The influence of process parameters on precursor evaporation for alumina nanopowder synthesis in an inductively coupled rf thermal plasma

J W Shin\textsuperscript{1}, H Miyazoe\textsuperscript{1}, M Leparoux\textsuperscript{1}, St Siegmann\textsuperscript{1}, J L Dorier\textsuperscript{2} and Ch Hollenstein\textsuperscript{2}

\textsuperscript{1} Swiss Federal Institute for Materials Science and Technology EMPA, Feuerwerkerstrasse 39, CH-3602 Thun, Switzerland
\textsuperscript{2} Ecole Polytechnique Fédérale de Lausanne, Centre de Recherches en Physique des Plasmas, CH-1015 Lausanne, Switzerland

E-mail: jong-won.shin@empa.ch

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Abstract

The process parameters of an inductively coupled thermal plasma used for nanopowder synthesis are experimentally investigated using various plasma diagnostics and \textit{in situ} powder monitoring methods. An enthalpy probe technique is applied to characterize the plasma properties under particle-free conditions. The nanoparticle synthesis from microscale alumina precursors is monitored \textit{in situ} by optical emission spectroscopy and laser light extinction measurements to investigate the powder evaporation. The synthesized powders are collected in a sampling unit and characterized \textit{ex situ} by particle size analysis as well as by electron microscopy. At low flow rates of the torch central gas, higher plasma enthalpy, a laminar powder flow and increased evaporation of the precursor have been observed. A precursor- and an energy-deficient regime related to the precursor feed rate and plasma enthalpy are found from the emission line intensities of aluminium metal vapour. The number fraction of plasma-treated precursors, which is an important process parameter, is calculated from the precursor number density obtained from laser extinction measurements.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Since the first inductively coupled plasma (ICP) torch was developed by Reed in the 60s \cite{1}, rf thermal plasmas have found a variety of applications in materials processing such as crystal growth, thermal spray coatings, spheroidization and vaporization of refractory materials \cite{2–4}. In recent decades, inductively coupled thermal plasmas have been used for the synthesis of high purity ultra fine powders, due to their unique properties such as high energy density, variable operating pressures and low product contamination. Successful applications of the ICP for the synthesis of a variety of nanocrystalline refractory materials of different compositions have been reported \cite{5–7}. In these ICP processes, powder properties like particle size, size distribution, phases and morphology are determined by various process parameters, including plasma properties and powder trajectory and interactions between powder and plasma. Understanding plasma–powder interactions and finding a correlation between process parameters and synthesized powder properties is an important task for process control and optimization. Several numerical modelling studies have been presented to describe the plasma properties \cite{8, 9} and powder behaviour in plasma \cite{10}. Buchner \textit{et al} \cite{11} demonstrated the influence of...
the residence time of the particles on copper evaporation using numerical simulation as well as spectroscopic measurements in the hot region of the Ar plasma. However, there is still lack of process-related experimental work investigating the correlation of process parameters with powder properties.

The objectives of the present work are to experimentally demonstrate, by using suitable plasma diagnostics and process monitoring tools and powder characterization, the influence of two relevant process parameters, namely the central gas flow (CG) and the precursor feed rate (FR), on precursor evaporation. Firstly, an enthalpy probe technique was applied to characterize the inductively coupled Ar–H₂ rf thermal plasma at different operating conditions. The enthalpy probe measurement is a well-established plasma diagnostic technique to obtain the locally resolved enthalpy, temperature and velocity of thermal plasmas [12–17]. Secondly, optical emission spectroscopy (OES) and laser light extinction (LE) measurements have been carried out to monitor in situ the injection of the alumina precursors and give real-time information on the precursor evaporation. The emission line measurements of the aluminium vapour are used to determine the dependence of various process parameters on precursor evaporation. Furthermore, monitoring the LE is used to calculate the number density of non-plasma-treated powders, from which the number fraction of evaporated powders can be deduced. Finally, powders have been collected after the synthesis process and their size and morphology have been characterized ex situ. These different measurements, plasma characterization, in situ process monitoring and ex situ powder analysis, demonstrate the influence of process parameters on alumina powder evaporation in an inductively coupled Ar–H₂ thermal plasma.

