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AQUEOUS SOL-GEL COATINGS OF PURE AND
DOPED TiO₂ FOR BIOMEDICAL APPLICATIONS

**INFLUENCE OF PARTICLE SIZE DISTRIBUTION
AND CHEMICAL COMPOSITION IN SOLS ON
TOPOGRAPHY AND MECHANICAL
PROPERTIES**

Abstract

Goal of this study was to investigate the properties of coated TiO₂, pure and doped, synthesised by a newly developed aqueous sol-gel process. Titanium as substrate was coated by spin coating and the coatings were then heat-treated at two different temperatures. Particle size distributions were measured using photon correlation spectroscopy. The influence of the particle size distribution and their different chemical compositions on the coating's topography and roughness was investigated using atomic force microscopy. And the mechanical properties of the coatings were measured by scratch test. Part of the results were not very conclusive, since the strong influence of oxide layer growth underneath the coatings was underestimated. Nevertheless, very stable sols could be produced with the new deagglomeration process, which is mainly due to a reduced average particle size of dimension as low as 30 nm.

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1 Introduction

1.1 General

Titanium implants are now widely used in the dental field, and also in total joint replacements. They show good properties and bond strongly with bone, a phenomenon called osseointegration¹. The surface properties of titanium play the most important role²⁻⁴. Ti has a naturally formed oxide layer of a thickness of approximately 5 nm. There is unanimous agreement that this layer is responsible for the material's bioactivity. These surface properties include topography/morphology, chemistry, physical properties and many others. One problem that occurs is that these properties are highly dependant on the bulk material's composition and pre-treatment^{5,6}. Thus, it is very hard to study the influence of each property in its biological response in a comparable and reproducible manner.

A synthetic coating of TiO₂, which mimics the natural oxide layer of titanium and is highly reproducible, can thus give very good results in the study of the biological properties of the surface⁷. The mechanical properties of a surface layer can also be improved by a coating compared to the natural oxide layer. Of course, a synthetic coating can also be applied to any other substrate material, which might have better properties as an implant than the commonly used titanium alloys.

In this study, a sol-gel coating method was used, which shows many advantages compared to other commonly used coating methods, such as plasma spraying for example. It enables very good control of stoichiometry, purity, homogeneity and chemistry⁸.

Several studies have investigated sol-gel coatings of TiO₂ via an alkoxide route and yielded very promising results⁹⁻¹¹. In this study a different method via an aqueous route was investigated. This route shows several advantages, being easy to handle, due to the absence of alcohols, and thus producing redispersible sols where the surface of the colloidal particles can be chemically adjusted.

1.2 Background

A new aqueous sol-gel method for TiO₂ has recently been developed in this laboratory. Stable sols with different chemical compositions could be synthesised. The phase evolution during the heat treatment in these sols, once converted to dried powders, has been investigated by TEM and XRD, as well as crystal size and growth.

The resulting sols were not always stable, due to agglomeration of the colloidal particles and subsequent sedimentation. Thus, a new process to deagglomerate the larger particles was

developed, and the particle size distribution could be adjusted. This could lead to a way of tailoring the topography of the coatings, which has a major effect on the biological response as mentioned above.

XPS studies have also been conducted, with which the chemistry and composition of the surface was resolved.

The surface properties of the coating have not yet been completely studied and need to be further characterised for further biological experiments.

1.3 Aim of this Study

The goal of this study was to investigate the effect of the deagglomeration process on particle size distribution, and its influence on topography and roughness. Three sols of different chemical compositions were analysed. In addition the influence of the sol's properties on its mechanical strength and adhesion was also to be investigated.

2 Experimental

2.1 Materials

Commercially pure titanium (c.p. ti) was used as substrate. The following three systems of aqueous sols were provided by other members of the group, pure TiO_2 , $\text{TiO}_2 + 4\% \text{ V}$ and $\text{TiO}_2 + 12\% \text{ Al}$ (dopants in molar fractions). These sols were produced in this laboratory, but the process cannot be described here for proprietary reasons (patent pending). The concentration of the precursors in the sols was 1 M, which roughly leads to a volume fraction of 4%, assuming precipitation of the majority of the precursor. The sols were divided into three portions, from which two were further used to obtain two different particle size distributions via a time dependant deagglomeration process, which can unfortunately not be disclosed, also for proprietary reasons.

