Synthesis of nickel coatings with high surface area on the ceramic powders

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Abstract. The study of the dynamic of the synthesis processes of nickel nanostructured coatings on the ceramic powders is presented. It has used the approach with the minimal set of reagents for the deposition of nickel coatings with high surface area. The Al₂O₃ is selected as a ceramic powder. As a result of the study, it has found the optimal conditions for the synthesis of Ni/Al₂O₃ composite powders with high surface area. It has studied the dynamic of the synthesis process of nickel coating by the scanning electron microscopy that allowed us to clarify the mechanism of the synthesis of nickel nanostructured coatings. The surface area of the synthesized composite powders was studied by nitrogen adsorption. The obtained results may have wide applications in catalysis and electrochemistry.

1. Introduction

A creation of new architectures of functional materials is important for combination of their unique properties, including heat conductivity and electroconductivity, strength and plasticity, stability and reactivity. This makes it necessary to synthesize new composite materials, as well as research of the conditions for the manufacture of new products based on them [1-2]. Nickel combined with alumina extremely interesting for use in many applications, such as catalysis, soldering, corrosion-resistant coating, functionally graded metal-ceramic composites, fuel cells and others [3-7]. Powder composites are interesting as building blocks for creation of new electrodes of chemical current sources based on them [8-10]. The presence of such a wide range of applications of nickel-alumina materials requires the development of existing methods of their synthesis [11-17].

In this work, the dynamic of the process of synthesis of nickel nanostructured coatings on ceramic powders has studied. The scientific novelty of this work is that the synthesis of coatings was carried out according to a procedure with a minimum set of starting reagents to avoid occurrence of residual impurities apart from known approaches [18-20]. Also, the nickel-coated powders with high surface area were synthesized.
2. Experimental section
The initial powders of the Al₂O₃ composition were spheroidized by inductively coupled plasma (ICP). Plasma system used spheroidization of powder materials consists of lamp high-frequency generator with frequency 5.2 MHz and power up to 60 kW with control unit, two-circuit water cooling system, gas supply system and plasma-chemical reactor.

For the synthesis of nickel-coated powders chemicals from Acros Organics were used: nickel chloride NiCl₂·6H₂O, hydrazine hydrate N₂H₄·H₂O; purity of reactants is 99+; no additional purification of reactants was used. Reaction was realized in distilled water solution. 18 g NiCl₂·6H₂O, 4 g of Al₂O₃ powder and 200 ml distilled water were putted at room temperature into a 500 ml round-bottom flask under stirring with magnetic stirrer. A green color of the solution was observed. After that mixture of 25 ml of N₂H₄·H₂O in 200 ml distilled water was dropped into the reaction zone under magnetic stirring, and the color changed to blue. The reaction temperature was 80 °C during 2 h. The reaction resulted in formation of nickel coating on the alumina powder. After the reaction the product was washed with distilled water and isopropyl alcohol. Also, the synthesis of nickel-coated powders with the concentration of nickel 6 times less has realized.

Optical microscopy, scanning electron microscopy (SEM) and X-ray diffraction (XRD) were used to characterize the structure and morphology of the powders. SEM has done on Auriga Crossbeam workstation (Zeiss). Optical microscopy has done on Axio Z2 optical microscope from Zeiss. XRD was studied on XRD-7000 diffractometer (SHIMADZU). Also, the specific surface area of the powders was determined by nitrogen adsorption on Autosorb-iQ MP surface area analyzer (Quantachrome). Brunauer-Emmet-Teller (BET) method was used to calculate the specific surface area of the powders.

3. Results and discussion
In figure 1 SEM-images of spheroidized powders of Al₂O₃ before and after nickel coating are shown. In figure 2 photos of coated powders at intermediate and final stages of synthesis are shown.

During the synthesis we can see the changing of the color of the synthesized powder from blue to black. In figure 3 SEM-images of coated powders at intermediate (25 min after heating) and final stages of synthesis are shown. The presence of loose uncrystallized phase around the Al₂O₃ particles could be explained as nickel complexes formed at intermediate stages of the synthesis [20-22]. This confirmed by XRD measurements that shown pure nickel for the final nickel product. It could be proposed the formation of \([Ni(NH₃)₆]Cl₂\) and \([Ni(N₂H₄)₃]Cl₂\) complexes for the intermediate product. The detailed study of intermediate substances will be done in future.

Figure 1. SEM-images of spheroidized powders of Al₂O₃ before (a) and after (b) nickel coating.
According to literature, blue solid product should be complex $[Ni(NH_3)_6]Cl_2$ [22-23]. It is known that reduction potential of Ni$^{2+}$/Ni is higher than reduction potential $[Ni(NH_3)_6]^{2+}$/Ni, so formation of nickel from this complex in solution is thermodynamically more favorable in comparison with nickel chloride [24]. The known approach is the decomposition of the complex in alkaline solution (pH~13) that resulted to the formation of $Ni(OH)_2$ [25-26], that could be reduced by $N_2H_4$ by the next reaction [27-30]:

$$2Ni^{2+} + N_2H_4 + 4OH^- \rightarrow 2Ni + N_2 + 4H_2O$$ (1).

