4.1 Introduction

Owing to the superior material properties of tungsten, like very high melting temperature (3410 °C), hardness (3.43 GPa), low vapor pressure, low thermal expansion coefficient (4.5×10^{-6} K^{-1}) and excellent thermal conductivity, this material is used for a wide variety of strategic applications for example in space for ignition tubes of rocket engine, thermionic emitters in spacecraft, in military applications for high kinetic energy penetrators, nozzles in rockets/jet vanes and electronic industry for electron emitter, grid wires, heat sinks [18]. Because of its low rate of sputtering and erosion, low tritium retention, tungsten currently is considered to be most
appropriate for controlled plasma fusion research, where it is used as the plasma facing material in the tokamak machines [113]. Production of tungsten in nanoparticle form is important, because they may be sintered more efficiently at a comparatively lower temperature to produce actual nanostructured materials with enhanced material characteristics [114]. The consolidation of tungsten micron particles processed by conventional powder metallurgical techniques requires very high temperature as a result of which grain growth occurs, and finally, product’s mechanical properties are compromised. Tungsten nanoparticles have also been used for catalytic reactions and for reinforcing metallic/intermetallic material systems [115]. It was recently demonstrated that incorporation of tungsten nanoparticles might positively influence the microstructure of the joining area during advanced brazing of stainless steel alloys [116]. Superfine tungsten particles are being utilized in the laboratory as a substitute for tungsten dust particles that are likely to form in ITER-like future Tokamaks due to extreme plasma surface interaction processes, mainly to understand their hydrogen retention characteristics, which is a significant safety concern in the field of controlled plasma fusion research [117].

Reports are available on synthesis of tungsten nanopowders by different techniques, including thermal decomposition of tungsten hexacarbonyl [W(CO)₆] [118], high energy ball milling [119], electric wire explosion [120], magnetron sputtering [121], self-propagating high-temperature synthesis (SHS) [122], chemical reduction synthesis [123], low temperature molten salt technique [124], etcetera. However, most of these techniques involve multistep, lengthy processes having meager production rate or are very low-temperature techniques which result in poor crystallization of the material. Thermal plasma assisted techniques have also been
used to synthesize this high-temperature material in nanometre sizes, which in general have the distinct advantage of bulk production rate, scalability and good product crystallinity [114]. In this communication, we are exploring the synthesis of tungsten materials by an essentially single step, almost continuous, expanded plasma jet assisted technique, through which we had before demonstrated excellent size control simply by manipulation of the ambient pressure in the sample collection chamber [60]. In this process, precursors embedded in the plasma jet undergo rapid and uniform cooling while expanding into a sample collecting vacuum chamber maintained at a low ambient pressure, which ensures nucleation of nanometer particle sizes with uniform size distribution. In this experiment, we investigated the effects of two experimental variables, which are the ambient pressure in the sample collection chamber and plasma current (power), on the characteristics of the final product material. To explore synthesis under the lowest possible pressure, we had in this experiment connected the chamber with a roots vacuum pump with very high pumping speed (4200 m$^3$/h), which had produced sub-mbar working pressure.

4.2 Experimental details

4.2.1 Thermal plasma assisted nanoreactor setup

The plasma jet assisted reactor along with essential peripherals, which we have been using for controlling the synthesis of different high-temperature nanomaterials for the last several years, is elaborately described in reference [57]. Fig. 4.1 shows the current system where certain modifications were made to the previous hardware. To produce particles over a wide range of pressure, we had in this experiment coupled the vacuum chamber with a very high throughput roots vacuum pump (EH 4200
backed with an E2M 275 rotary vacuum pump), that had allowed reducing the pressure down to the sub-mbar level.

![Diagram of the segmented plasma torch assisted experimental nanoparticle reactor system used for the synthesis experiments.](image)

**Fig. 4.1** Diagram of the segmented plasma torch assisted experimental nanoparticle reactor system used for the synthesis experiments.

