Influence of particle size distribution on micromechanical properties of thin nanoparticulate coatings

Nina Barth*, Carsten Schilde, Arno Kwade

TU Braunschweig, Institute for Particle Technology, Volkmaroder Straße 5, 38104 Braunschweig, Germany

Abstract

In this study the production of thin nanoparticulate coatings on solid stainless-steel substrates using dip-coating was investigated. Defined particle sizes and particle size distributions of Al₂O₃-nanoparticles were adjusted by stirred media milling using various operating parameters. Using nanoindentation the influence of particle size and width of the particle size distribution on the mechanical properties was investigated. In particular the establishment of nanoindentation routines for particulate thin films in contrast to hard coatings is discussed. Nanoindentation appears to be an efficient method for analysing mechanical properties of said thin coatings. It will be shown, that the influence of the substrate can be neglected for small indent depth while the coating’s surface roughness influences the employed routine of the nanoindentation. The effect of the median particle size and the width of the particle size distribution on the coating structure and the micromechanical coating properties will be discussed. As a result, the maximum indentation force decreases with decreasing particle size but rises again once the nanoparticles reach very small sizes. A change in the width of the particle size distribution influences the micromechanical properties and coating structure as well.

1. Introduction

Thin films are one of the most important forms for the application of nanoscaled products and are used in nano-coatings, e.g. superhydrophobic coatings and ultra-thin hard coatings [1-5]. Within these applications, the advantages of nanoscaled products, such as a high specific surface of the material can be utilized while using minimal amounts. For the production of nanoscaled and nanostructured thin films a number of different methods are available. In addition to well-established thin-film production techniques in the gas phase such as vapor deposition or sputtering [6], a number of solvent based methods are frequently used, in particular sol-gel processes [7]. The production of nanostructured thin films by sol-gel
processes is inexpensive and easily implemented in many fields of application. Furthermore, it is often used for the production of corrosion protective, hard, anti-adhesive or anti-reflection coatings [8, 9].

### Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>$x_{i,j}$</td>
<td>particle size, $i$: the value which indicates how many percent of the particles are smaller than the given size, $j$: this value indicates if the particle size related to the: 0 number, 1 length, 2 surface and 3 particle volume</td>
</tr>
<tr>
<td>$Q$</td>
<td>cumulative distribution</td>
</tr>
<tr>
<td>$\eta$</td>
<td>viscosity</td>
</tr>
<tr>
<td>$\dot{\gamma}$</td>
<td>shear rate</td>
</tr>
<tr>
<td>$t$</td>
<td>time</td>
</tr>
<tr>
<td>$F$</td>
<td>force/load</td>
</tr>
<tr>
<td>$N_i$</td>
<td>number of indents</td>
</tr>
<tr>
<td>$h$</td>
<td>displacement</td>
</tr>
<tr>
<td>$d$</td>
<td>coating thickness</td>
</tr>
<tr>
<td>$R_a$</td>
<td>coating roughness</td>
</tr>
<tr>
<td>$A_c$</td>
<td>contact area</td>
</tr>
<tr>
<td>$W$</td>
<td>deformation work</td>
</tr>
<tr>
<td>$W_{\text{plas}}$</td>
<td>plastic deformation work</td>
</tr>
<tr>
<td>$W_{\text{elas}}$</td>
<td>elastic deformation work</td>
</tr>
<tr>
<td>$W_{\text{tot}}$</td>
<td>total deformation work</td>
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Another possibility is the production of nanoscaled or nanostructured coatings based on nanoparticles or nanomaterials by means of solvent-based coating processes, used in this study. Currently the use of such coatings in various applications is continuously increasing, as simple solvent-based coating processes are much cheaper than gas phase deposition processes. While scratch-resistant coatings, anti-freeze layers or hybrid solar cells are made up of low to moderate volume fractions of nanomaterials embedded in a polymer matrix [10], an increasing number of applications require coatings consisting of a high proportion or almost entirely made of nanoparticles [11-14]. A well-known example of such nanoparticle films is the field of “printable electronics” where the use of particle suspensions allows cost-effective manufacturing of electronic components [15].

Application effecting properties of nanostructured coatings, e.g. the mechanical properties of the coating, are influenced mainly by the raw material properties as well as the final coating structure. These properties depend strongly on the used production process of the raw material and on the process and formulation parameters of each process step in the entire process chain: production of the particles, dispersing and stabilisation of the suspension, formulation of the coating suspension, application and coating.

