Plasma-solution synthesis of particles containing transition metals

K V Smirnova, D A Shutov, A N Ivanov and V V Rybkin

Ivanovo State University of Chemistry and Technology, Ivanovo, 153000 Russia

E-mail: smirnovakv1@gmail.com

Abstract. The paper proposes a new method for the synthesis of powders containing transition metals using a plasma-solution system. The reactor was an H-shaped glass cell, the two parts of which were separated by a cellophane membrane. A discharge consisting of two discharges - with a liquid cathode and a liquid anode - a high voltage is applied to titanium electrodes located above the surface of the solution. Aqueous solutions of zinc, iron, cadmium, cobalt, nickel, and copper nitrates were used as the liquid phase. Under the action of the discharge on the liquid anode, in the region of contact of the discharge with the solution the formation of a colloidal suspension was observed. The kinetics of the process of synthesis of solid-phase particles in solution under the action of a discharge have been studied. The chemical composition and morphology of the formed solid phase have been established. The mechanisms of chemical reactions occurring in the solution under the action of plasma, and the mechanisms of formation of transition metal oxides in the process of calcining the synthesized powders have been proposed.

1. Introduction

Transition metal nanoparticles are used in various industrial and biological applications such as homogeneous and heterogeneous catalysis, fuel cells, sensors and biosensors. They are widely used as conductive pastes, battery materials, magnetic recording media, etc. Due to the semiconducting properties of oxide nanomaterials have been found their application in microelectromechanical systems and optoelectronics. The recent areas of nanoparticles containing transition metals consumption is presented in figure 1.

Plasma-solution synthesis is one of the simple and effective methods for producing nanomaterials. The widespread use of plasma-solution systems is limited by the poor knowledge of the kinetics of processes in the "solution-discharge" system. High energy efficiency can be obtained from a discharge in direct contact with the solution being treated, including a glow discharge. [1, 2] The advantages of such systems is in the fact that when they act on water, a wide range of chemically active particles appear in it, which have both oxidizing and reducing properties. Oxidants are represented by OH radicals (standard oxidation potential \(E^0 = 2.85\) V), oxygen atoms \(E^0 = 2.42\) V), hydrogen peroxide \(E^0 = 1.68\) V), ozone \(E^0 = 1.51\) V), HO₂ \(E^0 = 1.70\) V), and reducing agents - atoms \(E^0 = –2.3\) V) and hydrogen molecules and solvated electrons \(E^0 = –2.68\) V). These particles are formed without the use of any chemical reagents, and the surrounding air as the plasma-forming gas can be used. The action of the discharge also leads to changes in the pH of solutions. Depending on the conditions, both acidic and alkaline media can be obtained.
It can also be noted that the number of works devoted to the study of the kinetics and mechanisms of the formation of ultradispersed materials under the action of gas discharges on solutions is extremely limited. The currently known works devoted to the synthesis of materials in plasma-solution systems are of a pronounced empirical character [2-4]. The description of the processes occurring in the solution is often hypothetical in nature, not supported by experimental data.

In this work, we present the main results and regularities of the formation of a solid phase from a solution of transition metal salts under the action of a gas discharge. This system is an H-shaped cell with two external titanium electrodes. This method is simple to implement, and there is no contamination of the samples by the material of the electrodes, thus, no additional cleaning is required. An additional motivation for using this method is the possibility of synthesis at sufficiently low concentrations (5 mmol/L), which in the future will make it possible to use this method for purifying wastewater from heavy metal ions.

![Figure 1. Application area of nanoparticles containing transition metals.](image-url)

2. Experimental methods
The scheme of the plasma-solution cell and the experimental procedure are described in detail in [5]. In this work, zinc, iron, cadmium, cobalt, nickel, and copper nitrates were used as starting salts (transition metal nitrates Me(NO$_3$)$_x$). The initial concentration was 5 mmol and 100 mmol. The discharge cell had an H-shape, divided into two identical parts by a cellophane membrane. The volume of each part was 100 ml. A direct current discharge was ignited above the solution surface in both cells in air at atmospheric pressure. Thus, the solution in one part of the cell served as the anode (A-cell), and in the other, the cathode (C-cell). External electrodes were made of titanium. The
electrode-solution distance was 5 mm. The discharge current varied in the range of 30-70 mA. After ignition of the discharge, a colloidal suspension is formed in the anode part of the cell for several minutes near the contact of the plasma with the solution. The formation of a solid phase in the liquid cathode is not observed. Obtaining and analysis of particles can be conventionally divided into two stages. First: plasma-solution synthesis (analysis of particles in solution and after drying); Second: calcination of the particles after drying and examination of the resulting oxides.

The process of formation of insoluble compounds consists of transition metals, initiated by the action of a direct current discharge of atmospheric pressure in air on aqueous solutions of nitrates has been investigated. The kinetics of the particle formation process was investigated using the method of turbidimetry. The intensity of the light passing through the layer (1 mm below the surface) of the solution with an AvaSpec-2048FT-2 spectrometer (Avantes, Netherlands) was measured. The optical length was 45 mm. The light source was a He-Ne laser (\( \lambda = 632.8 \) nm).

