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Droplet size prediction in ultrasonic nebulization for non-oxide ceramic powder synthesis

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ABSTRACT

Spray pyrolysis process has been used for the synthesis of non-oxide ceramic powders from liquid precursors in the Si/C/N system. Particles with a high thermal stability and with variable composition and size distribution have been obtained. In this process, the mechanisms involved in precursor decomposition and gas phase recombination of species are still unknown. The final aim of this work consists in improving the whole process comprehension by an experimental/modelling approach that helps to connect the synthesized particles characteristics to the precursor properties and process operating parameters. It includes the following steps: aerosol formation by a piezoelectric nebulizer, its transport and the chemical-physical phenomena involved in the reaction processes. This paper focuses on the aerosol characterization to understand the relationship between the liquid precursor properties and the liquid droplet diameter distribution. Liquids with properties close to the precursor of interest (hexamethyldisilazane) have been used. Experiments have been performed using a shadowgraphy technique to determine the drop size distribution of the aerosol. For all operating parameters of the nebulizer device and liquids used, bimodal droplet size distributions have been obtained. Correlations proposed in the literature for the droplet size prediction by ultrasonic nebulization were used and adapted to the specific nebulizer device used in this study, showing rather good agreement with experimental values.

1. Introduction

The spray pyrolysis process has been used to produce silicon nitride and silicon carbide based materials, which are interesting because of their thermal structural properties. It consists in the ultrasonic production of an aerosol from a liquid precursor which is then transported by a gas into a furnace where the precursor droplets are decomposed and then recombined to form solid ceramic powders. The spray pyrolysis allows to obtain spherical nanosized multi-element particles with variable compositions and size distributions. The synthesis of composites from a ceramic precursor allows a better control of powders composition in comparison with other conventional methods, like powder mixing, to obtain Si_3N_4/SiC composites [1–3]. The synthesis of non-oxide nanosized particles by spray pyrolysis was studied in the Si/C/N system, from hexamethyldisilazane (HMDS), and the as-formed powders are thermally and chemically stable with a relative narrow size distribution [4–6]. The use of HMDS, pure or with sintering aids, as a precursor, leads to the formation of Si_3N_4/SiC composites, and a variation of the size and composition of the yielded powders was observed depending on the synthesis atmosphere, temperature and the nature of the precursor [7,8]. In these studies, different parameters were investigated to find the optimal conditions for powder synthesis. The change in the pyrolysis atmosphere affected both size distribution and composition evolution. Generally, the presence of NH_3 in the atmosphere results in the reduction of the free carbon content in powders and a narrower size distribution is obtained with the addition of H_2 in the reaction gas [5,8]. These studies led to identify the optimal parameters for powder synthesis and to evaluate the characteristics of the powder obtained. Nevertheless, the involved mechanisms in the precursor decomposition and the ceramics powders formation are still unknown. For this reason, and considering that the formation of particles is governed by the *One Droplet One Particle* (ODOP) mechanism [9], this study aims to contribute to the comprehension and prediction of the powder characteristics depending on the liquid precursor properties by a dual experimental/modelling approach, for the specific system of hexamethyldisilazane precursor. Because of its complexity, the process is separated in two main parts: (i) the aerosol formation from the liquid precursor by the generator device and (ii) the thermal decomposition and recombination of species in the

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furnace. In this paper, the aerosol droplet size distributions were obtained experimentally with a shadowgraphy imaging device. An empiric modelling of the mean particle diameter depending of the precursor physical properties and nebulizer device was then carried out by adapting correlations laws proposed in the literature to the specific device and liquids used in this study. These liquids, which properties are close to the precursor of interest will allow to predict its behavior during the aerosol generation step. This model define an initial state of the precursor before entering in the reaction zone corresponding to the decomposition and recombination steps, establishing a clearer relationship between the aerosol and final powders characteristics and contributing to understand the mechanisms involved in the process.

1.1. Ultrasonic nebulization

In the spray pyrolysis process, the precursor aerosol is generated by ultrasonic nebulization. This process has been widely used in the medical field, but also in the production of nano-sized particles by spray pyrolysis [4,5,9–15]. Ultrasound waves are applied to a film or a volume of liquid by a piezoelectric actuator to cause its fragmentation into fine drops. The formation of a spray from a liquid by ultrasound waves is supposed to be caused by two principal mechanisms: the capillary wave instability development at the liquid surface and the cavitation phenomenon.

