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THERMAL PLASMA DECOMPOSITION OF NICKEL AND COBALT COMPOUNDS

ROZKŁAD TERMICZNY W PLAZMIE ZWIĄZKÓW NIKLU I KOBALTU

The paper presents the study on manufacturing of nickel and cobalt powders by thermal plasma decomposition of the carbonates of these metals. It was shown the dependence of process parameters and grain size of initial powder on the composition of final product which was either metal powder, collected in the container as well as the nanopowder with crystallite size of 70 - 90 nm, collected on the inner wall of the reaction chamber. The occurrence of metal oxides in the final products was confirmed and discussed.

Keywords: plasma, decomposition, cobalt, nickel

1. Introduction

Nickel, cobalt and other metals occur in Polish copper ores as the accompanying metals. They are recovered as the by-products of copper metallurgy in pyro- or hydrometallurgical processes. Nickel and cobalt are recovered in the form of sulphates or carbonates. Processing of these compounds into the metallic form is a continuity of the whole value chain from ore to metal. In this work the thermal plasma decomposition was used for this purpose. The advantage of plasma decomposition is a possibility of manufacturing of nanopowders (Np) by vapour condensation. Ni and Co nanopowders are magnetic materials and because of their specific characteristics have numerous applications. Ni-Np is used as anode and proton exchange membrane of solid oxide fuel cells, for production of automotive catalytic converters and catalysts for chemical reactions. Co-Np are used as medical sensors and as the agent for magnetic resonance imaging. For these reasons, thermal decomposition process of Ni and Co salts, usually carbonates or oxalates, was investigated in numerous works [1-6]. The disadvantage of thermal plasma decomposition method is the presence of both coarse fraction and nanopowder in a final product. Furthermore, the final product often contains undecomposed particles and chemical form of the product depends on a number of factors including morphology and grain size of the initial powder, parameters and conditions of the decomposition process. This paper presents studies of the thermal decomposition of Ni and Co carbonates in the argon/hydrogen atmosphere with different hydrogen content. The processes were performed in the reaction chamber of the plasmatron. X-ray phase analysis of examined powders was made with application of the SEIFERT – XRD 7 diffractometer using

CoK α radiation. The quantitative analysis of the crystalline phase in the decomposition products was carried out by Rietveld method [7] based on the digital diffraction patterns. Microstructural characterizations of both starting material and products were made by electron probe microanalyzer JEOL SUPERPROBE 8230 JXA.

2. Initial materials

The initial powders were prepared basing on by-products containing nickel and cobalt, recovered in Polish Copper Company. Nickel sulphate hydrate NiSO₄·6H₂O was transformed into Ni₃(CO₃)(OH)₄ · 4H₂O + Ni₂(CO₃)(OH)₂ by chemical way. The powder containing cobalt carbonate was identified by the x-ray analysis as the Co(CO₃)· 0.5Co(OH)₂· 0.11H₂O phase. Before powders were introduced into the plasmatron they were dried at temperature of 150°C/1hour for partial dehydration and then subjected to pressing and grinding. The fractions of grain-size 76-120 μ m and 120-220 μ m were selected by application of sieve analysis.

3. Experimental

Thermal plasma decomposition processes were carried out with application of AP50 plasmatron with power of 35 kW and equipped with reaction chamber of 2000 mm length and 220 mm diameter, made of stainless steel and cooled by water circulating between double walls. The plasmatron applied to studies uses argon/hydrogen arc as a source of temperature. The powder was transported from rotational pneumatic feeder to reaction chamber, using argon with flow of 2-4 l/min. and

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was inserted into the plasma stream through the nozzle placed 6 mm under the plasma torch anode.

4. Results and discussion

4.1. Decomposition of $\text{Ni}_3(\text{CO}_3)(\text{OH})_4 \cdot 4\text{H}_2\text{O} + \text{Ni}_2(\text{CO}_3)(\text{OH})_2$

Tests were performed under the following conditions: plasma torch current was 500A, hydrogen content in argon/hydrogen plasma gas varied in a range of 0-28%. Additional introduction of hydrogen to the reaction chamber made it possible to increase hydrogen content up to 49% in the chamber atmosphere. Pressure in the chamber was changed in the range of 1-0.3 bar. Intensity of powder feeding was changed in the range of 50-57 g/min. The results of selected tests presented in Table 2 show that with increasing content of hydrogen in the reaction chamber, NiO content in the nanopowder deposited on the chamber walls decreases but simultaneously increase of its content in powder collected in the container is observed.

