

Relationships between Pore Structure, Free Carbon Content, Particle Size Distribution and Deposition Stage of Ni/NiO Nanopowers

I.O. Dulina*, T.F. Lobunets, A.V. Ragulya

Frantsevich Institute for Problems of Materials Science of NASU, 3, Krzhyzhanovsky St., Kyiv 03142, Ukraine

(Received 12 June 2015; published online 27 August 2015)

Ni/NiO nanopowders have been prepared by using thermal decomposition of aqua solutions of nickel acetate ammine complexes in air at the annealing temperature range 300 – 500 °C, time of decomposition from 30 to 180 min. Particle size of powders has been investigated by scanning electron microscopy (SEM). Powders pore structure has been determined by low temperature nitrogen adsorption method.

Content of free carbon in powders is determined by stage of decomposition and annealing temperature. Decomposition of hydroxy-containing precursor occurred in 3 stages: 1) the primary formation of Ni; 2) decomposition of precursors with formation of NiO; 3) afterreduction of NiO to Ni by residuals of organic compounds and ammonia. The first two stages are characterized by highly endothermic effect that can lead to decreasing of acetic acid evaporation rate and resulted in high free carbon content of powders. Increasing of deposition time permits to remove of acetic acid from particle surface and decrease free carbon content in powder.

Keywords: Nickel ammine complexes, nanopowders, slit pore structure, free carbon content.

PACS numbers: 81.07.Bc, 81.16.Be

1. INTRODUCTION

Ni 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. At the same time these powders are used as electrode materials should fulfil requirements for morphology, particle size distribution, ability to dispersing in organic solvents and impurity composition. Every of this characteristics effects on properties of conductive paste for screen printing, electrode layers obtained from it and multilayered ceramic capacitor as a whole.

Size of solid particles, particle size distribution and powder ability to dispersing in organic solvents determines viscosity, rheological properties [1, 2] and sedimentation stability of paste in the first place. In the second place, they effect on continuity [3, 4] and roughness [2] of electrode.

Impurity composition effects on paste viscosity and electrical properties of multilayered ceramic capacitor. For example Na, K presence decreases powder electroconductivity and breakdown voltage of capacitor [5, 6]. Sulfur concentration in powder over 200 ppm leads to sizeable viscosity rising of electrode pastes for screen printing that complicates process of capacitors manufacturing [7, 8]. 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 [9].

Besides, complete or partial exchanging of Ni powder in green electrode layer on NiO can result in electrode thinning during annealing in reductive atmosphere due to powder volume decreasing [10]. In addition this exchanging can decrease BaTiO₃ concentration in electrode which is added with aim of balancing

of sintering speeds of electrode and dielectric layers [11, 12] 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 has a great importance.

In our previous papers [13-19] the method of obtaining of Ni/NiO nanopowder by thermal decomposition of nickel acetate amines in air was proposed. It was determined that this technique permits to obtain Ni/NiO nanopowders with monomodal particle size distribution. But powders free carbon content depends not only from acetate content in initial complex and temperature of decomposition. Specific surface area and pore size distribution have a significant effect free carbon content.

Thus paper is aimed to investigation of relationships between pore structure, free carbon content, particle size distribution and deposition stage of Ni/NiO nanopowders obtained by thermal decomposition of nickel acetate amines.

2. MATERIALS AND METHODS

Ni/NiO nanopowders have been prepared by using thermal decomposition of aqua solution of nickel acetate ammine complexes in air. Complexes have been obtained by adding of nickel (II) acetate tetrahydrate in ammonia aqua solution. Ammonia content in initial complex was 3.6 – 9.55 mol/mol Ni²⁺. Obtained complexes in porcelain crucible have been put in muffle furnace heated to 300 – 500 °C and annealed in air atmosphere during 30 – 180 min.

Concentration of free carbon has been identified as mass of insoluble residuals after dissolving of powders in HNO₃ and boiling during 2 hours. Particle size of powders has been investigated by TEM and SEM.

* i_risha@online.ua

Powders pore structure has been determined by low temperature nitrogen adsorption method. The particle size distributions have been obtained from measurement of 300 – 500 particles in SEM micrographs. Deviation in particle diameter measurements was 5 nm.

