THERMAL PLASMA SYNTHESIS OF CERAMIC MATERIALS
FROM LIQUID PRECURSORS

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Abstract

Thermal plasma generated by inductive coupling is used for material synthesis and deposition from liquid precursors. The process is presented and examples of SiC synthesis are given. Coatings with a relatively high porosity can be synthesized and deposited with a rate of up to 20 μm/min. The droplet size of the precursor spray has been identified as a controlling parameter in respect of the resulting coating microstructure.

1. Introduction

The synthesis of material in thermal plasma conditions has started in the late eighties with the use of either a radio frequency (rf) plasma or with a hybrid system (dc plasma torch associated with an rf plasma torch) [1,2]. First gaseous precursors have been used [3], and next liquid precursors mainly based on salts in aqueous solutions have been employed [4]. High deposition rates have been reached by such a process, which range from few μm/min to few tens of μm/min [5]. This is two to three orders of magnitude higher than the one observed in classic CVD methods [6].

This process has the following characteristics: since composition-controlled high-temperature vapors can be generated, preparation of multicomponent films may be easier; any gas can be used as the plasma gas; due to the high reactivity and the high particle density of an rf plasma, high rate deposition can be expected; the use of liquid raw material makes it easier to control the feeding rate of the dense source into the plasma continuously and accurately [7].

More recently, several works have been devoted to deposition of ceramic coatings from solutions by using inductively coupled thermal plasma, for yttria-stabilized zirconia from nitrates in aqueous solutions [8], for high temperature superconductor materials (e.g. NdBa2Cu3O7) from organometalligic sol [9], for titanium and/or aluminum nitrides (Ti1-xAlxN) from alkoxides in ethanol or toluene solutions [10, 11].

This paper presents the synthesis of Si-based ceramic materials by means of rf plasma from azeotropic liquid, being by-products coming from the silicone industry [12], i.e. chlorosilanols. The main difference concerning the process initially developed by Pfender and coworkers [4] and the one presented here is the raw material concentration in the
reactant and then the resulting feed rate of the liquid precursor which was around $10^{-3}$ mol/min for Pfender and which is 0.61 mol/min in our case. This explains two different phenomena of great importance in terms of material processing:

(a) The high deposition rate which can reach few tens $\mu$m/min.
(b) The deposition process and more especially the formation of solid material where the homogeneous nucleation is more likely to occur than the heterogeneous nucleation onto the substrate.

Figure 1 shows the principle of material synthesis under thermal inductive plasma. From this diagram one can distinguish four zones:

(i) spray formation and evaporation of the droplets in the plasma peak temperature zone,
(ii) gas phase chemistry starting,
(iii) aerosol formation, and
(iv) coating building onto the substrate.

![Diagram of aerosol formation through rf plasma synthesis](image)

Figure 1 - Principle of the aerosol formation through rf plasma synthesis.

2. Experimental

The plasma torch is schematically depicted in Fig. 2. The inductively coupled plasma (ICP) torch, a PL-50 model from TEKNA Plasma Systems Inc., is connected to a generator oscillating at 500 kHz and providing 60 kW maximum power. The liquid source is a fraction of carbochlorodisilanes (CDF) containing tetrachlorodimethylsilane (60 mol. %) as main component. The characteristic molar ratios of the whole fraction are C/Si=1.42 and Cl/Si=1.75. The liquid is injected by atomization (by using a plain-jet airblast twin-fluid type atomizer [13]) in the plasma core at the peak temperature zone. Coatings are deposited on
non-cooled Mo plates (40x40x3 mm). Table 1 summarizes the experimental conditions. The spray droplet mean size, measured by means of Dual Phase Doppler Anemometry (DPDA), ranges between 70-100 μm depending on the atomization parameters (liquid and atomization gas flow rates) [14].

![Figure 2 - Schematic of the thermal ICP deposition set-up.](image)

<table>
<thead>
<tr>
<th>Plasma gas flow rate</th>
<th>[slpm]*</th>
</tr>
</thead>
<tbody>
<tr>
<td>central</td>
<td>15</td>
</tr>
<tr>
<td>sheath</td>
<td>60/5-60 10 Ar/H₂</td>
</tr>
<tr>
<td>atomization</td>
<td>5-10 Ar</td>
</tr>
<tr>
<td>Disilane injection rate [ml/min]</td>
<td>0.5 - 2</td>
</tr>
<tr>
<td>H power [kW]</td>
<td>25-40</td>
</tr>
<tr>
<td>Spray distance, Z [mm]</td>
<td>100-200</td>
</tr>
<tr>
<td>Reactor pressure [kPa]</td>
<td>20</td>
</tr>
<tr>
<td>Experiment duration [s]</td>
<td>180</td>
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</tbody>
</table>

*standard litre per minute.

