NANO SIZED Pd PARTICLES IN A SiO_2 MATRIX BY SOL-GEL PROCESSING

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Abstract

Pd colloid 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 $Si(OEt)_3(CH_2)_3OCH_2CHCH_2O$. The amino complex formation is necessary to avoid spontaneous reduction and uncontrolled colloid formations in the liquid phase. This synthesis route leads to Pd colloid containing powders and coatings on glass. By thermal curing (temperatures up to 500 °C) using different atmospheric conditions (N_2, Ar, H_2/N_2) brown to deep black coatings on glass with transmission values from 80 to 0 % can be obtained. The average particle size can be controlled by varying the molar ratio of the used Pd salt ($Pd(ac)_2$) and the aminosilane.

INTRODUCTION

Metal colloids in SiO_2 matrices are interesting composite materials, since their high coefficients of extinction of about 10^5 l/(mole cm) open up the possibility to obtain intensively coloured, thermally stable glass like coatings already with thickness of less than 1 µm in thickness to be used for decoration, for solar energy control or nonlinear optical purposes. The optical properties depend strongly on colloid size and distribution and therefore the control of colloid size during the sol-gel synthesis route is of high importance. Pd was chosen as an example, since Pd already is used in technical applications as coating (Schott Calorex ®). Schubert et al. showed that the spontaneous reduction of $Pd(acac)_2$ in ethanolic sols from alkoxysilanes could be suppressed using amino functionalized silanes[1,2] and a relatively narrow size distribution was obtained after thermal densification, but no systematic investigations of the influence of reduction parameters on Pd particle size has been carried out so far.

EXPERIMENTAL

Pd nanoparticle containing Ormocers were prepared by the following route. 200 mg of $Pd(ac)_2$ was dissolved in 8 ml of acetone and an appropriate amount of the silane $NH_2(CH_2)_2NH(CH_2)_3Si(OR)_3$ (DIAMO) in an alcoholic solution of ethanol, propanol and butanol with a volume ratio of 70 : 15 : 15 was added to the $Pd(ac)_2$ solution at various ratios of $Pd(ac)_2$: DIAMO = 1 : y (with y=1,2,3,4,8,20). After 5 min. of stirring at room temperature 20 ml of GPTS/TEOS (γ-glycidoxypropyl trimethoxy silane / tetraethoxy silane) sol was added in order to obtain Pd nanoparticle containing powders, densified at temperatures up to 500 °C in N_2-atmosphere. The GPTS/TEOS sol was prepared by stirring 160 g of GPTS, 40 g of TEOS and 29 g of H_2O in 290 ml of ethanol at 60 °C for 15 hours. The thermal decomposition of $Pd(ac)_2$ was examined

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by thermal analysis airtight (DSC, Seiko DSC220C) and in Ar atmosphere (DTA/TG, Netzsch STA 409) as a function of the DIAMO concentration. For that $Pd(ac)_2$ was dissolved in acetone and the appropriate amount of DIAMO was added. The solvent was distilled at 100 mbar and 30 °C within 5 min and the resulting liqiud was dried at 60 °C for 12 h in air. The Pd colloid formation was observed by TEM (JEOL Jem 200 CX) and by WAXS measurements (Siemens D 500).

RESULTS AND DISCUSSION

$Pd(ac)_2$ was chosen as Pd precursor, since other Pd salts like $PdCl_2$, $Pd(NO_3)_2$ or $PdSO_4$ are hygroscopic and form unsoluble brown oxohydrates[3]. As ligand, DIAMO has been used since it is known that amines easily form complexes with Pd (II) compounds and, in addition to this, the silane can be used for further condensation with other orthosilicates or other organosilanes like GPTS to form solid systems (coatings or powders). In ethanolic solution $Pd(ac)_2$ is reduced and a black precipitate of Pd is obtained within 5 min. In presence of DIAMO this reduction and precipitation is increasingly suppressed with increasing DIAMO concentrations.

