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Розроблено електрохімічний метод синтезу тонкодисперсного порошку кобальту, призначеного для виробництва твердих сплавів. Запропоновано введення аміаку в електроліт, доведено формування при цьому амінокомплексу Co^{+3} . Показано утворення при 100 A/дм^2 ультрадисперсних $35\text{--}150 \text{ мкм}$ частинок Co коралоподібної форми, які легко піддаються розмолу до сферодних складових. Визначено максимальну температуру електроліту – 30°C , розраховано катодний вихід за струмом 39% та питома витрата електроенергії $48 \text{ кВт}\cdot\text{год/кг}$

Ключові слова: амінокомплекс кобальту ($+3$), порошок кобальту, тверді сплави, дендрит

Разработан электрохимический метод синтеза тонкодисперсного порошка кобальта, предназначенного для производства твердых сплавов. Предложено вводить аммиак в электролит, доказано формирование при этом амминокомплекса Co^{+3} . Показано образование при 100 A/дм^2 ультрадисперсных $35\text{--}150 \text{ мкм}$ частиц Co порошка кораллоподобной формы, легко размалывающихся на сферодные составляющие. Определена максимальная температура электролита 30°C , рассчитан катодный выход по току 39% и удельный расходом электроэнергии $48 \text{ кВт}\cdot\text{час/кг}$

Ключевые слова: аминкомплекс кобальта ($+3$), порошок кобальта, твердые сплавы, дендрит

DEVELOPMENT OF THE ELECTROCHEMICAL SYNTHESIS METHOD OF ULTRAFINE COBALT POWDER FOR A SUPERALLOY PRODUCTION

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1. Introduction

Ultrafine metal powders are widely used in various fields of engineering and manufacturing. Cobalt powder possesses

high electrical conductivity, electrochemical and catalytic properties and is used for various purposes. For instance, it is used in chemical power sources [1], including hydrogenation [2] or as anodic material [3].

Cobalt powder is also used as a binder for superalloys, in combination with nickel [4], or without [5]. Superalloys, which are also called pseudo-alloys, are not alloys by the classic definition, but are composites. Commonly, composite materials of organic [6, 7], inorganic [8] or mixed organic-inorganic nature [9, 10] are composed of a matrix-forming component and a filler, including cobalt compounds [11, 12]. The structure of superalloys is different: large numbers of hard material particles (usually W or WC) are bound together with a small amount of molten metal binder (particularly Co).

Workpieces from superalloys are produced by means of powder metallurgy: a mixture of hard component and metal binder [13] is placed into a mould which is then heated under pressure to obtain a metal-ceramic piece. Because of this procedure, there are special requirements for cobalt powder. First, cobalt powder must be free from volatile compounds or metals (zinc, magnesium), as they can lead to the formation of caverns inside the piece. Second, powder's particle size must be within 5–50 μm . Additionally, the pretreatment for manufacturing of superalloy pieces is grinding of metal powder mixture in alcohol [14]. Thus, another necessary requirement is susceptibility to grinding.

Based on the operation conditions of such pieces, one of the main parameters of superalloys is high heat resistance [15, 16]. This parameter is important for application in the aerospace industry [17]. Superalloys are used for manufacturing of turbines for plane and rocket engines. So, for manufacturing such pieces, the requirements to cobalt powder are more strict. And the composition is determined by synthesis conditions and method [18].

2. Literature review and problem statement

One of the principles of sustained development is recycling of materials or their repeated use. Based on this principle and considering the high cost of cobalt, it should be noted that the best cobalt source for the preparation of powder is various waste. First, this can be various cobalt-containing liquid wastes. Second, the source for the preparation of cobalt powder can be a scrap of superalloys with a cobalt binder. The scrap can be used as a source of solid cobalt or it can serve as a source of cobalt salts after selective dissolution [19, 20].

Another source of cobalt can be a scrap of supercapacitors with cobalt oxide-hydroxide electrode, dissolution of which would result in a solution of cobalt salts.