A motorized powder feeder was also integrated that made the possible injection of reactants to the plasma in the form of micron-sized particles (tungsten oxide). A segmented plasma torch was used for generation of plasma, which was connected vertically to a water-cooled converging nozzle that exhausted to the sample collection chamber kept at the bottom. The reactants are injected into the so-called injection section, which is positioned in between the torch anode and the nozzle below. The plasma power source was a full wave DC thyristorised power supply (200 V/400 A, Technocrats Plasma) with a high-frequency igniter.

### 4.2.2 Synthesis of nanosized tungsten powders

Argon was injected at the rate of 15 litres per minute (lpm) near the cathode using digital mass flow controller (Alborg make), for three different plasma currents of 150 A (7.5 kW), 250 A (15 kW) and 350 A (23 kW). WO$_3$ micron powder (99.98%
purity, Alfa Aesar) was fed to the injection section at a rate of 0.4 g/m using the powder feeder. Hydrogen was injected in the same location at 5 lpm using mass flow controllers through the powder feeder. In the hot plasma environment of the injection section, the oxide is subsequently reduced by hydrogen to the tungsten metal. Samples were collected from a substrate kept at a distance of 150 mm from the reactor nozzle, where a thick layer of powder was deposited within just a few minutes of the initiation of the synthesis experiment. For the 350 Ampere/400 mbar synthesis condition the production was 4.7 g/h. The samples were kept in a vacuum desiccator before being sent for various characterizations. The synthesis experiments were undertaken for three different plasma currents of 150 A (7.5 kW), 250 A (15 kW) and 350 A (23 kW). The experiments were also repeated for three different ambient pressure values in the sample collection chamber, as follows: 400, 20 and 0.8 mbar.

### 4.2.3 Characterization of tungsten powders and the plasma

The phase analysis of the as synthesised samples was done using an X-ray diffractometer (Rigaku, TTRAX-III), in the 20-range from 20° to 80°, step=0.03, at a scan rate of 2 deg min⁻¹, operated at 50 kV/100 mA, with Cu Kα radiation (1.546 Å) having monochromator in the detector side to block Kβ radiation. Quantitative phase analysis was performed by Rietveld structural refinement of the XRD profile using the FullProf program (version 2.05) [125]. The Williamson-Hall (W-H) analysis and size-strain plot method were used to study the individual contributions of crystallite sizes and lattice strain on the peak broadening of the α-tungsten phase. The crystallite size of the produced powder was estimated from the diffraction peak broadening using Scherrer’s equation. This measurement was supplemented by Laser Raman analysis carried out with a LabRam 010 (Horiba-Jobin Yvon) instrument from ISA.
using a 2.48 mW He-Ne laser (633 nm). The morphology of the particles at a relatively bigger scale was investigated by a field-emission scanning electron microscope (FESEM, JEOL JSM-7100F). For detailed morphological analysis of the samples at nanometre resolution, we had first utilized a JEOL, JEM 2100 HRTEM system (200 kV). An FEI, Tecnai G² F30, S-Twin HRTEM equipped with Gatan Orius CCD camera, operating at 300 kV was also used. This had a HAADF detector attachment from Fischione (Model 3000), to perform high angle annular dark-field studies. This also had an energy dispersive X-ray (EDX) spectroscope attached, which made a possible quantitative elemental analysis of the particles and their background with energy resolution ~130 eV, using Tecnai Imaging and Analysis (TIA) software from FEI. For all HRTEM measurements, the samples were first sonicated in ethanol and then deposited on carbon-coated copper grids for imaging. The surface area of these samples was measured by BET technique in a static volumetric adsorption surface area analyzer system using N₂ adsorption/desorption isotherm (Micromeritics ASAP 2010). The temperature of the substrate where from the samples were collected was measured with a K-type thermocouple.

For an understanding of the plasma chemistry and particle growth process specific to this particular material, we had analyzed the plasma emission coming out of the injection section with a McPherson 1.33 m spectrometer (1800 grooves/mm) and CCD camera (ANDOR DU940P, 2048×512 pixels). Assuming the plasma to remain at thermodynamic equilibrium in the relatively high pressure injection region, the temperature there was estimated by the ratio of hydrogen line intensity ratio technique, employing the hydrogen H₆ (656.28 nm) and H₆ (486.1 nm) atomic lines, from integrated light, collected over the line-of-sight by a fiber optic cable. The
profiles of the Hβ lines were fitted with a Lorentzian profile, and the FWHM were measured, from which the corresponding plasma density was also estimated assuming Stark broadening.