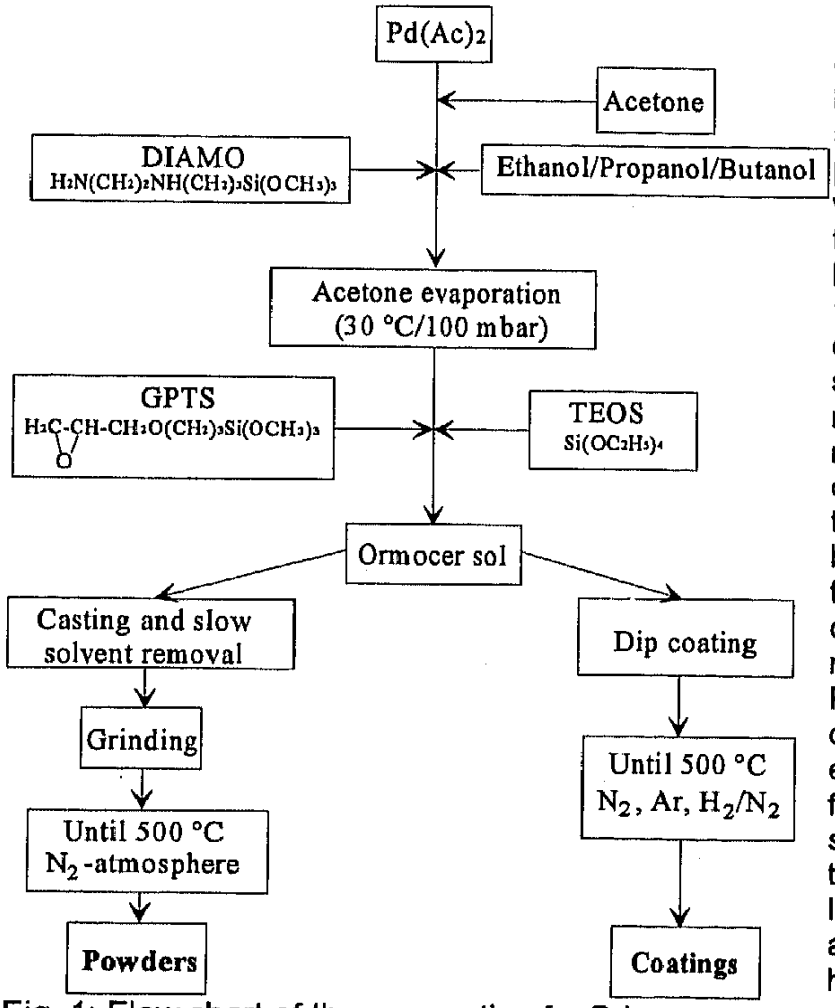

Fig. 1: Flow chart of the preparation for Pd colloid containing coatings and powders

For a $Pd(ac)_2$: DIAMO ratio of 1 : 1 the solution turns black through a brownish state and after 30 min. only precipitation was observed, whereas a ratio of 1 : 2 leads to precipitation after 12 hours. For ratios higher than 1 : 3 yellowish clear solutions are obtained that do not show any precipitation during several days. From this result the conclusion can be drawn that DIAMO stabilizes the $Pd(ac)_2$ against reduction by ethanol. To investigate the influence of the stability of the DIAMO on $Pd(ac)_2$, a method for the preparation of Pd containing inorganic-organic composites had been developed as shown in fig. 1. The experiment showed that no difference in the development of the colloids could be detected by adding the silane before ethanol addition or by adding a solution of DIAMO in ethanol. UV-VIS spectra of

$Pd(ac)_2$ dissolved in acetone show an absorption band at about 402 nm wavelength that decreases with increasing contents of DIAMO added and vanishes for Pd : DIAMO ratios ≥ 1 :3, but a quantitative analysis is very difficult because of superposition effects with acetone (strong absorption below 320 nm) an absorption around 350 nm indicating a reaction product between DIAMO and $Pd(ac)_2$. As known from[4] $Pd(ac)_2$ decomposes at 205 °C. Thermal analysis was carried out with pure $Pd(ac)_2$ and $Pd(ac)_2$ reacted with different amounts of DIAMO. DTA/TG measurements of $Pd(ac)_2$ in Ar atmosphere showed an exothermic decomposition peak of $Pd(ac)_2$ and a weight loss of 51 % at about 205 °C. In fig. 2, the DSC intensities, attributed to the trimeric („free") $Pd(ac)_2$ decomposition are shown as a function of the DIAMO added to the system.

