

PRODUCTION OF NANOPARTICLES UTILIZING WATER STABILIZED PLASMA

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Abstract

Water stabilized plasma torch (WSP®) generates plasma jet with max. plasma velocity in the nozzle exit 7000 m/s and temperature of 25000-30000 K. Reactants injected into the plasma jet undergo complicated radical reactions. Once the reactants leave the plasma jet, the reactions can become either a primary decomposition or secondary synthesis. Interaction of plasma with injected reactants depends on energy settings of the WSP plasma torch and lasts from 5 to 10 ms. Droplets of inorganic compound solution are fed to the plasma jet by pressurized spray nozzle device. Compounds of Ag^I, Al^{III}, Ti^{IV}, Pt^{IV}, V^V, and Cr^{VI} undergo decomposition in the extremely high plasma temperature and the decomposed products are collected in liquid separators. Outcome of the decomposition can be altered by choices of carrier gas and shrouding atmosphere. Size of the produced nanoparticles in unsettled fraction is from 10 to 200 nm and depends primarily on concentration of inputting aerosol particles. The reaction must be interrupted every 15 seconds to protect the periphery equipment from extremely high temperatures. In the case of 15 seconds reaction time and use of saturated solutions at 20°C, one can obtain colloidal solutions with silver, platinum, alumina, titania, vanadia, and chromia nanoparticles in concentrations of 3 to 180 mg/l. This production method is being further modified for the purpose of plasma deposition of nanoparticles on special substrates by means of solution precursor plasma spraying (SPPS or LPPS).

Keywords: Ag, Al, Ti, V, Cr, Pt – nanoparticles; nanoparticles morphology; plasma spraying; water stabilized plasma; photon spectroscopy;

1. INTRODUCTION

Nanoparticles of silver, gold, and platinum are subject of basic research and commercial applications not only for their optical and catalytical properties, but especially for their biological activity. Oligodynamic properties of gold and silver are known from antiquity, properties of platinum were discovered a few hundred years later, but their nanometric form gives them a new potential for great applications. Synthesis of metal nanoparticles by chemical methods is based on reduction of their salts in presence of chemicals that modify their morphology and size [1]. Tollens reaction is one example [2]. Metal nanoparticles are commercially offered in the form of suspensions with water-soluble polymers or in solutions containing up to 100 mg/dm³. Their aggregate stability in solutions is modified by various surfactants. Significance of inorganic compounds with nanometric dimensions is shown mainly in the fields of heterogeneous catalysis or powder metallurgy. Their synthesis is hindered by their difficult separation and possible pyrophoricity. There are other problems arising while processing of precursors into nanometric suspensions from incidental ions that cannot be removed from the solution and can later interfere in some applications [3]. The aim of this study is to verify a possible route of preparation of nanometric metal particles and their oxides by thermal decomposition of suitable compounds in extremely high temperatures of thermal plasma generated by WSP torch.

2. EXPERIMENTAL

Colloidal solutions of nanoparticles of silver, platinum, and Al, Ti, V, Cr oxides were obtained using a modified equipment described in paper about Solution precursor plasma spraying (SPPS) [4]. The equipment uses a graphite tube placed in the axis of plasma jet, into which water solutions of precursors (Table 1) are fed by a graphite nozzle with adjustable diameters. Feeding of aerosol droplets was accomplished by a system of low pressure atomizer. One end of the graphite nozzle was inserted into the graphite tube in which a stream of transport gas (air or nitrogen) carried off the aerosol droplets towards a place which was exposed to the front portion of the plasma cone generated by high-power WSP torch (up to 160 kW). The temperature field in the graphite tube is 300 mm long and assumes a conical shape. The graphite nozzle orifice was placed 50 mm in front of the graphite tube orifice and the output temperature was 25 000°C. The temperature of plasma jet dropped to approximately 4000 °C in the middle of the tube where the aerosol was injected. The solvent (i.e. water) of the solution precursors was evaporated in 3 to 6 milliseconds given the plasma jet velocity of approximately 900 m/s. The precursors were then thermally decomposed (to elemental metals in case of AgNO_3 a H_2PtCl_6 or to oxides in other cases), melted, spheroidized due to high surface tension, and finally rapidly condensed while coming into contact with water surface. The water was contained in a vessel (volume of 3 liters) placed 600 mm away from the output

nozzle of the generator. Construction details of the equipment/generator are shown in Fig. 1. Temperature field in individual equipment parts was monitored by thermal camera Micro-Epsilon TIM 160.