4.3 Results and discussions

4.3.1 X-ray diffraction and Rietveld Refinement analysis

X-ray diffraction measurements demonstrate that under most of the experimental conditions, the stable α-tungsten was the dominant material phase, with which metastable β-W and tungsten oxides (WO₃) were thinly mixed with (Fig. 4.2).

Fig. 4.2 X-ray diffraction patterns of (a) as received WO₃ feedstock, tungsten nanomaterials synthesized at the following experimental conditions (b) 150 Ampere plasma current and 0.8 mbar pressure, (c) 250 Ampere and 0.8 mbar, (d) 350 Ampere and 0.8 mbar, (e) 150 Ampere and 20 mbar, (f) 250 Ampere and 20 mbar, (g) 350 Ampere and 20 mbar, (h) 150 Ampere and 400 mbar, (i) 250 Ampere and 400 mbar, and (j) 350 Ampere and 400 mbar.
Stable $\alpha$-W is the preferred phase for tungsten, which possesses superior properties like high electrical conductivity and better mechanical strength compared to $\beta$-W [126]. The very high-temperature environment of a DC thermal plasma as well the typically very fast quenching rate associated with them, in general, is understood to have favoured the formation of this high-temperature stable crystal structure [114,127,128]. Microwave plasmas, on the other hand, are known to possess comparatively lower temperature, which is in agreement with the statement just made, was seen to produce a significant amount of $\beta$-W phases during the synthesis of the same material [129]. Moreover, in this particular technique, the precursors had enhanced residence time while remaining embedded in the relatively longer expanded plasma beam, which also, in general, might have contributed in promoting this particular material phase. The typically broadened XRD peaks confirm that crystallites of all material phases were in the nanometer size range. The crystallites size of $\alpha$-W phase for all the reported samples is recorded in Table 4.1. Corresponding sizes for the $\beta$-W under all experimental conditions always remained under ten nanometers. Lattice strain, as calculated from XRD data, was found to be of the order of $10^{-3}$ irrespective of plasma power and chamber pressure, indicating that the gas phase condensation method contributed very less strain to powder samples (also presented in Table 4.1).
Fig. 4.3 X-ray diffraction patterns of tungsten nanoparticles synthesized at (a) 350 Ampere plasma current under different chamber pressure of 400 mbar, 20 mbar, and 0.8 mbar, and (b) 400 mbar chamber pressure under different plasma current of 150 Ampere, 250 Ampere, and 350 Ampere.

Regarding phase purity (α-W), the high power, high pressure (350 Ampere/400 mbar) condition synthesized sample was observed to be of the best quality, which contained minimum quantities of other phases (Fig. 4.3). It is found that the relative composition of tungsten oxide in the nanoparticle samples increases with the reduction of both pressure and plasma current (Fig. 4.3a and 4.3b). β-W also follows a similar trend, which was almost absent in all high-pressure samples. The metallic substrate from where samples were collected gets heated up during the experiments, which is understood to have seriously influenced the quality of the as-synthesized material, by further reaction of the as-deposited tungsten nanoparticles with the residual oxygen inside the chamber. Under the lowest pressure (0.8 mbar) synthesis conditions, the plasma jet had exhibited a highly under-expanded configuration, which was seen to engulf the substrate holder completely. The corresponding substrate temperature could not be measured, but that must have been higher than 600 °C which was the substrate temperature measured for the 350
Ampere/20 mbar conditions (when the plasma beam was much shorter). At that temperature range, oxidation of tungsten is known to occur most rapidly, and that explains the dominance of oxides in the low-pressure samples [130]. On the other hand, at high pressure (350 Ampere/400 mbar), the visible beam was much shorter hardly even coming out of the nozzle, the corresponding oxidation at a substrate temperature of only 320 °C was also minimum. β-W followed almost the same trend as oxides, which is understood to get stabilized in the presence of the oxygen impurities.

