Kinetics of Formation of Ni-Co Bimetallic Nanoparticles

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Abstract. Development of new cheaper and more efficient methods of synthesis of Ni and Co based nanopowders is an actual task of nanochemistry due to promising of these materials for huge range of applications, for example for hydrogen storage systems [1] or hydrogen generation [2]. One of the simplest methods of synthesis of Ni and Co nanoparticles is low-temperature polyol process involved metal-hydrazine complexes as precursor of NiNPs and CoNPs. However, despite the huge range of references devoted to synthesis and utilizing of NiNPs and CoNPs the kinetics of metal nanoparticles and especially bimetallic nanoparticles formation in polyol solutions are studied insufficiently. That is why the aim of presented work was to investigate the kinetics and mechanism of bimetallic Ni-Co nanoparticles (Ni-Co-NPs) formation via reduction of Ni^{2+} and Co^{2+} by hydrazine in water-ethylene glycol solutions. The kinetics of synthesis of Ni-Co-NPs via reduction of Ni^{2+} and Co^{2+} ions by hydrazine was studied using the volumetric setup and obtained nanoparticles were studied using scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS) and XRD.

Introduction

Recently we have studied in details the kinetics of NiNPs formation in water/ethylene glycol solutions under conditions of homogeneous [3] and heterogeneous nucleation [4, 5] via the reduction of Ni^{2+} or $Ni(OH)_2$ by hydrazine. It was shown that these methods of synthesis of NiNPs are well reproducible, fast and cheap and obtained particles are characterized by narrow particles size distribution (PSD). At the same time it was found that synthesis of NPs in heterogeneous media is more preferable in comparison with homogeneous conditions due to lower in twice of activation energy of nucleation as well as due to possibility of obtaining of a lot of nanopowders. Besides, on the base of the kinetic investigations combined with the UV-vis spectroscopy data, the mechanism of NiNPs formation under conditions of heterogeneous nucleation was proposed. Such a mechanism involves *i)* partial dissolution of nickel hydroxide and formation of nickel-hydrazine complex; *ii)* the decay of formed nickel-hydrazine complex on the nickel hydroxide surface and formation of nuclei of nickel nanoparticles; *iii)* growth of nickel nuclei via the reaction with dissolved nickel-hydrazine complex; *iv)* coagulation of small nickel particles; 5) growth of nickel nanoparticles from the surface. These investigations allowed us to optimize the techniques of obtaining of Ni-based nanopowders and these optimal conditions were applied in this study for the synthesis of Ni-Co bimetallic nanoparticles.

