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Microstructural and Microanalytical Characterization of Pd Clusters in ORMOCER Matrix

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Abstract. — Noble-metal clusters dispersed in glass matrix are of great interest for their technological applications such as heterogeneous catalysis, in the realization of non-linear optical devices, in sensor technology, for absorption control in solar reflecting glasses (IROX[®] coatings) etc. The physical properties of these materials strongly depend on cluster concentration, size distribution and on their structural and chemical nature. High spatial resolution structural and analytical characterization techniques are needed to understand the cluster formation mechanism and the physical properties of these materials. In this work, palladium clusters dispersed in ORMOCER matrix *via* a modified sol-gel process are structurally and chemically characterized by conventional transmission electron microscopy, high-resolution electron microscopy, electron nanodiffraction and X-ray diffractometry, in order to obtain information on the clusters shape, structure, spatial distribution in the matrix and chemical nature. Samples heat treated both in inert N₂ atmosphere and in air at 400 °C for different times are analyzed in order to obtain a deeper insight in the formation and structural evolution of the clusters and in the oxidation process. In fact after heat treatment in air, clusters oxidation occurs and a PdO shell surrounding a core with different structure ~ 1.5 nm in diameter is formed. Heat treatment in inert N₂ atmosphere does not affect the clusters shape, structure and distribution.

1. Introduction

Noble metal doped glasses have been the subject of a great number of studies due to their interesting optical, electrical and catalytic properties arising from the nanometer dimensions of the clusters. They are very promising materials for many technological applications such as for heterogeneous catalysis, non-linear optical devices, in sensor technology and for absorption control in solar reflecting glasses (IROX[®] coatings) [1–3]. Several techniques have been developed in order to prepare clusters, e.g. high temperature glass melting and subsequent thermal heat treatment,

radio frequency sputtering, ion implanting, chemical vapor deposition and sol-gel [4–6].

The Pd clusters studied in this work were obtained by a modified sol-gel process [7], to allow the preparation of hybrid materials, the so-called ORMOCERS (organically modified ceramics) [8–12]. A Pd salt ($\text{Pd}(\text{Ac})_2$) was used as Pd source and initially solved in acetone. To avoid the formation of Pd clusters in the liquid phase solution, dynosilan DAMO from Huls ($\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OMe})_3$) was added to the solution as stabilizer, in a metal/stabilizer ratio = 1:2. In a further step, a GPTS/TEOS (γ -glycidoxypolytriethoxysilane/tetraethoxysilane) sol was added to the Pd containing solution, in order to promote the formation of the matrix. The solution was then distilled in order to partially remove the solvent and to promote hydrolysis and polycondensation reactions. The resulting solution was then heated up to 200 °C in N_2 , removing the volatile compounds and therefore leaving Pd clusters dispersed in an amorphous matrix. The matrix components are Si and O in a ratio 1:2, with nitrogen and carbon impurities. Further details about the cluster preparation technique are reported elsewhere [7]. The advantages of the use of the ORMOCERS in comparison to pure inorganic materials are that, thick film and uncracked bulk materials are easily obtained. Furthermore, metal particles can be uniformly dispersed in the matrix with narrow diameter distributions by using organofunctional silanes as complexing agents.

Despite the high number of experimental works, very little information regarding the physical mechanisms of growth and stabilization of the clusters is available. The mechanism of interaction between the noble metals and the matrix is not very clear and not much is known about the role played by the temperature and by the stabilizer in the process.

In order to obtain a deeper insight in the formation of the clusters and in their structural evolution, a detailed structural characterization has been performed. Samples have been investigated by conventional transmission electron microscopy (CTEM), high-resolution electron microscopy (HREM), electron nanodiffraction and X-ray diffractometry (XRD). The Pd $\rightarrow$ PdO phase transformation following the heat treatment in air is also studied.

2. Experimental

In order to evaluate the cluster formation process, their evolution with heat treatment, and the oxidation process, different parts of the same monolith were heat treated at 400 °C both in inert N_2 atmosphere and in air for 1 h as well as 4 h.

Transmission electron microscopy samples were obtained by scratching the monolith surface with a diamond tip and collecting the resulting fragments onto thin carbon support films obtained according to the procedure developed in our laboratory [13]. A thin carbon film was then evaporated onto the fragments, in order to avoid charging effects of the sample during the TEM observation.