Measurement of the pH of the solution before and after discharge treatment was carried out using a PHT-028 multi-parameter water quality monitor (Kelilong, China).

The average hydrodynamic diameter of the formed particles was determined by dynamic light scattering (DLS) using a Photocor Compact-Z size analyzer (Photocor, Russia).

For qualitative and quantitative analysis of the phase composition of the powders, X-ray diffraction analysis was used (X-ray diffractometer DRON 3M, Burevestnik, Russia, CuKa radiation). The diffraction patterns were processed using QualX2 software [6] and the open crystallographic COD database [7].

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of the obtained precipitates were performed on a STA 449 F1 Jupiter thermal analysis instrument (Netzsch, Germany). The temperature range was 20–900°C at a heating rate of 5°C/min in an argon flow using a platinum crucible.

The shape of the particles, their sizes and elemental composition of the powder were obtained using scanning electron microscopy (SEM, Tesla Vega 3SBH, Czech Republic) with an EDX analysis system (Aztec EDS, Oxford Instruments Ltd., England).

3. Results and discussion

Typical visible changes occurring in the anode cells were as follows. After igniting the discharge, the first seconds the solutions are a transparent liquid with a color characteristic of each metal (blue for copper, green for nickel, colorless for zinc and cadmium). During the first minutes, a visible color change is observed in the plasma-solution contact area. After several minutes of plasma treatment, an increase in the area of the colloidal solution and subsequent movement deeper into the cell is observed. The effective rate constants of the solid phase are shown in table 1.

It is well known that plasma is a source of a large number of both charged and neutral particles that can interact with the solution. As shown earlier, the main neutral particles are the •OH and •HO\(_2\) radicals, molecules of nitrogen oxides and H\(_2\)O [8]. At the same time, the solution (at the point of contact of the discharge with the solution) in both cells is heavily bombarded with electrons and ions for the A and C cells, respectively.

Active bombardment of the liquid anode with electrons may lead to the formation of hydroxide anion, for example by the reaction:

\[
H_2O + e = OH^- + H. \tag{1}
\]

Really, the action of the discharge leads to changes in the acidity of the initial solution. The solution in the A-cell becomes alkaline and the solution in the C-cell becomes acidic. The measured pH value after a few minutes of plasma-solution interaction reaches the required value for the precipitation of the solid phase to begin. In this case, the formation of hydroxide compounds in the liquid cathode of solutions of these salts of transition metals is thermodynamically impossible, which was observed experimentally.
In the A-cell the formation of basic low-soluble Me$^{2+}$ salts (hydroxonitrates) and the formation of metal hydroxide are possible.

Metal II nitrate, a salt that is readily soluble in water, is susceptible to hydrolysis, since it is formed by strong nitric acid and a weak base. Hydrolysis proceeds at the Me$^{2+}$ cation with the formation of an acidic environment. Possible processes in solution:

\[
\text{Me}^{2+} + H_2O \rightarrow \text{MeOH}^+ + H^+, \quad (2)
\]
\[
\text{MeOH}^+ + \text{OH}^- \rightarrow \text{Me(OH)}_2 \downarrow, \quad (3)
\]
\[
\text{MeOH}^+ + \text{NO}_3^- \rightarrow \text{Me(OH)}(\text{NO}_3) \downarrow. \quad (4)
\]

The chemical composition and typical particles sizes of the as-synthesized powders of different metals are bring together in Table 1. It should be noted that DLS measurements shows 2 different particles size fractions: nanometers and micrometers. Unfortunately, SEM images of the obtained substances before heat treatment for all metals have a well-developed structure (figure 2).

**Table 1.** Oxide metal particles synthesis in plasma solution system. Discharge current 40 mA. The initial concentration is 5 mmol and 100 mmol.

| Type of particles after calcination | Raw materials of solutions | Particle size | Rate constant, $10^{-3}$, s$^{-1}$ at two discharge currents (mA) | XRD and EDS of precursor |
|-----------------------------------|---------------------------|---------------|-------------------------------------------------------------|--------------------------|
|                                   |                           | The 1st fraction (nm) | The 2nd fraction (μm) | 30   | 70   |                                   |
| Cubic CoO                         | Co(NO$_3$)$_2$            | 50             | 1.2             | 9    | 10   | Co(OH)$_2$; Co(OH)(NO$_3$)$_2$    |
| β-NiO                            | Ni(NO$_3$)$_2$            | 73.5           | 1.2             |      |      | β-Ni(OH)$_2$                       |
| β-CuO                            | Cu(NO$_3$)$_2$            | 23             | 0.97            | 4.4  | 10   | Cu(NO$_3$)(OH)$_3$                 |
| Hexagonal ZnO                    | Zn(NO$_3$)$_2$            | 95.4           | 1.8             | 15   | 22   | Zn(OH)$_2$; Zn(OH)(NO$_3$)$_2$    |
| β-CdO                            | Cd(NO$_3$)$_2$            | 57.3           | 2.7             | 10   | 22   | Cd(OH)$_2$; Cd(OH)(NO$_3$)$_2$    |
| Cubic CoFe$_2$O$_4$              | Co(NO$_3$)$_2$, with Fe(NO$_3$)$_3$ | 92.9          | 1.4             | 5.6  | 19   | (CoO)(Fe$_2$O$_3$)                 |
| (ZnO)$_{0.92}$ (CdO)$_{0.08}$    | Zn(NO$_3$)$_2$, with Cd(NO$_3$)$_2$ | 51            | 3.4             | 1.3  | 12   | Zn(NO$_3$)$_2$OH·H$_2$O, Zn(OH)$_2$, γ-Cd(OH)$_2$, β-Cd(NO$_3$)$_2$OH·H$_2$O |

