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Features of Ni / NiO Nanopowder Synthesis by Thermal Decomposition of Nickel Acetate Amines: Effect of Annealing Temperature and Duration and Ammonia Content on Powder Composition and Particle Size

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Ni/NiO nanopowders with different metal and oxide phase ratio have been prepared by using thermal decomposition of nickel acetate ammine complexes which contain various ammonia concentrations at the temperature range 300-500 °C in air. Obtained powders have been characterized by IR-spectroscopy, XRD and TG, DTA, DTG, TEM, laser granulometry, adsorption-structural method and layer-by-layer Auger analysis. Thermal decomposition of nickel ammine complexes occurred with formation of crystalline hydroxide containing and amorphous carbonate containing precursors. Changing of precursors composition with different NH_3 content and annealing duration and temperature leads to different pore structure, agglomerate size of powders and determinates free and fixed carbon concentrations. 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, Auger analysis, Slit pore structure, Free and fixed carbon concentrations.

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1. INTRODUCTION

Nickel powders are widely used as electrode materials in multilayered ceramic capacitors. Tendency of ceramic and electrode layers thinning to 100-200 nm that is used for increasing of capacitor dielectric capacity leads to necessity of powders size decreasing to 10-20 nm. In addition powders those are used for capacitor electrode production should contain minimal impurity concentration because of high demands for electrical properties of capacitor. For example Na, K presence decreases powder electroconductivity and breakdown voltage of capacitor. Sulfur concentration in powder over 20 ppm leads to sizeable viscosity rising of electrode pastes for screen printing that complicates process of capacitors manufacturing. Carbon impairs powder conductivity and leads to increasing of Schottky barrier because of eutectic melting of electrode layers under sintering temperature as result of Ba/Ti/Ni alloys formation.

Complete or partial exchanging of Ni powder in green electrode layer on NiO can result in thinning of electrode during annealing in reductive atmosphere due to powder volume decreasing. In addition this exchanging can decrease $BaTiO_3$ concentration in electrode which is added with aim of balancing of sintering speeds of electrode and dielectric layers in the one hand and reduces the dielectric capacity of multilayered ceramic capacitor in the other hand.

Thus, development of technology of Ni/NiO nanopowders obtaining with particle size of 20 nm and less and minimal impurities content is of great importance.

2. MATERIALS AND METODS

Ni/NiO nanopowders with different metal and oxide phase ratio have been prepared by using thermal decomposition of nickel acetate ammine complexes which contain various ammonia concentrations at the temperature range 300-500 °C in air.

Chemical, phase composition and decomposition completeness of the products have been identified by IR-spectroscopy, XRD, chemical analysis and TG, DTA and DTG, respectively. Mean crystallite and particle size have been identified by TEM, SEM and laser granulometry. Pore size distribution of obtained powders has been measured by the adsorption-structural method. Elements distribution according to particle depth has been identified by layer-by-layer Auger analysis.

3. RESULTS AND DISCATION

3.1 Annealing Temperature Effect on Powder Composition and Particle Size

In accordance with TG (Fig. 1) and chemical (Fig. 2) analyses degree of initial complex decomposition depended on annealing temperature. Almost complete decomposition of nickel acetate hexaammine was observed at temperature range 375-500 °C. At lesser temperatures duration of annealing was insufficient for

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full decomposition and powders consisted sizeable concentration of nickel ammonia, aqua, hydroxide and carbonate complexes. Start of nickel and nickel oxide phases formation was observed at 325 °C as consistent with IR-spectroscopy and XRD data. But chemical phase analysis of obtained powders showed that per se NiO phase was formed at temperatures 400-450 °C only (Fig. 3). In our opinion this fact can be explained with presence of some amount of coordinated ammonia in oxide phase because of incomplete complex decomposition at annealing temperature 325-375 °C. At 500 °C process of ammonia removal was inhibited by rapid crystals grow in powder. This assumption was full coordinated with concentrations of free and fixed carbon in powders (Fig. 4). At temperature range 350-400 °C the minimal concentrations of free and fixed carbon were observed and this temperature range was the optimal for obtaining Ni/NiO powders with low carbon content.

