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COMPOSITES THEORY AND PRACTICE

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PRO-ECOLOGICAL METHODS FOR SYNTHESIS OF NICKEL NANOPARTICLES FOR COMPOSITE APPLICATIONS

Composites containing nickel nanoparticles dispersed in a ceramic polycrystalline matrix are widely utilized materials for different applications. They are utilized in ceramic matrix/metallic additive composites due to their profitable influence on both the mechanical (grain size growth control, stress relaxation on crack tip by plastic deformation) and functional properties. A zirconia/nano-Ni composite is an important material for solid oxide fuel cell electrodes possessing unique electrochemical properties. Another composite composed of alumina and nano-Ni is a widely investigated structural material showing excellent mechanical properties. The paper presents an innovative pro-ecological method for synthesizing nickel nanoparticles to be used in ceramic matrix/metal particle composites, which could be used as an alternative to traditional methods. The proposed biochemical syntheses minimise or even completely eliminate the amount of produced waste and could be implemented as sustainable processes accepting the basic principles of "green chemistry". The suggested method enables precise size control of the created nanoparticles and at the same time offers numerous advantages in comparison to conventional methods.

Keywords: nickel nanoparticles, biochemical methods, green synthesis, Ni/ZrO_2 composite

PROEKOLOGICZNA METODA SYNTEZY NANOCZĄSTEK NIKLU DO ZASTOSOWAŃ W KOMPOZYTACH

Nanocząstki niklu znajdują zastosowanie w wielu dziedzinach. Wykorzystuje się je m.in. w kompozytach ceramiczno-metalicznych, gdzie wpływają pozytywnie nie tylko na mechaniczne właściwości kompozytu (kontrola rozrostu ziaren, relaksacja naprężeń przy wierzchołku pęknięcia na skutek kontaktu z fazą plastyczną), ale również na jego właściwości funkcjonalne. Kompozyty zawierające nanocząstki niklu rozproszone w osnowie polikrystalicznego tlenku cyrkonu są wykorzystywane m.in. do budowy elektrod w ogniwach paliwowych z zestalonym elektrolitem tlenkowym (SOFC). Innym przykładem kompozytu zawierającego nanocząstki niklu jest materiał wykazujący znakomite właściwości mechaniczne zbudowany z nanocząstek niklu i Al_2O_3. W artykule przedstawiono proekologiczną, innowacyjną metodę syntezy nanocząstek niklu do zastosowania w kompozytach ceramiczno-metalicznych jako alternatywę dla metod tradycyjnych. Zaproponowana metoda pozwala nie tylko na precyzyjną kontrolę wielkości powstających nanocząstek, ale również ich równomierne rozłożenie w matrycy ceramicznej, realizując przy tym zasady „zielonej chemii".

Słowa kluczowe: nanocząstki niklu, metody biochemiczne, zielona synteza, kompozyt Ni/ZrO_2

INTRODUCTION

Nanotechnology is a rapidly developing branch of science, which can be applied in many fields due to its interdisciplinary nature [1]. Metal nanoparticles belong to the group of materials with potentially the widest range of applications. Their properties depend distinctly on the form of their structure. Decreasing the grain size to the nano-scale results in an increase in the specific surface area, which gives the nanoparticles some unique properties that their counterparts in the micrometric scale do not possess [2-4].

In recent years, the preparation of metal nanoparticles has received increasing attention from many researchers due to their unusual properties significantly different from individual particles and macro-scale materials due to their extremely small sizes, large specific surface areas and potential applications in optical, electronic, catalytic, magnetic materials, and so on. Nickel nanoparticles are used as an additive in greases, thermal pastes, the sintering of cermets, construction of electrodes or as a catalyst of numerous chemical reactions [1-7].

A number of techniques have been used for the preparation of nickel nanoparticles, such as photolytic reduction [8], the sonochemical method [9], chemical vapor deposition (CVD) [10], the wet chemical method [11], hydrothermal method [12] and the microemulsion method [13]. Despite the numerous methods for making nickel nanoparticles which have been developed, efforts to create new methods are constantly undertaken with more stress put on biochemical syntheses that aim at eliminating completely or minimising the amount of produced waste and to implement sustainable processes by accepting the twelve basic principles of green chemistry [5]. There are exciting possibilities of utilizing biological systems for nanoparticle synthesis. Natural material sources like plants, bacteria, fungi, yeast and honey have been used for synthesizing silver and gold nanoparticles [14-16]. Green synthesis provides advancement over the chemical and physical method as it is cost effective, environmentally friendly, easily scaled up for large-scale synthesis and furthermore there is no need to use high pressure, energy, temperature or toxic chemicals [17].

