{Na})-]_n$ (Na-PA) with molecular masses (M_w) of 1200, 5100 and 8000 (all as 45% aqueous solutions) (Sigma-Aldrich) were used as the stabilizers. Sodium hydroxide (NaOH, 50% aqueous solution) was of a highly pure grade.

2.2. Synthesis of nickel nanoparticles

Nickel nanoparticles were prepared by the reduction of nickel chloride in the presence of sodium polyacrylate, according to the published procedure [16]. The molecular weights of the polyacrylates used were 1200, 5100 and 8000. In a typical experiment, initially, appropriate amounts of nickel chloride and sodium polyacrylate at different molar ratios of nickel ions to monomeric unit of polyacrylate (Ni:Na-PA) were dissolved in ethylene glycol or propylene glycol under

stirring by heating in an oil bath to the desired temperature. Then a concentrated solution (100%) of hydrazine hydrate was added to the reaction mixture under continuous stirring at a nickel to hydrazine hydrate molar ratio of 1:14. To accelerate the reduction reaction rate, the process was carried out in the presence of sodium hydroxide (Ni:NaOH = 1:5). After the reaction was complete (the reduction time was 5–10 min), the mixture was air-cooled and the resultant nickel powder was collected by centrifugation, washed several times with ethanol to remove impurities and then it was dried in air at room temperature. The particle sizes and their morphology were investigated using various techniques.

2.3. Characterization of the nickel nanoparticles

XRD patterns were recorded on a D8 Advance powder X-ray diffractometer equipped with a one-dimensional Lynx-Eye detector and a $K\beta$ filter using $\text{Cu K}\alpha$ radiation. The crystallite size and lattice parameters were estimated by the Rietveld method [17] using Topas 4.2 software (Bruker AXS, Germany) for the profile and structural analysis. The broadening of the patterns due to the crystallite size was modeled by the “Double-Voigt” function. Analysis of the samples by transmission electron microscopy (TEM) was performed using a JEM 2010 electron microscope (JEOL, Japan) operating at 200 kV and having a resolution of 0.14 nm. The study of the samples by scanning electron microscopy (SEM) was performed using a Hitachi 3400 N scanning electron microscope (Hitachi Ltd., Japan). The magnetization of the samples was measured using a PPMS-6000 vibrational magnetometer within the temperature range of 4.2–300 K [18]. A powder sample of nickel nanoparticles was placed in a paraffin matrix. The variation of the magnetization as a function of the temperature (M - T curves) was measured in zero-field-cooled (ZFC) and field-cooling (FC) modes with an applied magnetic field of 1 kOe и 5 kOe.

The nickel concentration in the solutions was determined by complexometric titration using murexide as the indicator.

3. Results and discussion

3.1. Effect of the molecular weight of sodium polyacrylate and its concentration on the particle size

To study the effect of the Na-PA molecular weight and concentration on the size and morphological characteristics of the resulting nickel particles, the reduction of nickel ions was carried out in the presence of sodium polyacrylates of 1200, 5100 and 8000 molecular weights and at a temperature of 130 °C. It was shown that in the absence of Na-PA in the system, the particles formed have a nearly spherical shape and a quite narrow size distribution (Fig. 1). Their average size is

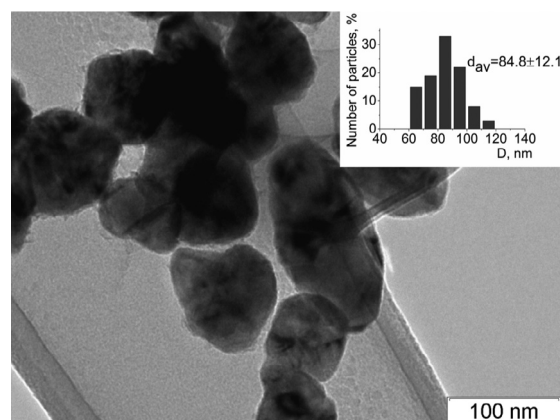


Fig. 1. SEM image of the nanoparticles prepared by reduction of nickel chloride in ethylene glycol with hydrazine hydrate in the absence of sodium polyacrylate at 130 °C.