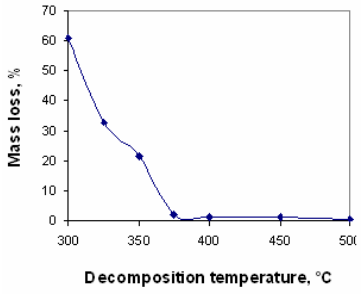

Fig. 1 – Mass loss vs. decomposition temperature for nickel acetate hexaammine decomposition products

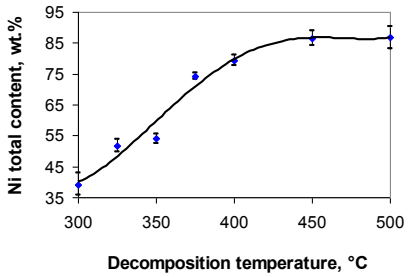

Fig. 2 – Nickel total content vs. decomposition temperature for nickel acetate hexaammine decomposition products

In accordance with analysis of powder microstructure the products with maximal area and volume of meso pores were observed at range 350-400 °C. Formation of slit pore structure with mean pore size 3-4 nm led to the most complete complex decomposition and carbon removal from powder at this temperature range.

In accordance with SEM microphotographs of powders obtained at 325-500 °C were characterized with presence of agglomerates with wide particle size from 50 to 700-800 nm for all powder. But in whole increasing of annealing temperature resulted in agglomerates size rising. For powder obtained at 300 °C formation of nanocrystallites was not observed due to insufficient annealing temperature. TEM microphotographs of powders showed that agglomerates mainly consisted crystallites of Ni and NiO phases. For powders obtained at 350 and 400 °C some amount of $Ni(OH)_2$ was observed which likely corresponded with ammonia-hydroxide precursors. Worth special mention that formation of crystalline phases of carbonate-containing precursors was not observed for XRD analysis and electron-diffraction patterns of TEM. This can be explained with formation of crystalline hydroxide containing and amorphous carbonate containing precursors during thermal decomposition of nickel acetate ammines. Layer-by-layer Auger analysis of elements distribution according to agglomerate depth showed that the outer surface of agglomerate consist of carbon layer with depth 1-2 nm and NiO crystallites monolayer with depth 4-8 nm. The main body of agglomerate consisted of uniformly distributed crystallites of nickel and nickel oxide.

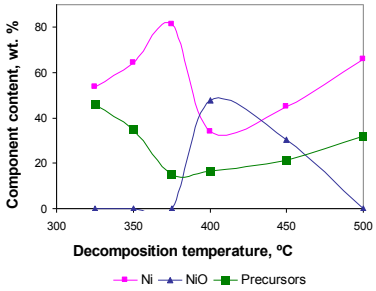

Fig. 3 – Chemical phase analysis vs. decomposition temperature for nickel acetate hexaammine decomposition products

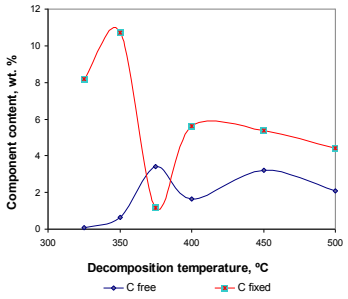

Fig. 4 – Carbon content analysis vs. decomposition temperature for nickel acetate hexaammine decomposition products

Mean crystallite size of nickel and nickel oxide depended on temperature. In the temperature range from 350 to 500 °C the crystallite size of nickel had grown from 40-60 to 40-70 nm and nickel oxide from 5 to 20 – 25 nm. Particle size of 5 nm for nickel hydroxide ammine remained unchanged with temperature.

In accordance with results of experiments temperatures 350 and 400 °C were considered the more promising for investigation of the process of thermal decomposition of nickel acetate ammines with aim Ni/NiO nanopowders obtaining.

3.2 Annealing Duration Effect on Powder Composition and Particle Size

In accordance with TG (Fig. 5) and chemical (Fig. 6) analyses almost complete decomposition of nickel acetate hexaammine was observed at 30 min of annealing at 400 °C and 60 min at 350 °C. Chemical phase analysis of obtained powders (Fig. 7) showed that at annealing duration less than 30 min and over than 45 min at

400 °C per se NiO phase was not formed. In our opinion this fact was generated because of incomplete complex decomposition at lesser annealing duration and formation of secondary precursor phases which consisted of NiO with coordinated ammonia after 60-80 min of decomposition. But at annealing temperature 350 °C increasing of decomposition duration led to full precursor decomposition with forming Ni and NiO phases and secondary precursors formation was not observed. Exchanging of nickel phase content in powders with increasing of decomposition time showed that decomposition process occurred in three stages: 1) Ni primary forming metal from precursors, 2) decomposing of residual nickel-containing precursors to NiO and 3) after reducing of NiO to Ni by ammonia and organic residuals.