Table 1 Sample overview

System	TiO_2	Name	$\text{TiO}_2 + 4\% \text{ V}$	Name	$\text{TiO}_2 + 12\% \text{ Al}$	Name
Processing time	as prepared	Tioasp	as prepared	TiVasp	as prepared	TiAlasp
	15 sec	Tio15s	15 sec	TiV15s	30 sec	TiAl30s
	30 sec	Tio30s	30 sec	TiV30s	60 sec	TiAl60s

2.2 Sample Preparation

For the substrate, 10 mm-dia. c.p. ti discs were punched from a 1 mm sheet. These were then glued onto a sample holder, 9 at a time, using a wax with a melting point around 60° C. To get a well-defined surface topography, the following grinding/polishing procedure was used: Plane grinding on SiC paper, grain size #240, 3 min; fine grinding by decreasing the grain size from #400, #800, #1200 (SiC), 3 min each, to #4000 (WC), 10 min and replacing the paper up to 4 times on the finest paper. Water was always used as lubricant. Finally the samples were polished on a cloth with the following mixture¹², 96% of silica colloid 0.06 µm (MetPrep, UK), 2% of H₂O₂ and 2% NH₃. By using this mixture, the polishing time to obtain a decent surface could be reduced from 2 h down to 20 min, compared to using the pure silica colloid. Of course this was a very important step to eliminate as many effects on the topography by the polishing process as possible.

The polished discs were then coated using a standard spin coater. First, the samples were cleaned by ultrasonication in acetone, industrial methylated spirit (IMS) and triply deionized water (TDW), 15 min each. The coater was run with a speed of 4500 rpm. The sols were dropped onto the spinning discs using a medical syringe pump with a flow of 0.6 ml/h and a syringe size 19G. After 7 to 8 drops, 8 min, giving an amount of ca. 0.075 ml, the samples were spun for another 2 min for drying. 2 to 3 samples were coated for each sol and then stored in air for further use.

Then the following heat treatments (HT) were used: 300° C, 18 h, for all coated samples and one as polished; 300° C, 1 h, for Tioasp and Tial30s; 600° C, 18 h, for all coated samples and one as polished. The heat treatment was performed in an open horizontal tube furnace in air. The samples were placed in the furnace and taken out at maximum temperature. The very long time of 18 h was used in light of recent experiments to investigate the phase evolution in the dried powders.

2.3 Characterisation

2.3.1 Particle Size Distribution

The particle size distribution in the different sols was measured by photon-correlation spectroscopy (PCS) using a Malvern 4700 PCS with an argon laser (485 nm) at 20.5 mW intensity. The sols had to be highly diluted with filtered TDW (triply deionized water). 6 to 12 scans were measured for each sol. The analysis model used is CONTIN, which is an industrial standard and gives the best results for nonmonomodal distributions.

2.3.2 Topography

The topography and roughness was measured with atomic force microscopy (AFM) using TopoMetrix TMX2000 Explorer. Standard pyramidal silicon probes were used. The measurements were done in contact mode. First a scanner with 2.3 μm scan range (x-y) was used and data obtained for all samples. Later a larger-scale scanner, 150 μm (x-y), was used to measure some samples. Only heattreated samples were measured, because the adhesion of the coating was too small prior to HT. Polished samples without coating were also measured, with and without HT, to get an idea of the topography underneath the coating. Before measuring, the samples were gently cleaned with a ball of cotton soaked in acetone to get rid of any small non sticking particles and dirt on the surface. The scan parameters (PID) were adjusted for each sample and tip used.

2.3.3 Mechanical Properties

To measure the mechanical properties of the coatings scratch tests were performed, using a machine manufactured in this laboratory. The setup is shown in Fig. 1. A scratch is made by a spherical diamond tip, diameter 0.5 mm. The force is increased with a speed of 50 N/min, while the sample is moved with 10 mm/min. The force at which the tip breaks through the coating, F_c , can be read in the graph as the point, t_c , where the frictional force changes slope. This value cannot be compared with literature values, but gives good comparable information about adhesion between the different samples.

