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A method for uniformly coating powdery substrates by magnetron sputtering

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ABSTRACT

DC magnetron sputtering was used to coat fine-grained powders, i.e. hollow glass microspheres (particle diameter approx. 2–70 μm). To accomplish the exposure of the whole surface of each powder particle the powder was put into a rotating vessel which makes the particles tumble so that they are coated uniformly. However, there are problems of sticking and cluster formation of the powder during the sputtering process, which prevent the complete coating of the particles. To resolve this issue a concussion mechanism had been used which now was completely redesigned for better upscalability. This newly designed mechanism is based on gravity and will be described in this work as well as its ability to deposit metal and oxide films on powder particles. For the better understanding of the trickling behaviour of the used particles (glass microspheres), experiments addressing this behaviour with regard to different particle size distributions have been carried out in vacuum with the concussion mechanism and without it. Furthermore the influence of the sputter beam is taken into account. It will be shown that it is possible to coat powders, which strongly tend to agglutinate in vacuum and even more under sputter conditions, by using the new concussion mechanism.

1. Introduction

Magnetron sputtering is one of the most widely used methods for thin film deposition. It can be utilised to manufacture nearly every metal coating or metal composite as well as nitride or oxide layers, thus making magnetron sputtering a most versatile coating method [1–3]. The possibility to coat large area substrates and the easy to handle process parameters of magnetron sputtering enable a wide range of industrially important applications. Although coating plane substrates is state of the art, coating powder-substrates, granulates and particles of approximately 2–600 μm diameter by magnetron sputtering is still a difficult task.

This is due to: (i): Each side of every single particle has to be exposed to the sputter beam in order to get coated uniformly; therefore a particle mixing or rotating mechanism is necessary. (ii): Small particles of different sizes and shapes become wedged together during the mixing process which prohibits most of the particles from being coated since they are not exposed to the sputtering beam. (iii): In vacuum the particles tend to stick together as coating proceeds, especially when the powder is coated with pure metal. This is because of the absence of any separation layer between the coating of two particles in contact, i.e. air, water film or an oxide layer.

To overcome these issues there are several approaches, such as (i): a rotating drum, where the axis of rotation is horizontal and the barrel can be shaped in different ways, e.g. circular [4,5] with inlets [6], hexagonal [7–12] or conical [13,14], and the targets are positioned within the drum or perpendicular to the drum. (ii): Vibration, where the sample stage is connected to an ultrasonic or electromagnetic vibration generator which keeps the particles tumbling [15–22], or (iii): tilted rotating vessels, which also can be of different shapes as described in [23,24].

Aside from magnetron sputtering there are some other methods to coat fine grained powders and granulates, e.g. sol–gel coating [25–28], electroless deposition [29] and chemical vapour deposition [30]. However, these methods offer only a limited choice in materials which can be deposited and will not be discussed further in this work.

This paper will deal with the improvement of the coating mechanism described in [24]. In this previous work, besides the specially shaped coating vessel, a concussion mechanism is described which is necessary to break up clusters of powder particles that form during the coating process. Therefore, the rotating coating vessel was periodically hit by coach springs. In the present work the principle of the concussion mechanism was changed from impulse transfer by springs to impulse transfer by gravity. This will be described later as well as the results of coating different types of substrates.

This paper is structured as follows: Section 2 describes the experimental details, the different granular substrates, the coating apparatus and the coating parameters. Section 3 presents the results of trickling experiments and coating runs with different parameters. In

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Section 4, finally, conclusions from experimental data are drawn and an outlook to further work is given.

2. Experimental details

In this section the different substrates used and their preparation will be described. The main focus is on coating glass microspheres, although the coating method can also be applied to different granular shaped substrates, as e.g. fibres and craggy particles.

2.1. Substrate — glass microspheres

Hollow glass microspheres or glass bubbles have a large variety of applications, e.g. thermal insulation, filling material or road marking to name just a few. Another possible application is storing hydrogen at high pressures which will be discussed shortly.

Hollow glass microspheres (type S38) from 3M™, used in this work, are filled with hydrogen by means of a diffusion process at high temperature and high pressure (approx. 300 °C, 70 MPa). After cooling down, hydrogen cannot escape the spheres unless they are destroyed or heated up again. To release the hydrogen, it is feasible to use an exothermal chemical reaction which itself also produces hydrogen [31]. Such reactions often require a catalyst to work properly [32–35] which can be applied onto the spheres, e.g. by magnetron sputtering.

The spheres, which were used in this work, consist of high grade low-alkali borosilicate glass and have typical diameters of 2–70 μm [36]. A histogram of the glass sphere size distribution (Fig. 1) shows that most of the spheres have a diameter smaller than 20 μm. The diameters were measured manually with the freely available software ImageJ (http://rsb.info.nih.gov/ij/) and with a particle detection algorithm integrated in ImageJ from scanning electron microscope images of the spheres. The sphere shell thickness was also acquired by scanning electron microscopy measurements and has a value of 0.8 to 1.1 μm. This value is important for the hydrogen storage capacity, but will not be further discussed in this paper. In the course of the experiments the trickling behaviour of the spheres in vacuum was examined. For that the spheres were sieved and thus separated into batches of bigger and smaller spheres. Sieving was carried out manually with a sieve of 50 μm mesh size. Fig. 2 shows a histogram of the sieved glass sphere size distribution. There are still spheres of small diameters (<20 μm) in the batch; most of the spheres, however, are larger and have a diameter of 30–70 μm.