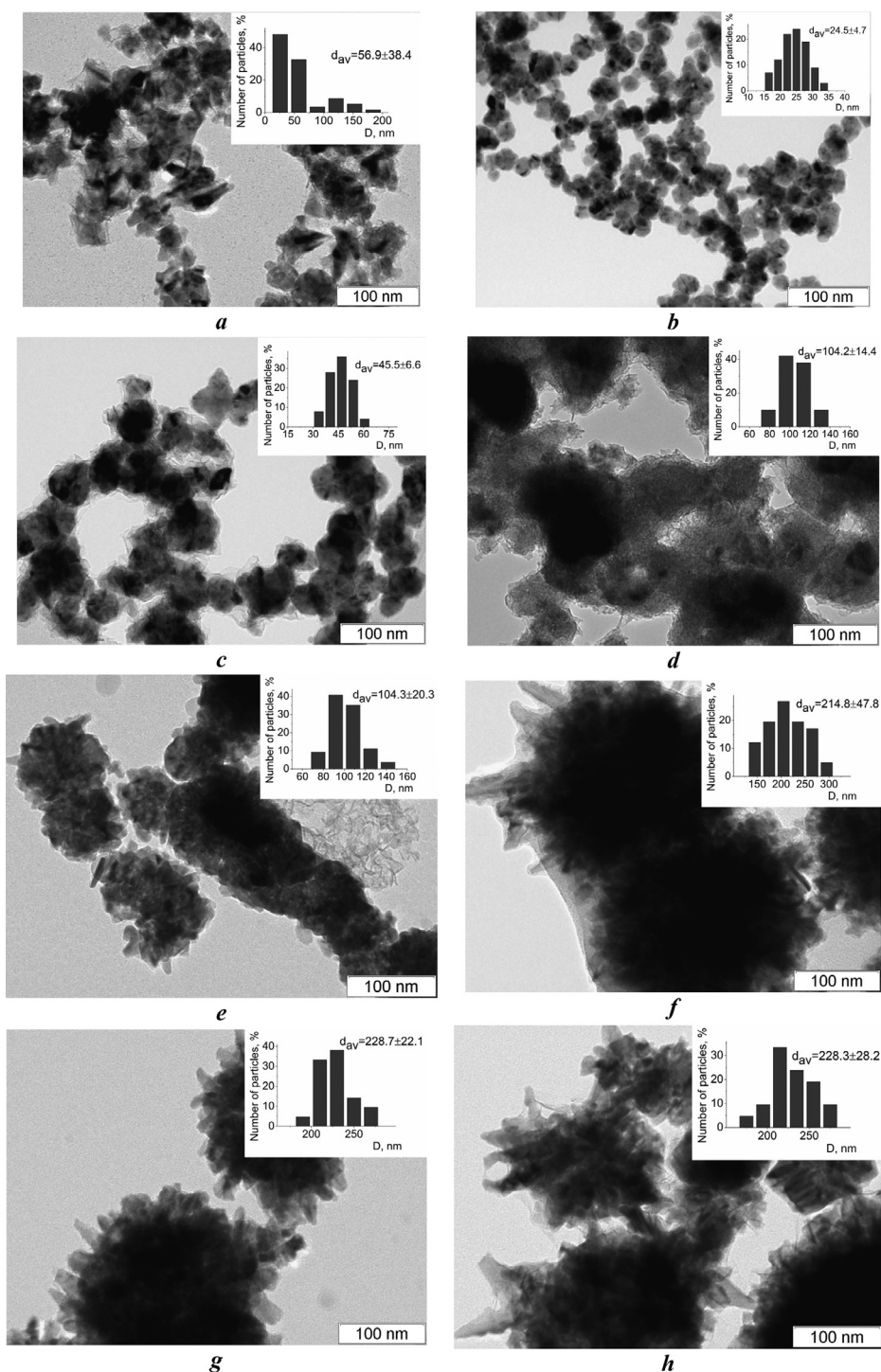


Fig. 2. TEM images of the nanoparticles prepared by reduction of nickel chloride in ethylene glycol with hydrazine hydrate in the presence of Na-PA-1200 (a–d) and Na-PA-8000 (e–h) of variable concentration. Ni:Na-PA = 1:1 (a, e), 1:5 (b, f), 1:10 (c, g) and 1:20 (d, h); T = 130 °C.

99 ± 7.8 nm. The introduction of Na-PA-1200 into the system at a Ni to Na-PA molar ratio of 1:1 results in a decrease in the average particle size to 56.9 ± 38.4 nm while the size distribution becomes much broader (Fig. 2a). At a Ni to Na-PA molar ratio of 1:5, the particles formed become more monodisperse and smaller. As seen from Fig. 2(b), the particles are spherical in shape and their average size is 24.5 ± 4.7 nm. A further increase in the Ni to Na-PA molar ratio to 1:10 and 1:20 results in an increase in the particles aggregation and their size up to 45.5 ± 6.6 and 104 ± 14.4 nm, respectively (Fig. 2c and d). Thus, in the case of sodium polyacrylate of 1200 molecular weight, the level of aggregation and the particle size are highly dependent on the polymer concentration so in order to minimize both

these parameters, the reduction process should be carried out at a Ni to Na-PA ratio of 1:5. In the presence of polymers with higher molecular weights (5100 and 8000), a similar trend has been observed: as the Na-PA concentration increases, the particle size increases. In the case of Na-PA-8000, by increasing the Ni:Na-PA ratio from 1:1 to 1:20, the particle size and their polydispersity were found to increase too. As seen from Fig. 2(e–h), at a Ni to Na-PA ratio of 1:1, the average particle size is 104 ± 20.3 nm, while at Ni:Na-PA ratios of 1:5 and 1:10, the average particle size is 214 ± 47.8 and 228 ± 22.1 nm. A further increase in the polymer concentration has no effect on the size of the particles and at a Ni to Na-PA ratio of 1:20, the particles of 228 ± 28.2 nm in size are formed. The XRD data show no characteristic peaks due to

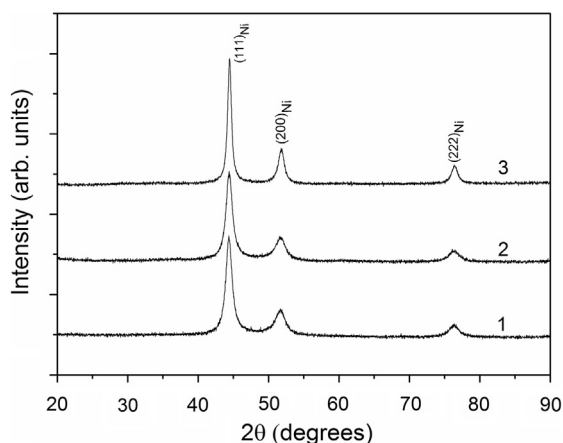


Fig. 3. XRD patterns of the samples obtained by reduction of nickel chloride with hydrazine hydrate in ethylene glycol in the presence of sodium polyacrylates of 1200 (curves 1 and 3) and 8000 (curve 2) molecular weights. Ni:Na-PA = 1:5; $T = 130\text{ }^{\circ}\text{C}$; curves 1 and 2 – freshly prepared samples; curve 3 – the sample prepared in the presence of Na-PA-1200 after keeping it in air for a year.

impurities of nickel oxides and hydroxides indicating that the final product in all cases is a pure metallic nickel with diffraction peaks at 2θ values of 44.5° , 51.98° and 76.4° (Fig. 3, curves 1, 2) attributed to the main characteristic peaks of the (1 1 1), (2 0 0), (2 2 2) crystal planes of face-centered cubic (fcc) nickel (space group $Fm\bar{3}m$ (2 2 5), JCPDS file No. 04-0850).

