Optimization of a container design for depositing uniform metal coatings on glass microspheres by magnetron sputtering

G. Schmid a, C. Eisenmenger-Sittner a,⁎, J. Hell a, M. Horkel a, M. Keding b, H. Mahr a

a Vienna University of Technology, Institute of Solid State Physics, Wiedner Hauptstrasse 8-10, A-1040 Vienna, Austria
b Austrian Institute of Technology, A-2444, Seibersdorf, Austria

ARTICLE INFO

Article history:
Received 11 June 2010
Accepted in revised form 18 August 2010
Available online 24 August 2010

Keywords:
Particles
Magnetron sputtering
Glass microspheres
Catalytic coatings

ABSTRACT

Coating granular substrates by PVD methods like magnetron sputtering is a very challenging process. Although many of such substrates may also be coated by other means like the sol gel method, there are coating materials (e. g. refractory metals) for which PVD processes are the method of choice.

One of these substrates is hollow glass microspheres with 2–80 μm diameter which can be used for hydrogen storage if a proper catalytic film is applied. To achieve a uniform film by magnetron sputtering on all the spheres a special apparatus was used which basically consists of rotating vessels positioned beneath the target. The arising problems of agglutination of the powdery substrate were solved by designing a special coating vessel, where the spheres are contained during deposition.

For testing the system first copper was used as a target material, which was then replaced by platinum since the glass microspheres are used for a catalytic application. The film thickness on the spheres was determined by optical absorption and matches well with the thickness calculated for the special vessel geometry. Additionally it is shown that the glass microspheres can be coated with a uniform layer by magnetron sputtering whereas coatings produced by a chemical deposition process are not continuous.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

To coat fine grained substrates with particle diameters of approximately 50–600 μm by PVD methods like magnetron sputtering is a very challenging task. Nonetheless several possible applications exist where other processes more suitable for coating granulates or fibers like sol gel coating [1–4], electrochemical deposition [5–7], Chemical Vapor Deposition (CVD) [8–10] or functionalization by immersion into liquids or gases [11–13] cannot be employed. Amongst these are the deposition of thin layers of refractory metals onto diamond granulates which may improve the thermal and mechanical properties of metal diamond composites [14,15] or the deposition of metallic catalytic layers on fragile glass substrates such as hollow glass microspheres with an approximate diameter of 2–80 μm which shall be utilized for hydrogen storage [16] and which are the subject of this paper. For these granulates often no suitable electrochemical process can be found because of the insulating nature of the particles to be coated. Also the thermal loads exerted onto the granulate in the case of CVD or PACVD processes may be too high [17,18]. MOCVD methods may be employed at temperatures close to room temperature, but are limited to a small range of materials due to the limited availability of proper precursors [19–21].

Magnetron or ion beam sputtering is the method of choice because of the low thermal load the substrates are subjected to. Several devices are employed for coating granulates or powders by sputtering [22–26]. Magnetron sputtering sources are solid and can therefore be positioned arbitrarily within the deposition chamber, a fact which is important if the granulate has to be filled into an open container. In this case a top-down sputtering geometry is necessary to avoid losing particles. The problems of moving and intermixing the granulate have partially been solved by the construction of a special coating device [27] at the Vienna University of Technology which is comparable to the set ups presented in [22] (rotating tilted turntable) and makes use of additional sliders as in [23,24] which are supposed to thoroughly intermix the particles. Nonetheless, for the task of coating fragile glass spheres the route chosen in [27] for intermixing the particles by sliders was unfeasible as will be described in detail in the following. A special container geometry was designed which prevents the agglomeration of the spheres as well as protect them from mechanical damage.

The paper is structured as follows: In Section 2 the general experimental parameters are presented along with a rough estimate of the film thickness that is to be expected on the microspheres. Section 3 describes the optimisation of the container geometry step by step. In Section 4 the coatings deposited on the microspheres by using the optimised container geometries are characterized. Finally, Section 5 summarizes the results and future work is discussed.