Several methods for the preparation of ultrafine cobalt powder have been developed [21]. A mechanochemical method for the preparation of a mixture of ultrafine Co and WC for the preparation of superalloys was proposed [22]. For the preparation of such mixture of ultrafine cobalt and tungsten carbide powders, paper [23] proposes direct reduction – carbidization. The downside of these methods is that they result in a concurrent mixture, while cobalt powder can be used in the preparation of superalloys with different composition. In the paper [24], it was proposed to utilize chemical evaporation – condensation for the preparation of mixed cobalt – iron powder from chloride precursors, however, this method requires the use of special equipment and the synthesis must also be conducted under an inert atmosphere. Paper [25] describes the process of preparing cobalt powder from an aqueous salts solution. It is proposed to use

polyols as reducing agents and also strong surfactants. The resulting powder would be contaminated with surfactant admixtures, which makes it unsuitable for the preparation of superalloys. One of the most commonly used methods for the preparation of cobalt powder is hydrogen reduction with the preparation of «cobalt cotton». In paper [26], it is proposed to precipitate cobalt as basic cobalt carbonate, followed by reduction with hydrogen to metal powder. The prepared cobalt powder is susceptible to grinding and does not contain any impurities, however, its production requires a hydrogen station and heating.

One of the most promising methods for the preparation of Co is electrolysis. The method allows for easy control over parameters of the resulting powder. The most suitable synthesis variant is direct electrolysis of cobalt salt [27, 28]. Like with the synthesis of nickel powder, the synthesis of cobalt powder must be conducted at current densities significantly higher than the limiting current density. However, the electrolyte layer at the cathode is basified resulting in cobalt precipitation in the form of hydroxide. To prevent this, the electrolysis of cobalt salt (usually sulfate) is conducted in the presence of ammonium salts. In the basic medium, ammonium cation transforms into ammonia, which can form a complex with cobalt. The latter passes through the basic layer to the cathode and upon its discharge the cobalt powder is formed [29].

Electrolysis of cobalt salt solution in the presence of ammonium salts (namely, chloride) allows for the synthesis of cobalt powder. However, in paper [29], it is stated that unlike nickel powder, cobalt powder, in addition to dendrite particles, also contains agglomerated particles of various sizes, and even particles of compact cobalt. This significantly limits the application of such powder in the manufacturing of superalloys, so, this promising method must be improved.

3. The aim and objectives of the study

The aim of the study is to develop an electrochemical method for the synthesis of ultrafine cobalt powder for manufacturing of superalloys. In order to achieve the set aim, following objectives were set:

- to propose a basis for the development of the electrochemical method for cobalt powder synthesis;
- to study the electrolyte composition and to determine the mechanism of reactions occurring during the preparation of cobalt powder;
- to study the dependency between the electrolyte temperature and properties of cobalt powder;
- to calculate the characteristics of cobalt powder synthesis.

4. Materials and methods

4.1. Basis for development of electrochemical method for cobalt powder synthesis

During the development of the electrochemical method for the synthesis of cobalt powder, the electrochemical parameters for the electrochemical synthesis of nickel powder [30] were used. Such choice was made because of similar properties of nickel and cobalt, and because the paper [30] describes the methodology for the synthesis of nickel powder for the production of superalloys.

4. 2. Study of electrode reactions during synthesis of cobalt powder

Electrode reactions have been studied by recording cathodic and cyclic cathodic-anodic polarization curves. For this purpose, a special three-electrode cell was used. Platinum was used as a counter-electrode. Reference electrode – Ag/AgCl (KCl sat.), submerged in saturated KCl solution. Stainless steel was used as a working electrode. In order to avoid the edge effect, the working electrode was placed in a Teflon cassette composed of two rectangular parts, one of which had a hole 12 mm in diameter. In order to establish a contact between the reference and working electrodes, a Luggin capillary filled with the studied solution was used. Polarization curves were recorded using a digital potentiostat Ellins P-8 (Russia). Scan rate 1 mV/s.