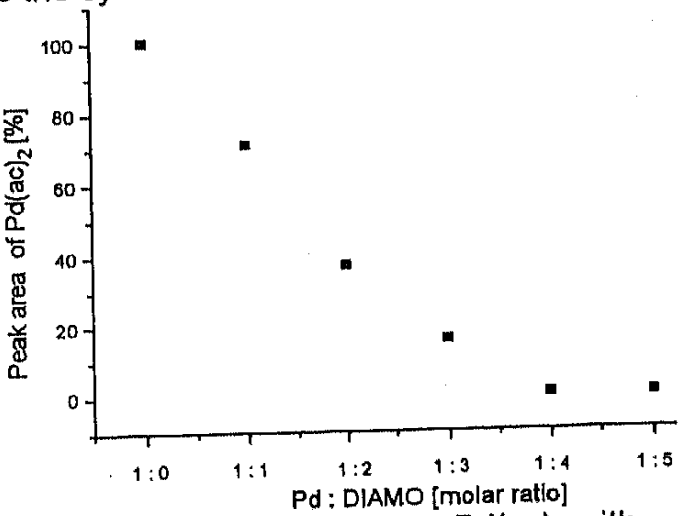

Fig. 2: Decrease of the free $Pd(ac)_2$ with increasing amounts of DIAMO

Simultaneously an endothermic peak at about 216 °C was measured that increased with increasing DIAMO content. It is known that the trimer structure of $Pd(ac)_2$ is broken by neutral amino (diethyl amine, triethyl amine, pyridine) and phosphine ligands or 2-dimethyl amino toluene, 8-methyl chinoline[5] according to eq. (1): $[Pd(ac)_2]_3 + 6\ L \rightarrow 3\ Pd(ac)_2L_2$ (1) where L is one of the ligands mentioned above. It seems plausible that DIAMO acts in a similar way and it can be concluded that with increasing amounts of DIAMO added an increasing fracture of the original trimer structure of $Pd(ac)_2$ is changed to monomers and for a $Pd(ac)_2$: DIAMO ratio of about 1 : 4 this change is complete. For the determination of the influence of the precursor structure on the particle forming process, the Pd/DIAMO system was immobilised by gelation with a GPTS/TEOS sol, dried, treated at different temperatures and analysed by electron microscopy (TEM) and x-Ray diffraction. In Table 1 the results of the experiments are summarized.

Table 1: Calculated average crystallite size (WAXS; Scherrer equation) and the average particle size calculated by TEM of powders, densified at 500 °C in N_2-atmosphere

Pd/DIAMO [molar ratio]	1 : 1	1 : 2	1 : 4	1 : 8
Crystallite size [nm]	3,2	2,7	2,1	1,8
Particle size [nm]	6,9	6,6	5,3	4,4

From TEM investigations it was evident that for a $Pd(ac)_2$: DIAMO ratio of 1 : 1 Pd colloids of about 4 nm in diameter forming agglomerates of about 10 nm in size were obtained in the gel, dried at 60 °C. The appropriate WAXS measurement showed only a small and broad [111] reflection at $2\ \Theta = 40{,}1$ °. For temperatures higher than 150 °C all reflections of cubic Pd appeared and the halfwidth of the [111] reflection decreased indicating an increase of crystallite size and concentration. For $Pd(ac)_2$:

DIAMO ratios of 1 : 2 and higher no colloid formation was observed by WAXS after drying the gels at 60 °C and it may be concluded qualitatively that the onset temperature of the colloid formation is shifted to higher values with increasing DIAMO content. However, for thermal treatments at 300 °C and 500 °C no differences in the crystallite size could be detected by WAXS. The number of detectable crystalline reflections of the cubic Pd decreased with increasing DIAMO content and for $Pd(ac)_2$: DIAMO ratios of 1 : 8 and 1 : 20 only a small and broad main reflection at 2 Θ = 40.1 ° was observed.

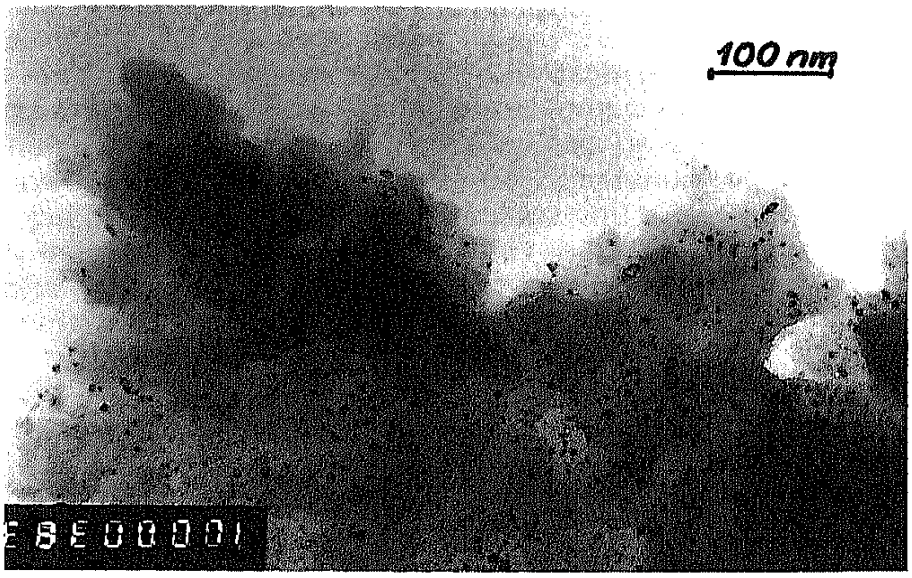

Fig. 3a: TEM micrograph of Pd colloids in Ormocer powder synthesized with a Pd : DIAMO ratio of 1 : 1 after thermal densification at 500 °C in N_2-atmosphere