⁎ Corresponding author.
E-mail address: christoph.eisenmenger@ifp.tuwien.ac.at (C. Eisenmenger-Sittner).
2. Experimental

2.1. Glass microspheres

The granular substrates used in the present work were hollow glass microspheres, manufactured by 3M Germany, brand name “S38”. This material is a common choice for thermal insulation and filling applications, since it has a very low thermal conductivity and density. According to 3M the thermal conductivity of the spheres at room temperature is 0.127 W/Km and the density is 380 kg/m³. The chemical composition is that of a typical soda–lime–borosilicate glass [28]. A German datasheet for the S38 microspheres can be obtained from 3M [29] (in German) or on the web [30] (in English).

The glass microspheres have been characterized both with an optical microscope (REICHERT POLYVAR MET) and a Scanning Electron Microscope (SEM, FEI Quanta 200F). An optical micrograph of hollow glass spheres. The broad size distribution is clearly visible. This material is a common choice for thermal insulation and filling applications, since it has a very low thermal conductivity and density. According to 3M the thermal conductivity of the spheres at room temperature is 0.127 W/Km and the density is 380 kg/m³. The chemical composition is that of a typical soda–lime–borosilicate glass [28]. A German datasheet for the S38 microspheres can be obtained from 3M [29] (in German) or on the web [30] (in English).

The glass microspheres were characterized both with an optical microscope (REICHERT POLYVAR MET) and a Scanning Electron Microscope (SEM, FEI Quanta 200F). An optical micrograph of hollow glass spheres. The broad size distribution is clearly visible. Generally a sputter run was performed as follows: approximately 16 cm³ of the as received glass spheres were filled into the rotatable cup shaped containers of the device described in detail in [27]. No further cleaning procedures have been applied to the spheres. Both, the containers as well as the base plate they are mounted on can be rotated independently. The angular velocity of the container is denoted by \( \omega \) and the angular velocity of the base plate is designated as \( \Omega \). In this work, however, the base plate rotation was not used. The containers can be tilted by an angle \( \alpha \) which was kept at 45° relative to the horizontal for the present experiments. Typical deposition parameters are given in Table 1.

The films on the samples were deposited from a 2-in. magnetron sputter source (AJA ST20) in unbalanced mode. The sputter target was concentrically mounted in a distance of 10 cm above the centre of the rotatable container, the target surface was horizontal and the tilt angle of the container relative to the target surface was \( \alpha = 45^\circ \). The deposition rate on the microspheres is not straightforward to assess in detail. The effects of the rotation of the container as well as the effects of mutual shadowing of the single microspheres have to be taken into account. To roughly calculate the deposition rate first the mass erosion rate \( \dot{m} \) of the sputter target can be computed using Eq. (1) which is valid for atoms which perpendicularly hit a flat target surface [31].

\[
\dot{m} = Y(E_i) \frac{I_i m}{e} \quad \text{[kg s}^{-1}] \tag{1}
\]

where:

\( Y = \) sputter yield [dimensionless],
\( E_i = \) ion energy [eV],
\( I_i = \) ion current [A],
\( e = 1.602 \times 10^{-19} \text{ [C]} \)

Inserting the appropriate numbers for material parameters and sputter yields as well as the experimentally determined currents into Eq. (1) \( Y_{Cu} = 2.3 \) at 600 eV, \( Y_{Pt} = 1.6 \) at 600 eV [31], \( m_{Cu} = 63 \text{ u}, m_{Pt} = 195 \text{ u}, I_{Cu} = 0.42 \text{ A at 200 W}, I_{Pt} = 0.25 \text{ A at 100 W, } I_{Pt} = 0.36 \text{ A at 200 W} \) the erosion rates given in Table 2 can be calculated (for the conversion of the erosion rate from kg s\(^{-1}\) to nm s\(^{-1}\) the target erosion was taken to be uniform and the target surface was 20 cm²). The erosion rates were considered as constant since (i) the measured currents varied less than 5% and (ii) the target erosion was negligible at the low sputter powers employed even after prolonged target usage.