4. 3. Synthesis of cobalt powder

Electrolysis was conducted in the flow-through polypropylene cell. A stainless steel cathode was placed into the cell. It was previously discovered [30] that during the synthesis of nickel powder, nickel anode behaves like a low-soluble electrode, it was decided to use two insoluble anodes. Nickel electrodes, plated with 3 μm of gold were used as insoluble anodes. Electrolysis was conducted at a current density of 100 A/dm². During electrolysis, a large amount of heat was produced. In order to evaluate the influence of temperature of the synthesis process, the electrolysis was conducted under the following conditions:

- without cooling;
- air-evaporative cooling: the cell was placed in a fabric sleeve located in water with airflow over it;
- water cooling: the cell was placed in a large container with cold water;
- snow-water cooling: the cell was placed in a large container with a mixture of water and snow;
- snow-salt cooling: the cell was placed in a large container with a mixture of snow and sodium chloride.

4. 4. Analysis of cobalt powder

After electrolysis, the cobalt powder was removed from the cathode and rinsed several times with distilled water and dried at room temperature.

Morphology and particle size of cobalt powder were evaluated using a Scanning Electron Microscope JEOL JSM-6510LV («JEOL», Japan).

5. Results of developing electrochemical method for synthesis of cobalt powder

5. 1. Development of electrolyte composition and electrolysis conditions for cobalt powder synthesis

The development of the electrochemical method for cobalt powder synthesis was based on the already developed method for the electrochemical synthesis of nickel powder. The paper [30] describes the following electrolyte composition of nickel powder synthesis: Ni²⁺ 0.1 mole/L, NH₄⁺ 1 mole/L, NH₃·H₂O until pH 11. Because the chemical properties of cobalt are similar to nickel, the following ammonium-sulfate electrolyte was proposed: Co²⁺ 0.1 mole/L, NH₄⁺ 1 mole/L. Cobalt sulfate CoSO₄·7H₂O was used as a source of Co²⁺, which was prepared by selective dissolution of VK20 superalloy (WC 80 %, Co 20 %), the source of NH₄⁺ – ammonium sulfate. Similar to the synthesis of nickel

powder and in order to avoid the formation of compact cobalt particles [29], it was proposed to introduce an aqueous ammonia solution until pH 11 is reached.

5. 2. Study of electrolyte composition and electrode reactions during synthesis of cobalt powder

Visual observations have revealed that the addition of aqueous ammonia (to pH=11) leads to the formation of a large volume of the brown-red precipitate. After the solution with the precipitate was stored for 1 week, the precipitate has dissolved with the formation of a purple-red solution. The obtained solution was then used for further studies.

The cathodic polarization curve recorded in the obtained solution is shown in Fig. 1.

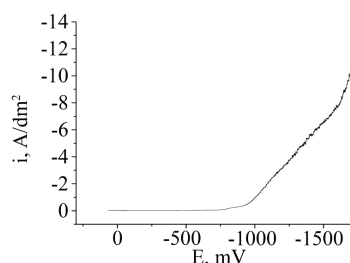


Fig. 1. Cathodic polarization curve recorded in the obtained electrolyte for cobalt powder synthesis

The cathodic curve for cobalt powder synthesis (Fig. 1) shows the limiting diffusion current density of 6 A/dm². However, no such limiting current is observed in the preparation of nickel powder [30]. This can indicate a multi-stage process.

In order to determine the possibility of the multi-stage process and to clarify the electrolyte composition, the cyclic cathodic-anodic curve was recorded (Fig. 2).

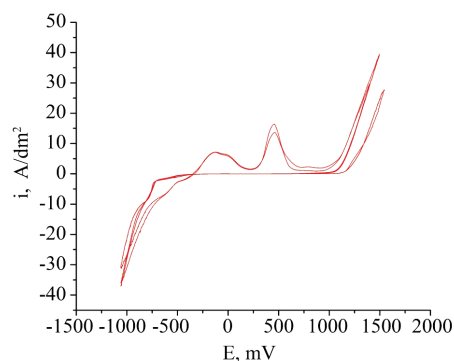


Fig. 2. Cathodic-anodic cyclic polarization curve, recorded in the electrolyte for the synthesis of cobalt powder (after precipitate dissolution)

The cyclic curve shows two limiting current plateaus in the cathode region and two pronounced oxidation peaks in the anode region. This indicates a two-stage character of the reactions that occur during the synthesis of cobalt powder.