In the paper, innovative synthesis of nickel nanoparticles with the use of a biochemical reduction is presented. The nanoparticles have been used for producing an Ni/ZrO_2 composite powder. This composite is an important material for solid oxide fuel cell electrodes possessing unique electrochemical properties.

Furthermore, nickel nanoparticles could be applied in different metal-ceramic composites where they have a beneficial effect not only on the mechanical properties of the composite (grain growth control, relaxation of stress at the tip of the crack due to contact with plastic phase), but also on its functional properties [6, 7, 18]. Another example of a composite in which nickel nanoparticles can be potentially used is one composed with nickel nanoparticles and alumina. This material is a widely investigated structural material showing excellent mechanical properties [19].

MATERIALS AND METHODS

Preparation of nickel nanoparticles

The method for synthesizing nickel nanoparticles is based on the reduction of nickel ions in an aqueous $Ni(NO_3)_2$ solution with the use of chemical compounds contained in Japanese Quince (Chaenomeles japonica) extract as a reducer and stabilizer and NH_4OH as a pH regulator. The characteristics of the raw materials used in this process are presented in Table 1.

TABLE 1. **Raw material characteristics**
TABELA 1. **Charakterystyka surowców**

Reagent	Chemical formula	Producer	Function
Nickel nitrate	$Ni(NO_3)_2$	POCH	Source of Ni^{2+} ions
Japanese Quince extract	-	-	Reducing and stabilising
Ammonium hydroxide	NH_4OH		Regulates pH (synthesis of nanoparticles) precipitating factor (synthesis of ZrO_2)
Zirconium oxychloride	$ZrOCl_2$	POCH	Substrate for synthesis of ZrO_2

In order to obtain the organic compounds contained in Japanese Quince, a fruit extract was prepared. Afterwards, the total polyphenols were measured in the above described extract with the use of the Folin--Ciocalteu reagent.

Six different suspensions in triplicate were made in order to examine the influence of individual parameters of the production process on the physical and chemical properties of the synthesised nickel suspensions (average size and electrokinetic potential). The individual input parameters of the processes may be found in Table 2.

TABLE 2. **Input parameters of produced nickel suspensions**
TABELA 2. **Parametry wejściowe syntezy nanocząstek niklu**

Sample no.	$Ni(NO_3)_2$ solution concentration [mol/l]	Concentration of polyphenols in extract [mg/cm^3]	pH of solution	Temperature of process [°C]
1	0.01	0.87	9	5.0
2	0.01	0.87	9	25.0
3	0.01	0.87	10	5.0
4	0.01	0.87	10	25.0
5	0.01	0.87	11	5.0
6	0.01	0.87	11	25.0

Each of these suspensions was made in a beaker with use of a magnetic stirrer by adding 25 cm^3 of the extract solution (with proper polyphenol amount) and a proper amount of sodium hydroxide (6.79 moles per litre) of NH_4OH solution to 80 cm^3 of an aqueous $Ni(NO_3)_2$ solution (of proper concentration) in order to obtain the defined pH. All these activities were performed under conditions of constant stirring at ambient temperature and under atmospheric pressure. Afterwards, the produced solutions were put inside plastic containers at a proper temperature.

The produced nickel nanoparticle suspensions were submitted for spectrophotometric analysis by a (UV/VIS) T 70 UV/VIS Spectrophotometer, which enabled examination of the influence of temperature and reaction time on the properties of the obtained suspensions. Dynamic light scattering analysis (DLS) by a Zetasizer Nano Range - Malvern Instruments was conducted in order to determine the average size and fractional distribution of the nanoparticles. Submitting the samples to these analyses allowed us to determine the influence of the input factors on the physical and chemical properties of the produced nickel nanoparticle suspensions.

Based on the principles of green chemistry, the parameters used in the nickel nanoparticle production process were selected. These nickel nanoparticles were used to produce the Ni/ZrO_2 composite (Fig. 1).