In the simplest case the containers implemented into the coating device are rotationally symmetric with a diameter of 9.3 cm and perpendicular walls with a height of 2.2 cm. The container was rotated with a frequency of \( \omega = 26–60 \text{ rpm} \) (see Table 1). Copper pretests were carried out at a sputter power of \( P = 200 \text{ W} \) to learn the characteristics and functionality of the configuration. Platinum deposition was done at powers of \( P = 200 \text{ W} \) and \( P = 100 \text{ W} \). The third column in Table 2 shows the deposition rate \( R_{dep} \) in the center of the rotating container which was estimated by first calculating the effective surface of the granulate exposed to the vapor beam. For a quadratic box shaped container (Fig. 2) tilted along one side by the angle \( \alpha \) the volume \( V \) and the surface \( A \) of the granulate ensemble

![100 μm](image)

**Fig. 1.** Optical micrograph of hollow glass spheres. The broad size distribution is clearly visible.
the material eroded from the target. Converting the mass of material condensing on – to pass. Taking into account the cosine shaped emission from each radius of 10 cm through which all material emitted from the target has been located 10 cm beneath the center of the target has to be considered. When one calculates the ratio of the surface of spheres which is exposed to the vapor beam to the total surface of spheres located within the volume by using Eqs. (2)–(5) it can be shown that the average deposition rate on all the spheres will again be significantly reduced in comparison to both the target erosion rate as well as the condensation rate on the exposed surface. In Section 3 an approach to optimise this ratio by tuning the container geometry will be discussed.

2.3. Film thickness measurement

The experimental film thickness determination on the coated spheres is no straightforward task. For determining the film thickness the transmission properties of metallic coatings for visible light are used. This method can be used here since (i) the microspheres acting as substrate are transparent and (ii) the metallic coatings are thin enough to transmit visible light. Green light with a wavelength of 550 nm was used. In a metallic coating electromagnetic radiation is exponentially attenuated according to the Beer Lambert Law [35]. The attenuation lengths for a wavelength of 550 nm are \( \kappa_{Cu} = 16.87 \) nm and \( \kappa_{Pt} = 11.8 \) nm for Cu and Pt, respectively [35]. Photographs of the glass microspheres were taken with an optical microscope and were analysed with the freely available shareware ImageJ [36]. For further processing the pictures were split into RGB colours and the green fraction was saved as an 8-bit grey scale image. Fig. 4 shows an image of the green fraction of copper coated glass microspheres. Mean values of the brightness were obtained by using histograms of areas of coated spheres (called “shell area” from now on) and areas without spheres. Both histograms to determine the mean brightness of the shell area (yellow) and the background (red) are indicated in Fig. 4.

\[
V = \frac{1}{2} \cdot x \cdot h \cdot L \quad \text{and} \quad A = y \cdot L = h \cdot L \cdot \sin \alpha
\]

(2)

(3)

For the rotation-symmetric geometry of a the real device, which was described above, the volume \( V \) and the surface \( A \) at a tilt angle of \( \alpha \) of the cup can be calculated in complete analogy (Eqs. (4) and (5)). The geometric situation is shown in Fig. 3.

\[
V = \int_0^\alpha \left[ r^2 \arccos \left( \frac{1}{r \cdot \tan \alpha} \right) - \frac{r - h \cdot \tan \alpha}{\tan \alpha} \sqrt{\frac{2 \cdot r \cdot x}{\tan \alpha} - \frac{x^2}{(\tan \alpha)^2}} \right] dx
\]

