Tungsten particles fabrication by a microjet discharge

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Abstract

As a consequence of interaction of a microjet discharge with the tungsten electrodes, tungsten material is released to plasma, and tungsten particles, of submicron size, are formed. The obtained particles were analyzed to establish a correlation of their morphology, size distribution and chemical composition with the discharge configuration and distance to collector. Experimental conditions were identified leading to spherical tungsten particles.

1. Introduction

The interest for nano and microparticles is increasing due to their occurrence in various applications [1], such as multi-functional biosensor-chips, by using Ag-coated polystyrene particles for glucose sensing [2] to textile industry, where mechanically alloyed MnAl particles are used for de-colorization of azo dyes compounds [3]. In medicine, AgNPs particles, used for improving wound healing, offer a new perspective for antimicrobial properties [4], and as drug delivery, AuNPs represent a valuable candidate for targeted therapy in pancreatic cancer [5].

Particles are present also in photoluminescence applications [6], solar cells, by using Si nanoparticles [7, 8], and so on. In addition, there are also concerns about the pollution with particles (e.g. iron, copper, nickel, tungsten, oxides) of urban atmosphere, terrestrial and marine environment caused by the human daily activities. Such pollution examples were reported from all over the world. Fe-containing particles, found in the atmosphere of Shanghai, could be assigned to anthropogenic sources of iron/steal industrial activities, and also, ultrafine particles, like black carbon (BC), have been tracked and investigated from the traffic emission, located near Metro facility, in Philippines. Moreover, metallic elements (e.g. Zn, Fe, Mn) and isotope of Pb were detected in wet precipitation, in South America urban areas [9–11]. In this line, the retention of radioactive particles (e.g. from U, Pt) in soils and sediments represents an important topic for investigating the impact over environment [12].

Particles are present in the marine environment, with a high potential of affecting the organisms living in the sea and oceans. Furthermore, was analyzed the effect of CuNPs and NiNPs over sea urchin (Heliocidaris crassispina) and Paracentrotus lividus organisms. In addition, the contamination with W, Mo and vanadium NPs was investigated, due to their presence in the marine basins, and also in Baltic Sea. At various concentrations, most of metallic NPs are toxic for the marine biodiversity, though NPs like Zn were found essential for these organisms [13–18]. In this line, the processes of particle generation are intensively studied. An interesting material is Tungsten, known as a transition metal with outstanding physical and chemical properties, a high melting point, around 3400 °C, having electrochemical properties [19], and a low sputtering rate. Tungsten and tungsten oxides are involved in large-scale applications in fusion technology, where we can note the importance of W material in the divertor region of ITER (International Thermonuclear Experimental Reactor) facility [20–22]. In addition, - one can find this attractive material used in defense applications, such as small caliber ammunition, armor plating, and high kinetic energy penetrators [1, 23]. In development of gas sensors devices, tungsten oxide NPs are used [24–26]; moreover, by using tungsten trioxide particles we can obtain a random lasing emission [27]. Tungsten oxide is present also in photochemical aerosol generators [28, 29]. With respect to fusion technology, due to plasma—wall interactions, tungsten particles are produced, having various shapes and sizes, and presenting a potential danger for humans and environment [21]; thus, details on particles formation at plasma contact with tungsten materials, and their properties are of wide interest.

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There are many methods of tungsten particle fabrication, which roughly can be divided in chemical and physical. Chemical methods involve a decomposition of the metallic compounds, for example, tungsten particles could be obtained by using chemical reduction of WCl₆ \([\text{E1}]\). Physical approaches for particles production include laser ablation in liquids \([\text{E2}]\), sputtering combined with gas aggregation \([\text{E3, E4}]\) and so on. In this paper, we focus on the generation and characterization of tungsten particles, produced with a plasma microjet, as result of plasma-electrode interaction. In spite of the fact that the experimental conditions are different from those used in fusion reactors, many of the basic processes are similar. In the present case, the erosion/melting/vaporization of the electrode surface at the contact with the microjet is observed (as discussed for Cu in \([\text{E5}]\)), followed by the solidification of droplets, nucleation and condensation of the removed material in the flowing plasma. In addition, the particles are produced without any use of chemical precursors, thus increasing the relevance of results for applications where pure materials are requested.