Several 5 mm scratches were carried out on each sample. Unless noted otherwise, the tip was brought into contact before the measurement was started, thus a small starting force was present from the beginning which was lower than the critical force, F_c . Between each scratch the tip had to be cleaned of adherent titanium from the substrate by doing a scratch with constant load, 8 N, on samples with a thick TiN coating. To confirm the results, some scratches were analysed by SEM and optical microscopy, where the distance could be measured from the start of the scratch to the point where the coating breaks. Also the nature of breaking or delamination was investigated.

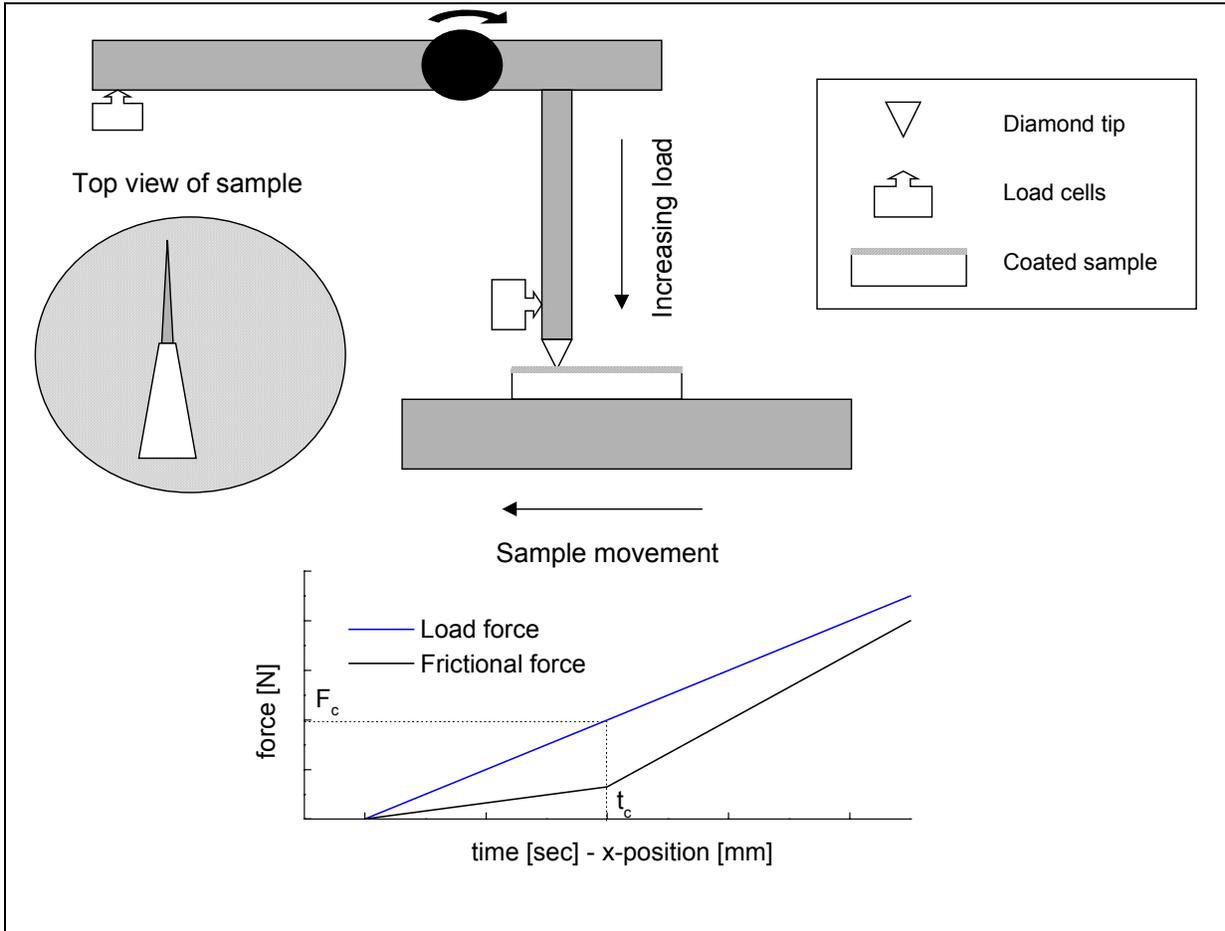


Fig. 1 Schematic setup of the scratch tester

3 Results and Discussion

3.1 Particle Size Distribution

Only one typical distribution from several measurements is shown in Fig. 2, while the exact and averaged results are shown in Table 2.