Figure 1 shows exemplary Scanning Electron Microscopy (SEM) images of three coatings consisting of aluminium oxide particles. The particles in the upper image are produced by real grinding in a stirred
media mill (SMM), the picture in the middle shows pyrogenic particles dispersed in a stirred media mill (SMM) while the third picture shows pyrogenic particles dispersed in a dissolver (DISS). Obviously, the three coatings appear to have a very different structure. From the pictures it can be concluded that the fractal dimension and, thus, the porosity of the number of contact points of the particles are different. As an effect of this difference the maximum force needed to indent to a specific depth the coatings varies considerably as shown in the diagram, exhibiting a decrease in nanoindentation force with increasing fractal dimension. However, in this example the median particle size of the particles $x_{50,3}$ stressed in the dissolver is considerably larger, which complicates evaluation of the results. Therefore, the influence of the median size and the width of the size distribution of $\alpha$-$\text{Al}_2\text{O}_3$-particles produced by real grinding on the micromechanical coating properties is systematically investigated in this study. A representative lab process will be used to produce thin coatings by dip-coating entirely made of nanoparticles.

Figure 1 SEM-pictures of three $\text{Al}_2\text{O}_3$-coatings (left) Load-displacement curves of three $\text{Al}_2\text{O}_3$-coatings (right)

2. Materials and Methods

2.1. Production and Characterization of the Suspension

As feed material, $\alpha$-$\text{Al}_2\text{O}_3$ (Martoxid MZS 1®, Martinswerk, Germany) with a mean particle size of 2 $\mu$m was used and dispersed in deionized water. A laboratory stirred media mill LabStar LS1 (Netzsch Feinmahltechnik, ®, Germany) was used for the milling experiments. Wear resistant, commercially available irregularly shaped alumina grinding media (Saint-Gobain ZirPro ®, SEPR Keramik, Germany) with sizes of 100, 320 and 660 $\mu$m were used to achieve different stressing conditions and thus create defined median particle sizes and distributions with different width. The grinding media have a density of 3910 kg/m$^3$ and a chemical composition of nearly 100 % $\text{Al}_2\text{O}_3$. The filling ratio of the grinding media in the milling chamber was set to 80 vol.-% for the experiments. When $\text{Al}_2\text{O}_3$ grinding media is used, only
wear of alumina is present in the resulting suspension. The comminution of the product was conducted in a circuit mode experimental setup [16]: From the stirred vessel, the suspension was pumped through a heat exchanger into the stirred media mill. After passing the mill, the suspension returned into the stirred vessel, where the pH value was measured. Electrostatic stabilization in the aqueous suspension was carried out with nitric acid with a pH-value of 5 for the experiments. Based on this pH-value the zeta potential reaches high values and ensures a well stabilized suspension. From the return flow, samples were taken to analyse particle size distribution and rheological behaviour. Sedimentation in a centrifugal field using a disc centrifuge (CPS Instruments ®, USA) was employed to determine the particle size distribution. The rheological behaviour was characterized with a rotational viscometer (Malvern Instruments ®, UK).

In order to investigate the influence of the median particle size and the width of the distribution on the micromechanical properties of the coatings, the particle size distributions were adjusted by varying the duration of the milling experiment as well as the grinding media size. The time necessary to obtain the required particle size was estimated using the kinetic model of Schilde [17]. Therefore the particle sizes of three short milling times were measured and fit to the model, providing a target time. In Figure 2 exemplary particle size distributions are presented. As a measure of the width of the distribution the ratio \((x_{90}-x_{10})/x_{50} \) [18] is applied, describing a wide distribution with a higher value.

The measurement of the viscosity is particularly important, as dip coating is a self-dosing coating method wherein the viscosity influences the coating thickness, as proposed by Landau and Levich [19]. The viscosity increases slightly with decreasing particle size because of intermolecular interactions (at a shear rate of 20s⁻¹ for example the viscosity increases from 0,0097 Pas to 0,00117 Pas). Yet, this increase in viscosity is not sufficient to induce the increasing coating thickness. Variation of the width of the distribution has nearly no effect on the viscosity of the suspensions.

2.2. Production and Characterization of the Coatings

The coatings were produced by dip-coating (Coater, Model, id Lab ®, Czech Republic) on solid stainless steel substrates, performed with a residence time of the substrate in the coating suspension of 60 s and a withdrawal velocity of 8.3 mm/s in nitrogen atmosphere at a humidity of about 5 %. A subsequent heat treatment at 120 °C in ambient atmosphere was applied for 2 h to dry the coatings. The thickness of the resulting coatings was determined by measuring profile and depth of a scratch. For this measurement a scratch with defined load and speed was applied to the coating, which completely removed the coating material locally without damaging the substrate, controlled by measuring with
energy dispersive X-ray spectroscopy (EDX). The profile was measured using a profilometer (dektak 8, Veeco®, USA). The additional measurement of surface roughness was performed using confocal laser microscopy (VK-9700K, Keyence®, Japan).