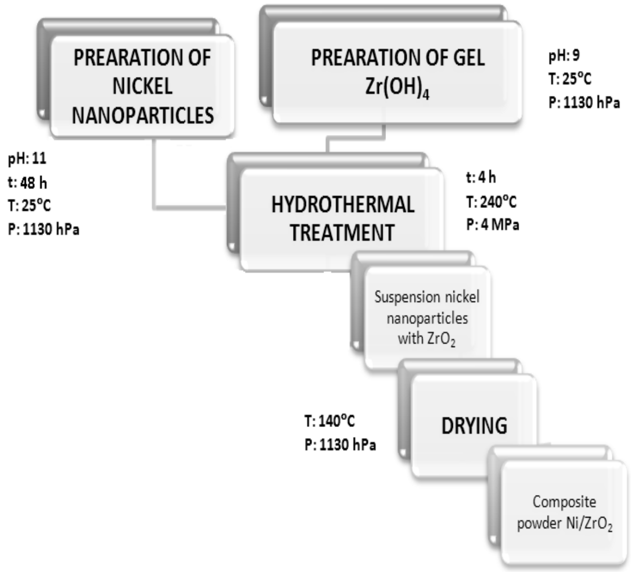

Fig. 1. Schematic preparation of Ni/ZrO_2 composite powder

Rys. 1. Schemat otrzymywania proszku kompozytowego Ni/ZrO_2

Preparation of $Zr(OH)_4$ gel

The ZrO_2 powder used during the research was synthesized by means of the precipitation method out of an aqueous salt solution with hydrothermal treatment of the produced hydroxide gel.

$ZrOCl_2$ in a concentration of 2.87 mol/dm^3 and NH_4OH in a concentration of 6.79 mol/dm^3 were used as the precipitation substrates. The precipitation can be presented as below:

$$ZrOCl_2 + 2NH_4OH + H_2O \rightarrow Zr(OH)_4 + 2NH_4Cl$$

In order to ensure complete reaction of $ZrOCl_2$, large amounts of the precipitating agent were used. The salt solution (2.4 cm^3) was introduced into an intensively stirred solution of NH_4OH and controlling the pH at the same time (pH should not drop below 9). Next, from the gel prepared in the above described way, NH_4Cl was removed by decantation by repeated washing with distilled water. The presence of chloride ions in the filtrate was controlled with the use of $AgNO_3$. Later, the prepared gel was filtered in a Büchner funnel.

Preparation of Ni/ZrO_2 composite powder

The produced hydroxide gel together with the suspension containing nickel nanoparticles was placed in a stainless steel autoclave and subjected to hydrothermal treatment (Fig. 1). The crystallization was performed at the temperature of 240°C and pressure of approx. 4 MPa for 4 hours. Next, the content of the autoclave was put into a crystallizer and dried in a laboratory dryer to a constant mass at the temperature of 140°C. The dried Ni/ZrO_2 powder was initially ground in a mortar made of α-Al_2O_3 and characterised.

RESULTS OVERVIEW

Characteristics of nickel nanoparticles

The spectrophotometric analysis and dynamic light scattering analysis has proved that nickel nanoparticles produced with use of the Japanese Quince extract are stable and comparable in terms of size to those produced with the use of traditional methods. The results of these analyses are presented in Table 3.

TABLE 3. **UV/VIS and DLS analyses results for produced nickel nanoparticle suspensions**

TABELA 3. **Wyniki analiz UV/VIS i DLS otrzymanych zawiesin z nanocząstkami niklu**

Sample no.	Average nanoparticle size [nm]	Stability (electrokinetic potential) [mV]	Sample reduction time [h]
1	15	–20.0	115
2	12	–31.0	68
3	12	–28.5	96
4	9	–30.5	58
5	7	–31.1	72
6	5	–31.8	48

Based on the principles of green chemistry, the parameters used in the nickel nanoparticle production process were selected. The most favourable process parameters were as follows: $Ni(NO_3)_2$ concentration: 0.01 mol/dm^3, concentration of polyphenols contained in the extract: 0.87 mg/cm^3, pH: 11, temperature: 25°C.

The size distribution of the produced nickel nanoparticles from this suspension is presented in Figure 2. The system comprises nickel nanoparticles of the size range 3÷7 nm and the modal value of 5 nm.

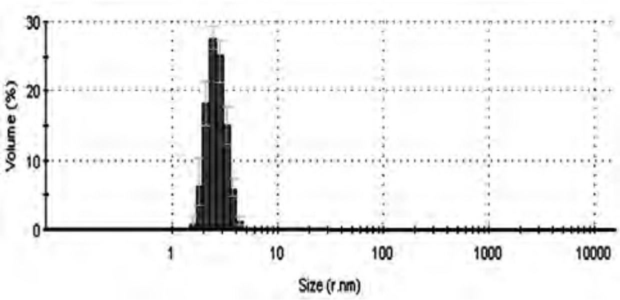

Fig. 2. Nickel nanoparticle size distribution by DLS

Rys. 2. Rozkład wielkości nanocząstek niklu wykonany metodą DLS

This suspension with nickel nanoparticles was used to produce the Ni/ZrO_2 composite (Fig. 1).

