SYNTHESIS OF ULTRAFINE POWDERS OF SILICA IN A DC TRANSFERRED PLASMA ARC FURNACE

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Abstract

Ultrafine silica powders are produced in a DC transferred arc plasma furnace. The raw materials is sand with a diameter range between 100 to 315 μm, and contained 98.5 % of SiO_2*. Different plasma forming gases (Ar,* Ar/H_2*, Ar/CO, and* Ar/O_2 *) were tested. The process consisted of : the vaporization and the dissociation of sand, then the oxidation of Si and SiO to reconstitute* SiO_2 *in the reactor and finally the nucleation and the growth of produced powders in the heat exchanger and into the baghouse.*

In order to optimize experimental running parameters, the thermodynamic equilibrium prediction and the heat and mass transfers between sand injected in the furnace and the arc plasma were studied.

The experiments show that the process used is very flexible. It allows the synthesis of amorphous and white powders, with various characteristics (spheric or fiber shape, specific surface from 17 m^2/g *up to 330* m^2/g*, powders contain until 99.0 % of* SiO_2*, ...) under different running parameters.*

Introduction

Ultrafine powders with high purity, diameter less than 1 μm and monodispersity, are of interest in the production of catalysts, ceramics, electronic devices etc. Generally, using conventional methods such as carbothermal reduction or milling and direct reaction between the metal and the appropriate gaseous reactant, to produce this type of powders is difficult and at some time is impossible. The thermal plasma has a very high temperature (up to a few 10^4 K), a high mass enthalpy and a high quenching rate ($\sim 10^6$ K/s and more), so that it has been used to synthesize the ultrafine Al_2O_3 [1], AlN [2], SnO_2 [3], SiO_2 [4, 5, 6], etc.

Ultrafine silica powders has for many years been applied as thixotropic additives in inks, paints and polymers, thickening for greasers, flow control agents for powders, reinforcing fillers for electronic, catalyst substrates and as raw materials for advanced glass [7, 8]. In last decade, ultrafine silica powders were found to be a suitable pore filler, so they were widely used to make the high strength concrete [9]. Commercial ultrafine silica powders is made by so-called the flame process using $SiCl_4$ as the starting materials [7, 8, 10]. The disadvantage of the flame process is the toxicity and corrosion of $SiCl_4$ and the disposal of HCl. Ultrafine silica powders have also been prepared by sol-gel process [11], direct oxidation of silicon process [12] and plasma process. For sol-gel or direct oxidation processes, the quality of product was good but the expensive raw materials and the small production limited its applications. Whereas, with the plasma process, the very low cost of sand can be used as raw material. For this process, Sayce [4] developed a centrifuge liquid-wall furnace, Lonza company 5, 13] have studied an alcohol liquid-stabilizing plasma torch to prepare silica powders. In these two furnace, sand was used as raw materials but the process was difficult to continuously operate. In 1987, Gauvin's group [6] produced the ultrafine silica powders by introducing sand into a plasma transferred-arc reactor.

The present work reported ultrafine silica powders synthesis by a transferred arc plasma process. This process consists of vaporizing sand particles in a plasma furnace which subsequently dissociates into SiO gas and oxygen. Then a quench of the gaseous mixture with oxygen reconstitutes SiO_2 in a fume form. Finally, the nucleation and the agglomeration of fumed silica simultaneously take place in the exit system. In order to assist the dissociation of SiO_2, various reacting gases (H_2, CO, or O_2) are also injected into the reactor.

To optimize the experimental parameters, on the one hand, a thermodynamic equilibrium analysis and on the other hand, a heating and evaporation of the particles injected in the arc plasma are investigated. Then a variety of operating conditions are tested. For each test, the products are analysed by X-ray, SEM, TEM etc.

1. Thermodynamic equilibrium analysis

A thermodynamic equilibrium analysis was performed to determine the vaporization/dissociation temperature, $T_{vap\text{-}dis}$, at which SiO_2 condensed phase disappears in the systems considered and the minimal necessary enthalpy of dissociation of SiO_2.

This analysis, under the assumption of the complete thermodynamic equilibrium, is based on the minimization of Gibbs free energy and mass conservation of the system [14].

In Figure 1, the chemical composition of $SiO_2/Ar/H_2$ system at atmospheric pressure, is plotted as a function of the temperature.

