SYNTHESIS IN AN R.F. PLASMA REACTOR OF SILICA POWDERS DOPED WITH ALUMINA

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ABSTRACT

This paper deals with the elaboration and characterization of ultrafine (30 to 90 nanometers) and ultra pure (total impurity content <1 ppm) silica powders doped with alumina. The basic materials : silicon and aluminum powders with particle size < 40 µm and purity > 99,999 %, are injected into an R.F. plasma reactor where occur their vaporization, oxidation and quenching. The other properties of synthesized powders are : grain size increase with alumina content, spherical shape, core doping and homogeneous chemical composition.

I. INTRODUCTION

R.F. plasma technology has been developed during the sixties by T.B. Reed (1) (2). Its application to silica synthesis by $SiCl_4$ oxidation has been investigated by Audsley and al. in 1969 (3). Later on, in 1975, Mac Pherson (4) (5), starting from halides ($AlCl_3$, $AlBr_3$) has studied silica doping conditions inside an R.F. plasma reactor. Moreover, since the laboratory realization of silica optical fibers with very low attenuation (<2 db/km) able to be used in the telecommunication field, the interest of the fabrication, in great quantities, of high purity doped or undoped silica has largely increased. Among the several methods presently used, those involving an R.F. plasma are taking a growing position due to their capability of high productivity in a pollution free atmosphere.
Unlike the other plasma methods the one presented here uses metallic powders as starting materials instead of gazeous halides.
The objective is to obtain ultrapure, ultrafine and chemically homogeneous silica powders doped with alumina which can be used in the elaboration of optical fiber preforms after a vitrification heat treatment.
The work presented here deals only with the elaboration and the characterization of the synthesized powders.

II. POWDER SYNTHESIS

Basic materials are silicon and aluminum powders with particle sizes ranging from 10 to 40 µm and purity > 99,999 %. The argon plasma reactor is powered by a 12 kW - 8 MHz generator. The reactive gases are oxygen or an argon-oxygen mixture. The reactor has been already described in

other papers (6) (7). It is formed by three vertical communicating chambers (Fig. 1).
Two essential conditions must be fulfilled to carry out the cycle of successive processes involved to synthesize silica powders doped with alumina :

- a 100 % chemical efficiency
- a very homogeneous grain composition.

To get the nearest of 100 % efficiency, it is essential to obtain at first the total vaporization of basic materials and secondly the complete oxidation of metallic vapours.
To get a homogeneous grain composition the metallic vapours have to be well mixed with the reactive gas during the initial stage of condensation in which appear SiO_2 and Al_2O_3 germs which grow afterwards by coalescence. The detailed process is explained in the following sections.

II.1. POWDER TOTAL VAPORIZATION

In order to obtain the total vaporization all the silicon and aluminum particles coming out from the injection probe must be vaporized when crossing over the plasma furnace. In fact we have found that the plasma resists to particle penetration. According to Chase (8) this is due to gaseous streams which create a point of maximum pressure nearby the induction coil center. (Fig. 2A)
Moreover the existence, on the symmetry axis, of two direction opposed streams prescribes the use of a central carrier gas jet for the basic powder injection (Fig. 2B).
We have checked the Chase's observations and moreover have pointed out a modification of the plasma shape when the carrier gas flow varies. For small flows, carrier gas and particles are thrown out to the plasma periphery (Fig. 2B). When the gas flow is such that the central jet enters more deeply into the plasma without crossing the point of maximum pressure (critical flow) the gas and the particles are again thrown out to the periphery (Fig. 2C). At higher flows the carrier gas breaks through the plasma creating, in its center, a cylindrical dark zone whose diameter is always equal to the probe external diameter (Fig. 2D). In that case the plasma becomes ring-shaped, the carrier gas is scattered on the length of the induction coil and a part of the gas and particles is still thrown out to the periphery. This phenomenum disappears when the end of the injection probe is placed at the maximum pressure point level. For that probe position and with a carrier gas flow slightly higher than the critical flow the best conditions of total vaporization are obtained (9). Thus the metallic vapours are guided in the middle of the plasma before entering the reaction and quenching chamber, so promoting the mixture homogenization.

II.2. COMPLETE OXIDATION AND MIXING

For the concerned reactor the experience shows that :
- the mixing ensuring the best metallic vapour homogenization is obtained with a reactive gas injected, under the induction coil level, through three symetric points disposed on a circle.
- the reactive gas flow must be, at least, two times the flow needed to meet the stoechiometric conditions and the oxidation efficiency does not change with flow as high as fifty times these conditions.

