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Synthesis of Ni/NiO Nanosize Powders with Different Phase Ratio by Thermal Decomposition of Nickel Acetate Amines

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Ni/NiO nanopowders with different phase ratio have been prepared using thermal decomposition of nickel acetate ammine complexes containing various ammonia content in air at the temperature range 300 – 500 °C. Obtained powders have been characterized by IR-spectroscopy, XRD and TG, DTA, DTG, TEM, laser granulometry and adsorption-structural method. Thermal decomposition of nickel ammine complexes occurred with forming nickel hydroxide, carbonate and hydroxocarbonate ammines precursors. Composition of the precursors depended on temperature and ammonia content in initial complex. Mean crystallite size of nickel depended on temperature only. In the temperature range from 350 to 500 °C the crystallite size of nickel has grown from 50 to 55 nm. Mean crystallite size of nickel oxide depended on temperature and ammonia content. In the temperature range from 350 to 500 °C the crystallite size of NiO has grown from 5 to 25 nm. Increasing ammonia content from 3.6 to 14.4 mol/mol Ni led to decreasing NiO crystallite size from 8 – 10 to 5 nm.

Keywords: Nickel Ammine Complexes, Nanopowders, IR-Spectroscopy, XRD Analysis, TG, DTA, DTG, Slit Pore Structure.

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1. INTRODUCTION

Nowadays, nickel powders are widely used as materials for electrodes manufacturing for multilayered ceramic capacitors. The specific capacity of the multilayered ceramic capacitors can be increased by thickness decreasing of ceramic and electrode layers and increasing number of electrodes. Both metallic and dielectric layers of 100 - 200 nm thick have to be manufactured from nanosize particles of Ni and $BaTiO_3$. Thus, development of Ni nanopowder of 20 nm and less is of great importance.

2. MATERIALS AND METODS

Ni/NiO nanopowders with different phase ratio have been prepered using thermal decomposition of nickel acetate ammine complexes containing various ammonia content in air at the temperature range 300 – 500 °C.

Chemical, phase composition and decomposition completeness of the products have been identified by IR-spectroscopy, XRD and TG, DTA and DTG, respectively. Mean crystallite and particle size have been identified by TEM and laser granulometry and the pore size distribution of obtained powders has been measured by the adsorption-structural method.

3. RESULTS AND DISCATION

Thermal decomposition of nickel ammine complexes occurred with forming hydroxide, carbonate and hydroxocarbonate ammines nickel-containing precursors (fig. 1). Precursors composition was identified by annealing temperature and ammonia content in initial complex and effected on Ni/NiO ratio in final powder. Temperature raising from 325 to 400 °C and ammonia content increasing from 3.6 to 14.4 mol/mol Ni led to decreasing content of nickel carbonate and hydroxocarbonate ammines precursors.

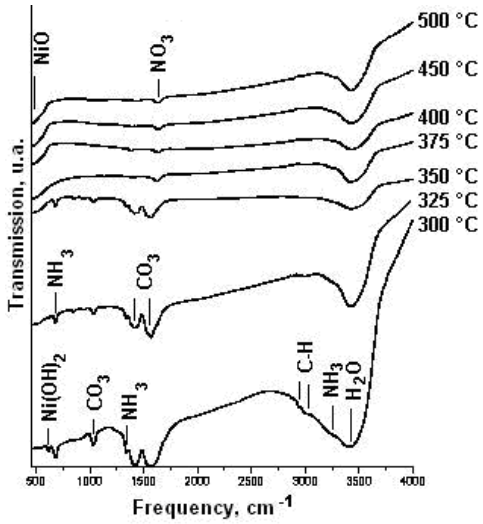

Fig. 1 – IR-spectra of nickel acetate hexaammine decomposition products obtained at different temperatures