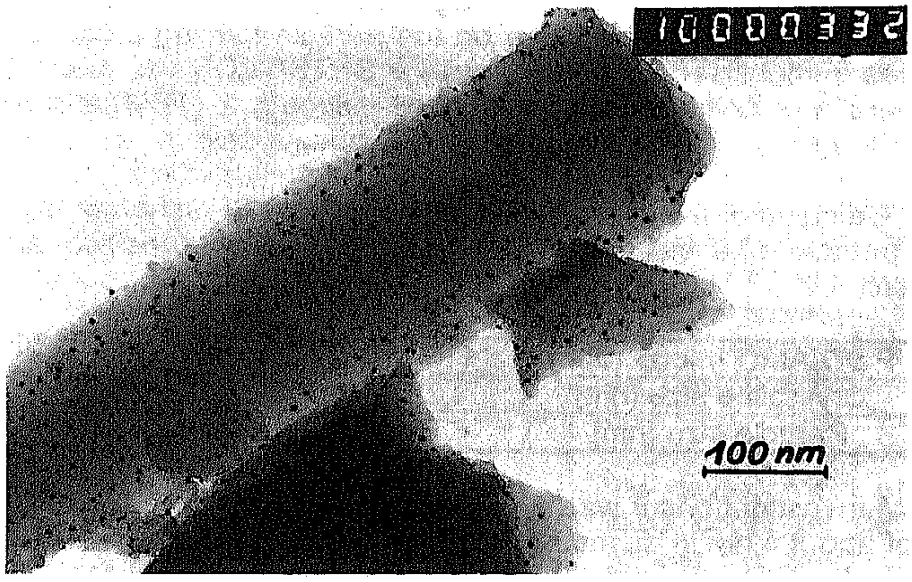

Fig. 3b: TEM micrograph of Pd colloids in Ormocer powder synthesized with a Pd : DIAMO ratio of 1 : 2 after thermal densification at 500 °C in N_2-atmosphere

From these results it has to be concluded that the Pd : DIAMO ratio influences as well the nucleation as the growth of the Pd crystallites. In order to explain the mechanisms, further investigations are required that allow the discrimination of nucleation and growth. In order to determine the size distribution of the Pd particles formed after thermal treatment at 500 °C TEM investigations were carried out for Pd : DIAMO ratios of 1 : 1 to 1 : 8. Fig. 3a represents the sample with a Pd : DIAMO ratio of 1 : 1, where the colloid formation was already obtained after drying the gel at 60 °C. Fig. 3b shows the result of a Pd : DIAMO ratio of 1 :2, where the onset of the colloid formation of about 120 °C was estimated from WAXS spectra. The particles in fig. 3a are partially agglomerated. This is not surprising due to the fact that agglomerates had been found in the dried gel already. Either for a Pd : DIAMO ratio of 1 : 2 (fig. 3b) nor for higher ratios, where an uncontrolled colloid formation in the sol was detectable, agglomeration is observed. For more general conclusions on the agglomeration behaviour of Pd colloids in presence of stabilizers experiments with higher Pd concentrations have to be carried out. Fig. 4 summarizes the results of the determination of the particle size distributions by TEM.

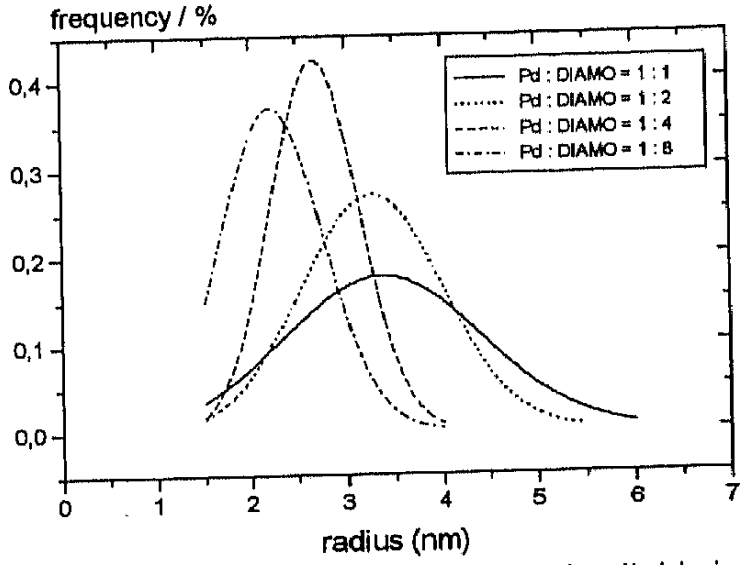

Fig. 4: Particle size distribution of Pd colloids in Ormocer powders, densified at 500°C in N_2-atmosphere determined by TEM