Calcination of the as-synthesized lead to the formation of metal oxides. The results of thermogravimetric and differential thermogravimetric curves for all metal powders calcination have a similar sequence.

A typical decomposition scheme (TGA) is shown in the figure 3 using the example of powders obtained from solutions of cadmium nitrate.

The first broad endothermic peak at low temperatures (typically up to 200°C) is apparently associated with the stepwise dehydration of nitrates by the reactions:
Me(NO$_3$)$_2$·xH$_2$O → Me(NO$_3$)$_2$·(x-1)H$_2$O + H$_2$O, \hspace{1cm} (5)

Me(NO$_3$)$_2$·(x-1)H$_2$O → Me(NO$_3$)$_2$·(x-2)H$_2$O + H$_2$O, \hspace{1cm} (6)

Me(NO$_3$)$_2$·(x-n)H$_2$O → Me(NO$_3$)$_2$ + H$_2$O. \hspace{1cm} (7)

Figure 2. SEM images of the surface of sediment formed at an initial salt (a) Zn(NO$_3$)$_2$ [9]; (b) Cd(NO$_3$)$_2$[5]; (c) Cu(NO$_3$)$_2$; (d) Co(NO$_3$)$_2$. 

The following peaks (typically after 300°C) can be associated with the following reactions of decomposition of nitrates and hydroxides of transition metals to oxides:

\[ 2 \text{Me(NO}_3\text{)}_2 \rightarrow 2 \text{MeO} + 4 \text{NO}_2 + \text{O}_2, \quad (8) \]
\[ \text{Me(OH)}_2 \rightarrow \text{MeO} + \text{H}_2\text{O}. \quad (9) \]

4. Conclusion
Based on reports available in the literature, it has been established that transition metal nanoparticles are an important class of materials used for various scientific and technical applications. Plasma-solution synthesis is a new and promising method for producing nanoparticles based on transition metals. In despite of the increase in the number of articles devoted to this issue, the mechanisms of the formation of particles in a solution under the action of a gas discharge have not yet been fully studied. In this article, we tried to describe the possible processes occurring during the interaction of a gas discharge with aqueous solutions of transition metal nitrates. In addition, the kinetic regularities of the formation of the solid phase are presented. The chemical composition and morphology of the synthesized and calcined powders were determined by X-ray diffraction spectroscopy (XRD), energy-dispersive X-ray spectroscopy (EDS), and scanning electron microscopy (SEM). The kinetics of the in-situ formation of the solid phase was studied by the methods of turbidimetry and nephelometry. The regularities of the processes occurring during calcination were investigated using thermogravimetric analysis (TGA) and scanning differential calorimetry (DSC).

Acknowledgments
This work was supported by the Ministry of High Education and Science of the Russian Federation, project No. FZZW-2020-0009.

The study was carried out using the resources of the Center for Shared Use of Scientific Equipment of the ISUCT (with the support of the Ministry of Science and Higher Education of Russia, grant No. 075-15-2021-671)
References

[1] Saito G and Akiyama T 2015 J. Nanomater. 2015 1–21
[2] Chen Q, Kaneko T and Hatakeyama R 2012 Appl. Phys. Express 5 086201
[3] Kruszelnicki J, Lietz A M and Kushner M J 2019 J. Phys. D: Appl. Phys. 52 355207
[4] Bruggeman P J et al 2021 J. Appl. Phys. 129 200902
[5] Shutov D A., Smirnova K V, Gromov M V, Ivanov A N and Rybkin V V 2018 Plasma Chem. Plasma P. 38 107–21
[6] Altomare A, Corriero N, Cuocci C, Falcicchio A, Moliterni A and Rizzi R 2015 J. Appl. Crystallogr. 48 598
[7] Grazulis S, Daskevic A, Merkys A, Chateigner D, Lutterotti L, Quiros M, Serebryanaya N R, Moeck P, Downs R T and LeBail A 2012 Nucleic Acids Res. 40 D420
[8] Shutov D A, Smirnov S A and Rybkin V V 2014 High Energ. Chem. 48 391
[9] Shutov D A, Rybkin V V, Ivanov A N and Smirnova K V 2017 High Energ. Chem. 51 65