Transmission electron microscopy (TEM) observations were performed using a JEOL 4000 EX II transmission electron microscope operating at 400 kV accelerating voltage, with an interpretable resolution limit of 0.16 nm. Bright field (B.F.) and selected area electron diffraction patterns (SADP) were obtained in order to evaluate the cluster shape, the diameter distribution and the lattice parameters. High-resolution electron microscopy (HREM) images were also obtained in order to evaluate the cluster subnanometric structure and their shape. Fourier transforms of digitized HREM images allowed us to evaluate the lattice parameters of the clusters. Nanodiffraction experiments were performed on a Philips CM 30 TEM/STEM microscope using a probe with a diameter of about 3.5 nm and a liquid nitrogen cooled specimen holder.

Computer simulations of experimental HREM images were obtained with the CERIU program [14].

Fig. 1. — Typical bright field TEM image of Pd clusters for the as synthesized sample. Similar images were obtained for the sample heat treated in N_2 . An average cluster diameter of (4.5 ± 0.5) nm was determined from the diameter distribution analysis.

X-ray diffraction measurements were carried out using a powder diffractometer (Philips PW1880) operating at 3 kW. Conventional $\theta/2\theta$ scans were performed in the 2θ angular range between 30° and 80° with a constant recording time of 12 h and by using CuK_α radiation.

3. Results

Figure 1 shows a typical B.F. image of the as synthesized sample. The cluster spatial distribution shown in Figure 1 is representative of the whole specimen volume, as derived from the analysis of several TEM images. It can be also seen that clusters are very uniform in diameter. The average diameter derived from the analysis of the clusters distribution is (4.5 ± 0.5) nm. Figure 2 shows a HREM image of some of the clusters shown in Figure 1, indicating the presence of nanotwins in most of the clusters. The image shows that the glass matrix is amorphous. Figure 3 is a nanodiffraction pattern from a Pd cluster. The nanodiffraction pattern shows a row of systematic reflections. The Pd(111) reflections corresponding to interplanar spacing $d_{111} = 0.22$ nm are indexed.

Similar results were obtained for the samples heat treated in N_2 . The analysis of the diameter distribution does not show any appreciable variation after the heat treatment, although a more

Fig. 2. — Typical HREM image showing some Pd clusters of the as synthesized sample. Similar images were obtained from the sample heat treated in inert N_2 atmosphere.

ordered nanostructure can be observed in most of the clusters. As in the as synthesized samples, the analysis of nanodiffraction patterns gives lattice parameters compatible with crystalline Pd.

Figure 4 shows a typical B.F. image of the sample heat treated in air for 1 h at 400 °C. Note the presence of some clusters like dark rings with a brighter core (we will call these particles “ring-like” particles in the following). Depending on the defocus and on the specimen thickness values, the “ring-like” contrast is more or less evident. Although in most cases the bright core is located approximately in the middle of the cluster and surrounded by a uniform dark ring, in some cases the ring seems to be incomplete, probably due to poorly formed spherical particles or to an anisotropic oxidation.

The analysis of the cluster diameter distribution shows that the average diameter has slightly increased to (5.5 ± 0.5) nm and that the distribution is slightly broader. Figure 5 is a typical HREM micrograph of one of the clusters: note the different contrast of the core compared to the outer ring. No subnanometric structure (nanotwins) is now evident from the HREM image in most of the clusters. The surrounding matrix is still amorphous. Figure 6 is a nanodiffraction pattern from a PdO cluster close to the $\langle 101 \rangle$ zone axis.

After heat treatment in air for 4 h at 400 °C, the “ring-like” particles were still present. The analysis of the diameter distribution does not show any significant changes compared to the 1 h treatment, showing that the oxidation process is already complete after 1 h. As in the sample

Fig. 3. — Nanodiffraction pattern from one of the clusters present in the sample heat treated in air. A systematic row of reflections is shown. The Pd(111) diffraction spots corresponding to planes with interplanar spacing $d_{111} = 0.22$ nm are indexed.

treated for 1 h, no evidence for any subnanometric structure inside the “ring-like” clusters was found in most of the images of the clusters.

Computer simulation of the experimental HREM images was also performed using the CERJUS program. This program was also used to evaluate the cluster diameter increase due to the oxidation process. To do so, a Pd cluster of a given diameter was built, and the relative number of atoms was evaluated. Then a PdO cluster was built assuming that all the Pd atoms of the starting cluster were oxidized. The resulting PdO cluster diameter was then measured and found to increase with respect to the initial Pd cluster, according to TEM and X-ray measurements.