3. Results and discussion

The coatings mainly constituted of rounded agglomerates or cauliflower structured grains are not completely dense. As shown with the scanning electron microscope (SEM) micrographs in Fig. 3, the size of the agglomerates depends on the atomization conditions, mainly on the size and distribution of the precursor spray.

![Figure 3 - SEM micrographs (top view) of SiC coatings](image)

(left) precursor feed rate 1.6 ml/min; Ar atomization gas feed rate 5 slpm; (right) precursor feed rate 0.8 ml/min; idem.
The droplet size is proportional to the following ratio [13]:

\[
D_{\text{droplet}} \propto \left( \frac{Q_l}{Q_g} \right)^{0.5}
\]  

(1)

\(D_{\text{droplet}}\) is the mean droplet diameter, \(Q_l\) the liquid flow rate, and \(Q_g\) the atomization gas flow rate. Varying the ratio of the liquid feed rate to the atomizing gas feed rate results in the modification of the mean diameter of the droplet injected in the plasma. The resulting coating microstructure is changed since the diameter of the "cauliflower" decreases with the droplet diameter. Smaller agglomerates are denser than the larger ones. One can consider two types of open porosity in the coating: (i) the macroporosity existing between the agglomerates, and (ii) the mesoporosity found within each agglomerate due to its poor densification.

Figure 4: SEM micrograph of a fractured SiC coating (left) with its corresponding X-ray diffraction pattern (right).

Fig. 4 shows a SEM image as well as the corresponding x-ray diffraction pattern of an as-synthesized SiC coating. The typical fractured coating SEM picture shows the formation of pseudo-columnar agglomerates oriented perpendicularly to the substrate surface. The X-ray diffraction pattern indicates the presence of pure SiC, mainly the \(\beta\) phase (the cubic polytype) with the \(\alpha\)-phase as secondary phase. The broad peak at low diffraction angle (20°-20°) is attributed to amorphous carbon, knowing that excess of carbon is present in the CDF raw material. No preferential crystallographic orientation has been observed despite the pseudo-columnar structure. It is worth noting that no trace of chlorine has been detected by means of energy dispersive X-ray spectrometry (EDS) on the as-synthesized SiC coatings. This is attributed to the high substrate temperature which impedes the trapping of chlorine coming from the precursor decomposition. The substrate directly heated by the plasma jet is in the temperature range between 1100 and 1400°C.

Fig. 5 shows the influence of the spray distance on the agglomerate diameter which forms the coating. For the same deposition conditions, an increase of the spray distance gives smaller agglomerates in diameter. Moreover, these agglomerates become denser with a longer spray distance meaning that a longer precursor dwell time in the plasma finally allows the deposition of denser agglomerates on the substrate. The coatings are still porous. One way to get denser deposits may be the injection of a finer precursor spray in the plasma jet leading to the formation of smaller agglomerates on the substrate. The lower limit for the mean spray droplet diameter with the atomizer design being used is around few tens \(\mu m\). The use of
atomizer or nebulizer already employed and especially developed for ICP-spectroscopy will permit to reduce the droplet diameter of one order of magnitude, namely few μm, conserving the same liquid feed rate.

Figure 5 – SEM micrograph (top view) of SiC coatings
(left) Z = 150 mm;
(right) Z = 100 mm.

4. Conclusion and outlook

The use of low-cost liquid source material for coating synthesis and deposition by means of thermal ICP gives the possibility to synthesize a broad range of ceramic materials. Here examples of SiC phase associated with a deposition rate of up to 20 μm/min have been achieved. The size of the atomized precursor droplets has been identified as an important parameter controlling the coating microstructure and thus the coating quality. Smaller droplet size and more narrowly sized-dispersed aerosol may lead to a fine-grained microstructure and also may improve the coating properties. The thermal ICP synthesis process is still in its infancy and thus needs further development in term of both experimental and in situ diagnostic aspects in order to follow the chemistry occurring in the plasma, as well as of the whole process modeling.

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References