It is evident, that with increasing stabilizer content the average particle size decreases and the size distribution gets narrower. It was concluded from the DSC measurements that the $Pd(ac)_2$ was modified completely into a thermodynamically more stable configuration for a Pd : DIAMO ratio of 1 : 4. For lower ratios a mixture of Pd compounds with different coordination spheres and therefore different thermodynamical stabilities are obtained. It may be assumed that for the two compounds the kinetics of nucleation and growth (controlled by thermal reduction and diffusion) are different.

Thus broader size distributions are obtained for ratios smaller than 1 : 4. This hypothesis also fits the WAXS result of an increasing onset temperature of colloid formation with increasing DIAMO content, that should lead to smaller average colloid sizes. Fig. 4 shows that for a Pd : DIAMO ratio of 1 : 8 the size distribution is broader and the average particle size is smaller than for the ratio of 1 : 4. It needs further investigations for the explanation of this result concerning the influence of the excess DIAMO on the Pd and the sol-gel matrix.
Comparing the average colloid sizes from TEM with the crystallite sizes determined from the halfwidth of the [111] reflection of the WAXS spectra it was found, that the colloid sizes were about the 2.4 fold of the crystallite size. First HTEM investigations indicate a polycrystalline morphology of the Pd colloids. The mechanisms for that are not understood yet.

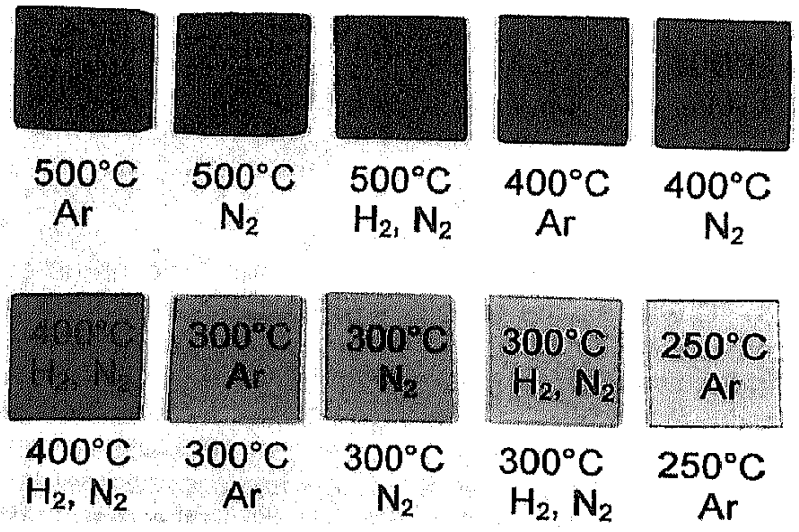

Fig. 5: Pd colloid doped coatings on glass with the same Pd : DIAMO ratio (1 : 4) but with different densification conditions (temperature, gas atmosphere (N_2, Ar, H_2/N_2)

Crackless coatings can be performed by Pd/ DIAMO/GPTS/TEOS sols by dipping and firing up to 500 °C The deepness of the brown colours can be controlled by firing conditions and different inertgas atmospheres (N_2; Ar; N_2/H_2). In fig. 5 a series of coatings is shown. After firing to 500 °C the Ormocer has been transformed to pure SiO_2 without cracking.

Conclusions

A new sol-gel synthesis route for nanosized Pd colloids in an SiO_2 matrix has been developed through inorganic-organic processing. $Pd(ac)_2$ is a suiteable precursor since its spontaneous reduction in ethanolic solutions can be suppressed by stabilization with DIAMO. The colloid formation can be induced thermally during the densification of the matrix and although this simple processing should be connected with a homogeneous nucleation of the Pd colloids, a relatively narrow size distribution is obtained, if the stabilization of Pd is complete. Thus the conclusion can be drawn that amino functionalized silanes can be used to control the colloid size by influencing the nucleation and growth kinetics at elevated temperatures.
This synthesis route also leads to Pd colloid containing coatings on glass, ceramic and other temperature stable substrates.

Acknowledgement

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