The paper has the following structure: first, the experimental details are presented. In Results and Discussions section, the peculiarities of this method of particle production are presented, and the characteristics of the particles produced in various conditions are described. Finally, we show that experimental configurations and parameters leading to tungsten particles with well-defined characteristics can be identified, which promote this technique as a facile, cheap and safe method for tungsten particle production at a laboratory scale.

2. Experimental

2.1. Particle generation setup

The experimental setup in which W particles were produced is schematically shown in figure 1. The system consists of two main parts: the plasma source and the deposition chamber.

The plasma source, mounted in vertical position on the top of the deposition chamber, has cylindrical geometry. It contains a central RF electrode manufactured from W introduced in a larger, insulating, dielectric tube. The upper end of the tube is used for gas entry, while the lower end leans on the flat surface of a metallic nozzle. The nozzle is grounded and is tightly connected to a water-cooled stainless-steel jacket externally surrounding the dielectric tube. By applying radiofrequency power (13.56 MHz) a discharge is established in the gap between the RF electrode and the nozzle. The discharge expands under gas flow, in the deposition chamber, as a plasma jet \([\text{E6}]\).

The deposition chamber accommodates the substrate (collector) holder and is attached to a vacuum system. By reaching the pressure for about 5 \(\times 10^{-2}\) mbar, the vacuum system is switched off. The gas inlet is provided through the plasma source. After filling the chamber with argon up to atmospheric pressure, an over-pressure...
non-return valve help the maintaining a clean argon atmosphere during the process. Thus, all depositions were performed at atmospheric pressure under continuous purging with Argon gas. Tungsten particles were produced from the eroded electrode, which is placed inside the plasma source, and were transported by the Ar plasma jet, through the nozzle, to the collector. The operating parameters were: 4000 sccm flow rate Ar gas, 200 W input power and pressure 1 atm. A deposition time of 20 min was used in all cases.

In this paper, we discuss two types of nozzle configurations (figure 2): the first one consists of a the stainless-steel disk in which was inserted a W pellet, with an inside aperture of 2 mm (figure 2(a)); in the second configuration, in the stainless-steel plate was inserted a W tube, with a length of 27 mm, and a diameter of 2 mm (figure 2(b)).

2.2. Investigation of plasma and particle properties
The plasma discharge was investigated with the OES high-resolution spectrograph (0.01 nm resolution) FHR 1000 Jobin Yvon. OES spectra were recorded by using an optical fiber, with an aperture of 60 μm, for a step—and—glue acquisition with an exposure time of 0.05 s and 20 accumulations.

The obtained W particles presents a specific arrangement on the Si collector: a central region and a marginal region. For both nozzle configurations, we have produced W particles by using various nozzle—to—substrate distances, in the range of 6 mm—40 mm. We studied, by varying the nozzle configuration and the nozzle—to—substrate distances, the influence of the parameters on the shape, sizes, and the arrangement of particle on substrate.

The particles morphology was analyzed by using the Scanning Electron Microscope (SEM) FEI Inspect S50. By loading SEM images in Imagej software, we obtained the statistical distribution of the particles upon size. Usually, particle dimensions can be measured automatically from SEM images with dedicated programs [36], but in this case, due to their multi-layered deposition, we chose to do it manually from the initial SEM images. In order to highlight only the morphology of the particles, the images presented in this paper were cropped from the original SEM images.

The elemental composition of the particles was evaluated by using a scanning electron microscope (FEI, model Inspect S) equipped with energy dispersive x-ray spectrometer (Element Silicon Drift Detector), and by using an energy of 5kV. Also, x-ray Photoelectron Spectrometer (XPS) K-Alpha Thermo Scientific (ESCALAB™ XI+), equipped with a monochromatic AlKα x-ray source, was used to establish the chemical composition of the obtained particles. The XPS spectra were measured by using an energy of 100 eV, and the obtained spectra were analyzed with Advantage software.