5. 3. Study of temperature influence on properties of cobalt powder

Because cobalt powder is subjected to grinding after the synthesis, the particle size is less important than susceptibility

to grinding. Thus, the powder characteristics (particle size and susceptibility to gridding) were evaluated quantitatively by placing a powder sample on the metal surface and grinding it with a metal spatula.

The results of studying the influence of the cell temperature on the qualitative properties of cobalt powder are presented in Table 1.

Table 1
Influence of cooling type and temperature on the properties of cobalt powder

Cooling type	Temperature, °C	Powder quality
No cooling	98	Very coarse powder with inclusions of compact metal
Evaporative cooling	81–82	Coarse powder, low susceptibility to grinding
Water-cooling	74	Moderately fine powder, can be ground with effort
Snow-water cooling	45–50	Ultrafine powder, easy to grind
Snow-salt cooling	28–30	Even finer powder, breaks down at minimum pressure

Lower temperatures result in finer powder with higher susceptibility to grinding. At high temperatures, the formation of compact cobalt particles is observed.

5. 4. Study of cobalt powder characteristics and electrochemical synthesis process

In order to study the characteristics of cobalt powder, the electrolysis was conducted at a cathodic current density of 100 A/dm². Two types of electrolytes were used for electrolysis:

- electrolyte decanted from brown-red precipitate;
- purple-red electrolyte after the precipitate dissolution.

Two types of cooling were also used: snow-water and snow-salt.

When the decanted electrolyte was used for electrolysis, a very low amount of powder was observed at the cathode, which was insufficient for further analysis. This indicates a very low concentration of cobalt in the solution.

Scanning Electron Microscope (SEM) images of cobalt powders prepared from the electrolyte with dissolved precipitate at different cooling types are shown in Fig. 2.

It can be seen; that powder is composed of small spherical particles that form coral-like grains of about 35–150 μm. These agglomerates break easily even when a small force is applied. With snow-water cooling (temperature below 50 °C), compact metal particles were observed in the prepared sample (Fig. 3, *b*).

The cathodic current yield and the specific power consumption for the electrochemical synthesis of cobalt powder at different cooling types were determined (Table 2).

Data presented in Table 2 show that lower temperature leads to lower current efficiency and higher power consumptions, however this also leads to a significant improvement in the cobalt powder quality.

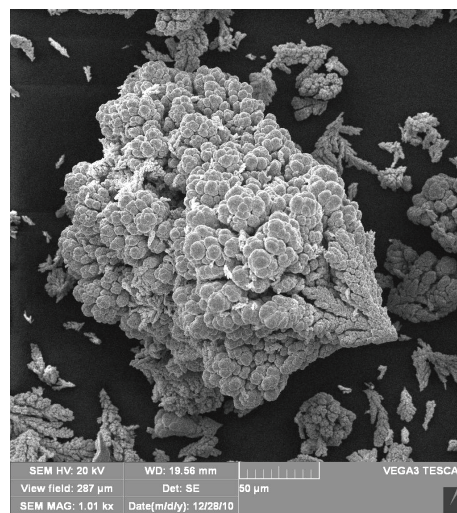
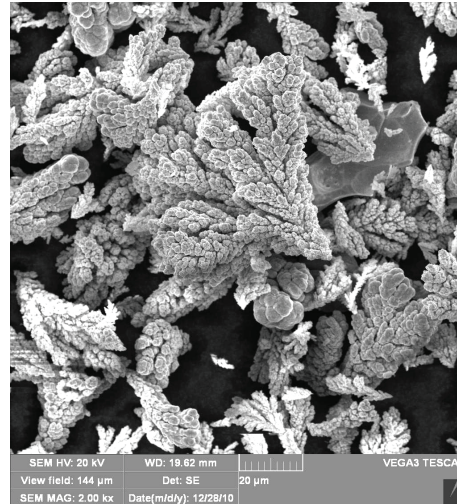