3. RESULTS AND DISCUSSIONS

In our previous papers [13-19] effect of annealing temperature and duration on chemical, phase composition and particle size for Ni/NiO nanopowders obtained by thermal decomposition of aqua solutions of nickel acetate amines have been investigated. It was determined that thermal decomposition of nickel acetate ammonia complexes occurred with primary formation of hydroxy-containing precursors which approximate composition is $Ni_x(OH)_yO_z(NH_{3-n})_p$. Presence of ammonia and its derivatives in precursors molecule results in possibility of formation Ni and NiO phases during decomposition process. Precursors decomposition with formation of crystalline Ni and NiO accompanied with formation of products with slit pore structure with mean pore size 3 – 4 nm. The maximal values of area and volume of pores with this diameter have been observed at temperature range 350 – 400 °C. This fact permits to determinate temperature range 350 – 400 °C as optimal for obtaining Ni/NiO nanopowders. At temperature 400 °C the maximal rate and velocity of decomposition and metal nickel content have been observed [13-15, 19]. But powders contained the maximal concentration of free carbon [19]. At temperature 350 °C [19] powders contained minimal free carbon concentration and had minimal particle size. At the same time samples demanded prolonged time of annealing for full decomposition and contained primary oxide phase. However, data obtained by thermogravimetry analysis showed that passing of different decomposition stages of accompanied with holding of nearly constant content of acetic acid in porous space [14]. Acetic acid evaporation may occur at the final stages of decomposition only. Rate and velocity of evaporation depended on morphology of decomposition products. At the same time the low organic carbon content in powders [19] showed that nonevaporated acetic acid converted in free carbon. Because of that the aim of this paper is investigation of effect of changings in powders structure on free carbon content depended on annealing duration at temperatures 350 and 400 °C.

Chemical analysis of powder composition showed that at temperature 350 °C (fig. 1) nearly full decomposition of prime precursors occurred at annealing duration 180 min and accompanied with formation primary nickel oxide. At 400 °C (fig. 2) nearly full decomposition of precursors was observed at 30 min. But fig. 2 shows that increasing of annealing duration led to formation of secondary precursors which are formed by gaseous adsorption on nanoparticles surface. Nickel and nickel oxide content had the difficult behaviour of dependence from annealing duration. Decomposition of hydroxy-containing precursor at 400 °C occurred in 3 stages: 1) the primary formation of Ni (10 – 25 min); 2) decomposition of precursors with formation of NiO (20 – 25 min); 3) afterreduction of NiO to Ni by residuals of or-

ganic compounds and ammonia (25 -60 min). The first two stages and was observed for every investigated temperature and resulted in formation of slit pore structure with mean pore diameter 3 - 4 nm (fig. 3). Because of is highly endothermic effect of these stages considerable decreasing of sample temperature is occurred. This fact can lead to decreasing of acetic acid evaporation rate and resulted in high free carbon content of powders obtained at 400 °C and annealing duration 25 – 30 min (fig.4). Increasing of deposition time permits to remove of acetic acid from particle surface and decrease free carbon content in powder.

At the same time, this tendency was not observed for powders obtained at 350 °C. This permits to suppose that at 350 °C evaporation of acetic acid isn't complicated by porous structure of sample. According to data of pore size distribution (fig. 3), specific surface area and (fig. 5) and particle size distribution (fig. 6 – 7), powders obtained at 400°C had a bigger size of nanoparticle agglomerates, smaller specific surface area than powders obtained at 350 °C. This fact allows make a decision that the main origin of complication of acetic acid evaporation from samples at 400 °C is too high

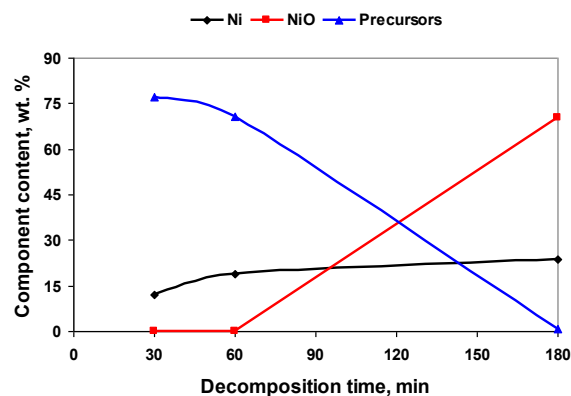


Fig. 1 – Ni, NiO and precursors content dependence from annealing duration for nickel acetate hexaammine decomposition products obtained at 350 °C

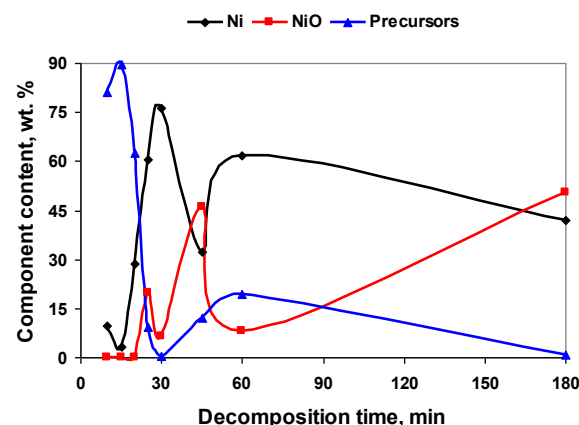


Fig. 2 – Ni, NiO and precursors content dependence from annealing duration for nickel acetate hexaammine decomposition products obtained at 400 °C