2. Experimental set-up

2.1. Inductively coupled plasma and powder synthesis system

The nanopowder synthesis system used for this study consists of an ICP torch, a synthesis chamber, a filtration unit and a powder feeder as schematically illustrated in figure 1. The 13.56 MHz ICP torch (PL-35, TEKNA Plasma System Inc., Canada) is mounted on the top of the synthesis chamber and is operated with argon and hydrogen up to a maximum input power of 35 kW. The torch comprises a water cooled four-turn copper coil, a ceramic confinement tube with an inner diameter of 35 mm and an intermediate tube separating central gas from sheath gas. The central gas is tangentially introduced through a metallic gas distributor giving rise to a swirl along the powder injection probe, while the sheath gas flows axially along the ceramic wall. Argon is used as central gas and a mixture of argon and hydrogen as sheath gas. Two flow rate ranges for the central gas are taken into consideration in this work. A flow rate between 6 and 12 slpm is referred to as a low amount of central gas (LCG) and a flow rate of 21 to 27 slpm as a high amount of central gas (HCG). The flow rate of the sheath gas is kept constant at 80 slpm of Ar and 6 slpm of H₂.

A water cooled stainless steel powder injector with an opening diameter of 3 mm is axially mounted on the central position of the torch at the height of the first induction coil. The powder exit is positioned 2 mm below the edge of the intermediate tube. This injection probe is connected to a commercial powder feeder (TWIN 10-2, Sulzer Metco, Switzerland) operating on a volumetric dosing principle. The precursor powder was introduced into the plasma using argon as carrier gas with a flow rate of 10 slpm. As precursor, α-alumina powder (AA-5, Sumitomo Chemical Co., Ltd, Japan) with a mean diameter of 4.7 µm was used in this investigation. This alumina powder has a very narrow size distribution (−6 +4 µm) allowing us a reliable calculation of powder number density from in situ laser extinction measurements. The water cooled synthesis chamber (1500 mm long) has several view ports for easy access of in situ process monitoring tools. These view ports enable a simultaneous process monitoring by at least two different techniques, e.g. OES and LE at various axial and radial positions as shown in figures 1 and 2. A working gas pressure of 40 kPa is maintained using a water ring pump and a butterfly-valve. A specially designed filtration unit comprising a small bypass membrane filter and a large production filter made of several woven metallic filters is connected to the synthesis chamber [18]. In the present work, the bypass membrane filter is used for on-line sampling of the synthesized nano-sized powders. The sampled powders are characterized ex situ by a particle size analyser (LS230, Beckman Coulter Inc., USA), a transmission electron microscope (TEM) (CM20, Philips, Netherlands) and a high resolution scanning electron microscope (HR-SEM) (S4800, Hitachi, Japan). Typical operating parameters used in this work are listed in table 1.

2.2. Plasma diagnostics: enthalpy probe

Under powder-free conditions, the Ar–H₂ plasma was characterized by a commercial enthalpy probe system (ENT-476 probe, Tekna Plasma Systems Inc.) equipped with a mass spectrometer (Prisma, Balzers) as illustrated in figure 1. The enthalpy probe technique is a reliable plasma diagnostic tool for high temperature thermal plasmas. The enthalpy probe is a water cooled gas sampling and stagnation pressure probe used to determine the enthalpy, heat load, temperature and velocity of the high temperature plasma jet. More detailed information on the basics of the enthalpy probe technique for thermal plasmas is given, for example, by Rahmane et al [15]. The tips of all enthalpy probes used have an inner diameter of 1.52 mm.

