Optical Measurements of heat treated silica samples

F.Mazzocchi[1], T. Scherer[1], R. Saavedra[2] , P. Martin Martinez[2]
[1]Karlsruhe Institute of Technology, 76344, Eggenstein Leopoldshafen (GER)
[2]Centro de Investigaciones Energeticas, Medioambientales y Tecnologicas, 28040 Madrid (ESP)

***Abstract* — In the following article the measurements performed at CIEMAT on several silica samples are described. The samples were treated in both N_2 and O_2 atmosphere, in a temperature range from 500 to 1000 °C. The measurements include UV – VIS – NIR absorption spectroscopy, FT-IR transmission and reflectance spectroscopy, and visual inspection of the treated samples with a confocal microscope.**

INTRODUCTION

WITHIN the studies required for the realization of the next generation nuclear fusion reactors, great focus has been posed on material analysis and treatment. The high power, high mechanical stress and high radiation and thermal load that the components of the various subsystems composing the reactor must endure require materials capable of enduring such harsh conditions without significant degradation in their performances. Silica, is a reference material for diagnostics windows. Therefore, the limits of the materials and the possible improvements given by surface treatment must be investigated. The samples analyzed consisted in three different kind of silica glass: KU1 and KS-4V high purity silica that are both reference material for

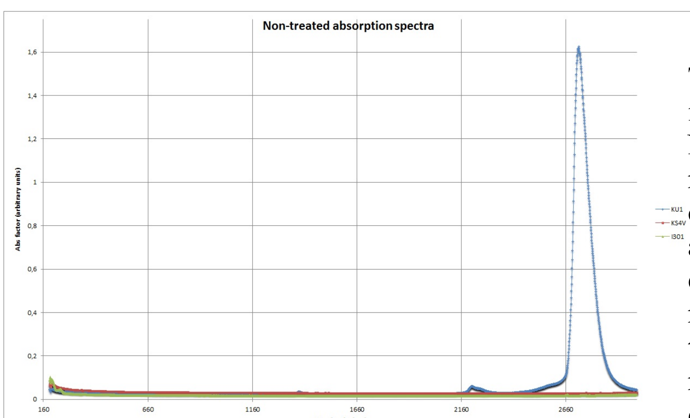

Fig.1 Absorbance spectra in the UV-VIS-NIR region. The KU1 spectra shows a peak in the 2700 nm region, where the OH impurities given by its "wet" nature absorb infrared light.

ITER and I301, a commercial glass from Heraeus. The various types of fused silica differ for the growing technique, the origin of the raw material (synthetic KU1 and KS-4V or natural for the I301) and the content of OH species, impurity and defects. KU1 is a of wet kind, produced by continuous high temperature hydrolysis of silicon tetrachloride - SiCl4 in hydrogen-oxygen flame, therefore presents a higher content of watery species that gives higher absorption in the IR region[1]. KS4V is produced by chemical gasification of silicon, oxidation of this gas to silicon dioxide (SiO2), and thermal fusion of the resulting ash in vacuum.[2] Focus of the annealing treatment is to allow the recombination of defects

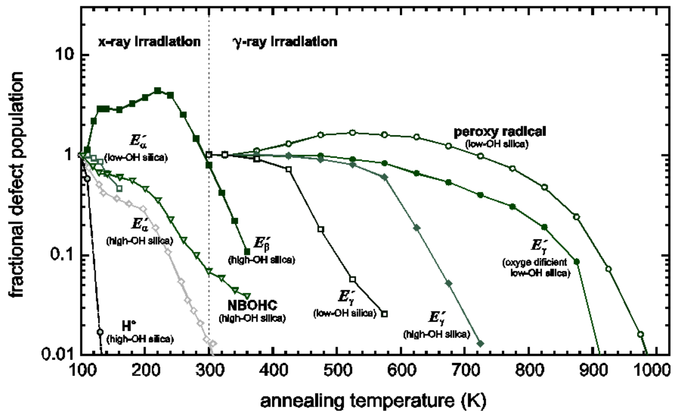

Fig.2 Fractional defects population vs annealing temperature

centers and water species diffusion through structural relaxation in the samples [3].

RESULTS

The experimental setup consisted of 3 different instruments: a Cary 5E UV-Vis-NIR (200 – 3000 nm), a Nicolet FT-IR spectrometer for both absorbance and reflection measurements and an optical Leica DCM8 confocal microscope, for visual inspection. For the annealing a programmable oven has been used. The electronics on the latter allowed to select temperature ramp up time (in 10°C steps) and the duration of the treatment. Differences are visible in the absorption and reflection spectra of the samples without treatments, especially in the IR (Fig.1). The treatment consisted in subsequent annealing of the sample, at 500, 800 and 1000 degrees for two hours, in N2 and O2 atmosphere. All the samples have been cleaned with acetone before and after every cycle in the oven and every measure inside the spectrometers. The composition of the atmosphere during the annealing doesn't seem to affect in a sensible way the performance of the samples. The treatment itself slightly improves the transmission properties of the materials. The major benefits of the treatment were observed in the KU1 samples, given the higher OH content. In particular, the first sample of this kind, shows generally a high reflectance that decreases after subsequent treatments. The analogous absorbance spectra from the very same instrument shows almost no changes through two different samples (N_2 and O_2 treated) and the whole set of treatment temperatures. This suggests that the biggest effect of the annealing process is located on the surface of samples , while is less effective in the bulk material. It may be possible that the 2 hour annealing time is not sufficient for the bulk defects to effectively recombine. Further investigation is required, in order to establish if extending