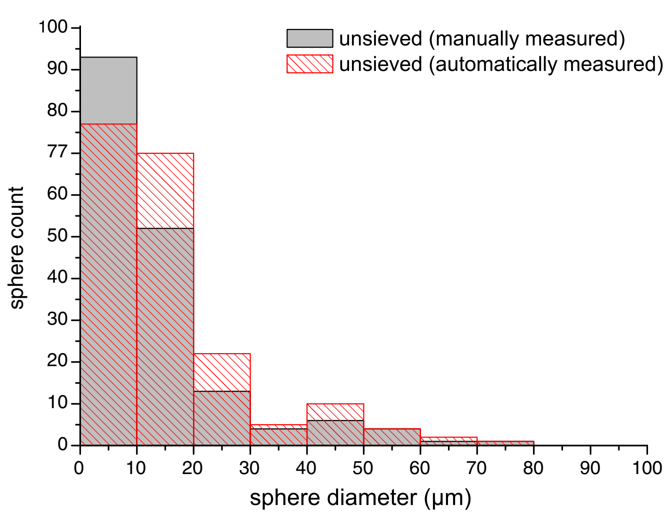

Fig. 1. Histogram of unsieved spheres, manually measured (grey) and automatically measured (dashed).

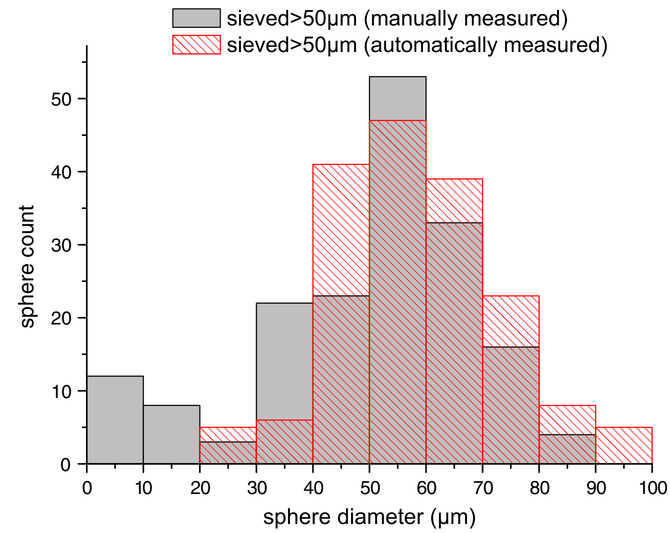

Fig. 2. Histogram of sieved spheres (>50 μm), manually measured (grey) and automatically measured (dashed).

2.2. Coating vessel and concussion mechanism design

In [24] a specially shaped coating vessel was designed to coat powders and other granular substrates. This vessel was tilted at an angle of $\alpha = \pi/4$ and rotating beneath the sputtering target. The special shape and the tilting angle allowed that per rotation period every surface of the vessel became vertical, thus enabling the powder to glide off the surface easily. The resulting movement of the powder, however, was not sufficient to break up the powder particle clusters that formed during deposition or to prevent sticking to surfaces completely. As a result it was necessary to use a concussion mechanism to induce additional momentum on the particles. This mechanism has been redesigned to work more reliably, to be constructed more simply and to be upscaled more easily.

2.2.1. Coating vessel

The basic coating vessel design is displayed in Fig. 3, where the coating vessel is put into a bigger plate (concussion plate). The coating vessel can be characterised by the following elements: a smooth inner surface (a), concave to the centre of the vessel and convex to the outer rim of the vessel, thus resulting in surfaces that are tilted toward opposite directions on the rim and in the centre of the vessel. Upon tilting the vessel this guarantees that the granulate is always located on a steep surface thus facilitating the sliding of particles (see also Fig. 5). To lift and mix the particles a small fin is fixed on the outer rim inside the vessel (b). Preliminary experiments have shown that the fin does not have to be very large; it has to transport only a certain amount of material to an elevated position to create particle trickling and thus stir the particles, gently. The detailed geometry of the coating vessel is currently subject to optimisation, but so far a coating vessel with an outer diameter of 93 mm was used in the experiments.

2.2.2. Concussion mechanism

The new concussion mechanism [37] consists of a rotating plate with a larger diameter than the coating vessel (Fig. 3). It has outer rim walls (2) so that the coating vessel (1) can move and glide within the plate and roll along its outer rim. Furthermore there are bolts attached to the outer wall of the plate pointing radially to the centre of the plate. When the coating vessel is put into the rotating plate (Fig. 4, A), the bolts lift the coating vessel (B) up to a certain point where the barycentre of the coating vessel is no longer supported by the bolt (C) and the coating vessel glides down (D). When the coating vessel hits the