The structural model for the refinement was constructed using crystallographic information files (cif) for different phases from the ICSD database viz. ICSD 44393 for α-W, ICSD 52344 for β-W, ICSD 80056 for WO₃ phases and the structural model reported in the literature [131]. The space group assigned for the α-W, β-W and WO₃ phases are Im-3m (SG No.229), Pm-3m (SG No.223) and P12₁/n1 (SG No.14) and the refined parameters were scale factor, background (fitted manually), sample displacement, lattice parameters, occupancy factors, temperature factors, etcetera. Fig. 4.4 shows Rietveld refined profile and the difference plot for XRD pattern of the high current/high pressure (350 Ampere/400 mbar) sample, which contained 90 (±4) wt.% α-W and 5.6 (±2) wt.% β-W while the oxide fraction (WO₃) consisted of ~4 (±2) wt.%.
Fig. 4.4 Rietveld refined XRD profile of the tungsten nanopowder synthesized at high plasma current, high pressure (350 Ampere/400 mbar) condition.

Rietveld refinement analysis for all the samples giving details about the lattice parameters (for different phases), the weight percentage of different phases ($\alpha$-W, $\beta$-W, and WO$_3$) is presented in Table 4.1.

Table 4.1 XRD measured structural and phase analysis details of the tungsten nanopowders.

<table>
<thead>
<tr>
<th>Sample synthesis condition</th>
<th>Lattice parameters ($\alpha$-W (Im-3m), $\beta$-W (Pm-3m), WO$_3$ (P1, 2/n1))</th>
<th>wt. % of different phases</th>
<th>Crystallite size (nm)</th>
<th>Micro-Strain</th>
</tr>
</thead>
<tbody>
<tr>
<td>350 Amps/400 mbar</td>
<td>$a= 3.16\text{Å}$ $a= 5.05\text{Å}$ $a= 7.29\text{Å}$ $a= 7.52\text{Å}$ $a= 7.68\text{Å}$ $\beta= 90.65$</td>
<td>90 5.6 4 35</td>
<td>$3.0\times10^{-3}$</td>
<td></td>
</tr>
<tr>
<td>250 Amps/400 mbar</td>
<td>$a= 3.16\text{Å}$ $a= 5.04\text{Å}$ $a= 7.30\text{Å}$ $a= 7.52\text{Å}$ $a= 7.66\text{Å}$ $\beta= 90.73$</td>
<td>76 5 19 29</td>
<td>$3.6\times10^{-3}$</td>
<td></td>
</tr>
</tbody>
</table>
4.3.2 Phase analysis by Raman spectroscopy

Laser Raman measurements were also undertaken just as a support to the XRD studies. Metals are not Raman active; hence this characterization is used just to demonstrate how the bulk oxide phases are minimized in the case of particular samples. Raman spectra show main bands in the regions 200-400 and 600-850 cm\(^{-1}\), all of which are assigned to oxides [132]. In complete agreement with the XRD results so far, it was observed that oxidation reduced with both pressure and current (Fig. 4.5a and 4.5b), the best sample being produced under the high power/ high-pressure conditions.
Fig. 4.5 Micro-Raman spectrum of the tungsten nanoparticles synthesized at (a) 350 Ampere plasma current under different chamber pressure of 0.8 mbar, 20 mbar, and 400 mbar, and (b) 400 mbar chamber pressure, under different plasma current of 150 Ampere, 250 Ampere, and 350 Ampere.

4.3.3 FESEM and TEM analysis

FESEM shows the formation of almost spherical fine particles in size range of 30-300 nm (Fig. 4.6a), under the same high plasma current, high pressure (350 Ampere/400 mbar) synthesis conditions, that we had identified before to produce material with the highest phase purity (α-W). The actual cubic/polyhedral morphologies of the particles were resolved in another micrograph containing just a few particles (Fig. 4.6b), which is understood to have formed under relatively slow thermal equilibrium processes. Under an electron microscope of limited resolution, these polyhedral morphologies may often look like spherical particles only. Careful observation of the first FESEM micrograph reveals that most of the particles are forming aggregates, remaining lightly sintered with their nearest neighbours. Z. Z. Fang et al. [133] had observed recently that even at low density and comparatively lower temperature of around 800 °C, tungsten nanoparticles start coalescing, where the relatively bigger ones start
devouring the smaller particles leading to larger average sizes. In this mechanism, a conduit may form between adjacent particles through which surface diffusion of mass occurs, resulting in a table-tennis bat-like structure; those morphologies were also identified in the FESEM pictures (Fig. 4.6c).