TABLE 1

Results of the selected decomposition tests of nickel carbonate powder and graphite mixture. Grain size of nickel carbonate initial powder was 120-220 μm

Test number	Pressure [bar]	H ₂ content [%]	Content of the components wt [%]			
			Container – powder		Walls – nanopowder	
			Ni	NiO	Ni	NiO
155	1.0	44.0	66.2	33.8	84.0	16.0
156	0.8	23.0	87.7	12.3	82.7	17.3

As shown in Table 1 (test 155), increase of hydrogen content in the reaction chamber causes increase of a content of metallic nickel nanopowder formed on the chamber walls as a result of vapour condensation in more reducing atmosphere. Test 156 proves that pressure in the reaction chamber has an impact on the yield of nickel powder collected in the container at the bottom of the chamber. Lower pressure, and consequently lower partial pressure of the oxygen vapour, suppresses oxidation of the Ni particles falling down to the container. X-ray local microanalysis of chemical composition of the spherical particles collected in the container carried out for test 156 indicates that these are Ni grains with diameter of about 10 μm surrounded by NiO deposition (Fig. 1).

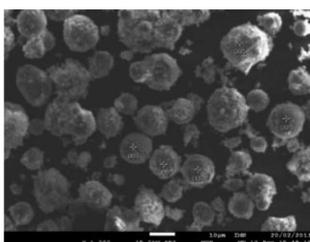


Fig. 1. Microstructure of the particles collected in the container and chemical composition in the marked areas – test 156. Magnification marker 10 μm

Fig. 2 presents nanopowder deposited on the chamber walls. Crystallite size of this nanopowder determined on the basis of the widening of X-ray diffraction lines was 74 nm for Ni and 88 nm for NiO.

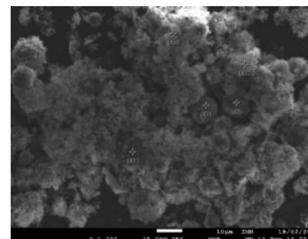


Fig. 2. Microstructure of the product deposited on the chamber walls and chemical composition in the marked areas – test 157. Magnification marker 10 μm

4.2. Decomposition of $\text{Co}(\text{CO}_3) \cdot 0.5\text{Co}(\text{OH})_2 \cdot 0.11\text{H}_2\text{O}$

The parameters of decomposition process were changed in the similar range as for nickel carbonate powder. Results of the selected tests are presented in Table 2. As shown in this table, the final product contains f.c.c (α) and hcp (ϵ) allotropic structures of cobalt and cobalt oxide CoO. The transformation in cobalt from hcp (ϵ) to fcc (α) takes place in the range from 430°C to 445°C on heating and from 400°C to 419°C on cooling [8]. Interesting structure of the particles has been revealed on their cross-section. As one can see at secondary electron images in Fig. 4, the particles consist of bulk inner part surrounded by a porous external layer. The point chemical microanalysis combined with the X-ray phase analysis (Fig. 6) confirmed that the inner part of the particles contains mostly Co(hcp) phase and some part – Co(fcc) phase. The external layer of the particles contains CoO and Co(fcc) with small content of Co(hcp). Analysis of the results presented in Table 2 shows that with increasing content of hydrogen in the chamber (test 174), content of CoO in the nanopowder deposited on the reaction chamber walls decreases. Influence of the initial powder grain size on the composition of final product is observed. The particles having a diameter twice the diameter of another particles (test 176) mean that volume is 8 times

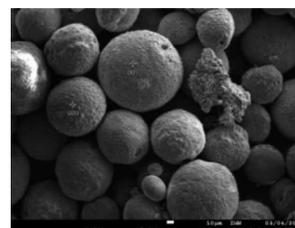


Fig. 3. Microstructure of the particles collected in the container – test 176. Magnification marker 10 μm

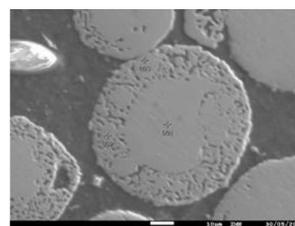


Fig. 4. Cross-section of spherical particles in the container – test 176. Magnification marker 10 μm

TABLE 2

Phase composition of the product from $\text{Co}(\text{CO}_3) \cdot 0.5\text{Co}(\text{OH})_2 \cdot 0.11\text{H}_2\text{O}$ powder decomposition at different process parameters. Atmospheric pressure in the chamber

Test number	Grain size [μm]	H_2 content [%]	Content of the components wt [%]					
			Container – powder			Walls – nanopowder		
			Co_{hcp}	Co_{fcc}	CoO	Co_{hcp}	Co_{fcc}	CoO
174	56-120	51	4.4	18.6	77.0	8.7	55.0	36.3
175	56-120	29	3.5	19.2	77.3	6.2	43.3	50.5
176	120-220	51	3.1	12.8	84.1	13.1	37.4	49.5

greater and consequently incomplete decomposition of cobalt carbonate takes place. Hence, both the final product collected in the container and the nanopowder deposited on the chamber walls have the highest CoO content.