We have proposed the next stoichiometric reaction for our approach with minimal set of reagents:

$$5N_2H_4 \cdot H_2O + NiCl_2 \cdot 6H_2O \rightarrow Ni + 2N_2 + 4NH_3 + 2NH_4Cl + 8H_2O$$ (2).

As discussed above, the growth of nickel included intermediate reactions with formation of nickel complexes also.

In figure 4 SEM-images of Al$_2$O$_3$ powders coated at optimal (a) and reduced (b) concentration of oxidizer NiCl$_2$·6H$_2$O are shown. It has found that at reduced concentration of nickel salt the nickel coating is not dense. Also, we have studied the specific surface area of the received products.
It has measured the specific surface area of Al₂O₃ powder with and without nickel nanostructured coatings synthesized at different concentrations of nickel salt (table 1). The Al₂O₃ ceramic powder has a specific surface area 0.75 m²/g, that much smaller than specific surface area of Al₂O₃ powder coated with nickel at optimal concentration of nickel oxidizer – 10.8 m²/g. The specific surface area of Al₂O₃ powder coated with nickel at reduced concentration of nickel oxidizer is 2.6 m²/g.

**Table 1.** Comparison of specific surface area of Al₂O₃ powders before and after nickel coating.

| Sample                                      | Specific surface area, m²/g |
|---------------------------------------------|-----------------------------|
| Al₂O₃ ceramic powder                        | 0.75                        |
| Nickel-coated Al₂O₃ powder at reduced conc. | 2.6                         |
| Nickel-coated Al₂O₃ powder at optimal conc. | 10.8                        |

The increased specific surface area of nickel-coated Al₂O₃ powder could be explained by roughened nanostructured surface of nickel coating. SEM of the surface of nickel coatings synthesized at different concentrations of nickel salt are shown in figure 5. It is visible that the surface morphology of nickel coatings is rough and formed by homogeneous distributing of nanocones on the coating surface. The height of nanocones is up to 600 nm – 750 nm for the coating synthesized at optimal concentration of nickel salt, and about 200 nm for the coating synthesized at reduced concentration of nickel salt. These results are fully correlates with the experimental data about specific surface area of the Al₂O₃ powders before and after nickel coating.

**Figure 4.** SEM-images of Al₂O₃ powders coated at optimal (a) and reduced (b) concentration of oxidizer NiCl₂.

**Figure 5.** SEM of the surface of Al₂O₃ powders with nickel coatings deposited at optimal (a) and reduced (b) concentration of oxidizer NiCl₂.
4. Conclusion
The nickel coatings with high surface area have synthesized on ceramic spheroidized Al₂O₃ powder. The new approach of synthesis of nickel coatings by procedure with a minimum set of starting reagents is presented. It has studied the dynamic of the synthesis process of nickel coating by the scanning electron microscopy (SEM). The surface area of the synthesized composite powders was studied by nitrogen adsorption. It has found that the specific surface area of the nickel coated Al₂O₃ powder could be reach 10.8 m²/g. That is related with roughened surface of the nickel coating formed by homogeneous distributing of nanocones with the height up to 600 nm – 750 nm on the Al₂O₃ powder surface. The obtained results may have wide applications in catalysis and electrochemistry.