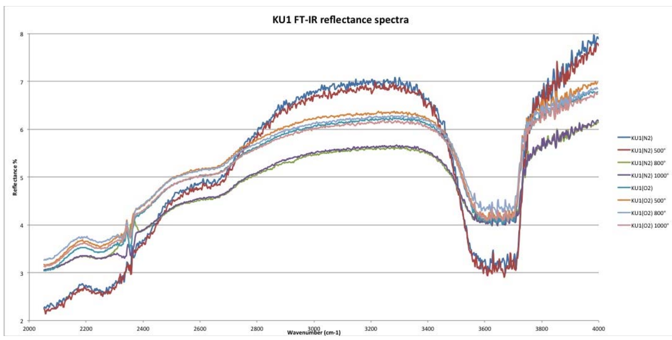

Fig.3 KU1 samples FT-IR reflectance spectra

the duration of the treatment or increasing the temperature can effectively reduce the amount of defects in the bulk material. It is also worth to be noted that the sample used in the N_2 annealing presented a higher reflectivity than the one treated under oxygen atmosphere, and that explains the bigger changes found in the reflectivity spectra of the two samples before and after the treatments. (Fig.3). The same situation is observed in the KS4V absorption and reflection spectra.

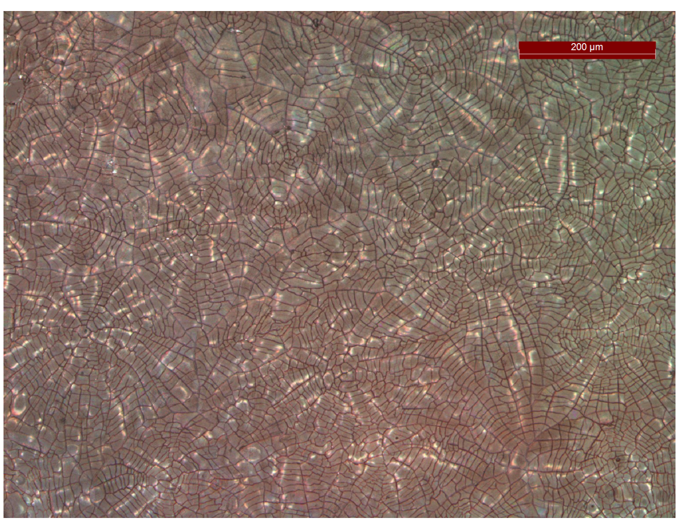

Fig.3 Microscope image of KS4V nucleation sites after annealing in O_2 atmosphere at 800 °C for two hours

We also noticed that annealing over 800° in oxygen promotes nucleation, at least for treatments lasting 2 hours. These phenomena are extremely clear as seen with the images coming from optical and confocal microscope. The devitrification effect is almost all in the surface, and is probably the major cause of the changes in the reflectivity of the material. These crystals appear to be crystobalite, a high temperature polymorph of silica. Crystobalite structure is tetragonal (α) or cubic (β) depending on the annealing temperature, and appears as octahedral or spherulites , or as microcrystals giving an "opal like" appearance [4]. Some of the other samples present opalescence under the microscope, further investigation is needed to determine the conditions under which each crystobalite form generates during the annealing process.

REFERENCES

[1] P. Martín, M. León, A. Ibarra, E.R. Hodgson, „Thermal stability of gamma irradiation induced defects for different fused silica", Journal of Nuclear Materials 417 (2011) 818-821

[2]I. I. Cheremisin , T. A. Ermolenko , I. K. Evlampiev , S. A. Popov , P. K. Turoverov , K. M. Golant & M. O. Zabezhajlov (2004) Radiation-hard KS-4V glass and optical fiber, manufactured on its basis, for plasma diagnostics in ITER , Plasma Devices and Operations, 12:1, 1-9

[3] M. Tomozawa, D. Kim, A. Agarwal, K. Davis "Water diffusion and surface structural realaxation of silica glasses", Journal of Non Cristalline Solids 288 (2001) 73-80

[4] A. F. Wright & A. J. Leadbetter (1975) The structures of the β- cristobalite phases of SiO2 and AlPO4 , Philosophical Magazine, 31:6, 1391-1401,

"This work has been carried out within the framework of the EUROfusion Consortium and has received funding from the Euratom research and training programme 2014-2018 under grant agreement No 633053. The views and opinions expressed herein do not necessarily reflect those of the European Commission."