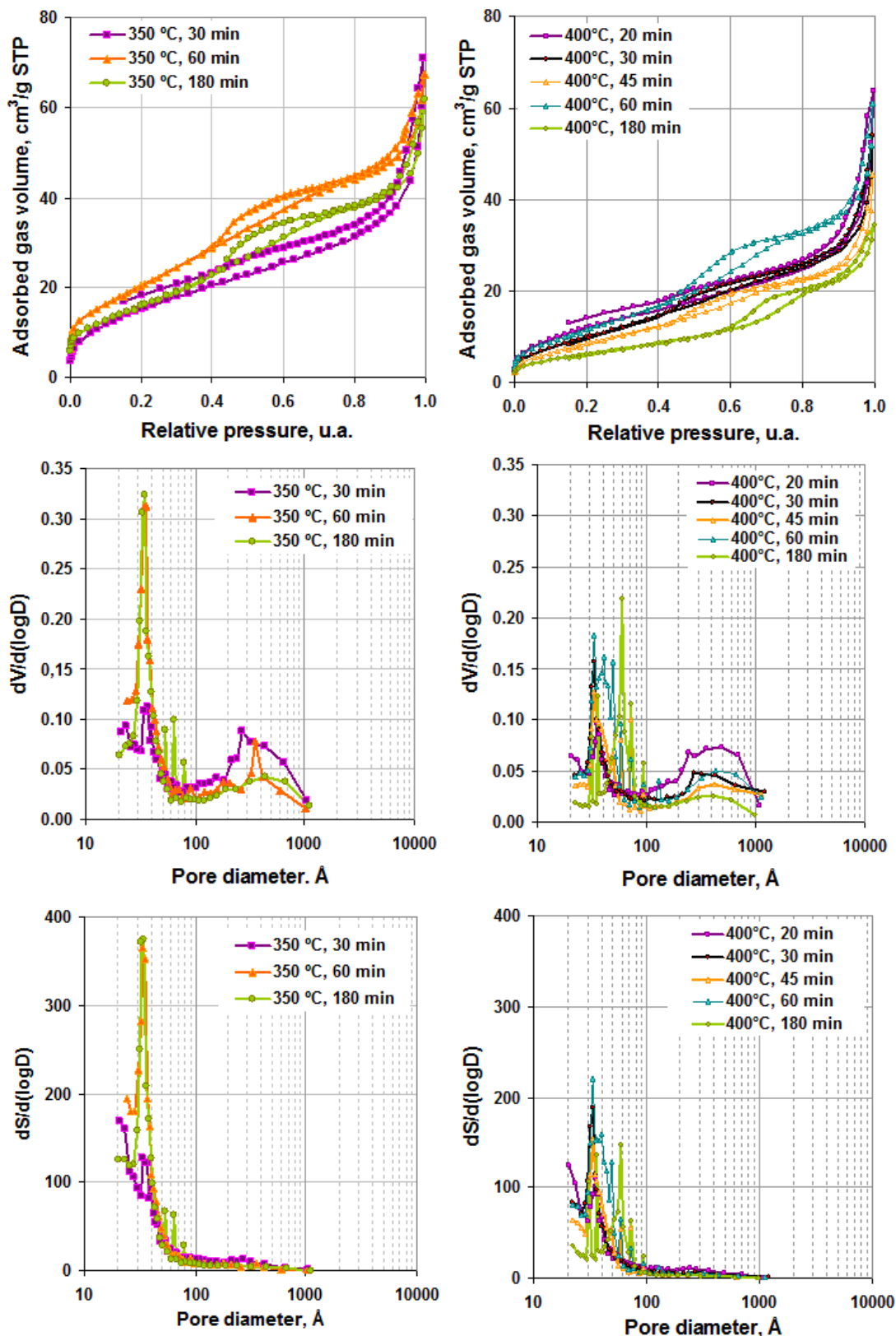


Fig. 3 – Adsorption isotherms, differential volume and area pore distributions of powders obtained at 350 °C, 400 °C with different decomposition duration

velocity of solid structure formation. At lowest velocity of solid structure formation the major value of acetic acid evaporated with water and some amount of ammonia. Nonevaporated part of acetic acid is placed on

surface and pore space of precursors and can evaporate at the last stages of decomposition only.