Fig. 3. SEM images of cobalt powder prepared at different temperatures: *a* – 50 °C (snow-water cooling, ×2000), *b* – 30 °C (snow-salt cooling, ×1010)

Table 2
Parameters of electrochemical powder synthesis

Conditions		Parameters	
<i>T</i> , °C	Cooling Type	Current efficiency, %	Specific power consumption, kW·h/kg
50	Snow-water	51	35
30	Snow-salt	39	48

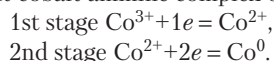
6. Discussion of results of developing electrochemical method for cobalt powder synthesis

Upon addition of ammonia solution to the solution containing cobalt and ammonium sulfates, the brown-red precipitate was forced. It was assumed that Co²⁺ forms the ammine complex with ammonia, however, the solubility of this complex turned out to be low. This hypothesis is supported by

that fact that after the electrolysis of the decanted solution, the amount of the formed cobalt was very small. This indicates a low cobalt concentration in the electrolyte, thus supporting the assumption of the low solubility of its ammonia complex.

However, upon storing the solution with the precipitate over a week, the precipitate gradually dissolved forming a purple-red solution. The most likely explanation is that over the period of storage, Co^{2+} was gradually oxidized to Co^{3+} with oxygen, resulting in the formation of soluble, stable ammine complex. The solution does not respond to a quality reaction for Co^{2+} , however, cobalt powder can be electrochemically synthesized from it.

The presence of the Co^{3+} ammine complex; allows explaining the presence of the limiting current plateau on the polarization curve (Fig. 1), while there is no such plateau in the synthesis of nickel powder. The most likely scenario is that the synthesis of cobalt powder from a solution of trivalent cobalt ammine complex occurs in two stages:



The limiting current is likely related to the first stage of Co^{3+} reduction to Co^{2+} . The two-stage process of cobalt powder synthesis from the Co^{3+} ammine complex electrolyte is also supported by cyclic cathodic-anodic curves (Fig. 2), which show two limiting current plateaus in the cathode region, and two oxidation peaks in the anode region. These data correspond to two subsequent reactions. To summarize, it can be concluded that the presence of cobalt as the Co^{3+} ammine complex leads to increased polarization and improved fineness of cobalt powder.

During electrolysis at $i = 100 \text{ A/dm}^2$, the electrolyte temperature would rise, because of significant Joule heating. The data presented in Table 1 reveal that lower electrolyte temperature leads to the formation of finer cobalt powder. This is in agreement with the theoretic basis, according to which higher polarization results in the smaller size of the formed particles. And higher temperatures decrease polarization of cobalt formation. These data correlate with data for nickel powder [30], however, at temperatures below $50 \text{ }^\circ\text{C}$ compact metal particles are observed in cobalt powder. This lowers the quality of cobalt powder for manufacturing of superalloys. So, the formation of powder suitable for manufacturing of superalloys requires electrolyte temperatures below $30 \text{ }^\circ\text{C}$, which requires powerful cooling of the electrolyte. Cobalt particles formed under these conditions are composed of agglomerated spherical primal particles, which can be easily broken with minimal effort.

Using formulas (1) and (2), the current yields and specific power consumption have been calculated for the synthesis of cobalt powder at $30 \text{ }^\circ\text{C}$ and $50 \text{ }^\circ\text{C}$.

$$Ke = \frac{m_{\text{Co}}}{I \cdot \tau \cdot k_{\text{Co}}}, \quad (1)$$

$$W = \frac{U}{k_{\text{Co}} \cdot Ke}, \quad (2)$$

where m_{Co} is the mass of cobalt powder prepared via electrolysis, g; I is the current during electrolysis, A; τ is the electrolysis time, h; k_{Co} is the electrochemical equivalent of cobalt, g/(A·h); Ke is the current efficiency, %; W is the specific power consumption, kW·H/kg.