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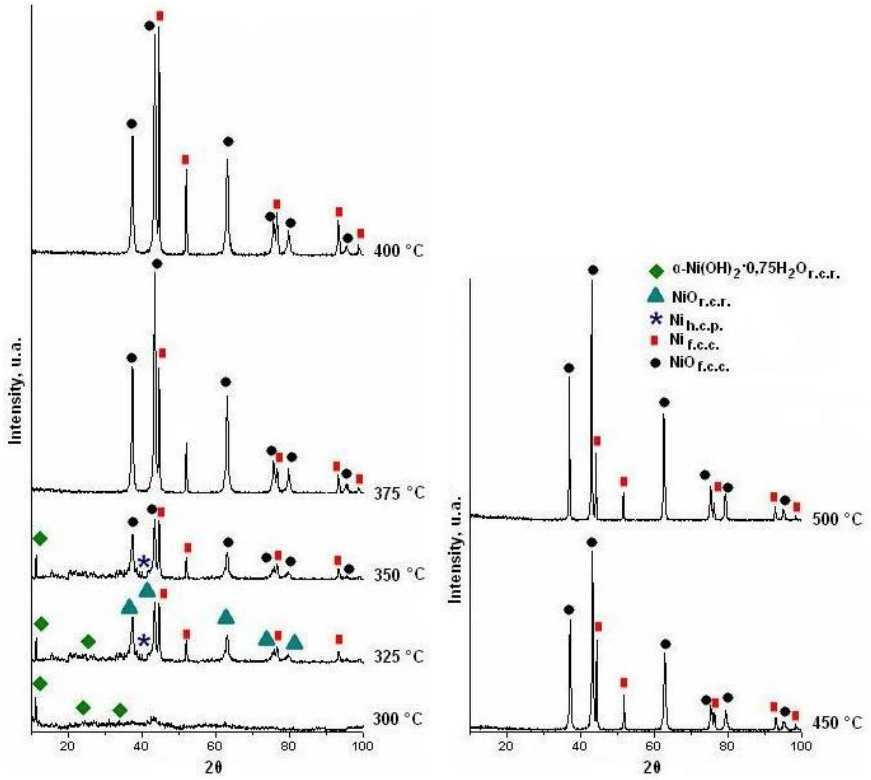


Fig. 2 – XRD patterns of nickel acetate hexaammine decomposition products obtained at different temperatures

Independently on initial complex composition complex decomposition process occurred in three stages: 1) primary forming Ni from nickel ammine-hydroxide complexes, 2) decomposing residual nickel-containing precursors to NiO and 3) after reducing of NiO to Ni by ammonia and organic residuals. Since formation of Ni phase can occur with thermal decomposition of nickel hydroxide ammines only and the thermal decomposition of nickel carbonate and hydroxocarbonate ammines led to forming NiO, ammonia content increasing resulted inrising nickel yield in precursor's decomposition stage and temperature increasing leads to increasing nickel yield on after reducing nickel oxide to metal nickel stage (fig. 2 – 3).

Temperature rising more than 400 °C accelerated reaction of nickel oxidation and led to increasing nickel oxide content in powder.

The first and the second decomposition stages led to forming slit pore structure with mean pore diameters of 3–4 nm in cases of sufficient annealing temperature (350 – 500 °C). Ammonia and organic compounds elimination from pores on the second stage led to decreasing particles size that consisted of nickel and nickel oxide phases particles. But after reduction NiO to Ni by ammonia and organic compounds adsorbed on pore surface resulted in rising mean particles size.

Crystallite size of 5 nm for nickel-containing precursors had remained unchanged with temperature and ammonia content (fig. 4a). Mean crystallite size of nickel depended on temperature only. In the temperature range from 350 to 500 °C the crystallite size of nickel has grown from 50 to 55 nm (fig. 5b, 6b). Mean crystallite size of nickel oxide depended on temperature and ammonia content. In the temperature range from 350 to 500 °C the crystallite size of NiO has grown from 5 to 25 nm (fig. 4b, 5a, 6a). Increasing ammonia content from 3.6 to 14.4 mol/mol Ni led to decreasing NiO crystallite size from 8–10 to 5 nm (fig. 7, 8).

4. CONCLUSIONS

1. Thermal decomposition of nickel ammine complexes occurred with forming hydroxide, carbonate and hydroxocarbonate ammines nickel-containing precursors. Composition of the precursors depended on temperature and ammonia content in initial complex.

2. Decomposition process occurred in three stages: 1) primary forming Ni from nickel ammine-hydroxide complexes, 2) decomposing residual nickel-containing precursors to NiO and 3) after reducing of NiO to Ni by ammonia and organic residuals independently on initial complex composition.