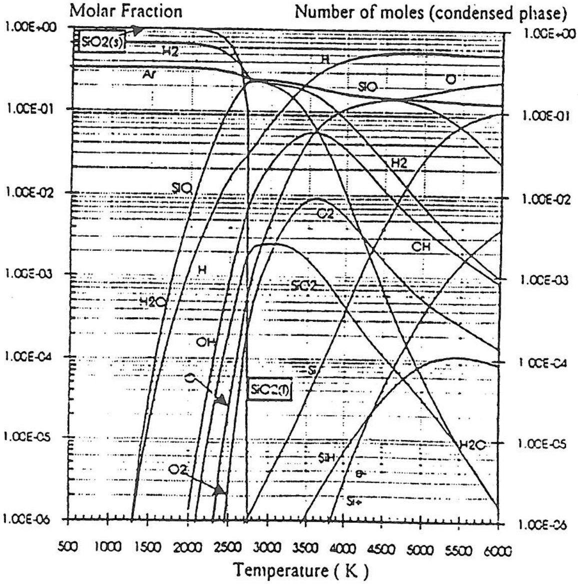


Fig. 1 : Chemical composition of the system $SiO_2/Ar/H_2$ versus temperature

At the low temperature, the SiO_2 solid is stable up to 1400 K. Beginning this temperature, the dissociation of SiO_2 occurrs and, at $T_{vap-dis}$ =2800 K, the concentration of SiO_2 in condensed phase decreases dramatically. Above this temperature, all species in the system are gases. It should be noted that the concentration of OH in the system is considerable. The presence of OH will form water when the gases become cold. The water could affect the silica particle growth process and would aid the formation of hydroxyl groups on the surface of particles, which impart strong thixotropic properties to aqueous suspensions of the materials. In addition, SiO gas is very stable for the computational temperature range.

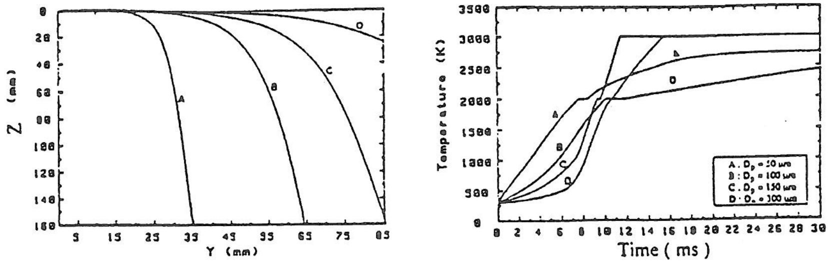
For different systems, $T_{vap-dis}$ and the minimal enthalpy of dissociation are listed on Table 1. It is obvious that the introduction of reducing gas permits to decrease $T_{vap-dis}$ of SiO_2 in condensed phase. The increases of the plasma gas feed rate and the fraction of reducing gas H_2 or CO lead to the decrease of $T_{vap-dis}$, but the higher energy consumption is needed. Among of reducing gases, the hydrogen has a very strong reducing effect. $T_{vap\ dis}$ of SiO_2 in condensed phase in the presence of H_2 can be 2630 K with 3 moles of H_2. In an inert atmosphere, this temperature is 3080 K. The system energy consumption of vaporization/dissociation of SiO_2 in the presence of H_2 is also found to be lower than the energy consummation of other systems.

Chemical System	$T_{vap-dis}$ [K]	$H_{300}^{SiO_2}(T_{vap})$ [kWh/kg]
SiO_2 + Ar	3080	4.822
SiO_2 + 2 Ar	3020	5.121
SiO_2 + 3Ar	2990	5.386
SiO_2 + Ar + O_2	3100	5.606
SiO_2 + Ar + 2 O_2	3040	5.996
SiO_2 + Ar + CO	2990	4.419
SiO_2 + Ar +2 CO	2930	4.618
SiO_2 + Ar + H_2	3010	4.352
SiO_2 + Ar +2 H_2	2800	4.415
SiO_2 + Ar +3 H_2	2630	4.519

Table 1 : Temperature and Enthalpy of vaporization/dissociation of SiO_2

2. Heating and Evaporating of sand in a transferred arc plasma furnace

The vaporization/dissociation of sand injected is a important stage to obtain a high quality of silica powders. For a single particle, the trajectories are calculated by solving a simplified Basset-Boussinesq-Oseen equation and the instantaneous particle temperature is determined by an energy conservation equation on the particle [15, 16]. The characteristics of the particle (surface temperature, position, velocity, diameter)are simultaneously determined versus the position in the experimental plasma furnace [17].