From these results it is possible to deduce that :
- a 100 % efficiency can be reached when the vaporization is total and the homogenization of chemical compounds is well ensured.
- above a certain threshold the efficiency does not depend on temperature and oxygen partial pressure.
- the oxidation reaction velocities are faster than the quenching reaction velocities (Table 1).

II.3. GRAIN GROWTH

Two mechanisms are possible to explain grain growth : from the vapour phase and by coalescence. Presently, as previously reported (4) (9) (10), we believe in the assumption of a coalescence growing mechanism. This mechanism is based on the inter-particle collisions from initial germ appearance temperature (≃ 2600°K for our experimental conditions) to the temperature of zero probability for coalescence (elastic collisions). The latter temperature being well below the melting point (5) (11). Moreover the silica liquidus temperature (11) decreases and the surface tension (12) increases when the alumina content increases. Consequently the coalescence time and therefore the particle size should increase with the alumina content.

III. POWDER PROPERTIES

Some results concerning the powder properties have been published elsewhere (13). These can be briefly summarized as follows :
- the pollution introduced in the basic material preparations and the chemical synthesis is lower than 1 ppm,
- the synthesized powder compositions fit very well the values calculated on the basic materials (no loss of dopant) and are homogeneous in the collecting chamber (isotropic reactor) for aluminum compositions varying between 0 and 15 % by weight.

The main results concerning the measurements of the particle sizes and the powder structure are the following :
- the SEM micrographs (Fig. 3) show the grain spherical shapes, the diameter increase with the aluminum content and make obvious the coalescence mechanism for the particle growth,
- the grain mean size increases linearly between 30 and 90 nanometers for aluminum content varying between 0 and 15 % by weight (Table 2, Fig. 4)
- the X ray diffraction analysis always show a total amorphous structure whatever the alumina content in silica is.
- the particle size distribution curves (Fig. 5) show an increase of the grain mean size and of the distribution width when aluminum content increases
- the linear variation of the grain mean size with aluminum content and the X rays diffraction results suggest, for the studied range of compositions, a core doping and an amorphous structure of each grain.

These above mentioned results emphasize our assumption of a coalescence growing mechanism.

IV. CONCLUSION

This work indicates that it is possible to obtain, with a low power (12 kW - 8 MHz) R.F. plasma reactor, the chemical synthesis of silica powders doped with alumina by using metallic powders as starting materials.

The noteworthy properties of synthesized powders are : purity, ultrafine grain size, spherical shape, homogeneous chemical composition and core doping.

In the future this work will be carried on with a powerful R.F. plasma reactor (40 kW) in order to realise, in situ, the vitrification of the synthesis products.

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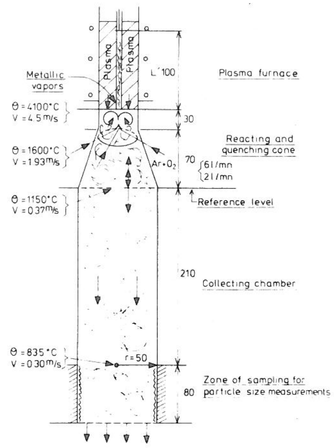


SCHEMATIC OF THE REACTOR FEATURING QUENCHING PROFILE

F.g.1 (Lengths in mm)