Kinetic peculiarities of reduction of Ni and Co hydroxides by hydrazine

As it was mentioned above, the kinetics of Ni-Co-NPs formation was studied at optimal conditions for the synthesis of monometallic NiNPs, namely: water/ethylene glycol ratio equal to 1/5, $\nu(Ni^{2+} + Co^{2+})$ = 0.0025 mol, $\nu(NaOH)$ = 0.05 mol, $\nu(N_2H_4)$ = 0.2 mol, temperature 70 °C. Due to reaction of metals reduction by hydrazine is accompanied by gas evolution (see gross-reaction 1), the kinetics of Ni-Co-NPs formation at different Ni/Co ratios was studied using volumetric setup.
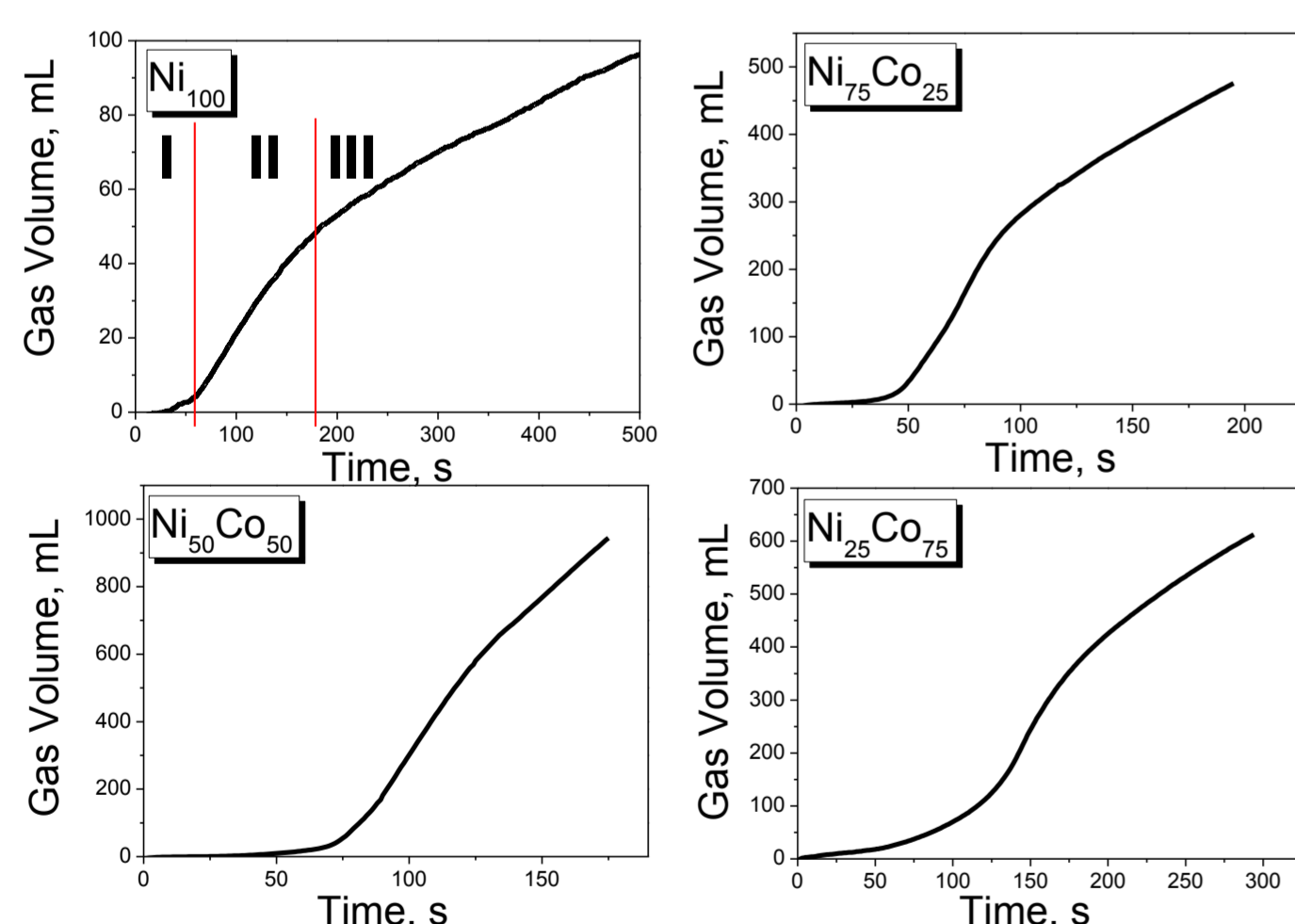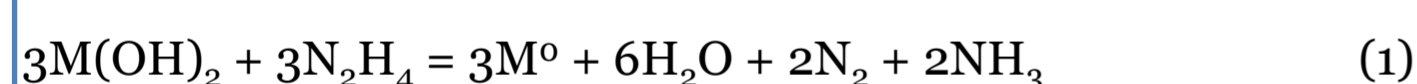
$$3M(OH)_2 + 3N_2H_4 = 3M^0 + 6H_2O + 2N_2 + 2NH_3 \quad (1)$$

Fig. 1. Kinetic curves of reduction of Ni and Co hydroxides by hydrazine.

It was found that the all kinetic curves are sigmoidal and consisted of 3 section (Fig. 1) which may correspond to nucleation (**I**, induction period), growth of nanoparticles (**II**) and decomposition of hydrazine catalyzed by Ni-Co-NPs (**III**).

Dependence of kinetic parameters of Ni-Co-NPs formation on the Ni/Co ratio

On the base of obtained data (Fig. 1) the kinetic parameters of formation of Ni-Co-NPs (namely, time of induction period (t_{ind}) and the maximal rate (dC/dt) of growth of nanoparticles) were calculated (Table 1).