The enthalpy is determined on the basis of a calorimetric two step energy balance measurement, and the plasma temperature under a given gas pressure can subsequently be calculated once the gas composition has been determined by mass spectrometer, assuming local thermodynamic equilibrium (LTE). The gas velocity of the plasma jet can also be obtained by using the Bernoulli equation assuming incompressibility of the gas flow and knowing the density of the plasma gas mixture from available tables [19]. The measurements were carried out at three different axial positions from the exit of the torch (z = 2, 22, 60 mm). The probe is also equipped with a displacement system so that the radial profiles can be measured. To avoid probe damage due to the extremely high heat load close to the torch exit, a lower input power (20 kW) was used.
2.3. Process monitoring

OES was used to observe the vaporized species resulting from reactions of the injected precursor with the plasma. The light emitted from the plasma was collected by an optical fibre and transferred to a spectrometer (S2000 Ocean Optics, Inc) equipped with a 2048 element linear CCD-array detector. The spectral sensitivity over the wavelengths used (from 340 to 880 nm) was calibrated by means of a tungsten filament lamp. For investigation of the evaporation of alumina precursor, the intensities of the spectral lines of the metallic aluminium vapour, which originates from the evaporating alumina, was measured under different conditions. The aluminium emission lines at 394.40, 396.15, 669.60 and 783.61 nm were investigated.

In addition to OES, a laser extinction measurement system was adapted to the synthesis chamber. A 10 mW HeNe laser at a wavelength of $\lambda = 632.8$ nm was installed at the location where the maximum emission line intensity of aluminium vapour was observed. The intensity of the transmitted laser beam was measured by a silicon photodiode detector. The number density ($N_P$) of the non-plasma-treated precursor powder can be obtained from the ratio of the transmitted ($I_T$) to incident ($I_0$) laser beam intensities under the assumption that mono-disperse particles are present. This intensity ratio is given by

$$\frac{I_T}{I_0} = \exp[-CN_P L],$$

where $C$ is the extinction cross section and $L$ is the laser path length. According to Lorenz–Mie theory describing the interaction between light and large spherical particles (for $R_p \geq 0.1\lambda : R_p$ is the particle radius, $\lambda$ is the wavelength
of light), the extinction cross section ($C_{\text{ext}}$) is a sum of the scattering cross section ($C_{\text{scatt}}$) and the absorption cross section ($C_{\text{abs}}$), and this can be solved by numerical calculation. We calculated the extinction cross section using the computer program provided by Bohren and Huffman in their book [20]. We used a value of $1.74 + 0.01i$ as the alumina refractive index and 4.7 $\mu$m as particle diameter.

Figure 2 shows a schematic top view of the experimental set-up for OES and laser extinction measurements.

3. Results and discussion

3.1. Influence of central gas flow rates

Since the early development of ICP torches, swirl flow of plasma gas has been widely used to stabilize the plasma [21]. In our investigation, the central gas is tangentially introduced, which causes a vortex flow, while the sheath gas flows down axially. This vortex flow leading to turbulent flows influences not only the plasma properties but also the flow pattern of the injected precursor powders. Figures 3(a) and (b) show the light emitted from the alpha-phase alumina precursor axially injected into the plasma at a CG flow rate of 6 slpm (a) and 27 slpm (b), respectively. A UV blocking optical filter is used for the visualization. The interaction between the injected powder and the plasma jet in the low central gas condition results in a broad, long and bright column, whereas at the high gas flow rate condition a widely-dispersed conical distribution is found. These different behaviours result from the trajectory patterns of the injected precursor powder as well as from the plasma properties such as enthalpy and temperature distributions, basically affected by the vortex of the CG. Therefore, it can be deduced from the visual observations that the low flow rate of CG would lead to a more laminar gas flow and a better confinement of the powder in comparison to the high flow rate of CG.

Figure 3 gives different profiles of the specific enthalpies measured with the enthalpy probe. The enthalpy of the plasma is one of the most important process parameters, since it plays a key role in precursor evaporation in the powder synthesis system. For these enthalpy probe measurements, to protect the probe tip from overheating, an Ar flow rate of 12 slpm was used for the low CG case instead of 6 slpm. Figures 4(a) and (b) show radial profiles of the plasma enthalpies measured at three axial positions for different CGs. The relative error on the enthalpy was in a range between 2% and 15%. Contour plots of enthalpy profiles made by interpolation of the measured axial profiles are presented in figure 5. A polynomial fitting was performed for the measurements data shown in figure 4. Since the contour images are built up on the basis of the measured datasets, the enthalpy profiles represent asymmetric features of the plasma.