(4)

\[
A = r^2 \arccos \left( \frac{1}{r \cdot \tan \alpha} \right) - \frac{r - h \cdot \tan \alpha}{\tan \alpha} \sqrt{\frac{2 \cdot r \cdot h}{\tan \alpha} - \frac{h^2}{(\tan \alpha)^2}}
\]

(5)

In Eqs. (4) and (5) \( r \) is the vessel radius and \( h \) is again the filling height. From Eq. (5) the exposed surface \( A \) can be calculated for the cup geometry given above, \( r = 4.6 \) cm, \( h = 2.2 \) cm, \( \alpha = 45^\circ \) and amounts to \( A = 12.2 \) cm². The exposed surface can be considered as static in a first approximation if the spheres are ideally gliding on the container walls. If a is horizontally located 10 cm beneath the center of the target surface, \( A \) is approximately 2% of the surface of a half sphere with a radius of 10 cm through which all material emitted from the target has to pass. Taking into account the cosine shaped emission from each point of the target which is given by the Hertz–Knudsen law [32] the mass of material condensing on \( A \) can finally be computed to be 4% of the material eroded from the target. Converting the mass \( m_A \) hitting \( A \) per unit time to a deposition rate by dividing \( m_A \) by the density of the material and by \( A \) yields the last column in Table 2. From there it is clearly visible that the deposition rate is much smaller than the erosion rate because of the geometric dispersion of the vapor beam.

The above considerations are basically valid for each substrate which is permanently exposed to the vapor beam. To estimate the deposition rate on a single small glass sphere first the total surface of 1 cm³ of micro glass spheres has to be assessed: From the data obtained with the SEM the mean surface \( S_0 \) and the mean volume \( V_0 \) of a single sphere are \( S_0 = 4893 \) µm² and \( V_0 = 61322 \) µm³, respectively. The filling factor of packed beds is \( f = 0.63 \) [33,34], thus 1 cm³ of spheres contains approximately 10⁹ glass microspheres. Hence the total surface of 1 cm³ of glass microspheres is \( S_{TOTAL} = 5.11 \) dm². To coat all spheres uniformly the total amount of sputtered material has to be distributed onto this surface. But during the deposition process not all spheres are located within the vapor beam for all times. The filling of the container has to be taken into account.

When one calculates the ratio of the surface of spheres which is exposed to the vapor beam to the total surface of spheres located within the volume by using Eqs. (2)–(5) it can be shown that the average deposition rate on all the spheres will again be significantly reduced in comparison to both the target erosion rate as well as the condensation rate on the exposed surface. In Section 3 an approach to optimise this ratio by tuning the container geometry will be discussed.

![Fig. 2. Geometrical situation for a tilted quadratic box filled with granular matter (grey).](image)

![Fig. 3. Geometrical situation for a tilted cylindrical cup filled with granular matter (grey).](image)

![Fig. 4. Green channel of an optical micrograph of Cu coated microspheres to illustrate the method for coating thickness determination by measuring the optical transmission of a coated sphere.](image)
The two values were normalized to the histogram mean values of uncoated spheres. So an uncoated sphere had a transmission coefficient of $T_{\text{un}} = 1$. The ratio of the two values (shell areas of coated spheres and areas around these spheres) then yields the transmission coefficient $T_c$ of the coating. Considering the exponential attenuation of the visible light within the metallic coating the thickness $d$ is given by

$$d = -\frac{\kappa}{2} \ln T_c$$

where the factor $\frac{1}{2}$ results from the fact that the microspheres are completely coated and the radiation has therefore to penetrate two films of (ideally) equal thickness. For each shell value a background value of the surrounding area has been subtracted, since most images did not have a constant background value (in Fig. 4 the upper left portion appears slightly darker than the lower right). If the size of the shell area and of the background area is changed by 10% the obtained thickness values only vary by about 2%. An analogous transmission measurement was applied to transparent Cu and Pt films deposited on plane glass substrates where the film thickness could also be assessed by mechanical profilometry. Within an error margin of 10% both methods (optical thickness assessment and profilometry) yielded the same results. A comparable method has also been successfully applied to determine the film thickness of metallic coatings on diamond granulates in [37]. Further information on technical issues can be found there.