The effect of polyacrylate molecular weight on the average size of the particles is shown in Fig. 4. As seen, an increase in the molecular weight of the polymer leads to an increase in the size of the nanoparticles and the degree of their aggregation. Thus, the reduction of nickel chloride in ethylene glycol at $130\text{ }^{\circ}\text{C}$ in the presence of sodium polyacrylate with a molecular weight of 5100 at a Ni to Na-PA ratio of 1:5, results in the formation of uniformly sized and shaped particles of about $197.1 \pm 30.6\text{ nm}$ in diameter (Fig. 4a). In the presence of sodium polyacrylate with a molecular weight of 8000, the particles formed are less uniform in size (they have a quite wide size distribution) and have a less regular spherical shape with a size of $214.8 \pm 47.8\text{ nm}$ (a crystallite size is 12 nm). The TEM analysis also shows that, in both cases, nickel dendritic crystals resembling spikes are formed on the surface of the nickel particles and the dendritic morphology becomes more pronounced as the molecular weight of the polymer increases. Thus, it was shown that an increase in the molecular weight of the polymer from 1200 to 5100 results in an increase in the average particle size by almost 10 times (from 24.5 ± 4.7 to $197.1 \pm 30.6\text{ nm}$, respectively), while the particles morphology

remains spherical or near-spherical in shape with the difference being that their surface is covered by thorn-like formations. However, as the molecular weight of the polymer further increases to 8000, the dependence of particle size on molecular weight is not so evident but the surface morphology of the particles change, and more pronounced thorny nanostructures are obtained.

3.2. Effect of the reduction temperature

The dependence of the particle size on the temperature regime of the reduction process in the presence of polymers was investigated. It was shown that in the presence of Na-PA-1200, at temperatures below $100\text{ }^{\circ}\text{C}$, the reduction of nickel chloride to metallic nickel does not occur. An increase in the reduction temperature from 100 to $170\text{ }^{\circ}\text{C}$ results in a decrease in the average particle size from 24 ± 3.9 to $16.5 \pm 2.1\text{ nm}$. The particles formed are spherical in shape and have rather uniform size distribution (Fig. 5a–c). In the presence of polymers with higher molecular weights (5100 and 8000), a similar trend is observed although the reduction of nickel ions can proceed at lower temperatures, e.g. at $80\text{ }^{\circ}\text{C}$. In this case, when using Na-PA-8000, the wire-shaped structures consisting of the spherical particles with a diameter of $98 \pm 16.9\text{ nm}$ are formed (Fig. 5d). A further increase in the reduction temperature up to 100 and $130\text{ }^{\circ}\text{C}$ (Figs. 5e and 2f) results in an increase in the average size of the particles up to 118 ± 22.5 and $214 \pm 47.8\text{ nm}$, respectively, effects on their shape and decreases their aggregation. The TEM analysis also shows that the particles formed are nearly spherical in shape with a thorn-like surface indicating the tendency of anisotropic growth. By further increasing the temperature to $150\text{ }^{\circ}\text{C}$, this tendency becomes stronger resulting in the formation of dendritic-like crystals on the surface of the nickel particles of $167 \pm 38.5\text{ nm}$ in size (Fig. 5f). Thus, the reaction temperature decreases the particle size and shows little impact on their shape when using Na-PA-1200 as the stabilizer, while in the presence of high molecular weight polyacrylates, an increase in the reaction temperature has little effect on the size and quite noticeable effect on the shape of the produced nickel nanoparticles resulting in the deviation from smooth spherical morphology and the formation of thorny nanostructures.

3.3. Effect of the polyol

In our earlier work [16], it was shown that the polyol solvent used as reaction medium when reducing nickel chloride with hydrazine hydrate affects both the shape and size of the resultant nanoparticles. Therefore, it was also of interest to find out how the type of polyol affects the size and morphology of nickel nanoparticles obtained in the presence of sodium polyacrylates. The reduction process was carried

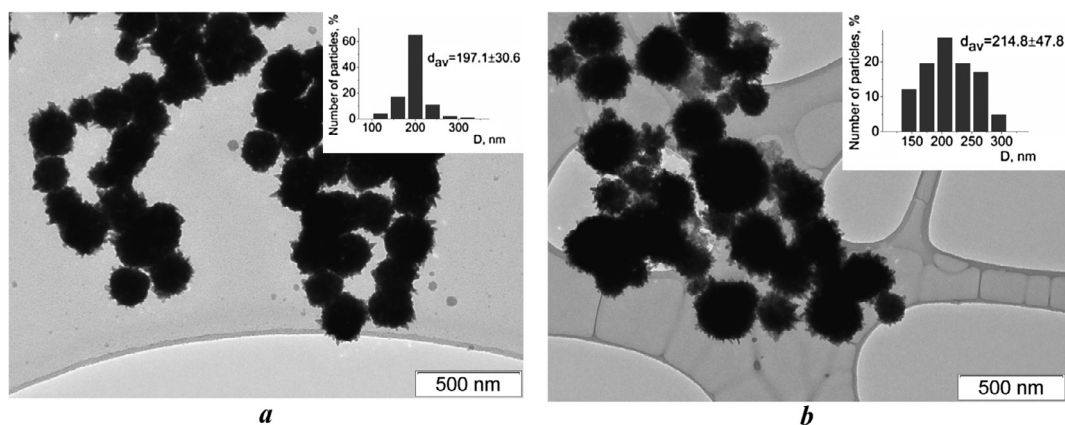


Fig. 4. SEM image of the nanoparticles prepared by reduction of nickel chloride in ethylene glycol with hydrazine hydrate in the presence of sodium polyacrylates of 5100 (a) and 8000 (b) molecular weights. Ni:Na-PA = 1:5, $T = 130\text{ }^{\circ}\text{C}$.