Higher enthalpies are measured for the LCG (figure 4(a)), in particular at the centre of the plasma, where the precursor powder trajectory is expected. For the LCG, the enthalpy drastically increases with decreasing axial distance from the torch exit, while it does not increase much for the HCG.
Furthermore, as the measurements are performed closer to the torch, larger enthalpy differences between LCG and HCG conditions are observed. The plasma in the LCG case (figure 4(a)) shows a faster cooling over this axial distance in the centre area. Figure 5 clearly shows the large difference of enthalpy gradients on axial and radial directions between the LCG and HCG cases. The low gradient of the enthalpy on the radial and axial directions of the HCG could be explained by a higher amount of vortex CG which enhances the gas mixing and the thermal diffusion. However, this radially flat profile of enthalpy on the radial axis is not the preferred condition for the synthesis of nanopowders, because the high enthalpy or temperature at the plasma boundary region would not contribute to melting and evaporation of the powders in the central stream. On the contrary, there is an energy loss by radiation [22]. The high enthalpies for LCG as shown in figure 4(a) are more advantageous to evaporate the injected powder. Finally, in figure 4(a), an off-axis enthalpy profile has been observed. The measured data show the maximal enthalpy with a radial deviation of 2 mm from the geometrical axis of the torch for all three axial measurements. This off-axis behaviour could be caused by an asymmetric power transfer from the working coils into the plasma, by a minor misalignment of the injection probe within the inner tube of the torch [23, 24] or by the enthalpy probe perturbing the plasma. The off-axis maximum becomes weakened by the addition of more central gas as shown in figure 4(b), which can also result from the better lateral mixing of the injected gases with an increasing vortex flow of CG as mentioned above.

The plasma–particle interactions have been investigated with OES as shown in figure 6. Micro-scaled alumina powders with an average diameter of 4.7 µm have been injected with various powder FRs axially into the Ar–H₂ plasmas studied previously. The emission line intensity of the aluminium metal vapour at 669.60 nm was chosen for investigating the dependence on CG flow rates. In fact, several lines from aluminium have been studied as described in section 2.3, and all aluminium emission lines showed the same tendency. Furthermore, aluminium is the main species appearing after evaporation of the alumina powder at high temperatures [25]. At 35 kW, the line intensities are drastically reduced when the flow rate of CG increases from 6 slpm to 18 slpm, whereas the intensity changes between 18 and 27 slpm are small (figure 6). At a lower input power, similar central gas dependence has been found. This central gas dependence can be explained by the results of the enthalpy probe measurement. The higher enthalpy of LCG (figure 4) allows an increased evaporation of the alumina powder which is evidenced by the higher intensity of the atomic aluminium emission line. Hereby the contribution of the excitation temperature ($T$) and the concentration ($N$) of aluminium vapour to the line intensity ($I$) were examined, since the emission line intensity depends

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**Figure 5.** Contour images of the specific enthalpy measured by the enthalpy probe: (a) 12 slpm and (b) 27 slpm.

**Figure 6.** Intensities of aluminium emission spectral line at $\lambda = 669.60$ nm and $z = 90$ mm versus flow rate of the central gas (SG: 80 slpm Ar + 6 slpm H₂, CaG: 10 slpm Ar, CP: 40 kPa, FR: 2.4 g min⁻¹).
where $E_i$ is the upper level energy and $k$ is the Boltzmann constant. Assuming LTE, temperatures of $T_{\text{LCG}} = 3820 \text{ K}$ and $T_{\text{HCG}} = 4200 \text{ K}$ at 25 kW are determined from the line intensity ratios and enthalpy probe measurements. With $N$ kept constant, the relationship $T_{\text{LCG}} < T_{\text{HCG}}$ would result in an intensity which should be lower under LCG than under HCG conditions. Hence the intensity increase observed in passing from HCG to LCG conditions can be attributed only to an increase in number density. Figure 7 shows the particle size distributions of the collected powders. For all three CGs investigated, multimodal particle distributions have been obtained. The measured particle size of the large particles (L) lies between 4 and 5 µm, which corresponds well to the mean size of the alumina precursor powder.

