PREPARATION OF COBALT AND NICKEL NANO-POWDERS BY THE THERMAL DECOMPOSITION OF HYDRAZIDOCARBONATES†

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Abstract

The preparation of nanosize cobalt and nickel metal powders and powders of solid solutions of cobalt and nickel from the thermal decomposition of $N_2H_5[M^{(n)}(N_2H_3COO)_{n+1}]\cdot H_2O$ and the intermediate $M^{(n)}(N_2H_3COO)_n\cdot N_2H_4$ obtained during this decomposition is described and discussed here. In an inert or reducing atmosphere these compounds decompose to metal particles of 50 to 70 nm in size. These particles are, in turn, composed of even smaller particles 5 to 7 nm in size. The advantages, disadvantages and possible ways of implementing this method for the preparation of nanosize products are discussed.

Introduction

The rapidly developing field of nanomaterials and nanocomposites has intensified research into methods for their preparation and even small-scale production. One of the possible methods for the preparation of new materials of nanoscale size is the thermal decomposition of suitable precursors. The starting compounds or precursors are chosen on the basis of the composition of the desired products. For the metal powder preparation, cobalt and nickel hydrazidocarbonates have been chosen. These compounds are derived from hydrazidocarbonic acid[1] by a reaction between its aqueous solution and a solution of a metal chloride hydrate. There are more than 66 different known hydrazidocarbonates up to the present. They differ in general type as well as in their metal cation (Table 1).

Early work on the properties of hydrazidocarbonates showed that some of the transition metal hydrazidocarbonates can be decomposed to a metal powder in an inert atmosphere[2]. This has also been observed for cobalt and nickel hydrazidocarbonates; metal sub micrometer particles can be obtained in this way as well.[3]

Table 1: Different types of hydrazidocarbonates

$M^{(n)}(N_2H_3COO)_n$	n = 1, 2, 3	
$M^{(n)}(N_2H_3COO)_n \cdot mH_2O$	n = 1, 2, 3	m = 0.5, 1, 2, 3
$M^{(n)}(N_2H_3COO)_n \cdot H_2O \cdot N_2H_4$	n = 2	
$M^{(n)}(N_2H_3COO)_n \cdot mN_2H_4$	n = 2	m = 1, 2
$K[M^{(n)}(N_2H_3COO)_{n+1}]$	n = 2	
$N_2H_5[M^{(n)}(N_2H_3COO)_{n+1}] \cdot mH_2O$	n = 2, 3	m = 1, 3

The purpose of this research work was to further develop this method toward nanoscale products and composites and to characterize the obtained products in order to determine possible uses.

Experimental

Hydrazidocarbonates of cobalt and nickel were prepared in a conventional way by dissolving metal chloride hexahydrate ($NiCl_2 \cdot 6H_2O$ p.a. Fluka; $CoCl_2 \cdot 6H_2O$ p.a. Kemika) in water into which a solution of hydrazidocarbonic acid (prepared from 80% N_2H_4, Merck) was added up to a 1:15 molar ratio of metal to hydrazine. Evaporating the solution in a shallow Petri dish caused colored crystals to grow in the solution after a day. The crystals were filtered off, washed with distilled water, and dried under vacuum. The results of the chemical analysis are given in Table 2. Mixed hydrazinium (1+) tris-hydrazido carbonates were prepared from solutions of cobalt and nickel chlorides hexahydrates in a 1:1 molar ratio. A solution of hydrazidocarbonic acid was then added until the molar ratio of 1:15 metal to hydrazine was reached.

Thermoanalytical studies were carried out on Mettler 4000 System and Netzsch STA 409 apparatus. Sample masses of 100 mg in 0.3 ml Al_2O_3 crucibles were used. For the decomposition of larger and unground crystals, sample masses of 230 mg in a 3.4 ml Al_2O_3 crucible were used. Heating rates were 4 K/min, except in the case of the decomposition of larger single crystals when it was lowered to 1 K/min. A dynamic furnace atmosphere made of a mixture of argon and 4 vol. % of hydrogen with a flow rate of 100 ml/min was used for all samples. Thermogravimetric measurements on the Mettler 4000 System were also made both with and without the presence of a magnetic field in order to determine the Curie temperature of the sample.