Table 1. Dependency of the kinetic parameters of Ni-Co-NPs formation on the Ni/Co ratio

Fraction of Ni, %	t_{ind}, s	dC/dt, s^{-1}
100	43±10	0.008±0.004
75	48±4	0.027±0.005
50	65±5	0.077±0.012
25	110±10	0.014±0.004

It was found that the rate of nucleation of Ni-Co-NPs (which is inversely to t_{ind}) is linearly decreased with decreasing of fraction of Ni in the reaction mixture but the rate of growth of nanoparticles is increased up to the Ni/Co ratio equal to 50/50 and sharply decreased for $Ni_{25}Co_{75}$ (Fig. 2).
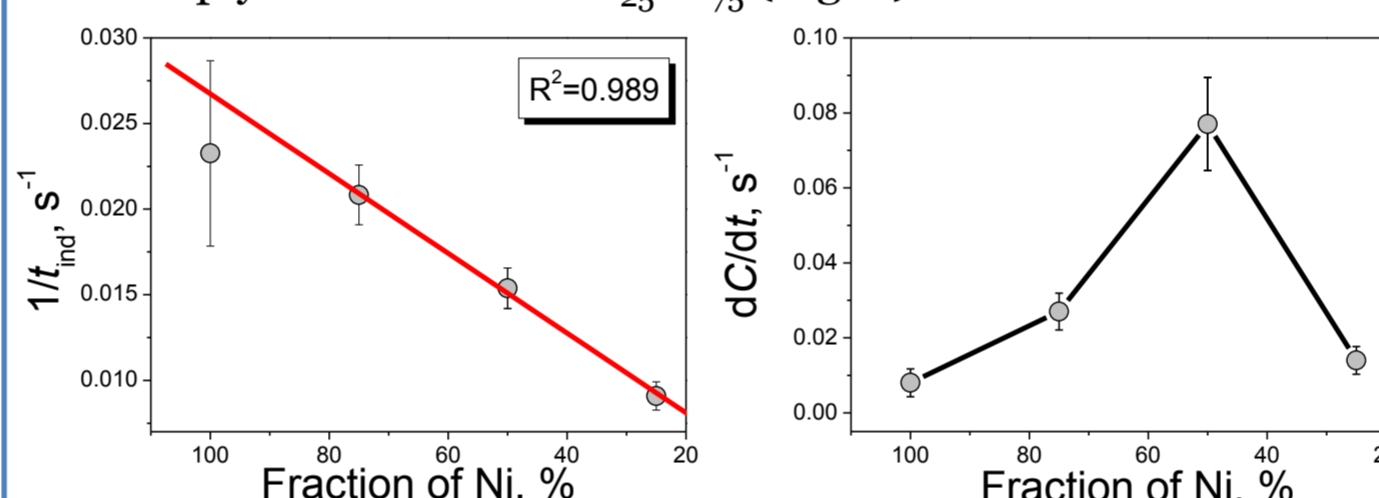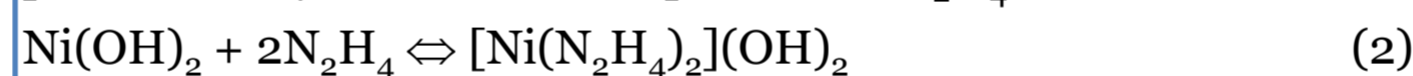

Fig. 2. Dependency of the rates of Ni-Co-NPs nucleation and growth on the fraction of Ni in the reaction mixture.
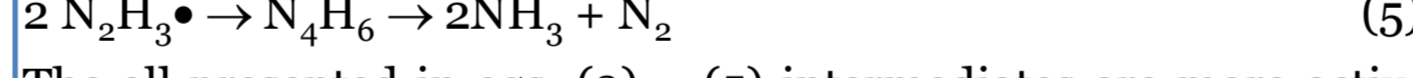
Such a fact may explained as follow.

1) As it was established in [5], the nucleation of NiNPs is occurred via partial dissolution of $Ni(OH)_2$ and formation on the surface of particles of hydroxide the complex $Ni^{2+} - N_2H_4$

$$Ni(OH)_2 + 2N_2H_4 \Leftrightarrow [Ni(N_2H_4)_2](OH)_2 \quad (2)$$

which easily ($E_A \sim 40$ kJ/mol) decompose forming the nucleus of NiNPs. Cobalt cannot form the complex compounds with hydrazine, thus, $Co(OH)_2$ does not dissolve and due to high redox potential of the half-reaction $Co(OH)_2 + 2e^- \to Co + 2OH^-$ (E_0 = -0.73 V) does not participate in the nucleation process. That is why the rate of nucleation linearly depend on the initial concentration of Ni^{2+} in the reaction mixture.