The presence of large particles (L) implies that a part of the injected precursor has not been plasma-treated probably due to the fact that they did not flow through the plasma plume but passed outside the plasma. However, a decrease in the volume fraction as well as in the mean size of these particles is observed with decreasing CG as illustrated by the line shift from X to X* in figure 7. Besides the non-plasma-treated particles, particles in the submicron ranges are observed. The particle size distribution shows two maxima after plasma treatment of the injected precursor powder [26, 27]. One peak is around 100 nm marked as S and the other is around 400–800 nm marked as M. The particles with size M are considered to be large hard-agglomerates of the fine particles. These hard-agglomerates cannot be separated from each other by external shear forces such as ultrasonic treatment performed before particle size analysis [28]. The particles with size S are expected to include the synthesized primary nanoparticles and small agglomerates. The transmission electron microscopic (TEM) image in figure 8 shows different shapes and sizes of the agglomerates (according to M sized particles in figure 7) consisting of primary nanoparticles in a size range of around 100 nm (S sized particles).

The low flow rate of CG features a drastic increase in S sized particles, volume fraction ($Y$ to $Y^*$) in comparison to the higher flow rates of central gas. This results from the more efficient precursor evaporation and the higher plasma enthalpy gradient as evidenced by the OES and the enthalpy probe measurements. This explanation is supported by scanning electron microscopy (SEM) as presented in figure 9. The images are taken from the same particle samples analysed in figure 7. Figure 9(a) shows the image of the particles synthesized with an HCG of 27 slpm, whereas the particles in figure 9(b) are produced with an LCG of 6 slpm. In figure 9(a) it is difficult to distinguish individual particles. The particles are irregularly shaped and mostly attached to each other, and no boundary around the particles can be found, which is called hard-agglomeration. The particles seem to have grown together in a liquid phase such as grain coalescence in the sintering process. This can be caused by an incomplete evaporation resulting in an inhomogeneous nucleation and growth. In contrast, figure 9(b) clearly shows the spherical single primary nanoparticles, which seem to be weakly bound to each other without sinter necks. These soft-agglomerates could be separated by an external shear force. Therefore, a remarkably high volume fraction of the S sized particles could be obtained for low CG flow rates.

### 3.2. Influence of precursor FR on the maximum evaporation rate

The intensity of the aluminium metal vapour measured by OES was used as an indicator for alumina precursor evaporation and is plotted in figure 10 versus the powder FR as a function of the input rf powers. The figure shows that a maximum in the aluminium emission line intensity exists up to 30 kW. At an input power of 25 kW, the aluminium emission line intensity increases first with increasing powder loading and reaches a maximum of $I_{\text{max}}$. Further increase in the precursor FR reduces...
the aluminium emission line intensity. The maximum in the aluminium emission line intensity indicates that for lower FRs, a precursor deficient regime ($P_{\text{deficiency}}$) is reached, while for higher FRs, an energy deficient regime ($E_{\text{deficiency}}$) occurs. However, the decrease in the aluminium line intensity at high FRs depends on the input rf power. At 35 kW, the aluminium line intensity at the higher feeding rate of 4.7 g min$^{-1}$ is considerably raised. Furthermore, the small difference in the aluminium line intensities at a FR of 2.4 g min$^{-1}$ between 30 and 35 kW means that most of the injected precursor within the plasma could have been evaporated with a power of 30 kW and hence, the additional power at 35 kW is then used for more evaporation. Therefore, it can be concluded that the maximum in the aluminium emission intensity ($I_{\text{max}}$) would be shifted towards higher FRs at higher input rf power.