Decreasing temperature leads to a non-linear decrease of polarization for cobalt formation and lower current yield,

which results in an increase of specific power consumption. However, this leads to insignificant improvement in powder fineness: particle size decreases from $70\text{--}120 \text{ }\mu\text{m}$ (at $50 \text{ }^\circ\text{C}$) to $35\text{--}90 \text{ }\mu\text{m}$ (at $30 \text{ }^\circ\text{C}$), significantly larger particles are also present. It should be noted that particles of compact metal are observed in the powder sample prepared at $50 \text{ }^\circ\text{C}$. This can be caused by local heating. The presence of such compact metal particles lowers the quality of cobalt powder for manufacturing of superalloys. Lower temperature prevents the formation of compact metal particles and enables the formation of agglomerates composed of particles with the sizes close to the size of primal particles. Due to grinding of the cobalt and hard component powder mixture as necessary pretreatment during manufacturing of superalloy pieces, the ability of powder agglomerates to be broken into smaller particles becomes more important than their size. The presence of compact metal particles that don't break down upon grinding significantly decreases powder quality. The obtained results indicate that Co powder synthesized at $30 \text{ }^\circ\text{C}$ is suitable for the formation of superalloy pieces.

It should be noted that electrolysis parameters and characteristics of the prepared cobalt powder were obtained using a laboratory model with the periodic character of the process. However, the modern trend in the development of chemical technology lies in the transition from periodic to continuous process, which provides better stability in properties of the product. Therefore, the obtained data must be evaluated under conditions of continuous synthesis, before industrial application, which requires developing a model electrolyzer for continuous synthesis of cobalt powder refining process parameters. This also includes process optimization with the aim to further reduce the particle size of cobalt powder after liquid-phase grinding.

The ultrafine cobalt powder without compact metal particles was prepared with a specific power consumption of $48 \text{ kW}\cdot\text{h/kg}$. This value is comparable to the specific power consumption for the synthesis of nickel powder ($51\text{--}53 \text{ kW}\cdot\text{h/kg}$ [30]). Given that the cost of cobalt is more than 4 times higher than of nickel, the effectiveness of the developed method for Co powder synthesis is rather high.

7. Conclusions

1. An electrochemical synthesis method for the synthesis of cobalt powder from the sulfate-ammonium electrolyte at a current density of 100 A/dm^2 has been developed. In order to improve the quality of cobalt powder, it was proposed to introduce ammonia to the electrolyte until $\text{pH} = 11$.

2. Introduction of ammonia to the electrolyte leads to the formation of the brown-red precipitate, which is likely Co^{2+} ammonia complex with low solubility. During storage of the precipitate in the mother liquor for a week, the precipitate has dissolved with the formation of a purple-red solution. By recording cathodic and cyclic cathodic-anodic curves, it was discovered that the solution with dissolved precipitate contained Co^{3+} . It was revealed that the synthesis process occurs in two stages « $\text{Co}^{3+}\text{--Co}^{2+}\text{--Co}^0$ », which results in the increased polarization and formation of ultrafine cobalt powder.

3. It has been determined that lower temperature leads to a smaller particle size of cobalt powder. At an electrolyte temperature of $90\text{--}95 \text{ }^\circ\text{C}$, the powder is very coarse and contains a large amount of compact metal. Lowering the temperature to $45\text{--}50 \text{ }^\circ\text{C}$ resulted in the formation of fine powder, which,

however, contains some number of compact Co particles. It was found that cooling down to 30 °C prevents the formation of compact cobalt particles and results in the formation of coral-like dendrites 35–150 µm long, which easily break into primal particles.

4. Current yield and specific power consumption for cobalt powder synthesis have been calculated for different temperatures. The ultrafine Co powder is formed at 30 °C with a current efficiency of 39 % and specific power consumption of 48 kW·h/kg.

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