2) It is known that reducing of metals by hydrazine is occurred with formation of hydrazile radical $N_2H_3\bullet$ subsequent by its recombination and formation of active short-lived intermediates:

$$2\,N_2H_3\bullet \to N_2H_4 + N_2H_2 \quad (3)$$
$$2\,N_2H_2 \to N_2H_4 + N_2 \quad (4)$$
$$2\,N_2H_3\bullet \to N_4H_6 \to 2NH_3 + N_2 \quad (5)$$

The all presented in eqs. (3) – (5) intermediates are more active reducing agents than hydrazine and can reduce $Co(OH)_2$. Moreover, bimetallic Ni-Co-NPs are more active catalysts for N_2H_4 decomposition (see Figs. 1, sections **III**) excepting $Ni_{25}Co_{75}$. However, in the case of bimetallic nanoparticles the intensive evolution of NH_3 was observed contrary to NiNPs which decompose the hydrazine in alkaline solution to nitrogen and hydrogen only. That is why we can assume that dC/dt is increased with increasing of Ni ratio due to higher catalytic activity of bimetallic nanoparticles but with increasing of Co content the fraction of reaction (5) is increased and the decreasing of the rate of particles growth is observed for $Ni_{25}Co_{75}$.

Characterization of Ni-Co-NPs

Using XRD (Fig. 3) it was found that obtained Ni-Co-NPs does not consist any impurities (such as unreacted hydroxides or oxides of Ni and Co).
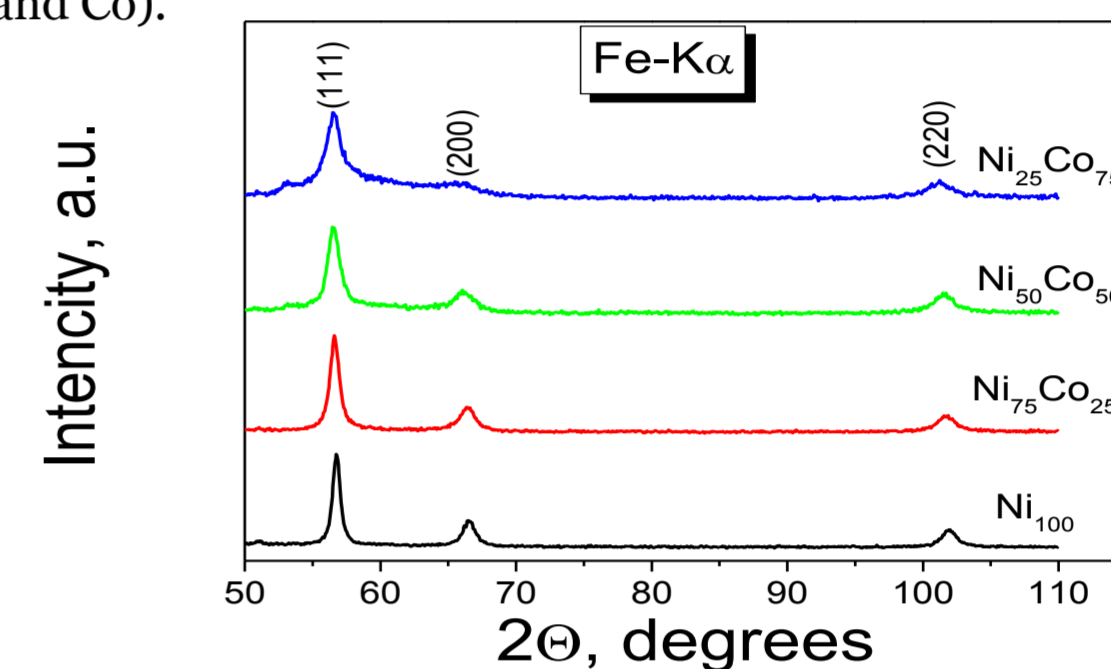

Fig. 3. XRD-patterns of Ni-Co-NPs.

At the same time element analysis (EDS) showed that the compositions of obtained products well correspond to the ratio Ni/Co in the initial reaction mixtures (Table 2).