Table 2 Averaged PCS results, values in brackets not averaged

TiO₂, as prepared		TiO₂, 15 sec		TiO₂, 30 sec	
Area by volume	Mean by volume	Area by volume	Mean by volume	Area by volume	Mean by volume
(88.6)	(62.8)	(97.2)	(39.4)	96.9	31.1
(11.4)	(179.0)	(2.8)	(109.8)	(4.4)	(74.3)
TiO₂ + 4% V, as prepared		TiO₂ + 4% V, 15 sec		TiO₂ + 4% V, 30 sec	
Area by volume	Mean by volume	Area by volume	Mean by volume	Area by volume	Mean by volume
68.8	87.8	97.2	42.7	98.5	35.7
31.2	265.2	2.8	148.4	(1.5)	96.3
TiO₂ + 12% Al, as prepared		TiO₂ + 12% Al, 30 sec		TiO₂ + 12% Al, 60 sec	
Area by volume	Mean by volume	Area by volume	Mean by volume	Area by volume	Mean by volume
68.7	92.6	96.0	51.5	97.8	40.5
31.2	332.5	4.0	133.0	2.4	114.4

The results from the PCS measurements (Fig. 2a-c) show for all three as prepared sols two populations of particles, one with a size below 100 nm and another one with rather large particles. After processing, the large particles start to break up and the average size of the smaller population decreases too. Obviously the particles are not yet fully deagglomerated, with the processing times used. Thus further experiments should be done to investigate the deagglomeration process.

These results mean that one can adjust some properties of the sols. E.g. the stability (no sedimentation) can be improved by breaking up the large agglomerates, viscosity can also be changed by changing the particle size distribution ¹³.

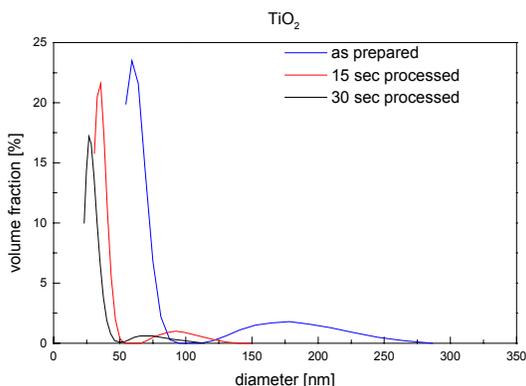


Fig. 2a PCS-result – TiO₂

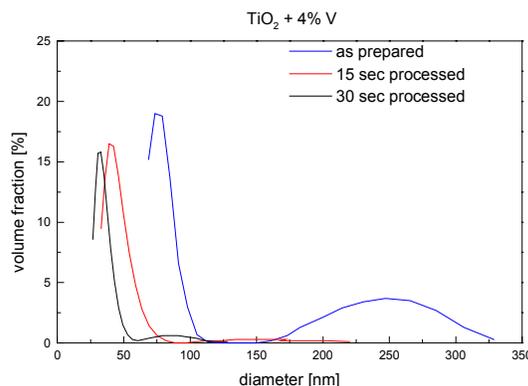


Fig. 2b PCS-result – TiO₂ + 4% V

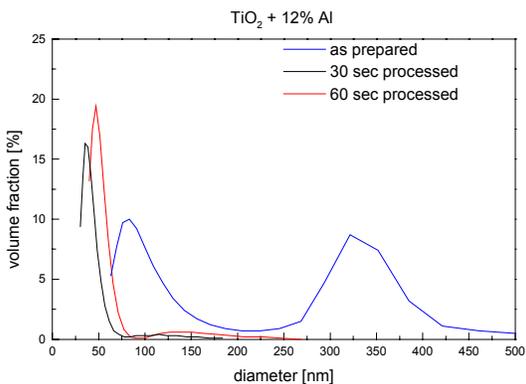


Fig. 2c PCS-result – TiO₂ + 12% Al

Fig. 2 PCS-results; One typical distribution of each sol

3.2 Topography

The picture of the polished surface without HT (Fig. 3a) shows that a really flat surface was achieved with the polishing method used, R_a value is only 2.3 nm. After the heat treatment at 300° C the surface looks very different (Fig. 3b) and the averaged R_a value has increased to

20.6 nm. The surface observed is oxidised due to the HT, and the oxide layer has grown and formed this topography.