Crystallite size of the nanopowder deposited on the chamber walls calculated on the basis of the widening of X-ray diffraction lines for test 176 were as follows: 95 nm for Co_{hcp} , 53 nm for Co_{fcc} and 76 nm for CoO.

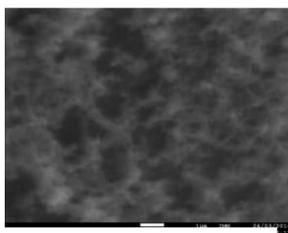


Fig. 5. Microstructure of the product deposited on the chamber walls - test 176. Magnification marker 1 μm

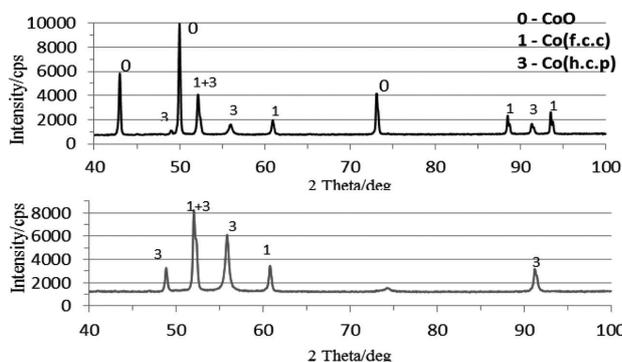


Fig. 6. The X-ray diffraction patterns of powder with test no. 176: at the top – the whole grains, at the bottom – cross-section of the grains

Plasma decomposition of the examined nickel and cobalt carbonates led to the formation of two grain-size fractions: nanopowder with crystallite size of 70-90 nm deposited on the reaction chamber walls and powder collected in the container. Both nanopowder (deposited on the reaction chamber walls) and powder (collected in the container) contain the fraction of metal oxide in the final product and its content depends on parameters of the decomposition process. The main parameters of carbonates decomposition in argon/hydrogen plasma stream are: grain size of the initial powder feed to plasma stream, pressure and gaseous atmosphere in the reaction chamber. Considering nickel carbonate it has been found that with

decreasing pressure to the level of 0.8 bar, content of NiO in the container decreases. In case of two examined carbonates it was also noted that higher content of hydrogen in the reaction chamber creates more reductive atmosphere and consequently reduces content of oxides in the final product. It can be supposed that presence of oxides in the final product, identified in every test, is connected with process technology and possibility of recombination of oxide with metal in the gaseous state. It is consistent with the results and their comments presented by C.S. Carney at all [1].

5. Summary and conclusions

To understand and to explain the obtained results it is necessary to take into account the following conditions of the thermal plasma decomposition processes:

- decomposition of chemical compounds in the reaction chamber occurs very fast and at very high temperature,
- some particles may avoid the region of highest temperature of plasma stream,
- the radius of the reaction chamber is 130 mm and its length is 1800 mm so the product of the reaction can contact the cooled walls of the chamber after covering the distance of 130 mm or 1800 mm, and the "history" of the products collected at the walls of the chamber and that collected in the container at the bottom of chamber differ from each other.

Shorter distance and hence shorter time for condensation and grain growth of particles from the gaseous state causes the deposition of the vapours at the walls of chamber in a form of metallic nanopowder. The condensed vapours of metal fall down to the container passing through the gaseous atmosphere of the chamber. They "have time" for possible oxidation so that we observed, as usually, some fraction of the oxides in the products of decomposed compounds both for Ni and for Co, collected in the container. Three-phase structure of the particles after decomposition of $\text{Co}(\text{CO}_3) \cdot 0.5\text{Co}(\text{OH})_2 \cdot 0.11\text{H}_2\text{O}$ was observed. The presence of low-temperature Co(hcp) phase inside the particles while the external layer contains mostly high-temperature Co(fcc) phase proves that this external layer was formed as a result of freezing of Co vapours on the surface of particles during falling. The presence of oxygen in the gaseous atmosphere of the chamber caused also formation of the Co oxide in the external layer of the particles.

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