3. Results and discussions
3.1. Spectral characteristics of the microjet
In the described experimental configurations, the discharge is shaped as a constricted/columnar jet, which is anchored with one end at the electrode surface and expands at the other end through the plate/tube nozzle in the deposition chamber.
In Figures 3(a) and (b), we can observe the OES spectra of the atmospheric microjet. Tungsten lines (W I) appear at 330.0 nm, 361.6 nm, 400.8 nm (the most intense W line observed), 407.3 nm and 429.3 nm. Also, we can identify the presence of spectral systems of radicals OH ($A^2\Sigma^+ - X^2\Pi$) and also the systems $\gamma$NO ($A^3\Sigma^+ - X^2\Pi$) and $\gamma$NH ($A^3\Pi - X^3\Sigma$). The atomic oxygen appears as triplet at 777.14 nm, 777.41 nm and 777.53 nm.

3.2. Morphological properties and size distribution of the obtained particles

In Figure 4, we present, as example, SEM images of the deposit with W particles collected on a Si substrate. The low magnification image (Figure 4(a)) shows that the particles do not present a uniform arrangement on substrate, two major regions being identified: the central region and the marginal region. Most particles are deposited in the central region and, in this example, are well individualized (Figure 4(b)). The marginal region (figures 4(c) and (d)), covers the rest of the Si collector surface and the predominant morphology is cauliflower-like. As observed from figures 4(b) and (d) the sizes and morphologies differ significantly in the two regions.

We analyzed the shape and the size distributions of the produced W particles, for the two plasma source configurations: with plate nozzle (shown in Figure 2(a)) and tube nozzle (shown in Figure 2(b)). Also, the nozzle—-to—substrate distance was varied form 6 mm up to 40 mm.

In Figure 5 we show images of the W particles obtained in the central region of the deposition by using the plate nozzle, for 6 to 35 mm nozzle - substrate distances. At 6 mm we obtained individual spherical W particles. By increasing the distance, we can identify the changes that occurred in the particle’s morphology. Starting with 15 mm, W particles morphology tends to suffer a transformation from spherical to cauliflower-like shape. This process denotes that the particles are sticking together, forming agglomerates with various dimensions. In addition, it is observed that the agglomerates are formed from small size particles.

Figure 6, presents images of W particles deposited in the central region with the tube nozzle. In contrast with Figure 5, here we can observe the presence of the spherical shape even at bigger distances, from 6 mm up to 20 mm. The cauliflower morphology is observed as well at large distances, where, accidentally, spherical individual particles can be also detected.

The size of the particles is an essential characteristic in applications (e.g. gas sensors). In this line, we investigated the W particles size distribution in the central and marginal zones, for the plate and tube nozzle configurations and for various nozzle—-to—substrate distances (6 mm, 10 mm and 15 mm).

The investigated area is of 35.52 $\mu$m$^2$ for both central and marginal zones. It is worth mentioning that at low distances individual particles were measured, while at large distances the distributions describe the size of the formed agglomerates, with cauliflower-like morphology.

The size distributions of the W particles obtained with the plate nozzle are shown in Figure 7. In the central zone, we can observe a tendency of increasing the particles size with distance, from a mean diameter of 176 nm (at 6 mm), up to a mean diameter of 604 nm (at 15 mm). Also, by increasing the nozzle—-to—substrate distances, the widening of the histograms is noticed. In the marginal zone, where the numbered particles represent agglomerations, the dimensions are only slightly dependent on distance. For example, in this zone the mean particle size in the range 600–800 nm, whatever the distance from nozzle.
Figure 8 presents the particles size distributions in case of using the tube nozzle, for 6 mm, 10 mm and 15 mm nozzle to substrate distances. At 6 mm distance, the size distribution is narrow, indicating that the particles present close dimensions, and with a mean size of around 157 nm. By increasing distance, the mean size...
of the particles increases and the histograms are larger indicating the existence of multiple particles categories. The mean particles dimension increases up to 347 nm for a nozzle—substrate distance of 15 mm.

Comparing to the plate nozzle, particle sizes are smaller in the case of tube nozzle configuration, at same distances for both central and marginal regions. In the marginal zone, an increase of size with distance is observed in case of nozzle-tube configuration, while it is difficult to establish a tendency in case of plate nozzle configuration.