Characteristics of Ni/ZrO_2 compound powder

The grain size and its phase compositions are the most vital parameters of the powders. The first parameter was determined on the basis of observation of the powder with the use of a transmission electron microscope and the second one - on the basis of X-ray diffractometry. The analysis of phase composition was carried out by means of an X'Pert Pro diffractometer produced by PANalytical.

Microscopic observations of the powder conducted with the use of a transmission electron microscope have shown an average size of powder grains of approx. 5 nm (Fig. 3).

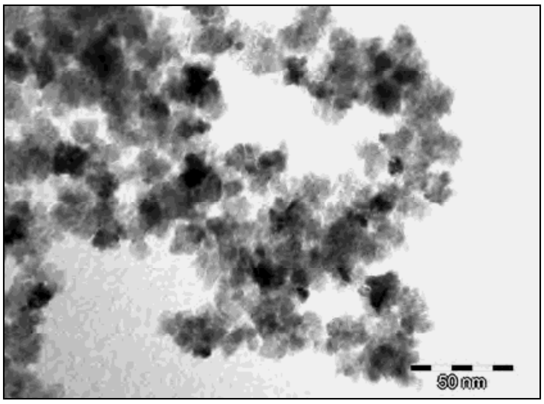

Fig. 3. TEM image of Ni/ZrO_2 composite powder

Rys. 3. Mikrofotografia TEM proszku kompozytowego Ni/ZrO_2

The phase analysis of the composite powder was performed utilizing the XRD method. The obtained diffraction pattern contained reflections corresponding to nickel and zirconium dioxide. The phase composition of the powder determined with the use of X-ray diffractometry is presented in Figure 4.

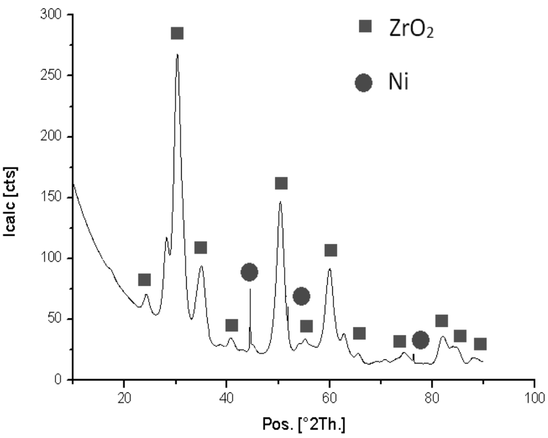

Fig. 4. Ni/ZrO_2 composite powder diffraction pattern

Rys. 4. Dyfraktogram proszku kompozytowego Ni/ZrO_2

CONCLUSIONS

This article presents an innovative method for producing nickel nanoparticle suspensions that complies with the rules of green chemistry, which allowed us to produce stable nanoparticles comparable in size to those produced by traditional methods.

It should be emphasized that the process of nickel nanoparticle production is a complex physical-chemical process influenced by all the examined input factors.

It has been noted that the size of nickel nanoparticles and their size distribution may be controlled by selecting proper reaction conditions. It has been proved that increasing the process temperature results in a smaller average size of nanoparticles since the kinetics of the reaction increases with the temperature growth, the reduction of nickel ions becomes rampant, which contributes to creating a large number of small points of low nickel concentration of nickel. The nanoparticles produced at higher temperatures exhibit a distribution close to the monomodal one.

It has been also proved that the pH of the solution influences to a great extent both the average size and the stability of the nanoparticles. By making the environmental pH more alkaline, the electro-kinetic potential is lower, which in turn makes the suspension more stable and its stabilisation time shorter. The nanoparticles produced from a solution of a higher pH had smaller average size in comparison to those obtained under a lower pH. Later in this paper, embedding nickel nanoparticles in the ceramic phase is described. Owing to this method, it is possible to obtain a finely dispersed nanocomposite powder with a microstructure characterized by even distribution of consistently sized nanoparticles and a nanometric size of ceramic matrix grains. The mentioned properties are ensured by the use of the electroless chemical method.

Nickel may affect not only the mechanical parameters of the designed composite, but also its functional properties. In most ceramic-metal composites, both the mechanical and functional properties of the nanocomposites are influenced to a great extent by the size of the matrix grains and homogeneous, even distribution of the metal particles. Actually, it is difficult to obtain such a perfect result. Common methods for producing ceramic-metal nanocomposites are based on grinding ceramic and metal powders (or metal oxides) together. However, these methods generally causes many problems in obtaining metal nanoparticles evenly distributed in the ceramic matrix.

The use of renewable plant extracts and a chemical method for synthesizing composite powders presents a wide range of possibilities for the further development of pro-ecological methods for synthesizing ceramic-metal nanocomposites.

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