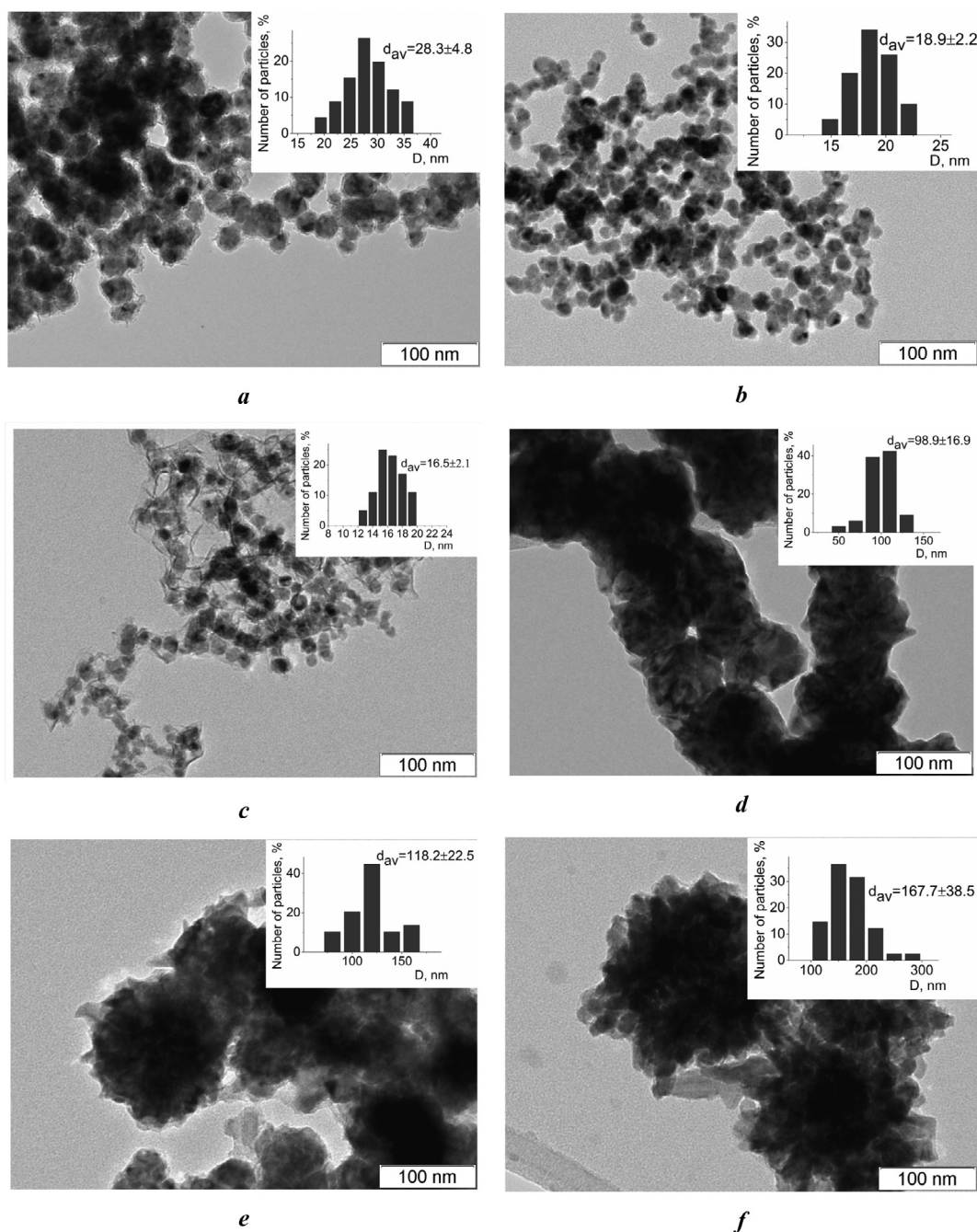


Fig. 5. TEM images of the nanoparticles prepared by reduction of nickel chloride in ethylene glycol with hydrazine hydrate in the presence of Na-PA-1200 (a–c) and Na-PA-8000 (d–f) at temperatures of 80 (d), 100 (a, e), 150 °C (b, f) and 170 °C (c). Ni:Na-PA = 1:5.

out in propylene glycol under the same conditions as in ethylene glycol. It was shown that, in the absence of sodium polyacrylate, nickel nanoparticles resulting from the reduction of nickel ions in propylene glycol were plate-like with an average size of 46 ± 7 nm (Fig. 6a). According to the XRD data, the crystallite size of the resultant nanoparticles was 15 nm. The introduction of a fivefold excess of Na-PA-1200 into the system results in the formation of nanocrystalline structures of predominantly spherical shape with an average diameter of 24 ± 3.9 nm and a relatively uniform size distribution (Fig. 6b). The introduction of a fivefold excess of Na-PA-8000 into the system, results in an increase in the particle size and the degree of aggregation. According to the XRD data, the crystallite size of the particles obtained is 10.5 nm and SEM images showed that the particles are highly aggregated and their size is around 30–70 nm. The surface of the resultant

nickel particles, like in the case of ethylene glycol, is covered with nickel dendritic crystals resembling small spikes. As the synthesis temperature decreases to 100 °C, the dendritic shape of the nickel crystals becomes more pronounced due to the formation of long needles on the surface and the average particle size decreases to 24.1 ± 9.7 nm (Fig. 6c). It should be noted that, in this case, the particles have quite a wide size distribution. In the presence of Na-PA-1200, the average particle size also decreases and reaches 16.8 ± 2.6 nm at 100 °C (Fig. 6d). An increase in the Ni to Na-PA ratio, as in the case of ethylene glycol, leads to an increase in the particle size. Thus, the use of propylene glycol as a reaction medium in place of ethylene glycol allows the reduction process to be carried out at lower temperatures, regardless of polyacrylate molecular weight, and thus production of smaller particles.