Exchanging of concentrations of free and fixed carbon (Fig. 8) in powders depended on annealing temperature. At 400 °C increasing of annealing duration led to decreasing free and fixed carbon content in powders. But at 350 °C increase of decomposition time over 60 min resulted in some rising of free carbon concentration. The minimal free and fixed carbon concentrations were observed for powder obtained by decomposition during 60 min at 350 °C.

Analysis of powders microstructure showed that at annealing temperature 400 °C increasing of annealing duration led to pores size growth which corresponded with powder agglomerates size growth. According to SEM, TEM and laser granulometry at annealing duration 20-25 min decreasing of agglomerates size was observed. Phase chemical analysis and IR-spectroscopy showed that this time range of annealing was corresponded to first and second decomposition stages. Annealing duration increasing led to pore and agglomerates size growth because of third decomposition stage start. However at annealing temperature 350 °C increasing of annealing duration led to area and volume rising of pore with size 3-4 nm. This process was accompanied with decreasing of powders agglomerates size. This fact showed that agglomerates size growth at third decomposition stage can be observed at sufficient annealing temperature only. Temperature 350 °C was an optimal one for obtaining Ni/NiO nanopowders with minimal agglomerate size.

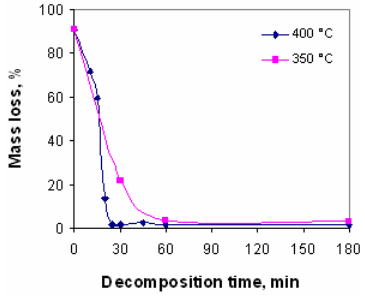

Fig. 5 – Mass loss vs. decomposition duration for nickel acetate hexaammine decomposition products

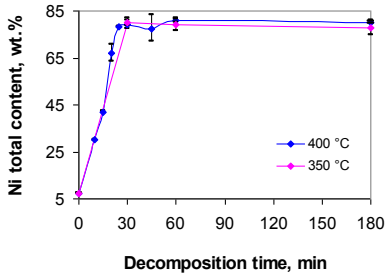

Fig. 6 – Nickel total content vs. decomposition duration for nickel acetate hexaammine decomposition products

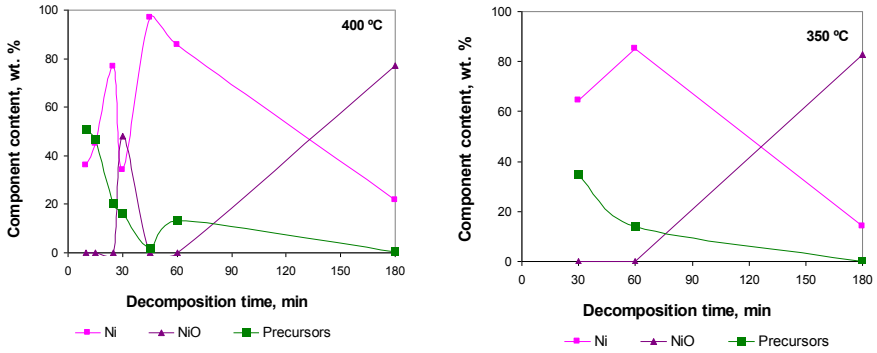

Fig. 7 – Chemical phase analysis vs. decomposition temperature for nickel acetate hexaammine decomposition products