The droplet formation due to capillary waves is based on Taylor's instability theory which explains the instability apparition and development at the interface between two fluids with different densities: this phenomena appears at relatively low frequency of ultrasound (20–100 kHz) and is represented by the formation of a well-structured wave pattern on the liquid surface, observed by some authors [16–19]. The waves produce drops from the ejection of their peaks when they are destabilized [17,20]. The cavitation phenomenon appears at higher frequencies (0.1–5 MHz), and is caused by local changes in pressure, due to high frequency waves through the liquid, that forms vapor cavities in the liquid volume until their implosion causes liquid rupture with droplet ejection [20,21].

Bouguslavskii and Eknadiosyants [22] have suggested that droplet formation by ultrasonic nebulization is due to the interaction between the two mechanisms described above, where the capillary waves in the liquid surface are disturbed by the shock caused by cavities implosion causing the droplet ejection from waves peaks. This assumption helps to explain the random behavior observed in nebulization at relatively high frequencies and the loss of uniformity in the pattern of capillary waves observed before droplet ejection [17]. To the best of our knowledge, neither of both mechanisms responsible of droplet formation have been modeled simultaneously in the literature; capillary waves have been described but in a schematically way. Cavitation phenomenological studies are mainly applied to the damage caused by this phenomenon to materials without focusing on mechanisms of droplet formation. Due to the complexity and lack of information about these mechanisms and the relationship between one another, the choice was made to experimentally determine the aerosol droplet size distribution in order to adapt the correlations laws of the literature to the experimental results.

Ultrasonic nebulization has been studied on a wide range of liquids by different authors, usually using an ultrasonic nozzle with a vibrating tip as nebulizer device. This kind of nozzle, schematized in Fig. 1, allows the nebulization of low amounts (a thin film) of liquid in an efficient way.

Some authors [16,18–20,23,24] were interested in determining the droplet size obtained with this type of device. One of the first works in this area was done by Lang [16] who measured the droplet diameter of re-solidified molten wax. The correlation of the experimental estimation of the drop diameter and the wavelength of capillary waves based on the Kelvin's equation (Eq. (1)) was used to propose an expression to predict drop median diameter (Eq. (2)). The Kelvin's equation was first developed to describe the change of vapor pressure due to a liquid-vapor curve interface and further used for the study of capillary waves phenomena [17,25,26].

$$\lambda = \left(\frac{2\pi\sigma}{\rho F^2}\right)^{\frac{1}{3}} \quad (1)$$

where λ is the wavelength (m), σ the surface tension (N/m), ρ the density (kg/m^3) and F the frequency of surface waves, considered as the half of the device ultrasound frequency f (1/s). In his work, Lang does not take into account the cavitation phenomena. For different liquids and nebulizer operating conditions, several other authors [18–20,23] proposed expressions of droplet diameter involving both capillary waves and the cavitation phenomena, represented by the combination of dimensionless numbers characteristic of the process. These expressions are presented in Table 1 (Eqs. (2)–(6)). The dimensionless numbers are the Weber number (*We*) that compares the effect of inertia forces and surface tension of the liquid, and the Ohnesorge number (*Oh*) that compares the effect of viscosity to inertia and surface tension. Rajan and Pandit [20] modified the original expressions of these numbers and introduced the intensity number (*In*) to take into account the nebulizer power rate delivered to the liquid film.where d is the droplet diameter (m), Q the liquid volume flow rate (m^3/s), η the dynamic viscosity (Pa·s), I the intensity of ultrasound (W/m^2). The constant, A, in Rajan and Pandit's expression is 0.1, and the parameter n in Avvaru's expression corresponds to the flow behavior index of

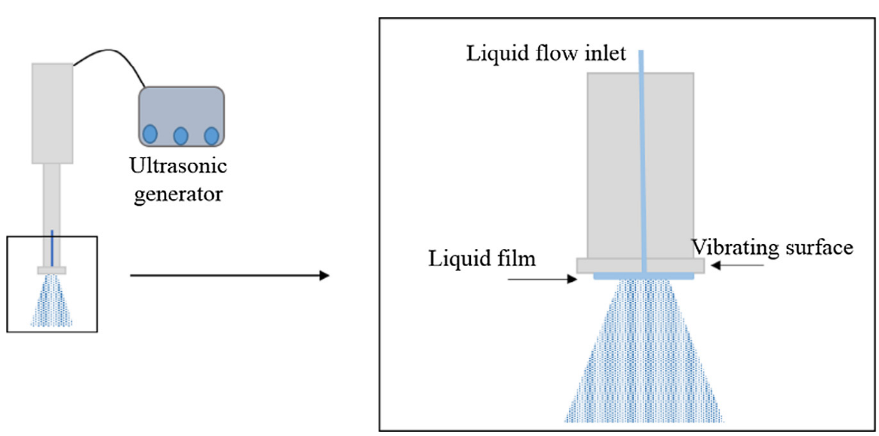

Fig. 1. Schematic representation of the ultrasonic nozzle used in several studies [18–20,23].