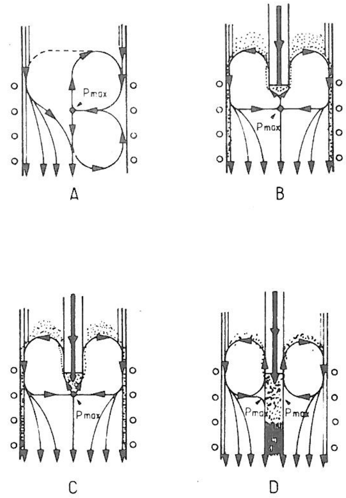
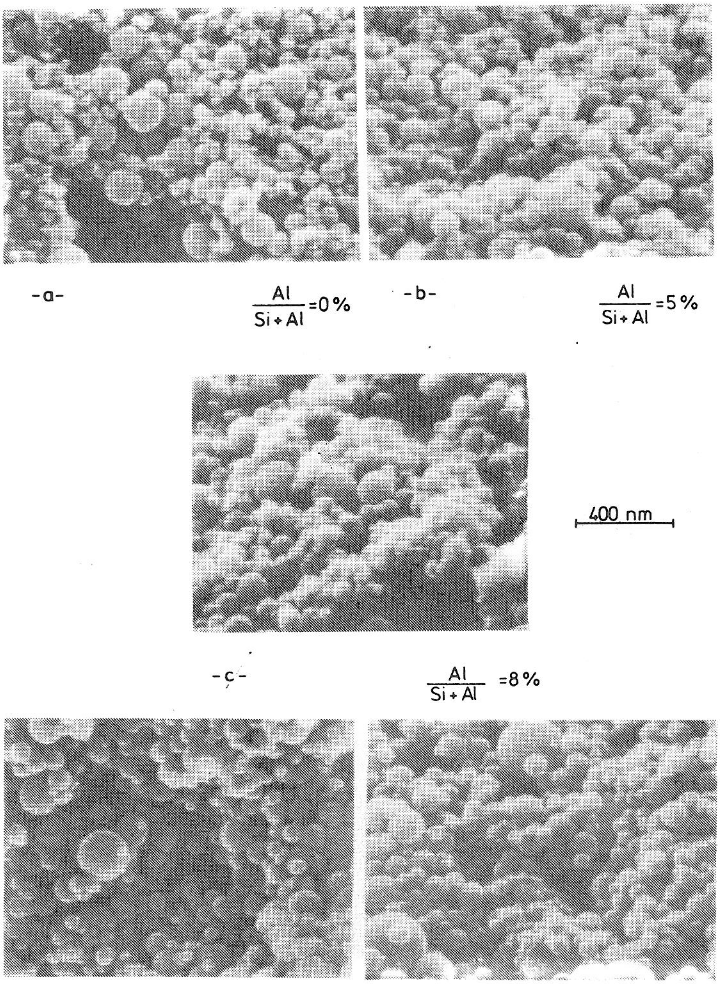


Fig.2 Powder Total Vaporization



-a- $\frac{Al}{Si+Al}=0\%$

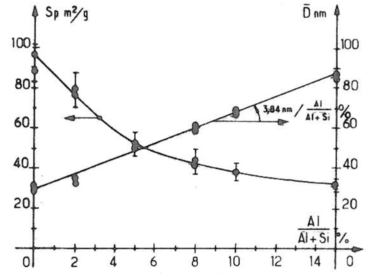
-b- $\frac{Al}{Si+Al}=5\%$

-c- $\frac{Al}{Si+Al}=8\%$

-d- $\frac{Al}{Si+Al}=10\%$

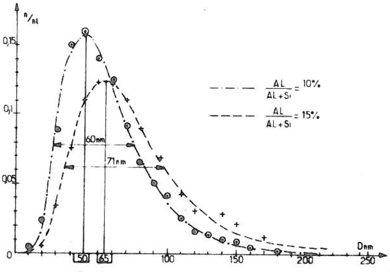
-e- $\frac{Al}{Si+Al}=15\%$

Fig.3 SEM micrographs of silica powders containing alumina .



● Particle size as a function of aluminum percentage

Fig. 4



Particle size distribution

Fig. 5

Table 1 _ Quenching velocities

Axial Temperature °C and measurement position Cm	Temperature gaps per centimeter °C	Corresponding time gaps Sec	Quenching velocity °C/sec	Added times in the reactor sec
4100 - 10	3000			
2900 - 9	1200	$2,6 \times 10^{-3}$	$4,60 \times 10^{5}$	$2,6 \times 10^{-3}$
2000 - 8	900	3,6	2,5	6,2 /
1620 - 7	380	5,2	$7,33 \times 10^{4}$	$1,14 \times 10^{-2}$
1400 - 6	220	6,7	3,280	1,810 /
1350 - 5	50	9,4	$5,3 \times 10^{3}$	2,75 /
1300 - 4	50	$1,22 \times 10^{-2}$	4,1	3,97 /
1255 - 3	45	1,55	2,9	5,5 /
1230 - 2	25	1,92	1,3	7,4 /
1180 - 1	50	2,33	2,1	9,77 /
1150 - 0	30	2,7	$1,10 \times 10^{-3}$	$1,25 \times 10^{-1}$
835 + 25	315	$6,6 \times 10^{-1}$	$4,8 \times 10^{-2}$	$7,9 \times 10^{-1}$

Table 2 _ Particle mean size

Aluminum content (mol %)	Specific surface B.E.T. sp m^2/g 1st mesure	2nd mesure	Mean size (nm.) BET $\bar{D} = \frac{6}{\rho S_p}$	ME $\bar{D} = \left(\frac{\Sigma n_i D_i^2}{\Sigma n_i}\right)^{1/2}$
0	94,8	88,5	28,3 30,8	
2	80	76,8	34 35,4	
5	51,8		52,2	
8	42,4	45,3	63,3 59,6	
10	39,3	38,6	68,2 69	68
15	30,7		86,9	85