

INTENSIFICATION OF PROCESSES NANOPOWDER PRODUCTION OF NICKEL OXIDE WHEN APPLIED ASYMMETRICALLY ALTERNATING CURRENT

E. Yu. Obraztsova, D. V. Obraztsov, **A. B. Kilimnik**

Tambov State Technical University, Tambov, Russia

*Reviewed by Doctor of Technical Sciences,
Professor N. Ts. Gatapova*

Keywords: asymmetrical alternating current; nanopowders; nickel oxide.

Abstract: The paper studies the influence of asymmetric AC on the speed of obtaining nanosized powder of nickel oxide. It is established that the maximum rate of formation of powder is observed when the ratio of anodic to cathodic density is equal to 2.5.

Production of nanosized powders of nickel oxide and creation of nanocomposites based on it is an important direction of development of modern nanotechnology. Nanodispersed powder of nickel oxide is used as electrode material in catalysis, including the synthesis of nanocarbon materials as active element of gas sensors. High-performance super frequency dielectrics is developed on the basis of complex mixtures of oxides of nickel and cobalt.

Nanodisperse powders of nickel oxide are obtained in various ways: precipitation pyrolysis, organometallics, copolymerization, sol-gel technology, hydrothermal synthesis, deposition of urea, carbonates of alkali metals and ammonia. These methods are conventionally divided into three groups: chemical, physical and physical-chemical methods.

Most of the described methods of obtaining nanosized powders of metals at the current level of development can neither control the growth of particles to obtain nanosized particles of definite composition and of the same size, nor synthesize powders with desired physical and chemical properties, except with the prior metal powders at a constant current. However, if the method is complicated by the use and maintenance of expensive equipment for rectifying

Образцова Елена Юрьевна – кандидат технических наук, доцент кафедры «Химия и химические технологии»; Образцов Денис Владимирович – кандидат технических наук, доцент кафедры «Уголовное право и прикладная информатика в юриспруденции», e-mail: odvru@ Rambler.ru; **Килимник Александр Борисович** – доктор химических наук, профессор кафедры «Химия и химические технологии», ТамбГТУ, г. Тамбов, Россия.

alternating current (AC), production increases. Thus, an important objective in the development of production technology of ultrafine environments is the transition from the stage of accumulation of data and empirical processing technologies to the stage of production of nanosized structures in a strictly controlled environment.

Electrolysis using the AC is a new promising direction of synthesis of nanoscale powders of oxides of metals. Directed electrochemical synthesis is one of convenient and affordable ways of forming metal-containing powders. The use of electrolysis is an environmentally friendly and cheap process; it allows you to create new materials with desired physical and chemical characteristics.

Alternating current is widely used in various fields of production. The use of AC makes it possible to carry out a variety of redox electrochemical reactions in solutions with or without the participation of the material of electrodes. In particular, the electrolysis with alternating current involves the processes of destruction of metals with the formation of nanosized powders.

The use of various forms of AC significantly intensifies the processes of anodic dissolution, eliminates passivation of electrode, and simplifies the production technology of nanodispersed powders. It was found that for the same current densities, the voltage when using the AC is almost twice as low as when using a direct current (DC), which makes the process energetically more favorable [1]. Besides, it was found [2] that the particle size and characterization of the porous structure of the materials during the AC process sets parameters of the electrolysis (density AC, composition and concentration of the electrolyte solution) and the subsequent processing modes. Therefore, under certain process parameters it is possible to obtain nanosized powders with desired properties.

The study of the electrochemical oxidation of metals with the use of AC is important for finding effective conditions for the synthesis of pure metal oxides, and determining the corrosion resistance of structural metallic materials under the influence of the currents of industrial frequency. Regularities of the processes on metals, occurring with the use of alternating current, are complex and insufficiently studied.

The effect of alternating current on the rate of dissolution of metals was reviewed in the literature [2 – 9]. The published materials contain experimental data on the dependence of the dissolution rate of metals on the frequency and density of the alternating current, composition and temperature of the electrolyte.

The passage of alternating current through the electrolyte solution is not supposed to decrease or increase the mass of the electrodes. When you change the direction of the current, the amount of metal passed into solution in the anodic half-cycle is compensated by the amount of metal deposited in the cathodic half cycle. However, there are many examples showing the possibility of destruction of metals by symmetrical alternating current [2 – 9]. Such a process is possible when changing the polarity of the current, the product of the anode reaction is not fully recovered in the cathodic half-cycle.