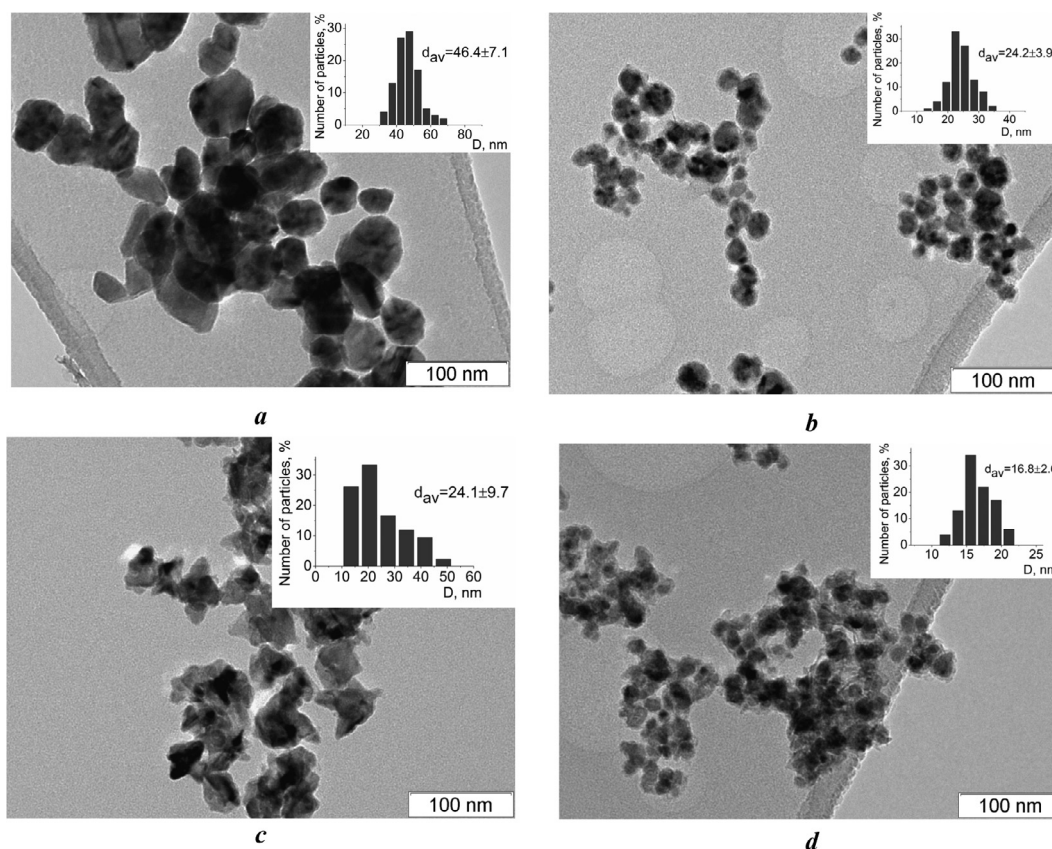


Fig. 6. TEM images of nickel nanoparticles synthesized by reduction of nickel chloride in 1,2-propylene glycol with hydrazine hydrate in the absence (a) and in the presence of sodium polyacrylates of 1200 (b, d) and 8000 (c) molecular weights and histograms of the particle size distributions. Ni:Na-PA = 1:5, T (°C): 130 (a, b) and 100 (c, d).

Table 1

Effect of synthesis conditions on the size and morphology of nickel nanoparticles prepared by the reduction of nickel chloride with hydrazine hydrate in a polyol medium in the presence of sodium polyacrylates. EG – ethylene glycol, PG – propylene glycol.

Sample	Na-PA molecular weight	Ni:Na-PA molar ratio	Temperature, °C	Polyol	Particle average size (TEM), nm	Morphology
1	–	1:0	130	EG	84.8 ± 12.1	Spherical nanoparticles
2	–	1:0	130	PG	46.4 ± 7.1	Plate-like nanoparticles
3	1200	1:1	130	EG	56.9 ± 38.4	Shapeless nanocrystals
4		1:5	130	EG	24.5 ± 4.7	Spherical nanoparticles
5		1:10	130	EG	45.5 ± 6.6	Spherical nanoparticles
6		1:20	130	EG	104.2 ± 14.4	Near-spherical nanoparticles
7		1:5	100	EG	28.3 ± 4.8	Spherical nanoparticles
8		1:5	150	EG	18.9 ± 2.2	Spherical nanoparticles
9		1:5	170	EG	16.5 ± 2.1	Spherical nanoparticles
10		1:5	130	PG	24.2 ± 3.9	Spherical nanoparticles
11		1:5	100	PG	16.8 ± 2.6	Spherical nanoparticles
12	5100	1:5	130	EG	197.1 ± 30.6	Spherical nanoparticles with a thorn-like surface
13		1:10	130	EG	$l = 3.5 \pm 0.5 \mu\text{m}$ $d = 318. \pm 36.8$	Wire-shaped nanostructures
14		1:5	130	PG	136.1 ± 16.8	Spherical nanoparticles with a thorn-like surface
15		1:10	130	PG	187.0 ± 46.2	Dendritic-like nanocrystals
16	8000	1:1	130	EG	104.3 ± 20.3	Thorny nanostructures
17		1:5	130	EG	214.8 ± 47.8	Spherical nanoparticles with a thorn-like surface
18		1:10	130	EG	228.7 ± 21.1	Spherical nanoparticles with a thorn-like surface
19		1:20	130	EG	228.3 ± 28.2	Dendritic-like nanocrystals
20		1:5	80	EG	98.9 ± 16.9	Wire-shaped nanostructures
21		1:5	100	EG	118.2 ± 22.5	Spherical nanoparticles with a thorn-like surface
22		1:5	150	EG	167.7 ± 38.5	Dendritic-like nanocrystals
23		1:5	130	PG	51.1 ± 5.7	Spherical nanoparticles with a thorn-like surface
24		1:5	100	PG	24.1 ± 9.7	Dendritic-like nanocrystals