2 a : Trajectories of particles

2 b : Surface temperature of particles

Fig. 2 : Evolution of the trajectories and the surface temperature of particles versus the dwelling time (Horizontal injection, Initial sand velocity : 10 m/s, maximal plasma velocity : 100 m/s

The trajectory and the surface temperature of sand of diameter of 50, 100, 150 and 300 µm are calculated. Typical results for argon plasma are shown in Figure 2 and 3. The trajectory of the particle is affected strongly by its size (Fig. 2a). In fact, the maximal radial distance reaches by the particles of diameter of 50 and 150 µm are 35 and 85 mm respectively (85 mm corresponds to the central line of the plasma column). As function of its trajectory, the surface temperature of the particle varies strongly (Fig. 2b). For example, at the end of a same computational time ($t = 30$ ms), the particle of diameter of 50 or 300 µm even can't attain the evaporation temperature (3000 K), but this temperature is quickly realized by the particles of 100 and 150 µm. These results are explained by the fact of which the middle size of particles enters easily the hottest zone of the plasma column. However, the particles with too small size can't enter into the high temperature region of the plasma due to the weak kinetic energy. With too large size of particles the dwell time in the high temperature region of plasma was too small for heating and vaporizing to occur. There are some optimal sizes of particle (diameter between 65 and 200 µm) for which the particle evaporation rate will be high.

Introducing reacting gas into argon plasma can effectively improve the evaporation rate of particles (Table 2). This effect is owing to the increase of the thermal conductivity and at same time the decrease of viscosity of plasma. So, from above theoretical studies, the sand chosen is suitable to the synthesis experiments and other gases introduces into argon plasma would facilitate the dissociation of sand.

Plasma gases	τ [ms] Dp =100 µm	τ [ms] Dp =150 µm
pure Ar	72.3	63.8
Ar : H_2 =1: 2	6.1	9.2
Ar : CO =1: 2	12.6	18.2
Ar : O_2 =1: 2	24.1	30.1

Table 2 : Minimal time τ for realizing a complete evaporation under different gases

3 . Experimental Set-up

The experimental device used in this study is shown schematically in Figure 3. The chamber of the transferred arc plasma reactor is made from a double wall of stainless steel with a water cool system. The thoriated tungsten cathode is protected by an argon injection when others gases such as : H_2, CO, O_2 or some mixtures of these gases are introduced in the shroud. This particularity of this reactor, running with a plasma forming gas containing an high proportion of oxygen, is the insignificant erosion of cathode. The sand to evaporate is injected into the furnace in a graphite crucible used as anode. Cathode and anode can be moved staight up or down, so arc length can varied between 1 and 20 cm. The arc current intensity used is in the range of 60 up to 1000 A.

In order to realize a high synthesis efficiency of ultrafine silica powders, the concentration of SiO or SiO_2 in vapor phase should be maximum at all time. Therefore, the furnace temperature must be maintained as high as possible. Due to the high temperature involved, the furnace is lined with a rigid graphite wool and two graphite furnaces to provide thermal insulation. A DC arc is struck between the cathode and the anode, then, the wanted arc length is adjusted. The exhaust gases are evacuated through the quenching module where approximately 100 Nl/mn of air or oxygen are introduced. Then, they run through a heat exchanger and two cyclones which are cooled by water. The powders elaborated are collected in a bag filter made of dralon.