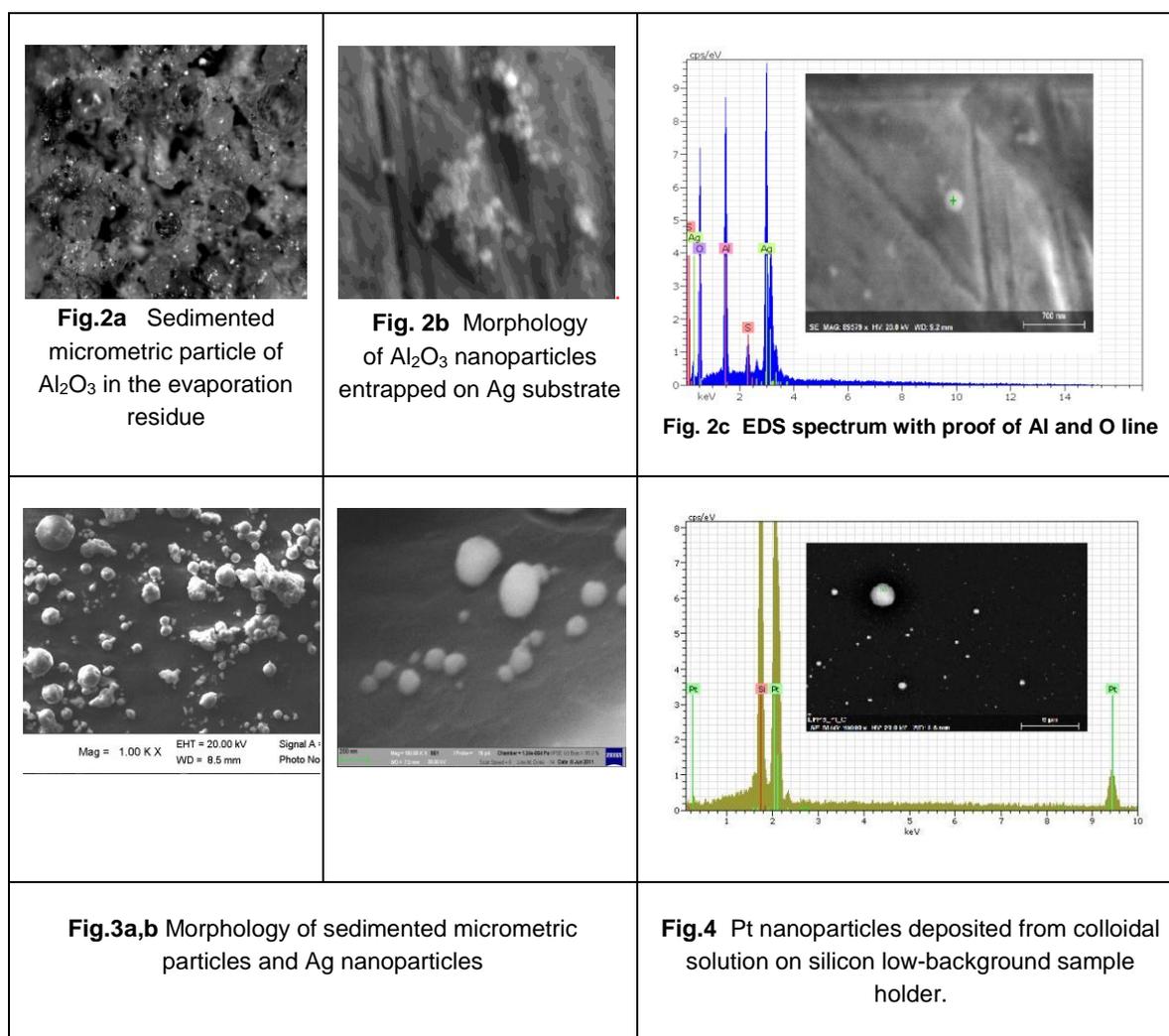
Fig.1 Overall view of the apparatus, detail of the graphite nozzles and picture of the ongoing experiment of plasma atomization