Fig. 4.6 FESEM micrographs of tungsten nanopowders, (a) prepared at 350 Ampere plasma current and 400 mbar chamber pressure, (b) few particles from the previous sample at higher magnification, (c) same sample showing typically sintered particle configuration, (d) the same sample showing mesocrystal-like microstructures, prepared at 150 Ampere plasma current and 400 mbar pressure, and (f) after annealing of the previous sample.

Along with the individual spherical particles, FESEM (Fig. 4.6d) shows the presence of some mesocrystal-like aggregated morphologies of particles of several micrometers in sizes, which appears to have been produced by agglomeration of individual nanoparticles [134]. Similar individual spherical nanoparticles, but with smaller average sizes were observed in the case of the low power/high pressure (150 Ampere, 400 mbar) sample also, which however was seen being mixed/covered with
particles with cheese plate/flower-like morphologies (Fig. 4.6e). They get eliminated on annealing at about 800 °C, under flowing hydrogen, which indicates that the material may be oxides of tungsten (Fig. 4.6f). This annealed sample contained some more exotic aggregated morphologies (Fig. 4.7a), which, however, might have formed just because of the additional heating process. On the other hand, cauliflowers like particle morphologies were produced during all low-pressure synthesis conditions. The sizes of the individual particles remained around few tens of nanometres only, while the aggregates were growing up to several micrometers in size (Fig. 4.7b).

Fig. 4.7 FESEM micrographs of tungsten nanopowder showing (a) exotic aggregated morphology observed in the annealed sample synthesized under 150 Ampere/400 mbar pressure conditions, and (b) cauliflower-like structures synthesized at 150 Ampere plasma current and 20 mbar working pressure.
Fig. 4.8 TEM images of tungsten nanopowders synthesized at plasma current of 350 Ampere and working pressure of (a) 400 mbar, and (b) 0.8 mbar, the inset shows the corresponding SAED patterns, (c) shows the TEM image of the first sample with higher magnification.

In the FESEM micrographs, very small particles are likely to remain hidden under bigger particles. Hence, to have a complete idea of the actual size distribution of the product, it was essential to go through high-resolution TEM analysis also. The as-synthesized samples were sonicated for thirty minutes before the microscopy. Therefore it is most likely that the bigger particles had settled down and HRTEM micrographs show particles from a few nanometers up to few tens of nanometers in sizes (Fig. 4.8a and 4.8b). The particle shapes are seen to be of cubes, spherical and faceted spherical morphologies. The corresponding SAED (as an inset in respective micrographs) consists of concentric circles with discrete spots, which reconfirms high-pressure particles as a whole are better crystalline compared to their low pressure counterparts. FESEM and TEM illustrate the two ends of the size distribution successfully. However, it was still not possible to construct a single size distribution because their relative abundance could not be estimated. In these TEM micrographs, under both pressure regimes, particles are seen remaining dispersed in a moss-like background, the extent of which apparently increases with lowering of
pressure that may indicate them to be oxides. Bernard et al. [135], while synthesizing nano tungsten by a laser-assisted method to utilise as fusion analogue dust particles had also reported similar foam like a backdrop, which they had assumed to be made up of small irregularly shaped aggregates. Under higher TEM magnification of the high pressure sample (Fig. 4.8c), individual crystal planes corresponding to the (110) planes of α-W becomes visible, where lattice spacing was measured in the range of 0.22-0.23 nanometers. To a lesser degree oxide crystallites also were identified (0.34-0.4 nanometers). However, part of the background could never be resolved, indicating they are amorphous in nature.