3. Formation of metal nickel phase can occur with thermal decomposition of nickel hydroxide ammine only.

4. Ammonia content increasing led to increasing nickel yield in precursor's decomposition stage and temperature increasing resulted in rising of nickel yield on after reducing NiO to Ni stage.

5. Mean crystallite size of nickel depended on temperature only. In the temperature range from 350 to 500 °C the crystallite size of nickel has grown from 50 to 55 nm.

6. Mean crystallite size of nickel oxide depended on temperature and ammonia content. In the temperature range from 350 to 500 °C the crystallite size of NiO has grown from 5 to 25 nm. Increasing ammonia content from 3.6 to 14.4 mol/mol Ni led to decreasing NiO crystallite size from 8–10 to 5 nm.

7. Particle size of 5 nm for nickel hydroxide ammine remained unchanged with temperature and ammonia content.

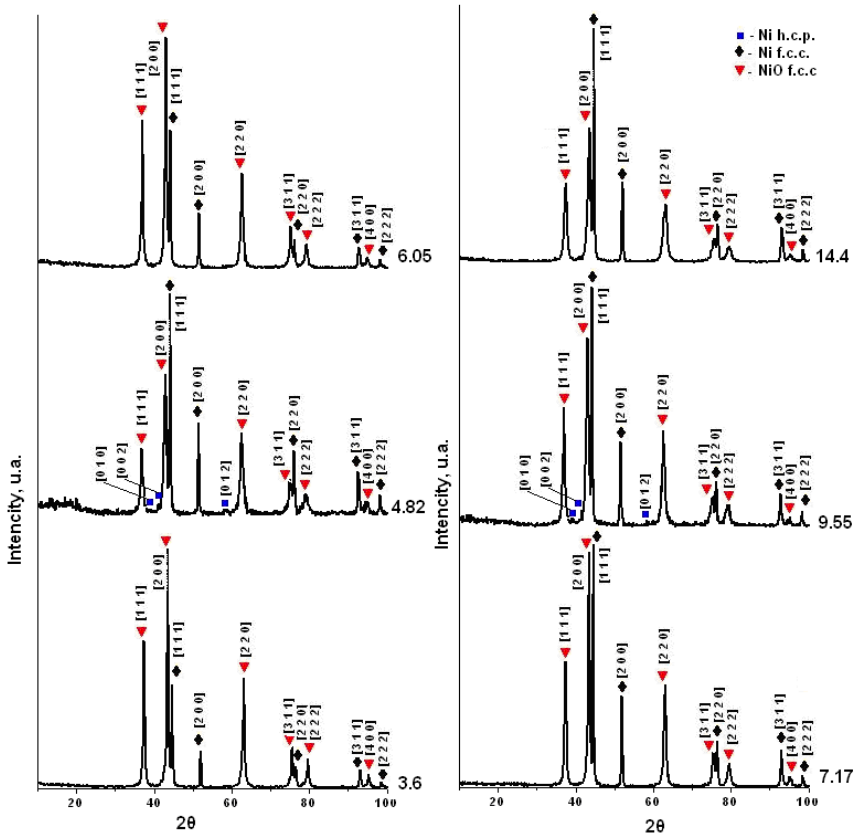


Fig. 3 – XRD patterns of Ni/NiO nanopowder obtained at different ammonia content in initial complex

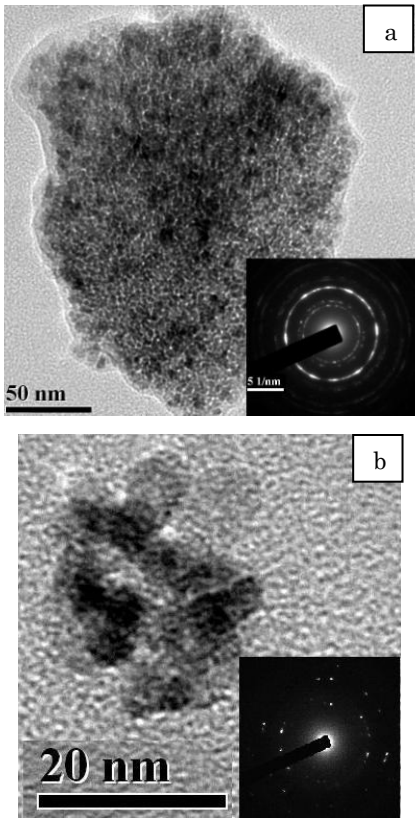


Fig. 4 – TEM micrographs of powder obtained with ammonia content 7.17 mol/mol Ni at 350 °C: a - nickel hydroxide amine precursor; b – NiO