Tab. 1. Characteristic of the precursors and its thermal plasma treatment products							
	Ag	Ag	Pt	Al	Ti	V	Cr
precursor	AgNO_3	AgNO_3	H_2PtCl_6	$\text{Al}_2(\text{SO}_4)$	K_2TiF_6	NH_4VO_3	$(\text{NH}_4)_2\text{Cr}_2\text{O}_7$
concentration w	0.1	0.2	0.0025	0.1	0.01	0.005	0.3
Product (XRD identification)	Ag	Ag	Pt	Al_2O_3	$\text{TiO}_2 + \text{TiO}_x$	$\text{V}_2\text{O}_3 + \text{VO}_2 \text{ VO}$	Cr_2O_3
Ions in solution $\mu\text{mol/l}$	NO_3^- <800	NO_3^- NO_2^- <20	* Cl^- , ClO^- *	SO_4^{2-} <1140	K^+ 115	NO_3^-	NO_3^-
pH	3.02	3.26	3.8	2.0	6.3	3.8	3.56
Mean particle size (nm)	19.4	82.9	21.0	164	122.4	58.7	92.6
** Colloidal product concentration (mg/l)	46.9	70.8	2.4	180	2.8	0.2	6.9
* only semiquant. analysis, ** After sediment filtration							

In the analytical part of this paper, the synthesized nanoparticles are studied by scanning electron microscope equipped with EDS spectrometer (SEM: Carl Zeiss SMT EVO MA 15, EDS: Bruker XFlash 5010). Analysis of dissolved compounds by AAS method was performed using a spectrometer for flame atomization technique (Spectr AA880 by Varian), the content of nitrates and nitrites was determined by spectrophotometry. pH was determined using pH-meter (Eutech Instr. pH 510). Photon correlation spectroscopy (dynamic light scattering) was used to determine size distribution of the nanoparticles. Measurement of Zeta potential was based on electroforetic mobility evaluation by means of Doppler laser microelectrophoresis. The measured signal was evaluated via the Stokes-Einstein relation and correlation function. The measurement was done using He-Ne laser at a wavelength of 632.8 nm and power of 4 mW. The detector was positioned at an angle of 173° with respect to the incident laser light. This configuration minimizes signal coming from large particles (e.g. dust) and enables measurement at high concentrations. The measurement was carried out using device Zetasizer Nano ZS by Malvern.

3. RESULTS AND DISCUSSION

Particles collected in the liquid collector spanned a wide size range from tens of nanometers to units of micrometers. After completion of the collecting process, the sedimented particles were separated from the clear solution by filtration using S4 frit. Micrographs of the sedimented particles (Fig. 2 and Fig. 3) show the largest particles to be of 2 - 5 μm in diameter. These large particles are mostly not spherical and their deformed shape is probably due to impacting of the molten droplets against water surface. Larger fraction of the deformed particles was found when using more concentrated solutions of precursors. Smaller particles assume regular spherical shape.