Products were also characterized by X-ray powder diffraction using CuK_α radiation and a Philips PW-1710 diffractometer. Particle shape and size were determined by electron microscopy on a Jeol T-300 scanning electron microscope and transmission electron microscope Jeol TEM – 2000 FX, with mapping using a JEOL 5800.

Results and discussion

The preparation of the hydrazinium (1+) tris-hydrazido carbonate precursors is rather simple and straightforward. The results of the chemical analyses are given in Table 2. By using a mixed solution of both metal cations, i.e. cobalt and nickel, mixed complexes with the desired ratio of both elements can be prepared.

Table 2: Chemical analysis of hydrazidocarbonates

Sample	$M_{obt.}$ %	$M_{calc.}$ %	$N_2H_{4\ obt.}$ %	$N_2H_{4\ calc.}$ %
$N_2H_5/Co(N_2H_3COO)_3/\cdot H_2O$	17.5	17.59	38.0	38.22
$N_2H_5/Ni(N_2H_3COO)_3/\cdot H_2O$	17.7	17.54	38.4	38.24
$N_2H_5/Ni_{0,5}Co_{0,5}(N_2H_3COO)_3/\cdot H_2O$	17,3	17,57	37,8	38,23

Large crystals several millimeters in size are produced in one day; these are quite stable on exposure to air and even after a month or two do not show signs of decomposition. Their stability decreases markedly when they are ground to a powder and after ten days the smell of ammonia can be detected, indicating the beginning of sample decomposition. The cobalt complex is an intense red color, whereas the nickel compound is blue. The crystals of the mixed complex with a molar ratio of cobalt to nickel of 1:1 are violet.

The ratio of both elements in a 1:1 precursor was determined by chemical analysis and atomic absorption spectrometry and the Curie temperature of the residue by the thermal decomposition in a magnetic field (Table 3).

Table 3: Results of the chemical analysis of $N_2H_5/Ni_{0,5}Co_{0,5}(N_2H_3COO)_3/\cdot H_2O$

Analytical method	Co. w.%*	Ni w. %*	M. w. %**
Atomic absoption spectrometry	53	47	17.3
Curie temperature of the residue (TG)	50,5	49,5	17.5
Element mapping	56	44	

* w. % of element of all metal present in the sample, ** w. % of metal in a compound

The chemistry of decomposition of these two hydrazinium (1+) tris-hydrazido carbonates in an inert atmosphere has already been described[4]. They both first decompose to hydrazido carbonates hydrazines accordingly to reaction:

$$N_2H_5[M\,(N_2H_3COO)_3]\cdot H_2O \rightarrow M(N_2H_3COO)_2.N_2H_4 + N_2H_4 + CO_2 + H_2O \qquad (1)$$

The second step of the thermal decomposition is closely followed by a smaller third step in the case of the cobalt compound, but not the nickel compound or mixed cobalt/nickel complex. In the case of pure cobalt or nickel hydrazinium (1+) tris-hydrazido carbonates, pure metal powders are produced accompanied by the evolution of carbon dioxide and varying ammounts of ammonia, nitrogen and hydrogen. The changeable concentrations of the last three components is the result of the thermal dissociation of ammonia to nitrogen and hydrogen:

$$2M(N_2H_3COO)_2.N_2H_4 \rightarrow 2M + 6NH_3 + 3N_2 + H_2 + 4CO_2 \qquad (2)$$

The mixed $N_2H_5/Ni_{0.5}Co_{0.5}(N_2H_3COO)_3/\cdot H_2O$ complex behaves upon heating like the monometal complexes. Thermoanalytical data are given in Figure 1.