3.3. Particles chemistry

3.3.1. EDS measurements
EDS measurements were made to highlight the presence of Tungsten in the obtained particles. For this analysis, in order to avoid the interference of W lines with the substrate Si lines, we have used a copper substrate to collect the particles. The recorded EDS signal was recorded from a small size area 143 $\mu$m$^2$ of the central zone of the deposition.

In figure 9 we can observe that particles composition includes tungsten (62.2%), oxygen (37.8%) and small quantities of carbon. Also, copper is not present in the results, indicating that the deposit of W particles on the substrate is thick enough for a reliable measurement.

More details on the composition of particles were obtained from XPS investigations.

3.3.2. XPS measurements of the obtained particles
XPS measurements were made for investigation of the chemical composition and bonding states in the obtained particles, for both nozzle configurations (plate nozzle and tube nozzle) at 6 mm nozzle—substrate distance. We did not investigate the central and marginal zone separately, the recorded signals corresponding to both zones. The survey spectra are presented in figure 10.

The atomic concentrations of the elements are presented table 1. Oxygen, Carbon and Nitrogen elements are incorporated by particles. Presence of Oxygen and Nitrogen can be correlated with the impurities from the process atmosphere, as detected also by the OES. In our case, carbon represents a normal contamination from the ambient atmosphere.

Aiming to assess the contamination effects, we performed etching at the surface with argon ions for 15 s. The signals of Carbon and Nitrogen elements almost disappeared, and the Oxygen quantity increased; so, in XPS the particles appear as formed dominantly from tungsten oxides. The origin of oxides is nevertheless difficult to interpret after depth profiling, because as other authors commented the exposure of tungsten particle deposits to argon ions beams leads to oxidation, even if it is performed in high vacuum [37].

In figures 11(a) and (b), the deconvolutions of W4f region recorded for both plate and tube nozzle cases, at 6 mm distance, are presented. By using the plate nozzle (figure 11(a)), the presence of the W metallic doublet is observed at 31.18 eV (W4f$^{7/2}$) and 33.29 eV (W4f$^{5/2}$) with a contribution of 19%, the WC doublet at 31.92 eV.
and 33.99 eV (W4f5/2) with a contribution of 44.73%, the WO3 doublet is observed at 34.86 eV (W4f7/2) and 36.97 eV (W4f5/2) with a contribution of 34.53%.

In the case of tube nozzle (figure 11(b)), the presence of the WO2 doublet is observed at 34.02 eV (W4f7/2) and 36.09 eV (W4f5/2) with a contribution of 37%, the WO3 doublet is observed at 35.75 eV (W4f7/2) and 37.89 eV (W4f5/2) with a contribution of 61%.

As can be seen the predominant component is tungsten trioxide, for both plate and tube nozzle configurations. Figure 12 presents the dependence of the WO3 component upon the nozzle to substrate distance, for both nozzle configurations. From the results presented in figure 12, the contribution of the tungsten trioxide is more intense in the particles obtained with the tube nozzle. While at large distances the curves look similar, indicating a WO3 content increasing with distance in the range 60%–90%, at 6 mm the WO3 content is much higher in the tube nozzle configuration. This behavior can be explained by the much higher temperature attained by the vapors during the transport inside the W tube; indeed, in this case, as can be even visually observed, the tube becomes hot red during experiments thus favoring faster oxidation in the presence of gas impurities. It is worth mentioning that pure tungsten bonding was

Figure 7. Case of plate nozzle geometry: dependence of size distribution histograms upon distance, for the central (upper row) and marginal (lower row) regions.
detected at short distance (figure 11(a)), indicating that metallic particles were formed initially, which are oxidizing during the transport to the collector.