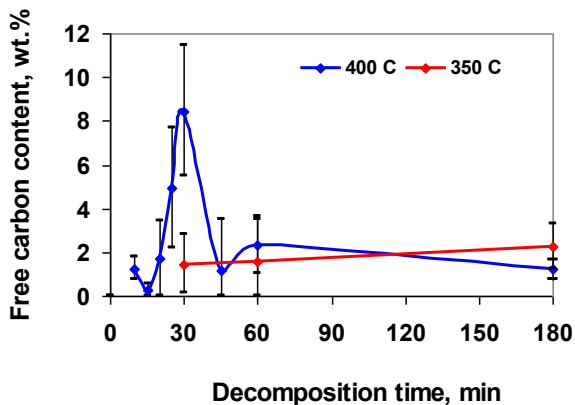


Fig. 4 – Free carbon content dependence from annealing duration for nickel acetate hexaammine decomposition products obtained at 350 and 400 °C

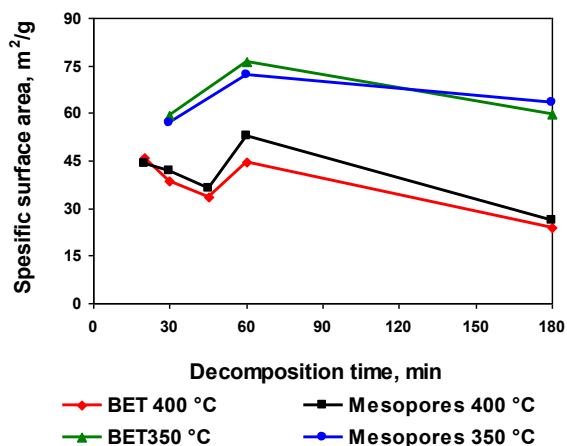


Fig. 5 – Specific surface area dependence from annealing duration for nickel acetate hexaammine decomposition products obtained at 350 and 400 °C

4. CONCLUSIONS

Decomposition of hydroxy-containing precursor at occurred in 3 stages: 1) the primary formation of Ni; 2) decomposition of precursors with formation of NiO; 3) afterreduction of NiO to Ni by residuals of organic compounds and ammonia. The first two stages is characterized by highly endothermic effect that can lead to decreasing of acetic acid evaporation rate and resulted in high free carbon content of powders. Increasing of deposition time permits to remove of acetic acid from particle surface and decrease free carbon content in powder.

The main origin of complication of acetic acid evaporation from samples is too high velocity of solid structure formation. At lowest velocity of solid structure formation the major value of acetic acid evaporated with water and some amount of ammonia.

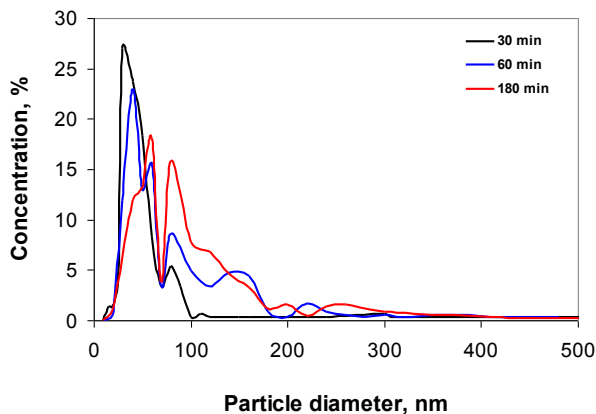


Fig. 6 – Particle size distribution dependence from annealing duration for nickel acetate hexaammine decomposition products obtained at 350 °C

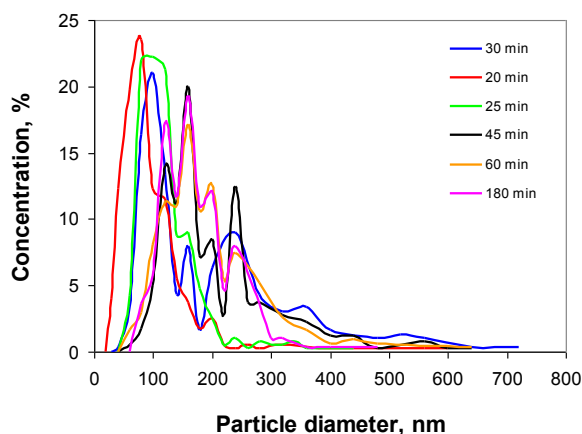


Fig. 7 – Particle size distribution dependence from annealing duration for nickel acetate hexaammine decomposition products obtained at 400 °C

Nonevaporated part of acetic acid is placed on surface and pore space of precursors and can evaporate at the last stages of decomposition only.