Table 2. Element composition of Ni-Co-NPs

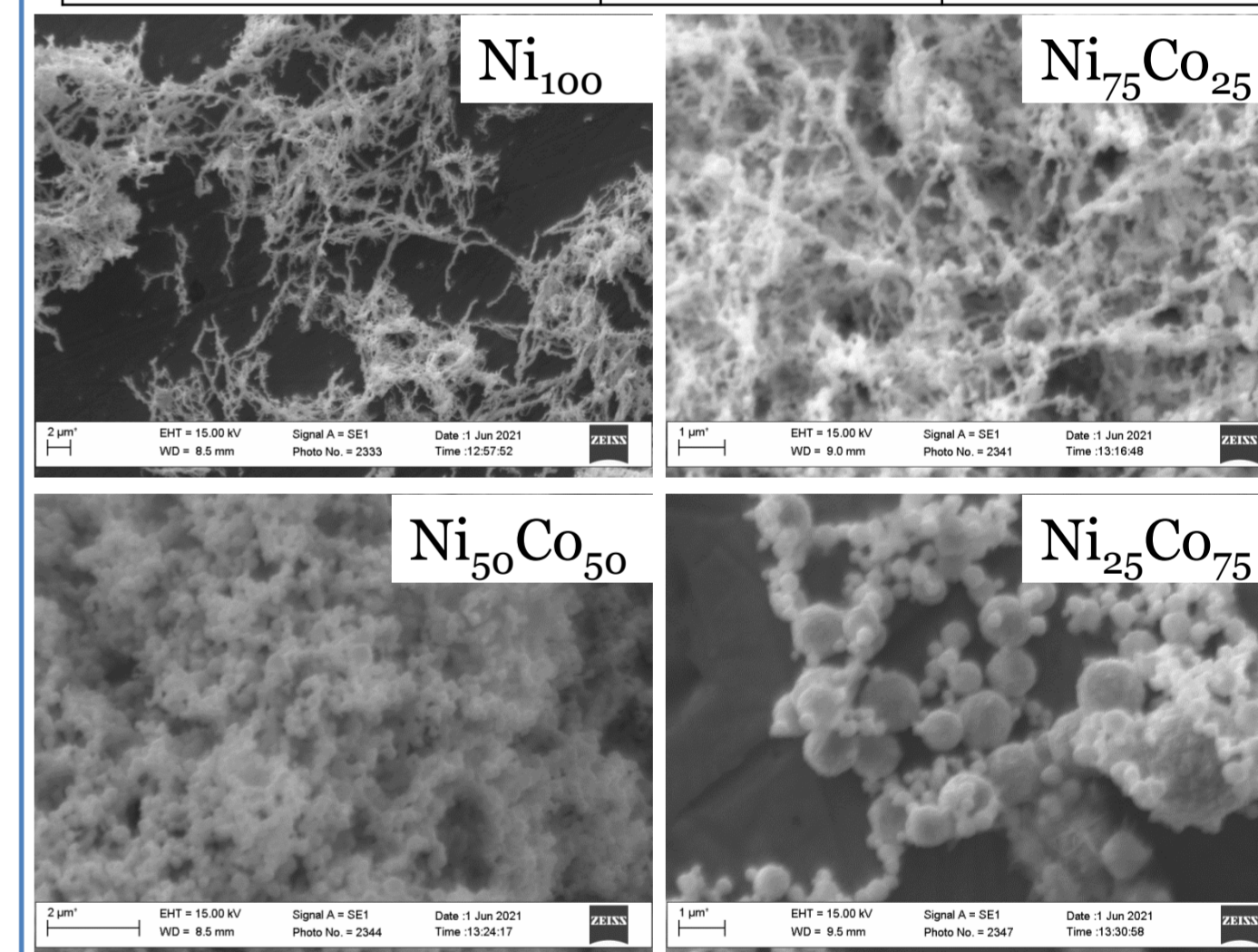| Ni/Co ratio in the reaction mixture	Content, % weight	
	Ni	Co
100/0	100	–
75/25	77	23
50/50	50.5	49.5
25/75	29	71

Fig. 4. SEM-images of Ni-Co-NPs.

Using SEM it was found that the size and polydispersity of Ni-Co-NPs does not change significantly with decreasing of Ni fraction up to 50 %. However, in the case of $Ni_{25}Co_{75}$ the sizes of particles are from 150 nm to 2 μm (Fig. 4). It was found that the big particles (point 1) are consisted of 25 % of Ni and 75 % of Co but the small ones (point 3) are consisted of 43% of Ni and 57 % of Co (see Figure at left). Such fact is in good correlation with kinetic investigations, namely: the high rate of NPs growth prevent the diffusive agglomeration of particles but with increasing of Co content the rate of Ni-Co-NPs growth is decreased that lead to formation of polydisperse and poly-compositive nanostructures.

Conclusions. In presented work we reported a cheap and fast gram-scale technique for the obtaining of bimetallic Ni-Co nanopowders. Using XRD, SEM and EDS the composition and the morphology of obtained Ni-Co-NPs have been evaluated. The correlations between the compositions and the sizes of obtained nanoparticles with the kinetics of their synthesis has been established.

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