In Figure 7a the X-ray patterns obtained from the as synthesized sample (curve 1a) and from the sample heat treated at 400 °C in N₂ for 1 h (curve 2a) and 4 h (curve 3a) are shown. The spectra reveal that Pd clusters are already present, embedded in the matrix, in the as synthesized sample and that the heat treatment in inert N₂ environment does not promote any detectable variation in the cluster phase. A slight increase in the intensity and a decrease in the width of the X-ray peaks occur with the increase of the heat treatment time. The shape and the width of the diffraction line profile are determined both by the mean crystallite size and by particular imperfections present in the crystalline lattice of the clusters [15]. As the TEM B.F. images show no significant variation in the Pd clusters diameter distribution with the heat treatment in N₂, the decrease in the intensity of the peaks width can be attributed to a lower defectivity in the crystallites. This is also confirmed by the HREM micrographs.

Fig. 4. — Typical bright field image of the sample heat treated in air for 1 h. The arrows indicate the “ring-like” particles. Similar images were obtained from the sample heat treated for 4 h. An average diameter of (5.5 ± 0.5) nm was determined from the analysis of the diameter distribution.

Fig. 5. — HREM image of one of the PdO clusters present in the sample heat treated in air. Note the crystalline outer shell surrounding the core of different contrast.

Fig. 6. — Nanodiffraction pattern from one of the clusters present in the sample heat treated in air, showing a PdO cluster close to the $\langle 101 \rangle$ zone axis.

Figure 7b shows the X-ray patterns of the as synthesized sample (curve 1b) and of the samples heat treated at 400 °C in air for 1 h (curve 2b) and 4 h (curve 3b), respectively. The analysis shows that the heat treatment in air produces oxidation of the Pd clusters already after 1 h of heat treatment, without any appreciable variation for longer heat treatment times. The X-ray peaks from the PdO phase are sharper and more intense than for the Pd precursor phase, indicating a higher structural perfection in the PdO clusters compared to the Pd precursors, in agreement with TEM results.

4. Discussion and Conclusions

A detailed structural analysis of Pd clusters in ORMOCER matrix was performed by the combined use of high spatial resolution transmission electron microscopy techniques and X-ray diffractometry.

Both as synthesized samples and samples heat treated in inert N₂ atmosphere at 400 °C for 1 h as well as 4 h were initially analyzed, in order to study the Pd cluster formation mechanism and the structural evolution of the clusters after heat treatment.

In the as synthesized sample Pd clusters are very uniform in diameter with an average diameter of (4.5 ± 0.5) nm and are homogeneously distributed on a micrometric scale in the whole amorphous matrix. Nanotwins are observed in most of the Pd clusters. Heat treatment in N₂ atmosphere does not produce any change in the diameter and spatial distributions of the clusters, showing that cluster formation is already completed at the end of the growth procedure; a better crystalline structure of the clusters is evident with increasing treatment time, which can be

Fig. 7. — a) X-ray patterns patterns of the as synthesized sample (curve 1a) and of the sample heat treated in N₂ for 1 h (curve 2a) and 4 h (curve 3a) respectively; b) X-ray diffraction patterns of the as synthesized sample (curve 1b) and of the sample heat treated in air for 1h (curve 2b) and 4h (curve 3b) respectively.

explained by defect recovery promoted by the heat treatment process.

It has been reported that the key parameters to obtain nanosized particles, which are uniformly distributed in the matrix, with the sol-gel technique, are the metal/stabilizer ratio and the thermal curing process [7]. In this work a single set of parameters (metal/stabilizer ratio, thermal curing temperature) was considered (see above), and the TEM and XRD data show that Pd clusters nucleate very uniformly in the matrix and with a very narrow size distribution. The further heat treatment at 400 °C in inert gas environment does not produce any further growth or modification of the clusters, indicating their high structural stability.

Finally the oxidation process was also analyzed by heat treating different parts of the same monolith in oxygen rich atmosphere for 1 h as well as 4 h. After 1 h heat treatment in air, oxidation of Pd clusters occurs. The resulting clusters show a characteristic “ring-like” shape, and consist of a PdO shell surrounding a core with different structure. The formation of this particular structure is attributed to phase transformation from Pd to PdO, which occurs at a temperature of 400 °C in air environment. The mean diameter of the PdO clusters, (5.5 ± 0.5) nm, is the same for 1 and 4 h heat treatment time. Computer simulations of Pd and PdO clusters matched the volume increase experimentally observed by TEM and XRD.

Further studies related to the influence of the metal/stabilizer ratio and the temperature of the thermal curing on the distribution of the clusters in the matrix are necessary for a better understanding of the clusters formation. Furthermore, the Pd $\rightarrow$ PdO phase transformation and the mechanism leading to the formation of the “ring-like” particles require further investigation to develop a deeper understanding. These studies are now in progress in our laboratories.

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