AKNOWLEDGEMENTS

Authors are grateful to V. Tkach from Bakul Institute for Superhard Materials of NASU, N. Danylenko from Frantsevich Institute for Problems of Materials Science of NASU and Yu. Romanenko from National Technical University of Ukraine “Kyiv Polytechnical Institute” for microscopic investigations.

REFERENCES

1. T.-N. Tsai, *Comp. Ind. Eng.* **374**, 54 (2008).
2. D.-H. Im, *Mater. Chem. Phys.* **228**, 96 (2006).
3. Pat. 2010/0208410 A1 US, Int. CI. H01G 4/008 (2006.01), C22C 19/03 (2006.01), B22F 9/16 (2006.01), H01B 1/02 (2006.01). *Nickel powder or alloy powder, having nickel as main component, method for manufacturing the powder, conductive paste and laminated ceramic capacitor* / I. Okada (JP), K. Koyama (JP).
4. Pat. 2011/0141654 A1 US, Int. CI. H01G 4/30 (2006.01), B22F 1/00 (2006.01), B01B 1/22 (2006.01), C22C 19/03 (2006.01). *Nickel powder or alloy powder, comprising nickel as main component, method for producing the same, conductive paste and laminated ceramic capacitor* / I. Okada (JP); assignee Sumitomo electric industries, Ltd. (JP).
5. Pat. 7,238,221 B2 US, Int. CI. B22F 9/24 (2006.01). *Metallic nickel powders, method for preparing the same, conductive paste, and MLCC*/S.-H. Kim, J.-Y. (KR); Samsung Electronics Co., Ltd (KR).
6. Pat. 2008/0043402 A1 US, Int. CI. H01G 4/008 (2006.01), C22C (2006.01), H01B 1/02 (2006.01). *Metallic nickel powders, method for preparing the same, conductive paste, and MLCC*/S.-H. Kim, J.-Y. Choi, D.-K. Kim, J.-H. Park (KR); Samsung Electronics Co., Ltd (KR).
7. Pat. 2009/0032780 A1 US, Int. CI. H01B 1/02 (2006.01). *Nickel paste* / T. Sugiyama (JP); assignee Noritake Co., Limited (JP).
8. Pat. 2010/0038604 A1 US, Int. CI. H01B 1/22 (2006.01). *Nickel paste* / T. Sugiyama (JP); assignee Noritake Co., Limited (JP).
9. M.M. Samantaray, K. Kaneda, W. Qu E.C. Dickey, C.A. Randall, *J. Am. Ceram. Soc.* **992**, 95, 3 (2012).
10. Pat. 2006/0171099 A1 USA, Int. CI. H01G 4/06 (2006.01). *Electrode paste for thin nickel electrodes in multilayer ceramic capacitors and finished capacitor containing the same* / D.E. Barber, I. Burn, J.J. Beeson, A. Tajuddin (US).
11. Pat. 6,366,444 B1 US, Int. CI. H01G 4/06. *Multilayer ceramic electronic part and conductive paste* / J. Yagi (JP); assignee Taiyo Yuden Co., Ltd. (JP).
12. Pat. 2009/0081372 A1 US, Int. CI. B05D 3/02 (2006.01), H01B 1/22 (2006.01). *Conductor paste for rapid firing* / K.-I. Sugimura, K. Hirao (JP); assignee Noritake Co., Ltd. (JP).
13. I. Dulina, O. Klochkov, M. Danilenko, A. Ragulya, *Nanostructural Material Science* **3**, 1 (2012) [in Ukrainian].
14. I. Dulina, T. Lobunets, O. Klochkov, A. Ragulya, *Nanostructural Material Science* **9**, 2, (2012) [in Ukrainian].
15. I. Dulina, T. Lobunets, O. Klochkov, Yu. Romanenko, A. Ragulya, *Nanostructural Material Science* **3**, 4 (2012) [in Ukrainian].
16. I.O. Dulina, O. Klochkov, M. Danilenko, A.V. Ragulya, *Proc. NAP 1* No1, 01PCN11 (2012).
17. I.O. Dulina, T.F. Lobunets, O. Klochkov, A.V. Ragulya, *Proc. NAP 2* No2, 01NTF35 (2013).
18. I.O. Dulina, T.F. Lobunets, L.O. Klochkov, A.V. Ragulya, *Proc. NAP 3* No2, 02NNPT02 (2014).
19. I.O. Dulina, T.F. Lobunets, O. Klochkov, A.V. Ragulya, *Nanoscale. Res. Lett.* **156**, 10 (2015).