3.4. Particle formation and transport

The physical situation in the present discharge relates to the behavior of plasmas when pressure is increased toward atmospheric values. Pressure increase leads to instabilities and to plasma constriction, denoting the tendency to arc transition. Such phenomena were examined previously by us, for an electrode geometry similar to that used in the present paper, in [38]. We have shown that by RF power control and using high gas flow rates we can attain stable situations at atmospheric pressure in which plasma can be either homogeneous, either constricted. In the constricted regime, the plasma column remained anchored on the RF electrode in a well-defined, small area zone (spot). OH radical emission simulations demonstrated that gas temperature in the constricted column is higher (but still in the range of room temperature) compared to the homogeneous plasma, and this temperature increases with power increase. In the constricted regime, the main part of current passes through this spot area, and it is expected that heat dissipation proceed at this zone, which may be thermally affected if power is high enough. Morphological investigations of the electrode surface were performed to

Figure 8. Case of tube nozzle geometry: dependence of size distribution histograms upon distance, for the central (upper row) and marginal (lower row) regions.
Figure 9. EDS measurement of W particles from the central area of the deposit obtained for $\Phi_{Ar} = 4000$ sccm, $t = 20$ min, $Prf = 200$ W (tube nozzle configuration with 6 mm nozzle to substrate distance).

Figure 10. XPS results: Initial survey spectra for tube/plate nozzle geometry (red & blue line); 15 s sputtering survey spectrum for plate nozzle geometry (green line).

Table 1. Atomic concentration of elements at surface of particles.

| Element | Plate Nozzle initial (6 mm) | Plate Nozzle 15s Ar sputtering (6 mm) | Tube Nozzle initial (6 mm) |
|---------|-----------------------------|--------------------------------------|-----------------------------|
|         | At (%)                      | At (%)                               | At (%)                      |
| O1s     | 38.82                       | 65.65                                | 41.67                       |
| C1s     | 29.74                       | 3.5                                  | 29.9                        |
| W4f     | 21.73                       | 30.63                                | 14.97                       |
| N1s     | 9.71                        | 0.22                                 | 0.52                        |
provide evidence for this process [34]. SEM images recorded at the spot area, for an applied power of only 20 W, are presented in figure 13.

On the low magnification image in figure 13(a) the plasma affected zone is clearly seen. Moreover, in the high magnification SEM image presented in figure 13(b), recorded at the margin of the affected zone, droplets are observed, solidified as result of vicinity with the colder region of the electrode around the spot area. The images indicate that during plasma operation the local temperature at spot place is high enough to produce melting, even in this case of W material. Therefore, it is naturally to assume that big particles observed on the collector originate from the droplets detached from the hot area and solidified at the contact with the colder Ar gas. Because of their size and large mass, these particles are reaching the collector by inertial impaction. Besides, a certain degree of material vaporization occurs as well, and W vapors are provided to plasma, as clearly demonstrated by the presence of W emission lines in the spectra. These atoms may contribute by attachment to bigger particle growth, but are also involved in the usual processes of particle nucleation and growth by atomic addition. Consequently, a second category of particles should be observed, of small size, which attains the collection zones by diffusion and gas entrainment. These particles are negatively and positively charged and agglomerate by electrostatic interaction, process consistent with the SEM images and the distribution of sizes determined at large collector distances. Other phenomena involved in particle transport that can be invoked,
related to electrical forces and thermophoresis, have presumable a little effect here because the electrical fields and temperature gradients are small downstream the nozzle.

4. Conclusions

Formation of tungsten particles was observed as effect of a plasma microjet action on the electrodes, in atmospheric pressure discharges with plate and tube nozzle electrode configurations. On the collectors, the deposit containing tungsten particles presents two zone, central and marginal; the morphology and size of the particles depend on the zone and distance to the nozzle. Spherical tungsten particles, in the hundreds of nanometer range, were obtained in both configurations, at short distance. However, in case of tube nozzle configuration, the spherical morphology is preserved at much larger distance, up to 20 mm. The particles obtained with this type of nozzle, show also a smaller size, and the deposition process shows better stability. As concerning the marginal zone, the deposits present agglomerations of much smaller particles, of tens of nanometer, coupled in cauliflower morphology. The formed tungsten particles are very prone to oxidation: XPS results showed that for both nozzle configurations, oxidation was an active process, the amount of oxide increased with the nozzle-to-substrate distance. For this experiment we did not proceed oxide reduction in hydrogen atmosphere. Both morphologies, spherical and agglomerated particles were observed also as dust in fusion experiments.

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