The reason for this may be the stability of the Ni-ethylene glycol and Ni-propylene glycol intermediates formed in the reaction medium which is not the same for different polyols and decreases when passing from a short chain polyol to a long chain polyol. As shown by Carroll et al. [20], the intermediate formed in the Ni-ethylene glycol system is more stable than that in the Ni-propylene glycol system which suggests that, in the latter case, the reaction proceeds at relatively lower temperature. The latter affects both the nucleation and growth steps resulting in the formation of smaller particles. The reduction conditions and the characteristics of the samples prepared are given in Table 1.

In order to verify the resistance to oxidation of the prepared nickel nanoparticles, the samples have been kept in air for 1 year and then were characterized using X-ray phase analysis. The results of the study show that the prepared nickel nanopowders remain stable and do not oxidize in air. According to the XRD data, after keeping the powders in air for a year, the qualitative and quantitative composition of the prepared powders do not change and the characteristic peaks assigned to the formation of nickel oxide were not detected in the XRD patterns (Fig. 3, curve 3). However, TEM analysis of the nickel nanoparticles carried out immediately after their preparation revealed the presence of a very small layer of amorphous nickel oxide on the nickel surface. The thickness of the layer does not exceed 1–2 nm and, as shown, it does not increase over time. It is obvious that this thin coating passivates the surface of the metallic nickel and does not allow it to oxidize further with time.

3.4. Discussion of the possible formation mechanism

The increase in the particle size and their degree of aggregation resulting from an increase in the molecular weight of sodium polyacrylate may be caused by several reasons. One of the reasons can be attributed to the difference in the adsorption mode of polyacrylates of different chain lengths on the surface of the nickel nanoparticles. Since sodium polyacrylates have a monomer unit containing the $-\text{COO}^-$ group, the stabilization of nanoparticles in the solution in their presence can occur through the coordination of the oxygen atoms of the carboxylate groups on the nanoparticle surface resulting in the formation of a protective layer thereon. Consequently, the adsorption of polyacrylate on the surface of nickel nanoparticles should prevent nickel atoms from direct contact between nickel ions with their nuclei and the subsequent particle growth by atomic addition. Obviously, the smaller the size of the Na-PA molecules, the more compactly they cover the surface of the nanoparticles, and, in contrast, the polymers with high molecular weights, due to steric effects between polymer chains, are not able to efficiently pack on a nickel surface, forming a less dense layer on it, and to prevent properly further nanoparticle growth by atomic addition [13].

Apart from that, the explanation of the polyacrylates effect on final size of the nickel nanoparticles can be found in different conformation states of polymer chains in various solvents [19]. As mentioned above, polyacrylates contain ionogenic groups that can dissociate into a charged polyanion and small counterions when dissolving in a polar solvent. In this case, due to electrostatic repulsion between ionogenic groups of the same charge, the chains polyacrylate macromolecule tends to unfold, while undissociated molecules, due to intramolecular motions and hydrogen bonding that occurs in polar solvents, tend to fold which results in the formation of various structures including coil-like one. Obviously, the longer the polymer chain is, the more likely the latter is to occur [19]. If this is a case, then we tentatively suggest that in the presence of polyacrylate of higher molecular weight (in our case, in the presence of Na-PA-8000), the formation of the coil-like polymer structures in the solution of ethylene glycol is responsible for the formation of larger particles than those formed in the presence of lower molecular weight polymers such as Na-PA-1200. The formation mechanism of nickel nanoparticles in the presence of sodium polyacrylates of different molecular weights illustrated in Fig. 7 was supported by the

results of transmission electron microscopy study. As seen from TEM images, primarily formed in the presence of Na-PA-8000 particles agglomerate forming a nanosphere (Fig. 2f and g) under the effect of overlapping of adsorbed polyacrylate molecule chains which behave as a kind of soft templates. TEM study clearly shows that, compared with the particles formed in the presence of Na-PA-1200 (Fig. 2a–d), the size of the particles prepared in the presence of Na-PA-8000, is enlarged and they resemble spheres of about 200 nm in size consisting of much smaller nanoparticles of about 20 nm in size.

In speculating why the trend of increasing particle size with increasing polyacrylate molecular weight takes place in the system under consideration, the kinetic features of the processes should also be taken into account. Thus, larger polymer molecules result in a larger particle because they require more time to diffuse to and passivate the growing nanoparticle.

3.5. Magnetic properties of the nickel powders

The magnetic properties of the samples prepared in the absence and presence of sodium polyacrylates with a molecular mass of 1200 and 8000 (Ni:Na-PA = 1:5, $t = 130^\circ\text{C}$) were investigated by analyzing the magnetization dependencies of the samples on the magnetic field strength (hysteresis and M - H curves) and on the temperature (M - T). Figs. 8 and 9 present the magnetic field dependences of the magnetization at different temperatures (4.2 and 300 K) for these samples. As can be seen, both samples exhibit a characteristic hysteresis behavior, which indicates that the nanoparticles obtained are ferromagnetic.