3. Optimization of the deposition device and the container geometry

3.1. Agglomeration

First pretests showed that sticking on the vessels inner surface and agglutinating of the glass microspheres would become a major problem. Significant agglomeration effects occur as soon as the pressure in the vacuum chamber falls below 10 Pa (±0.1 mbar) starting with the accumulation of granulate at edges and possibly existent chinks, because of the lack of the thin water layer between the glass microspheres. At room temperature water will start to evaporate at a pressure of approximately $p = 6 \cdot 10^2$ Pa (±6 mbar) according to the phase diagram of water [38]. The loss of the ubiquitous water layer leads to increased friction and, subsequently, at the mentioned areas more and more glass micro spheres will agglomerate until trickling stops completely. Thus only a few spheres located at the now immobile surface are coated.

There were three different approaches to solve this problem. At first the immobile spheres can be loosened by concussing the vessel. Second, the geometry of the vessel can be modified to improve the trickling. Third, the amount of filling can be varied. Only the combination of all three approaches led to a satisfactory result.

3.2. Preliminary approaches and working concept

The first experiments were carried out with a vessel with three diverters fixed in the cup which should rearrange the micro glass spheres [9]. The spheres preferably accumulated in corners and edges of the vessel or of the blades.

Because of this fact subsequent tests were carried out without any blades. By doing so the micro glass spheres had less spots to stick to. In this case, however, the spheres now stuck onto the flat bottom of the vessel. In addition, the micro glass spheres were very poorly stirred when they were still mobile because of the lack of the diverter blades.

To bypass this problem a scraper was attached to the vessel in a way that the vessel could rotate independently of the scraper (Fig. 5). The scraper could rearrange the spheres and prevent accumulation. Yet the micro glass spheres were nearly completely destroyed due to the mechanical stress exerted by the scraper as it is visible in Fig. 6. The inset in Fig. 6 shows the intact microspheres for comparison.

Another possibility to avoid the agglutination on the bottom of the vessel was to reduce the area available for sticking. Thus a cylinder was glued into the center of the vessel by a two-component adhesive. The adhesive was additionally used to form a smooth transition from the bottom surface of the vessel to the cylinder wall (Fig. 7). It was shown that the glass micro spheres do not adhere at the so formed smooth edge. Additionally, again three diverter blades were used to mix the spheres.

This configuration showed the best results with a flat vessel geometry as a base. The glass micro spheres were continuously rearranged, but still about 50% of them accumulated.

From the observations discussed above, the following points were identified as the main parameters influencing the mixing behavior of the microspheres within a given vessel.

3.2.1. Vessel geometry

There are two main conclusions which can be drawn from the above vessel geometry variations. First, edges and corners have to be reduced. Second, the vessel surface has to be as steep as possible to guarantee trickling and to avoid the accumulation of the glass micro spheres, but at the same time has to be flat to coat the spheres. Thus a completely new geometry was designed (Fig. 8).

It consists of a cone in the middle and a funnel shaped part at the wall of the vessel. These two parts are glued into the vessel and again the adhesive was used to form a smooth edge between the cone and the funnel. The vessel was named TK vessel (Trichter = funnel, Kegel = cone). The slope of both the cone and the funnel is 45°, so with a vessel tilted by an angle of 45° relative to the horizontal plane.

Fig. 5. Rendered image of the slider arrangement used to stir the spheres.

Fig. 6. Optical micrograph of glass microspheres destroyed by the mechanical stress which is exerted on them by the slider arrangement. Inset: optical micrograph of undestroyed spheres for comparison.
each part of the inner surface of the vessel becomes perpendicular one time per rotation. The spheres glide off easily.