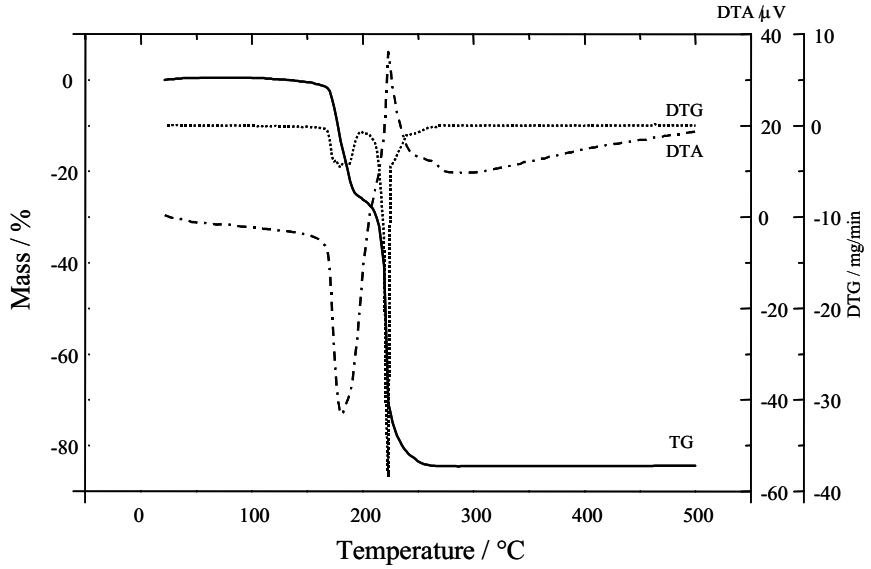

Figure 1. Thermoanalytical data for $N_2H_5/Ni_{0.5}Co_{0.5}(N_2H_3COO)_3/\cdot H_2O$

The decomposition proceeds in two steps with total mass loss of 82.4 %, although in the first step up to 205 °C only 25.5 % of the initial mass is lost. In the second step from 205 °C to 270 °C an additional 56.9 % is lost. DTG minimums are observed at 185.3 °C and 225.5 °C. The first decomposition step is followed by an endothermal peak at 186.2 °C, followed by an exothermal one with a maximum at 227.2 °C.

Similar decomposition in two steps occurs when large crystals are used instead of a powdered sample. The temperatures are shifted a little and the shapes of the curves are also modified. SEM photos show that crystals decompose into layered arrays of rods around 8-12 μm in length and 1-2 μm wide (Fig. 2).

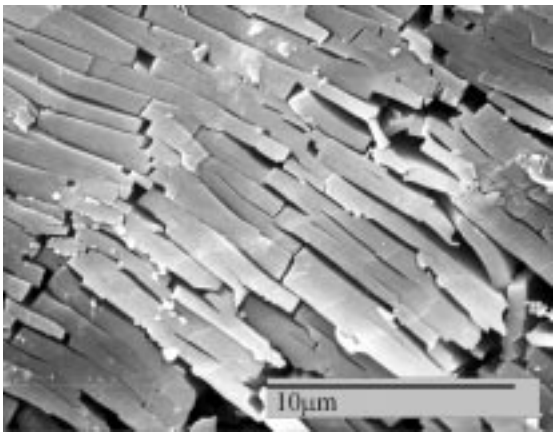

Figure 2. SEM photo of $Ni_{0.5}Co_{0.5}$ (top view)

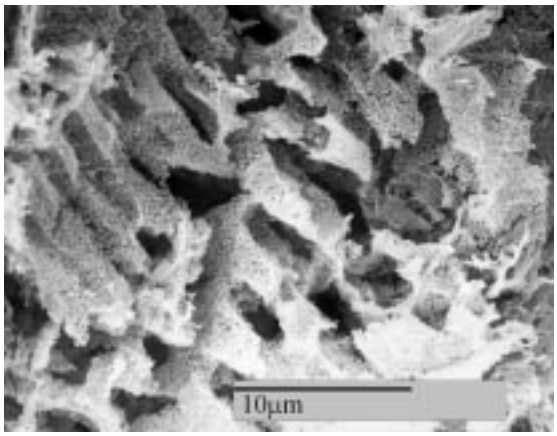

Figure 3. SEM photo of $Ni_{0.5}Co_{0.5}$ (side view)

From the side view, large cavities and channels can be seen through which the evolved gases left the sample (Fig. 3). The obtained products were ground and pressed into tablets using a pressure of 520 MPa. A photo of a thus prepared sample (Fig. 4) reveals that the particles are of a similar size, e.g. 50 – 70 nm. TEM photos show that these particles consist of even finer particles of around 5 - 7 nm in size (Fig. 5). Mapping of these powders shows that solid solutions are obtained since no distinct areas of predominantly one metal could be observed. The obtained Curie temperature of the sample of 845 °C is in good agreement with the value for the equimolar solid solution of cobalt and nickel (847.5 °C)[5].