Fig. 4.9 (a) STEM-HAADF micrographs of the tungsten nanoparticles synthesized at high pressure, high power (350 Ampere/400 mbar) synthesis conditions, (b) Energy Dispersive X-ray spectrum of the same sample, data collected from the red circle centered at the core of a particle, as shown in the HAADF micrograph in the inset, and (c) EDX spectrum obtained from the red circle concentrating on the moss like background, as shown in the HAADF micrograph in the inset.

To investigate the elemental composition of the product with even higher spatial resolution, thus to differentiate between the faceted particles and their background matrix, we have also performed high-angle annular dark field (HAADF) analysis. Fig. 4.9a represents the STEM-HAADF image of the high current/ high-
pressure sample, which in qualitative conformity to the previous HRTEM images, shows almost spherical particle shapes mixed homogeneously with a fainter background. Energy Dispersive X-ray spectrums were collected from two qualitatively different regions of the HAADF micrographs, such as from the particle core (Fig. 4.9b) and the background (Fig. 4.9c). It was estimated that the particle core comprises 97.83 wt.% tungsten and remaining 2.16 wt.% oxygen, whereas towards the background oxygen increases to 11.9 wt.% (Fig. 4.9c). Cu and carbon were also recorded that originated from the carbon-coated copper grid essential for the TEM measurements. This measurement conforms well to the XRD Rietveld analysis of the same sample reported before, which measured contributions averaged over both the well defined spherical particles and their apparently irregular backgrounds all together. EDX elemental mappings were undertaken for two more samples; all results are presented in Table 4.2. These measurements indicate the amorphous background mostly comprises tungsten, part of which remains in oxide form also. These finer material sizes are assumed to have formed under relatively higher super-saturation, hardly finding the time, even to crystallize, parts of which were oxidized because of the supposedly high specific surface area.

Table 4.2 EDX measured elemental composition (wt.%)

<table>
<thead>
<tr>
<th>Synthesis condition</th>
<th>At the particle centre</th>
<th>At the peripheral area</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tungsten</td>
<td>Oxygen</td>
</tr>
<tr>
<td>350 Amps/400 mbar</td>
<td>97.83 (± 0.68)</td>
<td>2.16 (± 0.09)</td>
</tr>
<tr>
<td>150 Amps/400 mbar</td>
<td>92.46 (± 0.98)</td>
<td>7.53 (± 0.36)</td>
</tr>
<tr>
<td>350 Amps/0.8 mbar</td>
<td>86.36 (± 0.80)</td>
<td>13.63 (± 0.38)</td>
</tr>
</tbody>
</table>
4.3.4 \( \text{N}_2 \) adsorption/desorption investigation of pore system

![Diagram](image)

Fig. 4.10 \( \text{N}_2 \) adsorption-desorption isotherm of tungsten nanopowder synthesized at (a) a plasma current of 350 Ampere and a working pressure of 400 mbar, (b) a plasma current of 350 Ampere and a working pressure of 20 mbar.

Measurement of the specific surface area of the W particles is important from the application’s point of view, particularly in catalysis or while being used to mimic fine dust particles generated inside tokamak fusion devices. In the latter case, tungsten dust may absorb hydrogen isotopes from the fusion environment giving rise to a serious safety concern, which is understood to be primarily dependent on the effective surface area of the basic material. Before the BET analysis, outgassing of the as-synthesised samples was carried out by heating at a temperature of 200 °C for 5 hours. BET surface area of the following two samples, 350 Ampere/400 mbar, and 350 Ampere/20 mbar, was measured as 34.9 m\(^2\)/g and 24.5 m\(^2\)/g, with the corresponding specific pore volumes as 0.265 cc/g and 0.084 cc/g respectively. \( \text{N}_2 \) adsorption-desorption isotherms for the same samples are presented in the Fig. 4.10a and 4.10b respectively. The curve in Fig. 4.10a is a typical H3 type hysteresis characterized by absorbents containing slit type pores [59,136]. In Fig. 4.11, BJH adsorption dV/dD pore volume is plotted against pore diameters of the samples,
which shows a multimodal distribution. For both the samples, pore volume decreases sharply at few nanometers, after which the high pressure/high power sample exhibits relatively higher pore volumes contributed by relatively bigger pore sizes. Contributions from the mesopores (pores with 2-50 nm sizes) were more pronounced for this particular sample, which in general, is known to lead to a higher specific surface area and absorption in materials [59]. This may be explained on the basis of the mesocrystal like morphologies that we had identified before in this sample. The pores may correspond to voids inside the particle aggregates. The specific surface area values reported here are much larger compared to those reported before for tungsten nanoparticles produced by various other methods [115,137].