With this geometry alone, however, the rearrangement of the spheres was still insufficient. Only a few glass microspheres which remain at the surface are coated, whereas the others serve as a floating bearing. To guarantee mixing a small blade shaped like the dorsal fin of a shark was assembled to the funnel part of the vessel (Fig. 8). It is important to note that the “shark fin” is parallel to the direction of rotation, thus making this design different from the setups presented in [23, 24, 27] where the diverter blades are mounted perpendicular or close to perpendicular to the rotation direction. The vessel was finally named TK-Hai vessel (Hai ≈ shark) because of the resemblance of the diverter blade to a shark fin.

3.2.2. Rapper

To concuss the vessel during rotation beaters made out of spring steel were attached to the middle of the driving disc and to the wall of the vacuum chamber. Three rods fixed onto the base plate were used to span the immobile springs mounted on the chamber wall if the base plate is rotated. The inner springs move with the disc which drives the rotation of the containers and are also spanned by the rods mentioned above. So the rapping device can be used with and without base plate rotation. Fig. 9 shows a rendered model (top view) of the rapper set up. Yellow: base plate, green: driving disc, red and blue: beaters, which are spanned by the three rods and hit the vessel after release.

The rapper can prevent (or rather postpone) agglomeration, but cannot avoid it completely. In the present work only the inner beaters (red) were utilized.

3.2.3. Filling of the vessel

The vessels with flat base geometry were always filled to the maximum as it immediately became apparent that low degrees of filling lead to more accumulation and to a very short time till no movement of spheres could be observed anymore. With the TK-Hai vessel some tests with different amounts of filling were carried out. It was ascertained, however, that the maximum filling worked out best here as well. Due to the mechanical impact of loose material to accumulated material there is always a rearrangement of the glass microspheres.

Fig. 10 shows the dependence of the ratio of the exposed surface of the spheres to the total surface of all spheres within the aggregate, $A_{\text{exposed}}/A_{\text{total}}$ in dependence on the filling volume for the three different vessel geometries (square box, cylindrical cup and TK-Hai) at a tilt angle of $\alpha = 45^\circ$. Due to the complex geometry the calculations were carried out with Wolfram Mathematica and SolidWorks in the case of the TK-Hai vessel. A higher value of this ratio means a higher exposed surface and is therefore desirable. The difference between the three container geometries is decreasing with the amount of filling since the bottom geometry of a vessel with very high walls becomes more and more negligible. Still, the TK vessel shows the best behavior followed by the cylindrical flat vessel geometry at the filling amounts used in this work which are approx. 16 cm$^3$.

4. Results and discussion

Since the combination of the rappers and the optimised TK vessel proved to be a suitable solution for the problems of agglomeration and grants a reasonable ratio $A_{\text{exposed}}/A_{\text{total}}$ even at relatively high filling amounts, several batches of microspheres were coated with different materials (Cu and Pt) to investigate the properties of the films on the granulate.

4.1. Coating of the glass microspheres

The TK vessel was filled with 16 cm$^3$ of glass microspheres (maximum) at every deposition run. All other geometrical parameters and deposition parameters are described in Section 2.2.

![Fig. 7. Rendered image of the arrangement containing a central cylinder for reducing the sticking area and with 1 diverter blades for intermixing the microspheres.](image1)

![Fig. 8. New optimized vessel geometry, called “TK-Hai” (details concerning this designation: see text). (a): schematic cross section, (b): rendered image.](image2)