Evaluation of this method for nano metal powder preparation shows that hydrazinium (1+) tris-hydrazidocarbonates metalates monohydrates of cobalt and nickel decompose in an inert atmosphere to metal powders of high purity if very pure furnace gasses are used. The obtained metal powders have high specific surface areas which makes them very reactive and they exhibit pyrophoric properties upon contact with air. Very pure argon or nitrogen of at least grade 5.0 should be used as furnace atmospheres in combination with oxygen and moisture adsorbents. In this part of our research a gaseous mixture of 96 vol. % of argon and 4 vol. % of hydrogen has been used in order to prevent any subsequent oxidation of the samples and to assure the preparation of oxide free metal powders, although hydrazidocarbonates can also decompose to metal in an inert atmosphere.

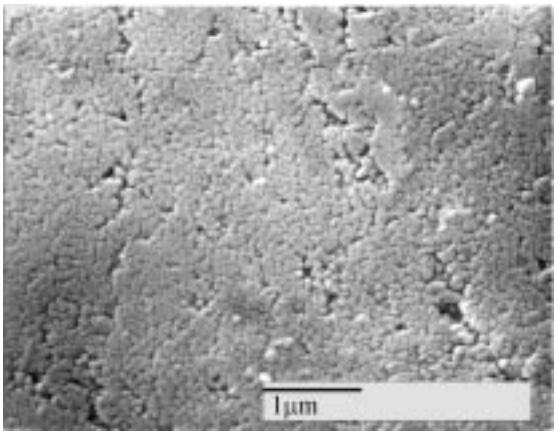

Figure 4. SEM photo of $Ni_{0.5}Co_{0.5}$ (pressed into tablets) - 300 °C

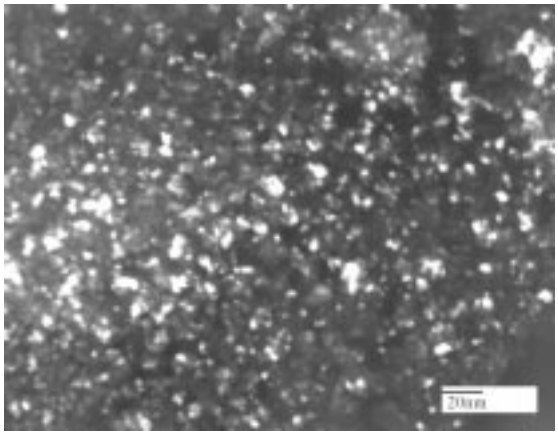

Figure 5. TEM photo of $Ni_{0.5}Co_{0.5}$ - 300 °C

The preparation of the precursors is not problematic if we take into account the physiological properties of hydrazine[6]. The cobalt and nickel complexes decompose to metal powders via an intermediate, $M(N_2H_3COO).N_2H_4$. This intermediate is more stable than the hydrazinium (1+) complex and can be isolated in the case of cobalt compounds, whereas the decomposition of the nickel precursor proceeds over a less pronounced intermediate but shows two distinct DTG peaks. The metal residue depends on the metal cation used for the precursor preparation and exceedes 17 % of the initial mass of the sample. Better metal yields can be obtained if, instead of the hydrazinium (1+) tris-hydrazido carbonate metalate monohydrate, the intermediate compound, $M(N_2H_3COO)_2.N_2H_4$, is used. This can be prepared by an alternative method[4]. In this case more than 24 % of metal residue is obtained.