The values of saturation magnetization (M_s), remanent magnetization (M_r) and coercivity (H_c) of the nickel samples evaluated from the M - H curves at 4.2 and 300 K are listed in Table 2. For comparison, the values for both nickel nanoparticles prepared in the absence of sodium polyacrylates and bulk nickel are given also. As seen from the Table, the M_s , M_r and H_c values depend on the nanoparticle size. Thus, an increase in the particle size results in an increase in the M_s values and a decrease in the M_r and H_c values. It can also be seen from the Table that the saturation magnetization values at a temperature of 300 K for nickel nanoparticles with an average size of 24.5 ± 4.7 and 214.8 ± 47.8 nm are smaller than that for nickel prepared in the absence of Na-PA and bulk nickel (31, 32.5 and 40.5, 54.4, respectively). A decrease in the saturation magnetization values of the nanoparticles as compared to that of bulk nickel can be attributed to the formation of a disordered or amorphous layer on the surface of the nickel nanoparticles whose atoms do not exchange with internal atoms and, therefore, do not contribute to M_s (the so called “magnetically dead” surface layer). The reason for the formation of this layer can be both the surface oxidation of nanoparticles and the presence of polyacrylate adsorbed on their surface. The thickness of this layer can be estimated from the equation [21]:

$$M_s = M_{s\text{bulk}}(1 - 6t/D),$$

where M_s and $M_{s\text{bulk}}$ are the saturation magnetization values of the nickel particles and their bulk counterpart, respectively, t is the thickness of the magnetically dead layer and D is the diameter of the nanoparticles. Using this equation, the t/D values were found to be 7.25% and 4.3% for nanoparticles prepared in the presence and absence of Na-PA-1200, respectively. As seen, a decrease in the particle size results in an increase in the surface-to-volume ratio of the Ni nanoparticles followed by an increase in the percentage of the magnetically inactive layer. For thorny-like nanoparticles prepared in the presence of Na-PA-8000, the value of the magnetically inactive layer has not been found as the particle shapes deviate from a smooth spherical morphology which complicates such calculations.

A clear increase in the coercivities of the nanosized samples as compared to that for bulk nickel is due to the fact that the H_c of the multidomain ferromagnetic nanoparticles and their sizes are linked by the formula: $H_c \sim 1/D$ [22]. Since the single-domain size of nickel is

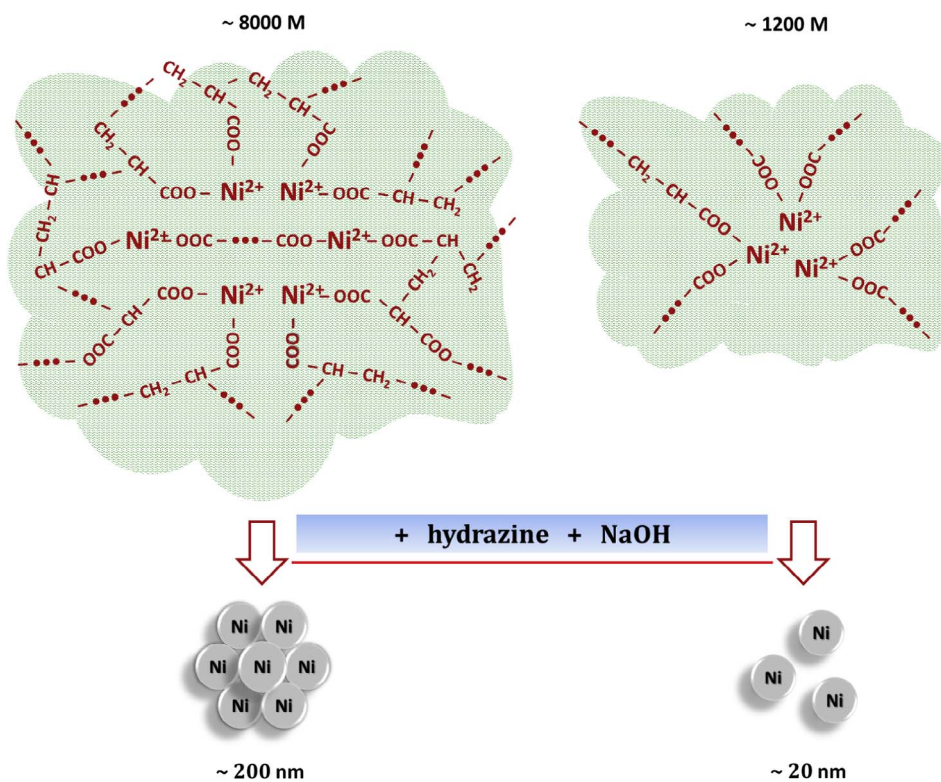


Fig. 7. Schematic illustration of the formation of nickel particles in the presence of sodium polyacrylates of 1200 and 8000 molecular weights.

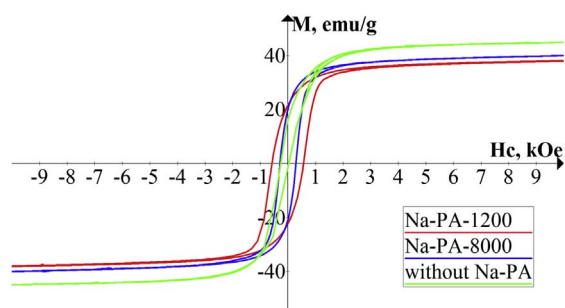


Fig. 8. Magnetic hysteresis curves measured at 4.2 K for nickel nanopowders prepared in the absence and presence of Na-PA-1200 and Na-PA-8000.

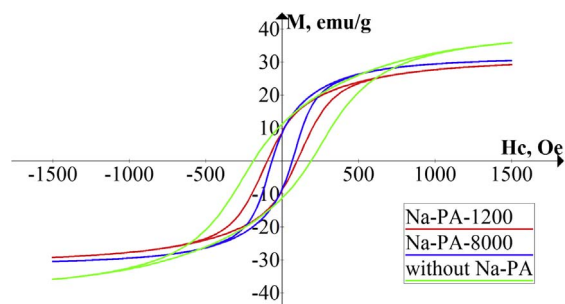


Fig. 9. Magnetic hysteresis curves measured at 300 K for nickel nanopowders prepared in the absence and presence of Na-PA-1200 and Na-PA-8000.