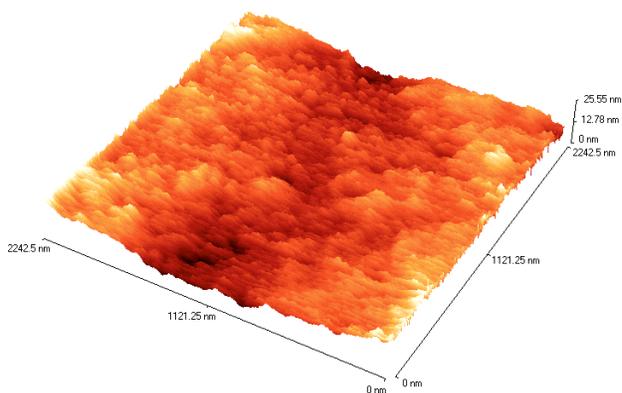


Fig. 3a as polished, no HT

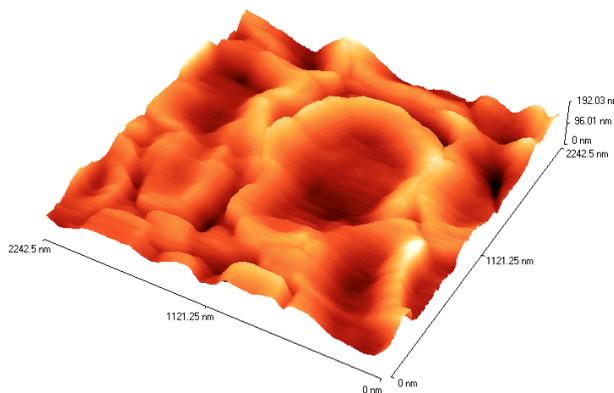


Fig. 3b as polished, HT @ 300° C, 18 h

Fig. 3 AFM of polished surfaces

In the measurements of the coated and heat treated surfaces a problem occurred because of the quality of the probes and the method used. Some examples are shown in Fig. 4. One can clearly observe flat round features, which are repeated very regularly. This was observed in all the pictures taken from the samples heat treated at 300° C, shown in Appendix 1. Also the features did not differ in size and shape between the samples. However, when the same sample was measured again, using another probe (Fig. 4b), the size of these features changed considerably. This led to the conclusion that all these features are simply artefacts; in fact they are pictures of the probe itself, which was obviously very blunt. This happens if the true features on a sample have sharper angles than the probe.