This method has its advantages as well as disadvantages. One advantage is the straightforward preparation of the precursors. By the use of a precursor of a single cation, pure powders of the corresponding metal can be prepared. If a mixture of two or more cations with similar chemical properties is used solid solutions of the metals are obtained, as was the case with cobalt and nickel. The final temperatures of the decompositions are relatively low depending on the heating rates. By the isothermal decomposition at lower temperatures, e.g. 200 ºC, decomposition proceeds to the metal powder also. The relatively low temperatures of preparation are important in order to prevent sintering of the obtained nano powders. Products obtained at 900 ºC show growth of the particles to particle sizes of 100 -150 nm.

The possible uses of cobalt or nickel complexes with hydrazidocarbonic acid are, for example, the preparation of catalysts and oxygen scavengers. The relatively low metal content of hydrazinium (1+) tris-hydrazidocarbonates metalates monohydrates of around 17 % and 24 % for metal hydrazidocarbonates hydrazines can be also advantageous for special applications. Preparations of mixtures of these precursors with green ceramic materials can, after thermal treatment of the mixture, result in porous materials made of a ceramic matrix in which fine particles of metal are dispersed. Hydrazine decomposes in an inert atmosphere by a homogenous reaction into ammonia and nitrogen according to the reaction scheme (3):

$$3N_2H_4 \rightarrow 4NH_3 + N_2 \quad (3)$$

Ammonia is not stable at higher temperatures and dissociates to its constitutive elements, particularly in the presence of catalysts. In addition to these gasses, carbon dioxide is also released during the decomposition of the hydrazidocarbonate group. The calculation based on the starting composition of precursors shows that, assuming the decomposition reaction proceeds to gaseous products such as nitrogen, ammonia, carbon dioxide and water vapor, 11 moles of gasses are obtained for each mole of precursor. In the case of the other extreme, when all of the ammonia dissociates to its constitutive elements, it is possible for even 16 moles of gasses to be released. For $M(N_2H_3COO)_2.N_2H_4$ these values are 7 and 10 moles of gasses per mole of starting compound. Evolved gases form pores and channels on leaving the sample, as was also observed in the case of the decomposition of pure hydrazinium (1+) tris-hydrazido carbonates.

Conclusions

Hydrazinium (1+) tris-hydrazido carbonates monohydrates of cobalt, nickel, or a mixed complex with both cations decompose to the metal. The final temperatures of the decomposition can be as low as 200 ºC and particles of nano size dimensions from 50 – 70 nm are obtained. TEM reveals that these particles are composed of even smaller particles several nanometers in size. These particles exhibit high reactivity and pyrophoric properties upon contact with air. Large amounts of gasses are evolved during the process, which can be advantageous for the preparation of porous materials.

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References

1. Stolle R.; Hoffman, K.; *Chem. – Ztg*. **1905,** *98*, 1273.
2. Slivnik, J.; Rihar, A.; Sedej, B., *Monatsh. Chem.* **1967**, *98*, 200.
3. Maček, J.; Hrovat, R.; Novosel, B. *J. Thermal Anal.* **1993**, *40*, 335-340.
4. Maček, J.; Rahten, A. *Termochimica Acta* **1989**, *144*, 257-266.
5. Hansen, M., *Constitution of binary alloys*, McGraw-Hill, 2nd Ed., New York, 1958, pp 485-487.
6. Schmidt, E. W, *Hydrazine and its Derivates*, John Wiley, New York, 1984, pp 528-599.

Povzetek

Priprava kobaltovih in nikljevih prahov nano velikosti in prahov trdnih raztopin kobalta in niklja s termičnim razkrojem $N_2H_5[M^{(n)}(N_2H_3COO)_{n+1}]\cdot H_2O$ in intermediata $M^{(n)}(N_2H_3COO)_n\cdot N_2H_4$ je opisana in diskutirana. V inertni ali redukcijski atmosferi te spojine razpadejo na kovinske delce velikosti od 50 do 70 nm. Ti delci so sestavljeni iz še manjših delcev velikosti od 3 do 5 nm. Podane so prednosti in slabosti te metode ter možnosti za njeno uporabo za pripravo nanoproduktov.