![Fig. 9. Rendered image of the spring set up to concuss the container during either base plate rotation (not used in the present work) or container rotation.](image3)
For a deposition time \( t \) of 10 min the film thickness \( d_{\text{film}} \) can be calculated according to

\[
d_{\text{film}} = \frac{A_{\text{exposed}}}{A_{\text{total}}} \cdot R_{\text{dep}} \cdot t
\]

if \( A_{\text{exposed}}/A_{\text{total}} \) (obtained from the data given in Fig. 10) is taken into account. The deposition rate \( R_{\text{dep}} \) for Cu and Pt at different sputter powers is given in Table 2 (last column). As Fig. 11 shows the calculated film thickness matches the thickness determined by the photometric method described in Section 2.3. The good quantitative agreement in the case of Pt may be fortuitous, but the deviation in the case of Cu seems to be significant because the calculation predicts a higher deposition rate in comparison to Pt due to the higher sputter yield of Cu (see Table 2). But in fact, the measured Cu thickness is even lower than the measured one for Pt. This difference can be attributed to gas phase scattering. The heavy Pt atoms (mass Pt: 195 u, mass Ar: 40 u mass ratio \( \text{Ar/}^{195}\text{Pt} = 0.2 \)) basically do not change their direction upon the collision of Pt with an Ar atom. The mean scattering angle for Pt/Ar collisions as it can be derived for classical hard sphere collisions [39] is only 17°. For Cu, however, which has an atomic mass close to Ar (mass Cu: 63.5 u, mass Ar: 40 u mass ratio \( \text{Ar/}^{63.5}\text{Cu} = 0.63 \)) the mean scattering angle per collision amounts to approx. 53°. The mean free paths for both materials are approximately 1 cm at 0.4 Pa [39], therefore both atoms undergo the same number of collisions between target and substrate. Because of the higher mean deflection angle the Cu atoms are scattered into distant regions of the chamber more likely and therefore may not even hit the exposed surface of the granulate.

Nonetheless, Fig. 11 shows that the simple approximations presented in Section 2, combined with knowledge about \( A_{\text{exposed}}/A_{\text{total}} \) allow for a reasonable prediction of the film thickness on the spheres. The difference between measured and calculated values is below a factor of 2 in all cases (Fig. 11). The error regions given in Fig. 11 were calculated by first measuring the film thickness of about 50 spheres within different optical micrographs as mentioned in Section 2.3. The thickness value determined for a single sphere varies by about 2% if measurement conditions are changed. Then the thickness values obtained for the single spheres were averaged. The mean square deviation was found to be about 20% and can therefore be taken as a measure of the thickness variation within this ensemble of spheres since it is significantly higher than the measurement error for a single sphere. The error bars can therefore be considered as a measure for the uniformity of the coating thickness within the total ensemble of microspheres located in the container. From these data it can be concluded that (i) basically all spheres are coated and (ii) the coating thickness uniformity is about 20% around the mean coating thickness.

### 4.2. Comparison of sputter deposited films with coatings obtained by reduction of platinum chloride

Pt films can be obtained by the reduction of platinum chloride. For this purpose platinum chloride (II) (98%) from Alfa Aesar was dissolved in bi-distilled water. 100 ml of glass bubbles was slowly added into the solution during vigorous stirring. The metal cations presumably adsorbed on the glass surface were reduced with \( \text{NaBH}_4 \) according to the chemical reaction

\[
\text{NaBH}_4 \rightarrow 2\text{H}_2 + \text{NaBO}_2.
\]

The mixture was then heated up to 100 °C to remove the rest of water and stirred by a mechanical stirrer.

Even a first inspection of coating morphology by optical microscopy shows significant morphological differences of the two coatings as it is visible in Fig. 12a and b. Fig. 12a shows microspheres coated with platinum by the means of magnetron sputtering at a power of \( P = 200 \) W, whereas Fig. 12b shows microspheres coated with platinum by the chemical method. The different character of the coatings can be recognized immediately. Whereas the spheres coated by sputtering show a uniform film the spheres coated by chemical reduction only show small scattered particles of platinum attached to the surface of the spheres. Loose Pt particles are also present between the spheres (see indications in Fig. 12b). In addition Fig. 12b shows an aggregate of platinum particles and parts of broken spheres. The spheres coated by sputtering, on the other hand, did not show any signs of damage (Fig. 12a).