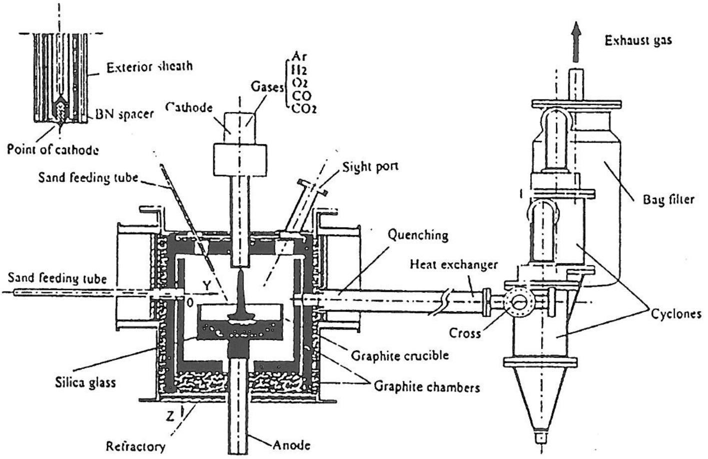


Fig. 3 : Experimental set-up

The silica sand used had a particle size classification of 85% in a range from 100 to 250 μm and a purity of 98.5% of SiO_2. The sand is introduced into the furnace by a horizontal or oblique injecting tube. The carrier gas of sand is argon (10 Nl/mn).

Typical operating conditions are : current : 300 - 800 A, voltage : 70 -160 V, argon : 10 - 60 Nl/mn, electrode gap : 100 - 180 mm, power : 21 - 128 kW, sand feed rate : 30 – 60 g/mn and other gases (H_2, CO, O_2, etc.) rates dependent on test.

The energy distribution throughout the system depends on the type of the sand injection when sand was horizontally injected into the furnace, the thermal losses are as following :15 to 37 % at the anode, 20 to 23 % on the walls of the reactor, 7 % in the cathode and equipment that gotogether, and, the other losses are distributed in the other parts of the system.

The powders deposited in the reactor are white. The X-ray diffraction spectrum does not present any peak. It indicates the powders are amorphous. Chemical analysis of the powders collected in the bag filter give a purity of SiO_2 of 98.5 %. The main contamination in the products are Al_2O_3, CaO, C and volatile gases. These originates from the raw materials, the furnace refractory and the formation of H_2O, CO_2. If the products are treated by a post thermal stage, the impurities will be significantly eliminated.

TEM photomicrographs of the products show that the average size of powders is about 140 nm and the powders agglomerate each other to form some three-dimensional aggregates (Fig. 4). Fig. 5 presentes the diameter distribution of the products issued from the bag filter. The range of the particles size is from 20 to 700 nm and most particles have a diameter between 50 and 400 nm. The BET measurement

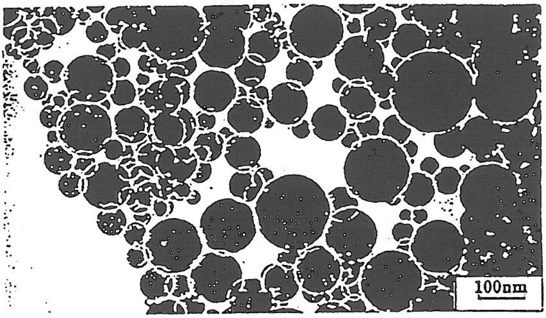
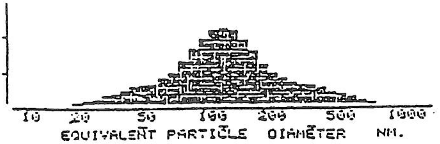


Fig.4 : TEM picture of the particles collected in the bag filter

for this product is 75 m^2/g. When CO is added into argon plasma as reducing gas, high value of the specific surface of powder (until 330 m^2/g) can be realized. In this case, the powders have strong agglomerating tendency. The density of powders produced varies from 1.60 to 2.07 g/cm^3. It increases with the decrease of the BET values.



characteristical size (nm)	cumulated mass (< %)
47	13
133	71
381	16

Fig. 5 : Size distribution of the powders collected in the bag filter

Conclusion

The production of ultrafine silica powders is carried out in a DC transferred arc plasma furnace by injecting sand as raw materials (a diameter range from 100 to 315 µm, and contains 98.5 % of SiO_2). Under different operating conditions, the process used allowed the synthesis of amorphous and white powders, with different characteristics (spherical or fiber shape, specific surface from 17 m^2/g up to 330 m^2/g, SiO_2 contains until 99.0 %,...). The experiments show that this process is very flexible and is in continuous manner.

Acknowledgments : The authors wish to acknowledge Lafarge Nouveaux Materiaux for its financial support and G.Guillevic for his kindly help. The authors thank J.P. Laval, P. Lortholary and J.P. Lecompte (University of Limoges, France) for their participation in the powder characterizations.

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