During electrolysis [3], the use of alternating current causes the change of the electrode potential under conditions far from equilibrium, resulting in the occurrence of a number of electrode reactions. Thus, it becomes possible to form oxide products with different degree of oxidation of the metal. The cycle polarizing voltage causes two sequential processes on the surface of the electrode: the first is the formation of oxide nuclei (anodic half-cycle current); the second is the discharge of protons to produce hydrogen, which contributes to the removal of oxide particles from the surface (cathodic half cycle current). Assuming that the anode half-cycle mechanisms of nucleation are the same as the DC, then we should expect the formation of nanosized structures because the stages of formation of centers of growth are limited by the frequency of changing polarity of the electrodes. In the cathodic half-cycle, the current of the oxide film does not have time to recover fully due to the difference of speeds forward and reverse reactions. Nanosized particles, due to weak adhesion forces, detach from the surface of the electrode and move into the electrolyte solution, forming a colloidal system.

As known from the literature [8, 9], the use of asymmetric alternating current allows for significant intensification of the process of anodic dissolution of metals. A special installation was designed to obtain an asymmetric AC with different amplitude and the same duration of half-cycles of anode and cathode currents.

We studied the effects of ratios of values of the densities of the currents in the positive and negative half-cycles in the destruction of nickel. The experiments showed that nickel electrodes where the value of the current density in the negative half-cycles of current is less than in the positive half-cycles begin to break down more rapidly.

Table 1 presents the experimental data on the dependence of the rate of consumption of nickel on the magnitude of the ratio of i_c and i_a 17 M sodium hydroxide solution. As can be seen from the above data, the dependence of the

Table 1

The values of the flow rates of Nickel at different ratios of the densities of the currents in the cathode and anode half-cycles

The current density, A/cm ²		K, mg/(cm ² h)
I_a	I_c	
2.5	2.5	25
2.5	2.0	35
2.5	1.5	42
2.5	1.0	64
2.5	0.5	35
2.5	0.1	5

rate of consumption of nickel from the cathode current density (i_c) at constant value of the anodic current density ($i_a = 2.5 \text{ A/cm}^2$) passes through a maximum ($i_c = 1 \text{ A/cm}^2$). At current densities in the cathode half-cycles of less than 1 A/cm^2 the intensive potentials of hydrogen evolution are not reached and decline in the mass of the electrodes is reduced. When the current density in the cathodic half-cycle is more than 1 A/cm^2 the reduction in the rate of consumption of nickel can be explained by the fact that the electrode is an intensive evolution of

hydrogen, the oxidation in the anodic half-cycle of the consumed current. Accordingly, the share of current leading to the formation of oxides decreases. The maximum rate of the consumption of nickel was observed when the ratio of the current density in the cathodic and anodic half-cycles was equal to 2.5.

The ratio of the current density i_c and i_a affects not only the rate of consumption of nickel in sodium hydroxide solution, but also the color

of the resulting powders. So when $i_a > 0.25 \text{ A/cm}^2$ in all cases black powders are obtained, and when $i_a < 0.25 \text{ A/cm}^2$ the color of powders becomes greenish, which corresponds to the formation of nickel oxides with a lesser degree of oxidation (Table 2).

Thus, by setting the ratio of the current density in the cathodic and anodic half-cycles, one can obtain nanodispersed powders of nickel oxide with a specific chemical composition.