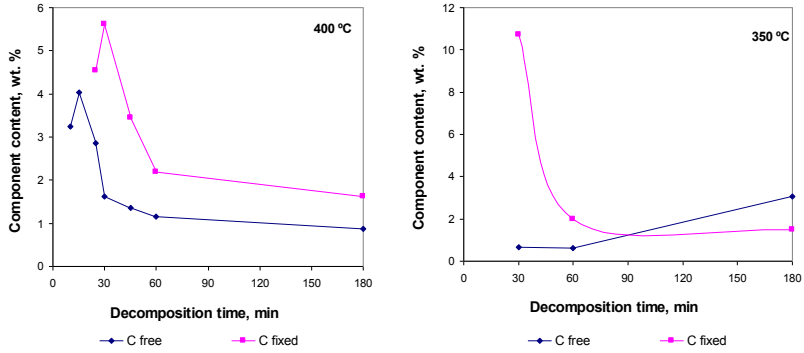

Fig. 8 – Carbon content analysis vs. decomposition temperature for nickel acetate hexaammine decomposition products

In accordance with results of experiments annealing times 60 and 30 min at 350 and 400 °C correspondently were considered the more promising for investigation of ammonia content effect on the process of thermal decomposition of nickel acetate ammines.

3.3 Ammonia Content Effect on Powder Composition and Particle Size

TG and chemical analyses (Fig. 9) of powders obtained at 30 min of annealing at 400 °C and 60 min at 350 °C from nickel acetate ammines with different ammonia content in initial complex showed that powder decomposition degree depended on ammonia concentration for annealing at 400 °C only. Almost complete decomposition of nickel acetate complexes was observed for complex ammonia content 6.5-9 mol/mol Ni^{2+} at 30 min of annealing at 400 °C and 6.5-8 mol/mol Ni^{2+} at 60 min and 350 °C.

Analysis of powders microstructure showed that NH_3 content changing in initial complex effected on pore size distribution. Decomposition process of complexes resulted in pore formation with mean size 3.3 and 3.7 nm. Rising of NH_3 concentration in initial complex resulted in decreasing pore volume with size 3.3 nm and increasing with 3.7 nm. This fact showed that decomposition of ammonia-hydroxide and ammonia-carbonate precursors occurred with formation of different pore size 3.7 and 3.3 nm correspondently.

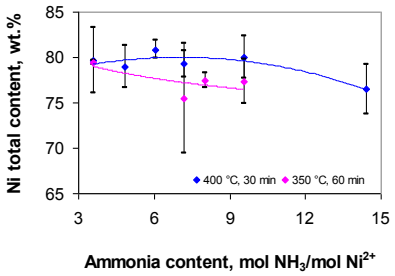

Fig. 9 – Nickel total content vs. ammonia content in initial complex for nickel acetate ammines decomposition products

SEM, TEM and laser granulometry analyses showed that rising of NH_3 concentration in initial complex led to decreasing agglomerate sizes in powders. Mean crystallite size of nickel crystallites was unchanged with ammonia content. However increasing ammonia concentration from 3.6 to 14.4 mol/mol Ni^{2+} resulted in decreasing NiO crystallite size from 8-10 to 5 nm at 30 min annealing at 400 °C.

In accordance with results of experiments ammonia concentration in initial complex of 6.5-9 and 6.5-8 mol/mol Ni^{2+} were considered the more optimal ones for Ni/NiO nanopowders obtaining by thermal decomposition of nickel acetate ammines at annealing times 60 and 30 min at 350 and 400 °C correspondently.

4. CONCLUSIONS

1. Thermal decomposition of nickel ammine complexes occurred with formation of crystalline hydroxide-containing and amorphous carbonate-containing precursors. Decomposition of ammonia-hydroxide and ammonia-carbonate precursors occurred with formation of different pore size 3.7 and 3.3 nm correspondently.

2. Decomposition process occurred in three stages: 1) Ni primary forming from nickel ammine-hydroxide complexes, 2) decomposing of residual nickel-containing precursors to NiO and 3) after reducing of NiO to Ni by ammonia and organic residuals. These stages were accompanied with exchanging of powders pore structure and agglomerate sizes.

3. The most optimal condition for Ni/NiO nanopowders obtaining by thermal decomposition of nickel acetate ammines were considered ammonia concentration in initial complex of 6.5-9 and 6.5-8 mol/mol Ni^{2+} at annealing times 60 and 30 min at 350 and 400 °C correspondently.

4. The minimal free and fixed carbon concentrations were observed for powder obtained by decomposition during 60 min at 350 °C.

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 of ammonia content from 3.6 to 14.4 mol/mol Ni led to decreasing NiO crystallite size from 8-10 to 5 nm.

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