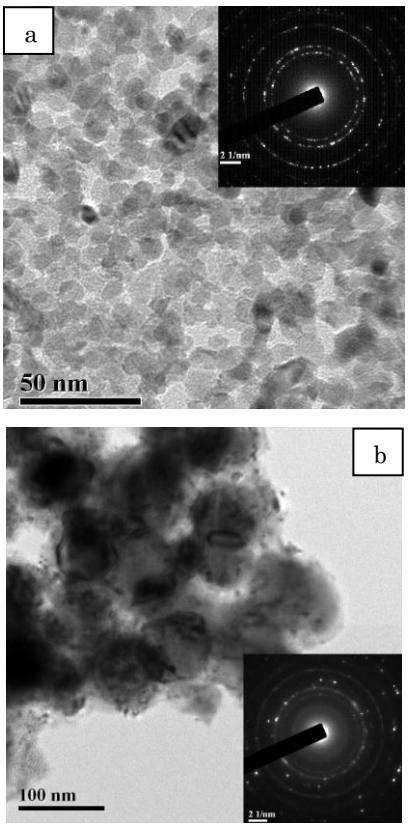
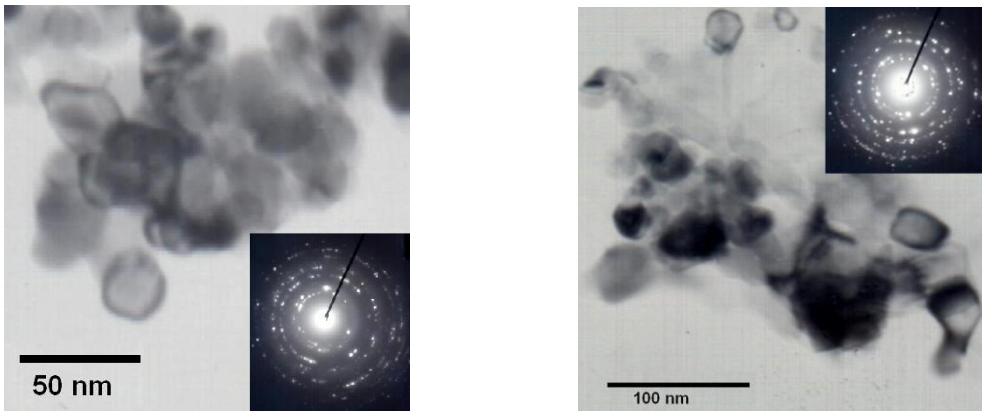


Fig. 5 – HR TEM micrographs of powder obtained from complex with ammonia content 7.17 mol/mol Ni at 400 °C: a - NiO; b – Ni



a b

Fig. 6 – TEM micrographs of powder obtained with ammonia content 7.17 mol/mol Ni at 500 °C: a - NiO; b – Ni

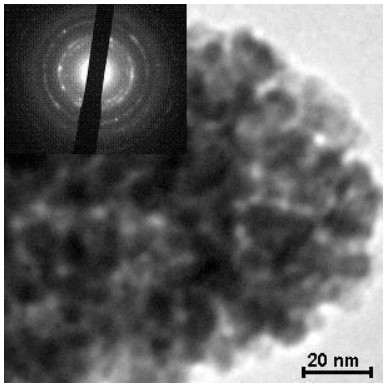


Fig. 7 – NiO particles TEM micrographs of powder obtained with ammonia content 3.6 mol/mol Ni at 400 °C

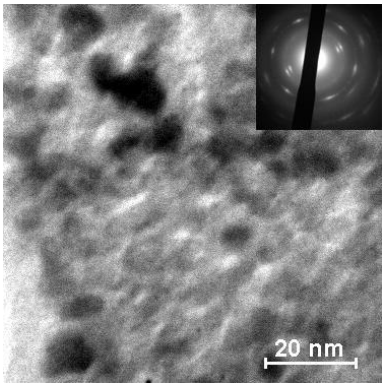


Fig. 8 – NiO particles TEM micrographs of powder obtained with ammonia content 14.4 mol/mol Ni at 400 °C

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