References

1. Shul'gin L.P. [Over-voltage electrode reactions in solution during the passage of the symmetrical AC], *Zhurnal fizicheskoi khimii* [Journal of Physical Chemistry], 1979, no. 3, pp. 2048-2051. (In Russ.)
2. Ozerov A.M. *Nestatsionarnyi elektroliz* [Unsteady electrolysis], Volgograd: Nizhne-Volzhskoe izdatel'stvo, 1972, 160 p. (In Russ.)
3. Shul'gin L.P. *Elektrokhimicheskie protsessy na peremennom toke* [Electrochemical processes ac], Leningrad: Nauka, 1974, 74 p. (In Russ.)
4. Korobochkin V.V., Khanova E.A. [Destruction of nickel and cadmium alternating current in the electrolysis in an alkaline electrolyte], *Izvestiya Tomskogo politekhnicheskogo universiteta* [Bulletin of the Tomsk Polytechnic University], 2003, no. 1, pp. 36-41. (In Russ.)
5. Boiko A.V. [Electronic processing of metals], *Elektrokhimiya* [Electrochemistry], 1975, vol. 11, no. 1, pp. 60-65. (In Russ.)
6. Belov S.F., Bryukvin V.A., Levin A.M., Kuznetsova O.G. [Investigation of the process of dissolution of metallic nickel under the influence of the AC power frequency in sulfuric acid electrolytes], *Tsvetnye metally* [Non-ferrous metals], 2005, no. 1, pp. 39-41. (In Russ.)
7. Mikhailovskii Yu.N. [Electrochemical mechanism metal corrosion by AC], *Korroziya metallov i splavov* [Corrosion of metals and alloys], Moscow: Metallurgizdat, 1963, pp. 222-242 (In Russ.)
8. Kukoz F.I., Kudryavtsev Yu.D., Makogon Yu.O. [Nickel Behavior AC electrolysis in alkaline solutions. I. Effect of alkaline nature and the current density], *Elektrokhimiya* [Electrochemistry], 1971, no. 7, pp. 990-994. (In Russ.)
9. Kudryavtsev Yu.D., Makogon Yu.O., Fesenko L.N. [Nickel Behavior AC electrolysis in alkaline solutions, coulometric and potentiodynamic measurements], *Elektrokhimiya* [Electrochemistry], 1976, vol. 7, no. 6, pp. 1362-1368. (In Russ.)

Table 2

The elemental composition of the nickel oxide powders obtained at different modes

$i, \text{ A/cm}^2$	$i_a = i_c = 2.5$	$i_a = 0.25,$ $i_c = 2.5,$ $i_k = 2.5$
Ni	39.93	48.08
O	58.30	49.82
Impurities	1.77	2.08
O/Ni	1.46	1.01

Список литературы

1. Шульгин, Л. П. Перенапряжение электродных реакций в растворах при прохождении симметричного переменного тока / Л. П. Шульгин // Журн. физ. химии. – 1979. – № 3. – С. 2048 – 2051.
2. Озеров, А. М. Нестационарный электролиз / А. М. Озеров. – Волгоград : Нижне-Волж. изд-во, 1972. – 160 с.
3. Шульгин, Л. П. Электрохимические процессы на переменном токе / Л. П. Шульгин. – Л. : Наука. – 1974. – 74 с.
4. Коробочкин, В. В. Разрушение никеля и кадмия при электролизе переменным током в щелочном электролите / В. В. Коробочкин, Е.А. Ханова // Изв. Том. политехн. университета. – 2003. – № 1. – С. 36 – 41.
5. Бойко, А. В. Электронная обработка металлов / А. В. Бойко // Электрохимия. – 1975. – Т. 11, № 1. – С. 60 – 65.
6. Исследование процесса растворения металлического никеля под действием переменного тока промышленной частоты в серноокислых электролитах / С. Ф. Белов [и др.] // Цветные металлы. – 2005. – № 1. – С. 39 – 41.
7. Михайловский, Ю. Н. Электрохимический механизм коррозии металлов под действием переменного тока / Ю. Н. Михайловский // Коррозия металлов и сплавов / редкол.: Н. Д. Томашов [и др.]. – М. : Металлургиздат, 1963. – С. 222 – 242.
8. Кукоз, Ф. И. Поведение никеля при электролизе переменным током в растворах щелочей. I. Влияние природы щелочи и плотности тока / Ф. И. Кукоз, Ю. Д. Кудрявцев, Ю. О. Макогон // Электрохимия. – 1971. – № 7. – С. 990 – 994.
9. Кудрявцев, Ю. Д. Поведение никеля при электролизе переменным током в растворах щелочей, кулонометрические и потенциодинамические измерения / Ю. Д. Кудрявцев, Ю. О. Макогон, Л. Н. Фесенко // Электрохимия. – 1976. – Т. 7, № 6. – С. 1362 – 1368.

Интенсификация процесса получения нанодисперсных порошков оксида никеля при наложении асимметричного переменного тока

Е. Ю. Образцова, Д. В. Образцов, А. Б. Килимник

ФГБОУ ВО «Тамбовский государственный технический университет», г. Тамбов, Россия

Ключевые слова: асимметричный переменный ток; нанопорошки; оксид никеля.

Аннотация: Рассмотрено влияние асимметричного переменного тока на скорость получения нанодисперсного порошка оксида никеля. Установлено, что максимальная скорость образования порошка наблюдается при соотношении анодной плотности к катодной, равной 2,5.

© Е. Ю. Образцова, Д. В. Образцов,
А. Б. Килимник, 2016