In order to quantify the mechanical properties of the coatings, nanoindentation measurements were conducted using a TriboIndenter TI 900 (Hysitron Inc.®, USA), equipped with a Berkovich tip. The tip is a triangular pyramid whose three surfaces meet at an angle of 65.3° between central axis and surface. When indenting the coatings load-displacement graphs were recorded. The measurements were performed in displacement controlled mode meaning a certain indentation depth was set to be achieved and the resulting indentation forces were measured as a function of the indentation depth. Different maximum displacements were measured ranging from 50 to 250 nm. Figure 3 (left) shows the load function of the nanoindenter. The used loading and unloading speed of the indentation was set to 20 nm/s. Using a constant velocity results in longer indentation times with increasing indentation depth but ensures the comparability of results, because the coatings exhibit a very distinct plastic and viscoplastic behaviour and the creep phenomena stay the same at the same depths. Using different velocities would result in the same time for one indent (independent on indentation depth), but in this case the results are not comparable because the viscoplastic behaviour doesn’t depend linear on the time. In order to increase the confidential level for each maximum displacement 40 indentation measurements were performed. The nanoindentation is a fully automated process. Patterns were distributed uniformly over the sample and performed automatically, so that the operator has no influence on the results.

Particulate systems usual exhibit a log normal distribution for a variety of properties, e.g. particle size distribution, porosity and contact number. The distribution of these properties results in a log normal distribution of the indentation force as well. Therefore Figure 3 right shows the mean and the logarithmic standard deviation of the maximum indentation force depending on the number of indents. The figure shows that both the mean and logarithmic standard deviation reach a constant value thus indicating that 40 indents per indentation depth provide sufficient statistical certainty [20]. Thus also allowing conclusions about the distribution of mechanical properties [20, 21]. Graphs showing the maximum indentation force always depict the mean value of the log-normal distribution.

According to Oliver and Pharr [22], typical models for determining hardness and elastic modulus based on the load-displacement curve cannot be applied due to the highly plastic and viscoplastic deformation and the high surface roughness of nanoparticulate coatings [23, 24]. Therefore, different characteristics for describing the micromechanical coating properties such as the maximum indentation force as well as the plastic and elastic deformation work may be used. The determination of the proportions of plastic and elastic deformation work is shown in [21]. The areas are calculated within

![Figure 3 Stress function of the nanoindenter (left); average of the maximum indentation force as a function of the number of measured indents (right)](image-url)
(plastic deformation work) and below (elastic deformation work) the load-displacement curve of nanoindentation measurements [21]. Due to the very plastic and viscoplastic behaviour, as shown in [23], significantly greater indentation depths (up to 40% of the coating thickness) are possible without any influence of the measurement by the substrate.

3. Results

3.1. Thickness of the Coating

In Figure 4 the coating thickness $d$ as a function of particle size for various particle sizes with either narrow or wide distribution is shown. Regardless of the width of the distribution, the coating thickness increases with decreasing particle size. A possible explanation is based on the ratio of the attractive forces between particles and the gravitational force acting upon the particles. This ratio increases with decreasing particle size. Additionally, since the coating thickness increases with decreasing particle size, the same solids content in the suspension should result in an increase in porosity of the coating for smaller particles, which has to be investigated further. Moreover, with a narrower particle size distribution the number of small particles in the coating and thus the ratio of attractive forces and gravitational force increase even more at small median particle sizes resulting in a higher coating thickness.

![Figure 4 Coating thickness as a function of particle size for various widely and narrowly distributed systems](image)

3.2. Roughness of the Coating

Figure 5 shows the arithmetic mean surface roughness $Ra$ of the coatings for different particle sizes ($x_{50,3}$) and two different distribution widths. Regardless of the width of the distribution at first, the roughness decreases with decreasing particle size, which suggests a more uniform coating structure. However, once the particle size decreases further, the ratio of attractive forces and gravitational force increases, probably resulting in an increase in porosity and hence the surface roughness. This can already be observed for the smallest particles of the wider particle size distribution. Furthermore it is apparent that the wider distribution shows a reduced roughness for most particle sizes, possibly because the small particles even out the larger particles’ pores.
3.3. Micromechanical Properties of the Coatings

Figure 6 depicts the maximum indentation force related to the contact area as function of indentation depth for different median particle sizes but similar distribution width. The results for an indentation depth of less than 100 nm should not be taken into account as the surface roughness is of a similar magnitude. The results for indentation depth greater than 200 or 250 nm should be excluded due to the low coating’s thickness, since the influence by the more elastic substrate cannot be excluded, as shown in [23]. Therefore, the values at an indentation depth of 150 nm can be considered to be reliable and to show a decrease in maximum indentation force related to the contact surface with decreasing particle size.