~ 21 nm [21] which is smaller than the size of the nickel particles in the synthesized powders, a decrease in the coercivity with an increase in the particle size is caused by their multidomain state.

The magnetization temperatures for the resultant nanoparticles are given in Figs. 10, 11 and 12. The dependences were obtained in the ZFC (zero-field cooled) and FC (field cooled) regimes in magnetic fields of 1 kOe and 5 kOe. In the low-temperature region, there are clear anomalies accompanied by the biggest divergence in the behavior of

the $M(T)_{FC}$ and $M(T)_{ZFC}$ dependences. It is also seen that an increase in the external field results in a shift of the maxima of the $M(T)_{ZFC}$ dependences toward the low-temperature region (or their disappearance). Since the nanoparticles under investigation are not single-domain, it is obvious that the observed behavior is not related to the processes of superparamagnetic blocking of the particles. The spin-glass-like behavior of surface atoms is a logical explanation for the observed anomalies [23–26]. The existence of the spin-glass-like subsystem correlates with the fact that the saturation magnetization values (M_S) of the nickel nanoparticles are noticeably smaller than that of bulk nickel.

4. Conclusions

Nickel nanoparticles have been prepared by the reduction of nickel chloride with hydrazine hydrate in a polyol medium using sodium polyacrylates of different molecular weights as the stabilizing agents. The average particle size and the degree of aggregation were shown to increase as the molecular weight of the polymer increases. The smallest nickel nanoparticles of 20–50 nm in size were obtained in ethylene glycol at a five molar excess of Na-PAK-1200 over nickel at 130 °C. The use of propylene glycol as a reaction medium allows the reduction process to be carried out at lower temperatures and thus the production of the particles of less than 20 nm in size which are nearly 10 times smaller than that obtained in the absence of sodium polyacrylates. In the presence of Na-PAK-5100 and Na-PAK-8000, an increase in their concentration and the reaction temperature was shown to contribute to the anisotropic growth resulting in the development of thorny nickel nanostructures. The formation mechanism of nickel nanoparticles prepared in the presence of sodium polyacrylates of different molecular weights has been discussed. The as-synthesized nickel nanopowders were shown to be stable and not to oxidize in air for 1 year. Magnetic measurements showed that compared with bulk nickel, the nanoparticles exhibited an enhanced coercivity which increases as the particle size decreases.

Table 2
Magnetic characteristics of the synthesized nickel nanopowders and bulk nickel.

Sample	M_s (4.2 K), emu/g	M_s (300 K), emu/g	M_r (4.2 K), emu/g	M_r (300 K), emu/g	H_c (4.2 K), Oe	H_c (300 K), Oe
Na-PA-8000 $d = 214.8 \pm 47.8$ nm	42.2	32.5	20	8.6	290	67
Na-PA-1200 $d = 24.5 \pm 4.7$ nm	44.1	31	22	8.8	560	97
Without Na-PA $d = 84.8 \pm 12.1$ nm	45.5	40.5	20	12.9	260	180
Bulk nickel [23]		54.4		2.7		6

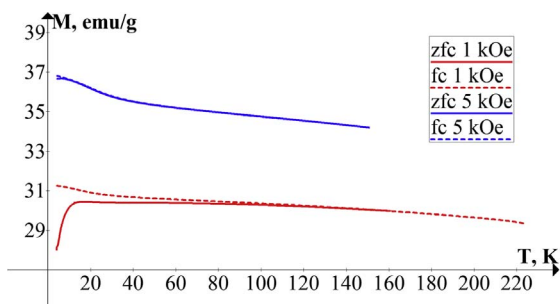


Fig. 10. Temperature dependences of the magnetization of the nickel nanoparticles prepared in the presence of Na-PA-1200 ($d = 24.5 \pm 4.7$ nm) in FC and ZFC regimes in external magnetic fields of $H = 1$ kOe and 5 kOe.

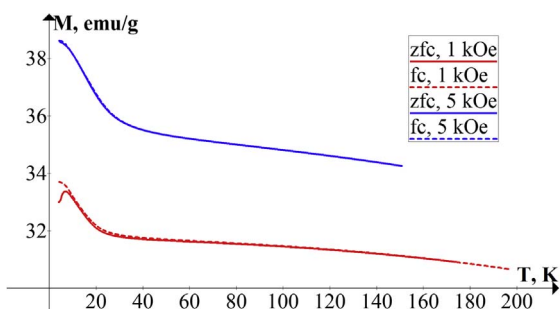


Fig. 11. Temperature dependences of the magnetization of the nickel nanoparticles prepared in the presence of Na-PA-8000 ($d = 214.8 \pm 47.8$ nm) in FC and ZFC regimes in external magnetic fields of $H = 1$ kOe and 5 kOe.

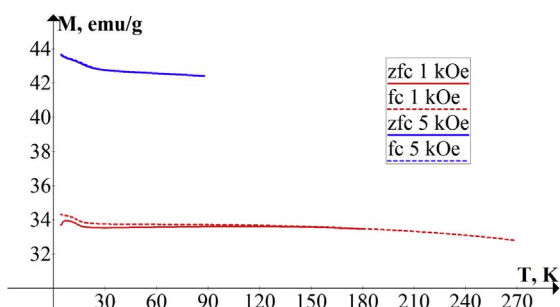


Fig. 12. Temperature dependences of the magnetization of the nickel nanoparticles prepared in the absence of Na-PA ($d = 84.8 \pm 12.1$) in FC and ZFC regimes in external magnetic fields of $H = 1$ kOe and 5 kOe.

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