![BJH pore size distribution plot of tungsten nanopowders synthesized with 350 Ampere plasma current and working pressure of 20 mbar and 400 mbar.](image)

**4.4 Particle growth mechanism**

Light from plasma coming out of a small annular hole at the injection section was analyzed with a 1.33 m optical spectrometer. A host of tungsten emission lines (365.4 nm, 368.2 nm, 370.8 nm, 371.9 nm), even including ionized ones (373.6 nm) were
identified, which confirmed the oxide reactant gets reduced to tungsten atomic vapour immediately after being injected into the reactor (Fig. 4.12). The emission spectra of the plasma coming out of the nozzle end into the vacuum chamber could be observed through a window in the chamber; however, no tungsten lines could be recorded under any experimental conditions in this case. By using the technique of the line intensity ratio of the hydrogen $H_\alpha$ and $H_\beta$ lines, the plasma temperature at the injection section for the 350 Ampere/400 mbar synthesis condition was estimated to be 6900 K (the corresponding plasma density was $1.5\times10^{21}$ m$^{-3}$).

![Plasma optical emission spectrum](image)

Fig. 4.12 Plasma optical emission spectrum collected from the injection section, which shows tungsten atomic (365.4 nm, 368.2 nm, 370.8 nm, 371.9 nm) and ionic (373.6 nm) spectral lines.

The temperature at the nozzle end was too low that no plasma emission adequate for temperature analysis could be collected from that location. Comparing these measurements to the evaporation (6200 K) and melting (3700 K) temperatures of bulk tungsten, it may be concluded that in this experiment W had started condensing immediately downstream of the injection position, much upstream of the
nozzle end. That had allowed achieving only a small value of super-saturation at the position of condensation, and that is why the average sizes of our tungsten particles were bigger, compared to the other nanomaterials, we had synthesized before using the same technique, under an almost same plasma parameter regime [58,138]. Nucleation at high temperature and pressure ensured the further growth of the nucleated particles, which were still in the liquid stage, through collision with others that resulted in still largely spherical morphologies of the final product. In our previous experiments, we had demonstrated efficient size control of different nanomaterials simply by manipulation of the ambient pressure in the sample collection chamber. However, the average sizes of the particles were at most a few tens of nanometers only even at high pressure, which had reduced to even below ten nanometers under reduced chamber pressure conditions of around 10-20 mbar. Here, we can cite a particular example of the aluminum-oxide, spherical, free-flowing nanoparticles, which we had synthesised using the same technique [58]. The melting and evaporation temperature for alumina is 2345 K and 3250 K respectively, which had ensured in the first place, that for the almost same plasma regime, particles nucleated far downstream of the nozzle almost at the end, where a relatively higher saturation ratio is achieved, that translated to tiny particle sizes. Nucleation at a relatively lower temperature and also at a lower ambient pressure also ensured insignificant subsequent growth through collisional processes. It may be noted that for a supersonic flow, the effect of reduced chamber pressure may be felt only at the end of the supersonic nozzle, which was realised by the alumina vapor in our previous experiments under the low pressure conditions. Coming back to tungsten, the basic crystallite sizes, as measured from XRD peak broadening, was measured to
be smaller for low pressure synthesis conditions, which shows tungsten vapour also
could see the reduced pressure in this experiment. We can conclude here that the
characteristics of tungsten nanoparticles could be enhanced further simply by
increasing the temperature, at what the atomic precursor vapour is produced, and
cooling is initiated. One of the simplest ways to achieve the same was by increasing
the plasma current, which however was not possible in this case because of the
limitation of the DC power supply. We can here point out another gas phase
nanoparticles synthesis technique, the wire explosion process, which produces
smaller, un-agglomerated ideal tungsten nanoparticles, must be primarily because of
the higher initial temperature to which the metal vapour is produced in the first place
[120]. While highlighting the fine morphological control associated with this
particular technique, S. Dine et al. [115] however, had also pointed out that the
corresponding size control is not very efficient and a significant part of the powder
crystallizes in the β-W structure.