The coatings exhibit a very distinct plastic behaviour between 80 and 90 %. Additionally, the elasticity increases with decreasing particle size.

Figure 7 shows the maximum indentation force related to the contact area dependent on indent depth for different particle sizes, but for very broad particle size distributions. The influence of particle size on the decrease in force is comparable to the previous one, but less pronounced.
Figure 7 Maximum indentation force related to the contact area dependent on indent depth for different particle sizes with wide distributions.

Figure 8 visualize schematically possible explanations for the results that were described above, with only the extremes in particle size and distribution width listed. There are relatively large particles with an average size of about $x_{50,3} = 180 \text{ nm}$ and comparatively small particles with an average size of about $x_{50,3} = 100 \text{ nm}$, both sizes once with a narrow and once with a wider distribution. A theoretical value $d/x$ was created for each of the four cases dividing the measured coating thickness by the mean particle size. This value $d/x$ gives an indication of how many particles are present in each layer on top of one another, schematically shown on the right side of the figure. The wider distributions possess more contacts between the particles than the narrow distributions; at the same time the number of contacts increases with decreasing particle size.

A possible explanation for the observed effects is based on the number of contacts and the number of particle layers in the coating. Narrow distributions and thin coatings with large particles have fewer contacts resulting in a comparatively direct transmission of force to the substrate. Therefore, with an increasing number of contacts either due to a wider distribution or smaller particles or a combination of the two, the force is relayed to more particles and thus reduced. Considering the number distribution the change becomes more apparent: With decreasing particle size the ratio $d/x$ increases by a factor of 1.4 for the wider distribution. In contrast to this, for a narrow distribution this factor elevates to 3.3. Figure 9 shows the maximum indentation force related to the contact area as function of median particle size for three different distributions at a constant indentation depth of 150 nm. For larger particles as shown on
the right sight of the figure, the proportion of direct transmission of force dominates. With decreasing particle size, shown in the middle of the figure, the influence of the increasing number of contacts between the particles rises. This behaviour is more distinct for the narrower distribution, which may be due to the larger absolute number of smaller particles. Considering an even narrower distribution (triangle symbol) the force falls off more steeply, which corresponds to the theory of increasing number of smaller particles. When reducing the particle size further as shown on the left side of the figure, the force starts to increase again for the narrowest distribution indicated with triangle symbols, possibly because the coatings are more homogeneous and have fewer defects. It is therefore also imaginable that this behaviour could be observed for the narrow and the wide distribution as well, once the particle size drops below a certain value which will have to be determined in future work.

Figure 9 Maximum indentation force related to the contact area as a function of particle size for different distribution width

4. Conclusion

In a stirred media mill suspensions with defined particle size distributions of alumina were produced and subsequently processed to produce coatings by dip-coating. The coating thickness, the surface roughness and micromechanical properties were characterized. It was shown that not only the particle size, but also the width of the distributions has an influence on the coating thickness, the surface roughness and the maximum indentation force.

With decreasing particle size the coating thickness increases while the surface roughness decreases. The maximum indentation forces decrease initially, but rise again once the particles reach a certain size. A change in distribution width leads to a decrease in coating thickness and roughness with decreasing distribution width. The narrower the distribution, the stronger the decrease in indentation force with decreasing particle size. For the narrowest distribution the force starts to increase for the shown particle size range. According to the present state of knowledge, the observed effects are based on the number of contact points and the number of particle layers in the coating. The comparatively direct transmission of force to the substrate for narrow distributions and thin coatings with large particles is a result of the comparatively few contact points. Consequently, an increase in the number of contact points - either due to a wider distribution or smaller particles or a combination of the two – would result in a reduction in force due to the distribution to more particles.

Acknowledgment

We would like to thank “European Regional Development Fund”, which supports the programme “Europa fördert Niedersachsen”, especially the project Nanokomp - Nanostrukturierte Kompositmaterialien – von der Entwicklung in die Produktion.
References