A further test to evaluate the response of the coatings to changing environmental conditions was to immerse both types of coated spheres into water. Since undamaged spheres are floating on the water surface, they can easily be recognized. The main part of the sputtered spheres was unharmed by the coating process, whereas about 50% of the chemically processed spheres were broken and therefore were sinking to the bottom of the test vessel. The high number of destroyed spheres is a consequence of the stirring employed during the immersion of the glass microspheres into the solution and during the heating phase which removes superfluous water. Additionally, the chemically obtained coating did not adhere to the spheres and most of the coating material was found on the bottom of the water containment. This was shown by the chemical analysis of the dried residues taken from there. Therefore it can be concluded that the sputtering process (i) allows for a more gentle coating of the glass spheres and that the sputter deposited coating is (ii) more resistant to severe environmental changes as they are inevitable if e.g. the spheres are filled by Hydrogen [33]. Of course there is still a potential to optimize the chemical process by e.g. minimizing the mechanical load by stirring, but this is not the objective.
of this work. From the economical point of view the costs of the Pt precursor are comparable to the costs of metallic Pt so that the favorable properties of the sputter deposited coatings may justify the more expensive PVD process.

5. Conclusion

In this paper it has been shown that fragile glass spheres can uniformly be coated by a magnetron sputtering process. To achieve this the geometry of the vessel containing the glass spheres was carefully adjusted and optimised (i) to avoid agglomeration of the granulate, (ii) to achieve good intermixing behaviour, and (iii) to allow for a portion of the granulate as large as possible to be exposed to the vapor beam. This has been achieved by (i) implementing a concussion mechanism into a pre-existing system constructed for coating granular materials, (ii) by designing a special vessel with a geometry that leads to a permanent trickling of the granulate if it is tilted by 45° and (iii) by optimising the ratio of the surface of spheres exposed to the vapor beam to the total surface of spheres located in the vessel.

The key step in the optimization of the vessel was the reduction of sharp edges and crevices which led to the prevention of agglomeration. The adhesion of the glass microspheres on these smooth surfaces was low enough to allow for their detachment by a simple concussion mechanism. A very small diverter blade parallel to the direction of container rotation is sufficient to guarantee proper intermixing of the spheres. This is an important point since other devices based on rotating cups [23,24,27] make extensive use of different arrangements of relatively large diverter blades which are perpendicular or close to perpendicular to the rotation direction. In the present work it has been found that the implementation of diverter blade arrangements comparable to [23,24,27] provided many positions (sharp edges and crevices) where the particles first came to rest and then were rigidly attached. From these positions the particles could no longer be removed by concussion. Therefore the optimization of the size shape and direction of diverter blades is an important issue for future work. Coating the surface of the container to reduce the adhesion of the particles does not seem to be a viable option because the container will be coated with the respective target material long before the film on the particles has reached sufficient thickness.

Finally it is important to note that the top-down sputtering geometry allows for the implementation of different sputter sources which, in consequence, can be used to produce multilayered systems on the granulate if the base plate which carries the container is rotated. This is different from the set ups described in [23–25] which consist of a single central source within a rotating drum-shaped container. This type of set up makes it extremely difficult to implement a second sputter source because of geometrical limitations.

It can therefore be concluded that the special granulate container presented here is capable of coating sufficient amounts of granulate also for applications which require larger batches of material. In principle the whole set up can be scaled up, provided larger magnetron sputter sources which today are state of the art. In addition, of course, the sputtering process provides a basically unlimited range of materials which can be deposited, as there are metals, oxides or nitrides. Finally, as it is easy to implement more than one sputter source, arbitrary multilayered films can be produced which may have applications in different fields such as catalysis, thermal engineering or surface modification of granular matter.

Acknowledgements

The support of the Austrian “Fonds zur Förderung der Wissenschaftlichen Forschung” (FWF) for the construction of the basic coating device within Grant P-19379 is gratefully acknowledged.

References