It is well known that under relatively slow thermodynamic control, crystals
grow into macroscopic shape bounded by specific crystal planes characterized with
the lowest surface energy. The planes with relatively higher surface energy develop
faster whereby they soon get depleted, upon which the low energy surfaces
effectively get exposed. Cubic systems like tungsten are usually defined by six
numbers of low energy [001] crystal planes, which however is frequently found as
polyhedral particles with few additional relatively high energy faces exposed, as these
atomic surfaces may not get entirely consumed during the limited time allowed for
growth [134]. In this experiment for nanometric bcc tungsten, we have identified both
cubic and polyhedral morphologies. However, under the limited resolution,
polyhedral morphologies may often look like spherical particles only. We had observed before that particle remains lightly sintered to each other in the final product, which was commented before to have resulted because of coarsening. This is assumed to have happened after deposition on the heated substrate.

In this experiment, along with the regular polyhedral tungsten crystals, we have also observed deposition of mesocrystal and cauliflower-like microstructures, which represent a deviation from equilibrium crystal morphologies. Vaterite or Aragonite, polymorphs of calcium carbonate, exhibit similar cauliflower like morphologies with the same micrometer scale lengths, which are known to precipitate at high saturation index, which may transform to the stable calcite having Hopper crystal like morphology, as the driving forces for precipitation decrease later. K.K. Sand et al. [110] had argued that the classical theory of spherulitic growth, adequately describes the formation mechanism of these exotic crystal structures and there is no need to invoke the popular hypothesis for nonclassical growth by the oriented self-assembly of nanocrystals. At high supersaturation, spherulites can form by the process of growth front nucleation when new crystal grains nucleate at the surface of the parent with a little different orientation than the previous, which eventually leads to the splaying growth at larger length and time scales [108]. Diverged materials have been observed producing spherulitic microstructures, including polymers, minerals, metals and alloys and even elements [108]. During a recent experiment in plasma surface interaction (PSI) with a tungsten target, we had demonstrated the simultaneous formation of spherulitic, hopper and polyhedral particles, where also a variation of the super-saturation as experienced by the molten metal in the PSI region was considered to have led to those diverged morphologies [139]. Concerning the
same PSI configuration, carried out with a similar segmented plasma torch, Bystrov et al. [96] had pointed out that the intense plasma regime may drive the system far out of equilibrium, producing similar non-equilibrium structures of carbon as well. Coming back to the present experiment, the experimental configuration here represents yet another system with extreme plasma parameters, which therefore we may conclude to have led to interesting non-equilibrium morphologies through kinetic control.

4.5 Conclusion

Tungsten nanoparticles were synthesized by an almost continuous, high-throughput, single step plasma expansion process, by variation of plasma current and pressure in the sample collection chamber. Almost phase pure α-tungsten particles with sizes up to 300 nm were produced under high current/pressure (350 Ampere/400 mbar) synthesis conditions, whereas contribution from β-tungsten and oxides were increasing both with reduction of plasma power and pressure. In this experiment W vapour nucleated much upstream of the converging nozzle at a relatively smaller saturation ratio, that was responsible for the relatively bigger average sizes of the tungsten particles. Nucleation at high temperature and pressure also led to further growth of particles by collision with others. Particles deposited on the substrate were observed to remain lightly sintered with each other, which is considered to be the initiation of a particle coalescing process which in extreme cases may jeopardize the prospect of achieving actual nanostructured material during the sintering process. Smaller crystallite sizes resulted during the low pressure operations, which however had cauliflower-like morphologies, which is suspected to have formed through
spherulitic growth processes. Particles were seen remaining dispersed in an amorphous matrix, the extent of which increased with the reduction of power and chamber pressure that was concluded to be a mixture of tungsten and its oxides. BET measurements demonstrated highest specific surface area for the above mentioned best tungsten nanoparticle sample, which is considered to have contributed by the voids inside the aggregated particles.