ICEM 13-PARIS
17-22 July 1994

TEM Characterization of Pd Colloids in ORMOCER Matrix

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1. INTRODUCTION

Glasses doped with metal particles have been extensively studied for their interesting optical, electro-magnetic and catalytic properties. During the last few years, theoretical studies have demonstrated that metal particle embedded glasses exhibit an enhanced third order non-linear optical susceptibility $\chi^{(3)}$ ($10^{-9} \div 10^{-8}$ esu), comparable to that observed for glasses containing semiconductor colloids (Ricard 1985). The high value of $\chi^{(3)}$ was attributed to contributions from the electron quantum confinement effect and the hot photoexcited electrons (Hache 1988). Pd colloids supported by amorphous matrix are very interestng catalytically active materials for inorganic molecule synthesis, electroless deposition and for their utilization as gas sensors(Yasumoto 1992). In this work Pd colloids prepared by chemical route (sol-gel process) in an organic-inorganic matrix have been studied by both Conventional and High Resolution Electron Microscopy (HREM).

2. EXPERIMENTAL RESULTS

2.1 Preparation of Pd colloids

Pd colloids containing Ormocers (organically modified ceramics) have been prepared from Pd amino complexes of the type $Pd[(NH_2CH_2CH_2NH(CH_2)_3Si(OMe)_3]_2ac_2$ by hydrolysis and condensation (sol-gel reaction) of the silane together with $Si(OEt)_4$ and $Si(OEt)_3(CH_2)_2OCHOCH_2$ (γ-glycidoxypropyltriethoxysilane). The amino complex formation is necessary to avoid spontaneous reduction and uncontrolled colloid formation in the liquid phase. After solidification and solvent evaporation the colloids have been obtained by heating the system to 200°C in N_2 atmosphere. Nucleation and colloid growth take place starting from 100 °C very uniformly and without agglomeration.

2.2 Electron Microscopy

TEM samples were obtained by scratching the monolith surface and collecting the resulting powder onto Copper grids previously covered with a thin Carbon film. The samples were observed in a JEOL 4000EX II TEM operating at 400kV accelerating voltage, with an interpretable resolution limit of 0.16nm. Both Conventional Bright-field (B.F.) images and Selected Area Diffraction Patterns (SADP) were obtained in order to analyze the colloid diameter distribution and the lattice parameters of the Pd colloids.

Fig. 1 is a typical B.F. image showing the Pd colloid distribution. The colloids are very uniform in diameter, and are also uniformly distributed in the matrix. Fig. 2 is a histogram showing the colloid diameter distribution. The average diameter, derived from the histogram

analysis is 4.5nm. Fig. 3 is a HREM image of some Pd colloids. The largest clusters show a subnanometric structure. They are formed by different nano-grains. Amorphous areas are visible in some of the clusters.

From the TEM data we can conclude that the colloid preparation technique described above allows to obtain Pd colloids uniformly distributed in the matrix, with almost constant diameters.

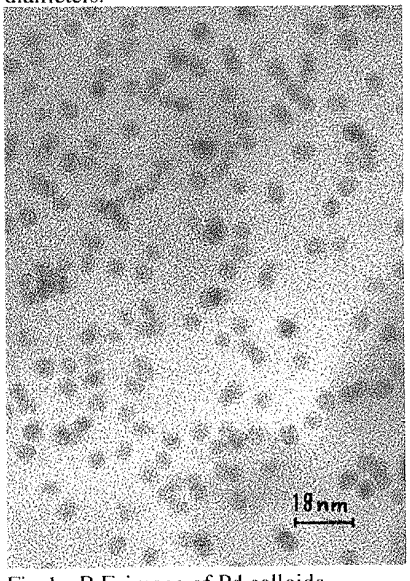

Fig.1: B.F. image of Pd colloids.

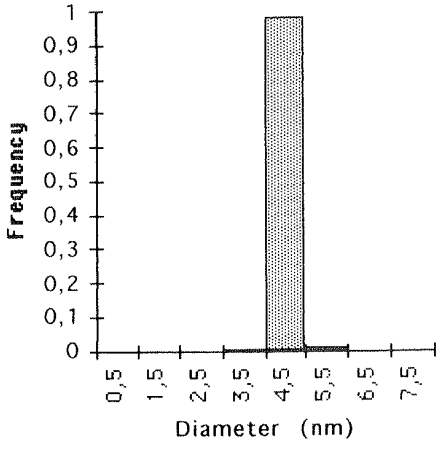

Fig.2: Histogram showing the colloid diameter distribution analysis.

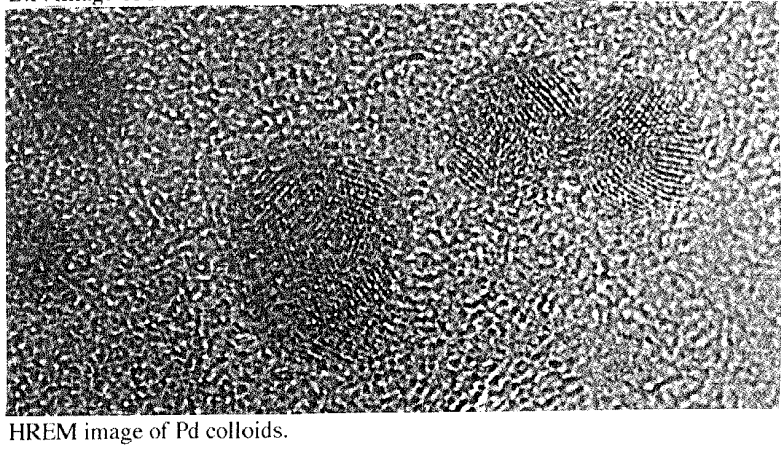

Fig.3: HREM image of Pd colloids.

Acknowledgements
The authors would like to thank L. De Caro for suggesting the TEM specimen preparation technique and M. Palmisano for his skilful preparation of TEM samples.

Richard D, Roussignol P and Flytzanis C, Opt. Let. 10, 511 (1985)
Hache F, Richard D, Flytzanis C and Kreibig U, J. Appl. Phys. A47, 347 (1988)
Yasumoto K, Koshizaki N, Suga K, SPIE 1758, Sol-Gel Optics, 604 (1992)