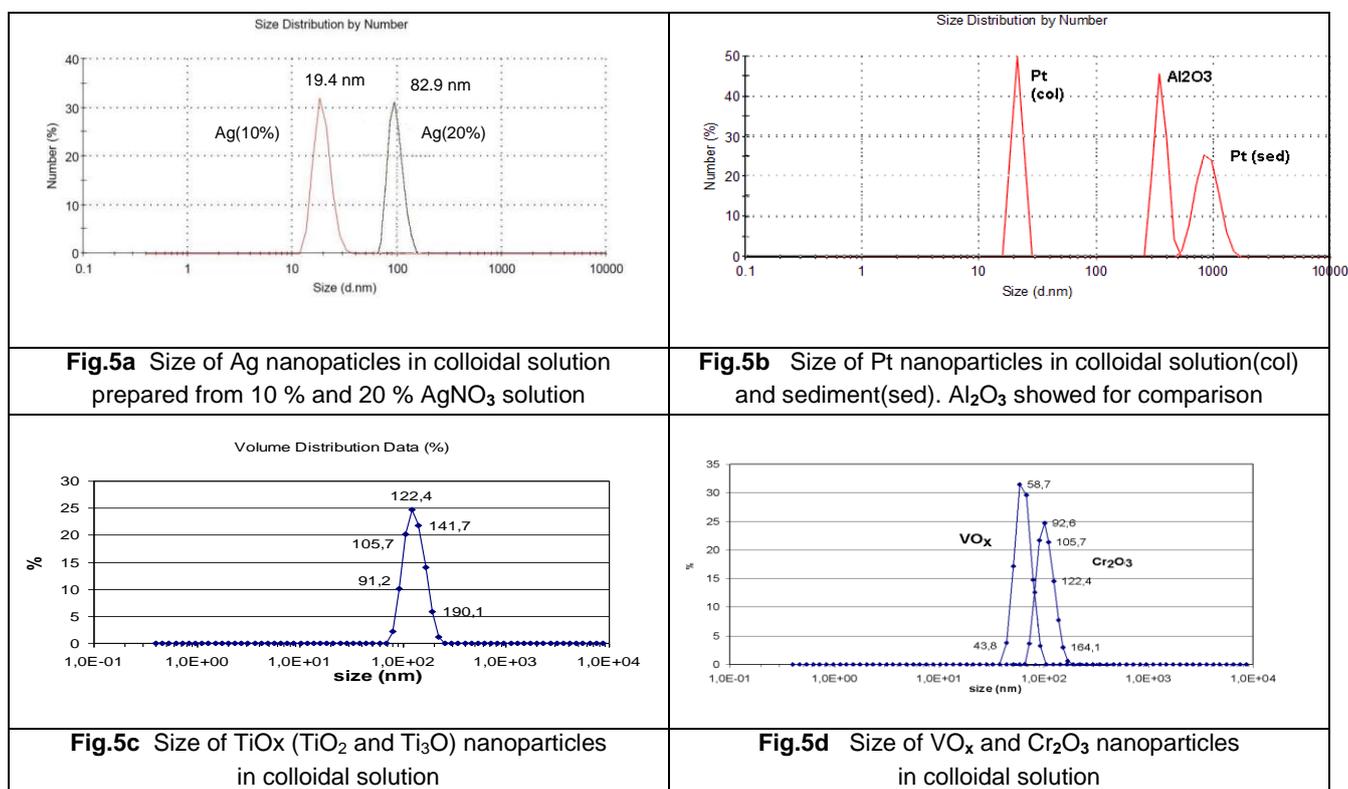


Formation of both nanoparticles and micrometric particles during one spraying session may be explained by various trajectories of solution droplets injected into the plasma jet due to their different size and velocity (momentum). Due to the very low density of water stabilized plasma (2 mol H₂O/min in idealized volume of 880 – 4100 dm³), some aerosol droplets can pass through the plasma and impact the opposite wall of the heated graphite tube where they form micrometric particles. External cooling keeps the wall temperature at 1200±100°C as controlled by thermo camera. Such temperature of the inner wall is high enough to enable thermal decomposition of the dried precursor followed by local aggregation and gradual detachment of the aggregates and their fall into the water collector. Hydrodynamic and aerodynamic conditions have major influence on the process. It was shown that dilution of solutions by 10% (especially considering NH₄VO₃ with solubility of 0.5 g/100 ml/20°C) can substantially minimize occurrence of the large particles. Detailed research of this issue from the chemical and engineering point of view will be presented in the next paper which is under preparation.

Measurement of particle size for colloidal solutions after filtering of sedimented particles is illustrated in Fig. 5. Average size of the nanoparticles may be evaluated from

$$\phi = 2r = 2 \cdot \sqrt[3]{\frac{3V \rho_{(sol)} w_{(prec)} mW_{(prod)}}{4\pi \rho_{(prod)} mW_{(prec)}}} \quad (1)$$

where Φ – diameter of particle, w – the solution concentration (wt%), $\rho_{(sol)}$ – density of the precursor solution, $\rho_{(prod)}$ – product density; mW – molar mass; V – volume of the droplet of the original precursor solution produced by the spray nozzle. Volume of the droplet is significantly influenced by the surface tension of the solution. For example, higher surface tension of the (NH₄)₂Cr₂O₇ solution ($\gamma = 78.97 \text{ mNm}^{-1}$ as measured by stalagmometric method) provided by its higher concentration when compared to NH₄VO₃ (surface tension of 74.56 mNm⁻¹), results in a higher diameter of the sprayed solution droplets and therefore bigger size of the nanoparticles of the solid product (mean size 58 nm and 122 nm – see Fig. 5d).



After previous measurements, the colloidal solutions were evaporated on the silicon wafer, which served also as a low-background sample holder, and subjected to XRD analysis.