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References
[1] Török T I, Pázmn J, Szabó M and Janó V 2013 Laboratory preparation and characterization of electroless nickel coated powders of industrially produced aluminium and iron (III) oxides Mater. Sci. Forum 752 284-93
[2] Gromov A A, Nalivaiko A Y, Ambaryan G N, Vlaskin M S, Buryakovskaya O A, Kislenko S A, and Arnaoutov A N 2019 Aluminum-alumina composites: Part I: Obtaining and characterization of powders Mater. 12(19) 3180
[3] Kim P, Kim Y, Kim H, Song I. K and Yi J. 2004 Synthesis and characterization of mesoporous alumina with nickel incorporated for use in the partial oxidation of methane into synthesis gas Appl. Catal., A 272(1-2) 157-66
[4] Latiff M I A, Nuruzzaman D M, Basri S, Ismail N M, Jamaludin S N S and Kamaruzaman F F 2018 Preparation and characterization of 6-layered functionally graded nickel-alumina (Ni-Al₂O₃) composites IOP Conference Series: Materials Science and Engineering 342(1) 012063
[5] Hanyaloglu S C, Aksakal B and McColm I J 2001 Reactive sintering of electroless nickel-plated aluminum powders. Mater. Charact. 47(1) 9-16
[6] Wen G, Guo Z X and Davies C K L 2000 Microstructural characterisation of electroless-nickel coatings on zirconia powder Scripta mater. 43(4) 307-11
[7] Karayannis V G and Moutsatsou A K 2012 Synthesis and characterization of nickel-alumina composites from recycled nickel powder Adv. in Mater. Sci. and Eng 2012 1-9
[8] Holzer L, Iwanschitz B, Hocker T, Münch B, Prestat M, Wiedenmann D and Graule T 2011 Microstructure degradation of cermet anodes for solid oxide fuel cells: Quantification of nickel grain growth in dry and in humid atmospheres J. Power Sources 196(3) 1279-94
[9] Morozov M, Ivanov S, Kadirov M and Bund A 2021 Facile synthesis of a binder-free 3D Ni/NiO microwire network with a nanostructured fiber surface for a negative electrode in Li-ion battery J. Appl. Electrochem. 51(5) 815-28
[10] Liu C, Li C, Ahmed K, Mutlu Z, Ozkan C S and Ozkan M 2016 Template free and binderless NiO nanowire foam for Li-ion battery anodes with long cycle life and ultrahigh rate capability Scientific reports 6(1) 1-8
[11] Luo L M, Lu Z L, Tan X Y, Ding X Y, Huang L M, Cheng J G and Wu Y C 2013 A specific chemical activation pretreatment for electroless nickel plating on SiC ceramic powders Powder technol. 249 431-5
[12] Luo L, Wu Y, Li J and Zheng Y 2011 Preparation of nickel-coated tungsten carbide powders by room temperature ultrasonic-assisted electroless plating Surf. Coat. Technol. 206(6) 1091-5
[13] Lucchini M A, Testino A, Ludwig C, Kambolis A, El-Kazzi M, Cervellino A and Canepa F 2014 Continuous synthesis of nickel nanopowders: Characterization, process optimization, and catalytic properties App. Cat. B: Environmental 156 404-15
[14] Hirata Y, Hatano H, Kyoda H and Hamasaki K 1995 Synthesis of alumina/nickel composite by electrodeposition of nickel. J. mat. res. 10(11) 2697-9
[15] Haag S, Burgard M and Ernst B 2006 Pure nickel coating on a mesoporous alumina membrane: preparation by electroless plating and characterization Surf. Coat. Technol. 201(6) 2166-73
[16] Lin Y J and Jiang B F 1998 Sintering and Phase Evolution of Electroless-Nickel-Coated Alumina Powder. J. Am. Chem. Soc. 81(9) 2481-4
[17] Uysal M, Karslioglu R, Alp A and Akbulut H 2013 The preparation of core–shell Al2O3/Ni composite powders by electroless plating Ceram. int. 39(5) 5485-93
[18] Choi J Y, Lee Y K, Yoon S M, Lee H C, Kim B K, Kim J M and Lee J H 2005 A chemical route to large-scale preparation of spherical and monodisperse Ni powders. J. Am. Chem. Soc. 88(11) 3020-3
[19] Liang-Hsing C H O U, Wen -Ching H U N G and Maw -Tien L E E 2016 On the preparation of nickel nanoparticles by chemical reduction method: X-ray absorption spectroscopy. Mater. Sci. 22(2) 305-8
[20] Eluri R and Paul B 2012 Synthesis of nickel nanoparticles by hydrazine reduction: mechanistic study and continuous flow synthesis. J. nanopart. res. 14(4) 1-14
[21] Nicholls D and Swindells R 1968 Hydrazine complexes of nickel (II) chloride J. Inorg. Nucl. Chem. 30(8) 2211-7
[22] Guo L, Liu C, Wang R, Xu H, Wu Z and Yang S 2004 Large-scale synthesis of uniform nanotubes of a nickel complex by a solution chemical route. J. Am. Chem. Soc. 126(14) 4530-1
[23] Rejitha K S, Ichikawa T and Mathew S 2011 Thermal decomposition studies of [Ni(NH3)6]X2 (X= Cl, Br) in the solid state using TG-MS and TR-XRD J. Therm. Anal. Calorim. 103(2) 515-23
[24] Ningthoujam R S, Gajbhiye N S and Sharma S 2009 Reduction mechanism of Ni2+ into Ni nanoparticles prepared from different precursors: magnetic studies Pramana 72(3) 577-86
[25] Li Y D, Li C W, Wang H R, Li L Q and Qian Y T 1999 Preparation of nickel ultrafine powder and crystalline film by chemical control reduction Mater. chem. phys. 59(1) 88-90
[26] Gao J, Guan F, Zhao Y, Yang W, Ma Y, Lu X and Kang J 2001 Preparation of ultrafine nickel powder and its catalytic dehydrogenation activity Mater. chem. phys. 71(2) 215-9
[27] Chen D H and Wu S H 2000 Synthesis of nickel nanoparticles in water-in-oil microemulsions Chem. Mater. 12(5) 1354-60
[28] Boudjahem A G, Monteverdi S, Mercy M and Bettahar M M 2004 Study of support effects on the reduction of Ni2+ ions in aqueous hydrazine Langmuir 20(1) 208-13
[29] Zheng H G, Liang J H, Zeng J H and Qian Y T 2001 Preparation of nickel nanopowders in ethanol-water system (EWS) Mater. Res. Bull. 36(5-6) 947-52
[30] Park J W, Chae E H, Kim S H, Lee J H, Kim J W, Yoon S M and Choi J Y 2006 Preparation of fine Ni powders from nickel hydrazine complex Mater. chem. phys. 97(2-3) 371-8