LE measurements are presented in figure 11. The measurements show that about 15–25 s are needed after precursor injection until the feeding is stabilized. The LE at this axial position is assumed to take place by scattering and absorption of the incident laser beam only from the particles which are not treated by the plasma. The extinction intensity of the particles below 0.1 µm is smaller by a factor of $10^4$ in comparison to that of precursor particles. Therefore, the nano-sized particles do not contribute to the extinction even though they might exist. The large hard-agglomerates shown as M sized particles in figure 7 are also believed not to exert influence on the extinction intensity, because the agglomeration is expected to occur during a condensation process at lower axial positions.

No difference in the extinction was measured for the powder FRs below 2.4 g min$^{-1}$, whereas a higher extinction is clearly observed at the highest FR. This phenomenon can be well explained by the result of emission spectroscopy shown in figure 10. The increase in the aluminium emission line intensity by changing the FRs from 1.4 g min$^{-1}$ to 2.4 g min$^{-1}$ implies higher precursor evaporation. Hence, at the FR of 2.4 g min$^{-1}$, no additional LE by coarse powders is observed. At the highest FR, the decrease in the aluminium line intensity in the energy deficiency regime indicates more presence of the coarse powders, which corresponds to the increase in the laser extinction.

The number density of the non-plasma-treated coarse powders is calculated using equation (1). The known mean particle size and the narrow distribution of the alumina precursor allow an easy determination of the extinction cross

Figure 9. High resolution SEM images of the synthesized alumina nanoparticles (SG: 80 slpm Ar + 6 slpm H$_2$, CaG: 10 slpm Ar, CP: 40 kPa, FR: 2.4 g min$^{-1}$). Scale bar on images = 50 nm, (a) 27 slpm and (b) 6 slpm.

Figure 10. Intensity of the Al(g) emission spectral line ($\lambda = 669.60$ nm) measured at $z = 90$ mm versus FRs for three different input power levels.

Figure 11. Time-development of the normalized transmittance of the laser intensity for different FRs at $z = 90$ mm (IP = 30 kW, CP = 40 kPa).
Figure 12. Calculated number density of the non-plasma-treated powders measured at $z = 90$ mm.

Figure 13. Estimation of the number fraction of the plasma-treated precursor powder for different FRs and plasma powers at $z = 90$ mm.

In figure 12 the calculated number density is plotted as a function of input rf power for various FRs. For all three FRs, the calculated absolute number densities decrease as the input power increases.

Figure 13 shows the number fraction of the precursor evaporation versus the FR as a function of input rf power. This number fraction has been estimated from the number density ($N_p$) of the non-plasma-treated powders. For each FR, the calculated number densities are normalized by the $N_p$ without plasma. With the assumption that the plasma-treated precursor powders do not contribute to extinction intensity, the number fraction of the evaporated powders can be obtained by subtraction from 100%. A steeper gradient of plasma enthalpy axially and radially is observed for LCG compared with HCG. OES of powder-plasma interaction shows much higher emission intensities of aluminium vapour from evaporation of the injected alumina powders for LCG, which is related to the high plasma enthalpy and better confinement of the precursor powder. Size distribution of the collected nanopowders indicates that more precursor powders are plasma-treated and more fine powders are synthesized as CG decreases. Consistent with this, operation conditions with a low flow rate of central gas show more evaporation of precursor, a higher fraction of fine particles and more spherical shapes of particles at even lower gas consumption, i.e. higher efficiency.

OES shows that the intensity of the aluminium emission lines can be used as a reasonable monitor for the evaporation of the Al$_2$O$_3$ precursor powders. The maximum in the aluminium emission intensity as a function of the powder feeding rate indicates that for low FRs a precursor deficient regime is reached. The Al emission intensity decreases for higher FRs indicating that the energy deficient regime is obtained. This observation was consistent with the laser extinction measurement showing the calculated number fraction of the plasma-treated powders. The laser extinction measurement supports the emission spectroscopy measurements for the precursor evaporation study as the path-integrated concentration of the micron-sized non-plasma-treated precursor can be determined.

The reasonable explanation of the influence of process parameters on powder evaporation on the basis of experimental results shows the usefulness of the in situ plasma process monitoring and a large potential for controlling the nanopowder synthesis process, in particular in industrial applications.

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