In case of Ag and Pt, XRD analysis proved decomposition of their precursors on individual elements. Morphology and EDS spectra of the nanoparticles are illustrated in Fig. 2 and Fig.3. XRD analysis of the Al^{III} , Ti^{IV} , V^{V} a Cr^{VI} precursors is a subject for further research. For example, extreme thermal decomposition of aluminium sulphate in plasma leads to formation of dominant cubic gamma Al_2O_3 phase with spinel structure $\text{Al}_{2,67}\text{O}_4$ – Fd-3m instead of expected trigonal corundum which was according to the semiquantitative XRD analysis present with less than 10% of mass fraction. This phenomenon was also in the field of plasma chemistry already described in 1976 by Shirasuka [5]. From the image of sedimented micrometric products (see Fig.2a), higher amount of transparent spheroidal particles is apparent than it would correspond to the amount of non-metallic corundum phase. Assuming that the spheroidal transparent particles could be formed only from the molten aluminium oxide, spheroidization of the cubic gamma phase is a newly observed phenomenon which will be a subject of further research. The produced titanium oxide is also not homogeneous, as beside rutile, high contents of cubic TiO and suboxide Ti_3O were found in the evaporation residue as well. Accordingly, decomposition of the ammonium vanadate led to the formation of multi-phase product, where besides V_2O_3 also VO_2 and cubic VO were identified. Content of the expected V_2O_5 was below the detection limit of the used method. Contrariwise, formation of the chromium (III) oxide (Cr_2O_3) from the ammonium dichromate was unambiguously proved by XRD.

3. CONCLUSION

Presented introductory experiments with plasmo-thermic decomposition of aqueous solutions of silver, platinum, aluminium, titanium, vanadium and chromium at extremely high temperatures provided several findings which will serve for further modification of nanoparticles fabrication in order to achieve even smaller particle sizes and improve process efficiency. Based on the qualitative measurements of the particles content in both colloidal solution and evaporation residue, it may be stated that stoichiometric losses in the used apparatus were not higher than 5 %. Reprocessing of the undesirable oversize powders (micrometric) using chemical processing is then relatively easy. Regarding costs of energy needed to evaporate the water and its transformation to the superheated steam, we can assume known values of the water evaporation heat $\Delta H_{\text{evap}} = 40,6$ kJ/mol, specific heat $c_p = 37,5$ J/mol and typical output power of WSP system 160 kW and efficiency of 60 %, resulting in the value of 60,9 kg H_2O /hour at 1000°C. Further calculations incorporating energy needed to heat up the solid particles formed from the evaporated solution at temperatures significantly higher than their melting point or temperature of thermal decomposition are not straightforward since for so high temperature range, the thermal capacities and other thermodynamic properties have to be roughly extrapolated (if some data are available at all). However, the energy needed is comparable to the energy needed to heat the injected water. It may be therefore estimated that due to the low concentrations of the solutions, up to 60 kg of solution may be processed per hour.

Obtained results also indicate that smaller size of the produced nanoparticles may be achieved when using less concentrated solutions and that the size-concentration relation is proportional. For example when using 10 wt% AgNO_3 as the input solution, approximately 6 kg of AgNO_3 may be processed per hour into nanometric particles (colloidal solution with powder size <100 nm and concentration up to 50 mg Ag/l). For the solution of 20 wt% AgNO_3 , content of produced colloidal nanometric particles is decreased while the amount of micrometric particles is increased. In case of platinum with 20 ± 5 nm colloidal particles (see Fig.4), concentration of 2.4 mg/l was achieved and corresponding volume of particles with size above 1 μm were produced in the sediment. However, products obtained in this way always need further processing in order to stabilize the nanoparticles since due to the ageing of the solutions colloidal stability of the nanoparticles is deteriorated and their agglomeration takes place. Due to this effect, some of the suspensions showed after two months no significant amount of nanoparticles when tested by the dynamic light scattering method. It is however possible to stabilize the colloidal suspensions by surfactants modifying surface tension of the liquid and Zeta potential of the nanoparticles. Regarding the presented images obtained from the scanning

electron microscopy, it has to be stated that some agglomerates could be formed during the sample preparation.

Measurement of Zeta potential demands a rather high nanoparticle concentration which was in our case obtained only for aluminium oxide. In this case, potential value was -4 mV. Increase in the stability of colloidal solutions may be achieved also for example by change of pH to the value of Zeta potential more far from isoelectric point (minimally +40mV resp. -40mV). During plasma spraying in the open atmosphere, nitrate and nitrite ions are formed which may be absorbed by the produced colloidal solution, and increase the acidity of the solution up to pH = 3 (in case of sulphate ions up to pH = 2). This phenomenon may be controlled by so called shrouding by inert gas, which prevents introduction of the ambient atmosphere into the plasma jet, or by reactive gasses. In this way, stability of the produced colloidal solution as well as the surface of the resulting nanoparticles may be easily modified.

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