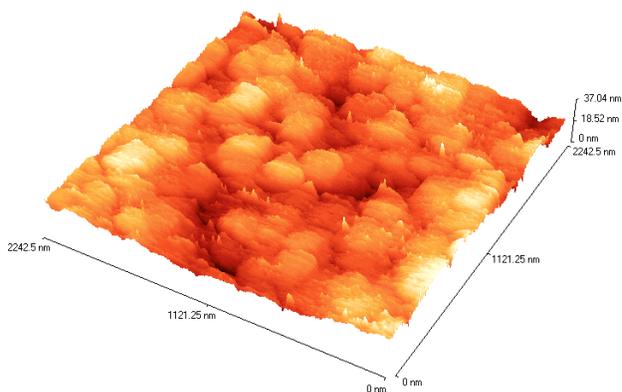


Fig. 4a tioasp, HT @ 300° C, probe 1

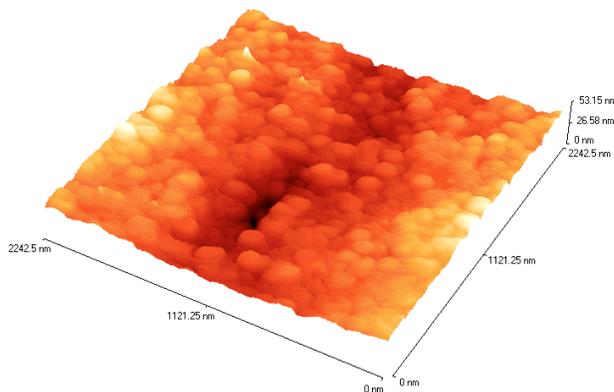


Fig. 4b tioasp, HT @ 300° C, probe 2

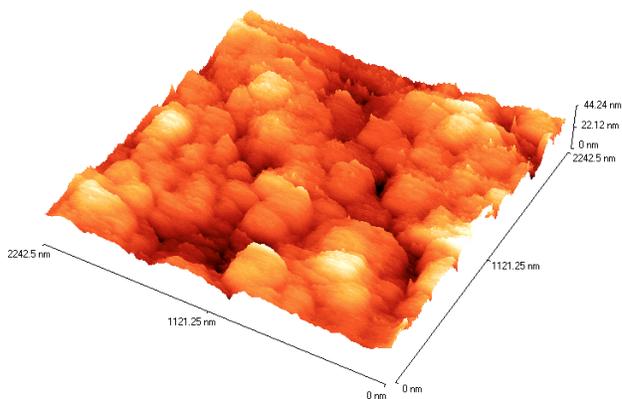


Fig. 4c tialasp, HT @ 300° C, probe 1

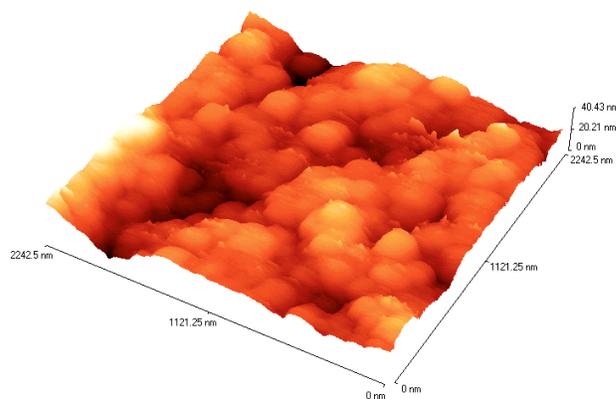


Fig. 4d tiv30s, HT @ 300° C, probe 1

Fig. 4 Selected AFM of different samples, HT @ 300° C, and different probes (4b)

The samples heat treated at 600° C have been measured with other probes (Appendix 1), one of them yielding really poor results, as one can see from the strange shape of all the features in some samples.

Taking this into account, there is only very little information that can be obtained from the AFM measurements and great care has to be taken concluding any results. At a given HT temperature for example no major difference in topography can be seen, neither due to the chemical composition nor due to the particle size distributions. However this cannot be proved by these measurements.

Table 3 Roughness values measured by AFM, colours represent different tips

Sample	Roughness, R_a value	
	HT @ 300° C	HT @ 600° C
Tioasp	3.11 nm	53.0 nm
Tio15s	3.63 nm	41.6 nm
Tio30s	3.96 nm	-
TiVasp	4.22 nm	32.6 nm
TiV15s	4.70 nm	41.3 nm
TiV30s	4.28 nm	34.3 nm
TiAlasp	4.60 nm	16.0 nm
TiAl30s	6.52 nm	20.9 nm
TiAl60s	4.53 nm	15.5 nm

Looking at the roughness values, R_a , listed in Table 3, it is clear that there is a big difference between the two heat treatments. But again, great care has to be taken concluding any results, because three different probes were used (one for HT 300° C, two for HT 600° C). Thus, the only thing that can be concluded is the general increase in roughness from 300° to 600° C. This will be discussed later in chapter 3.4.

But what does the real topography look like? One sample has been measured using an AFM at ETH-Zürich, the pictures being obtained in tapping mode using a standard silicon probe for

tapping. The result is shown in Fig. 5. Clearly this is very close to the true topography, because the particles can be seen and they also show individual shapes themselves, which means that it is the particles that are being imaged and not the probe. Still the shapes are slightly elongated in the horizontal direction due to the quality of the probe.

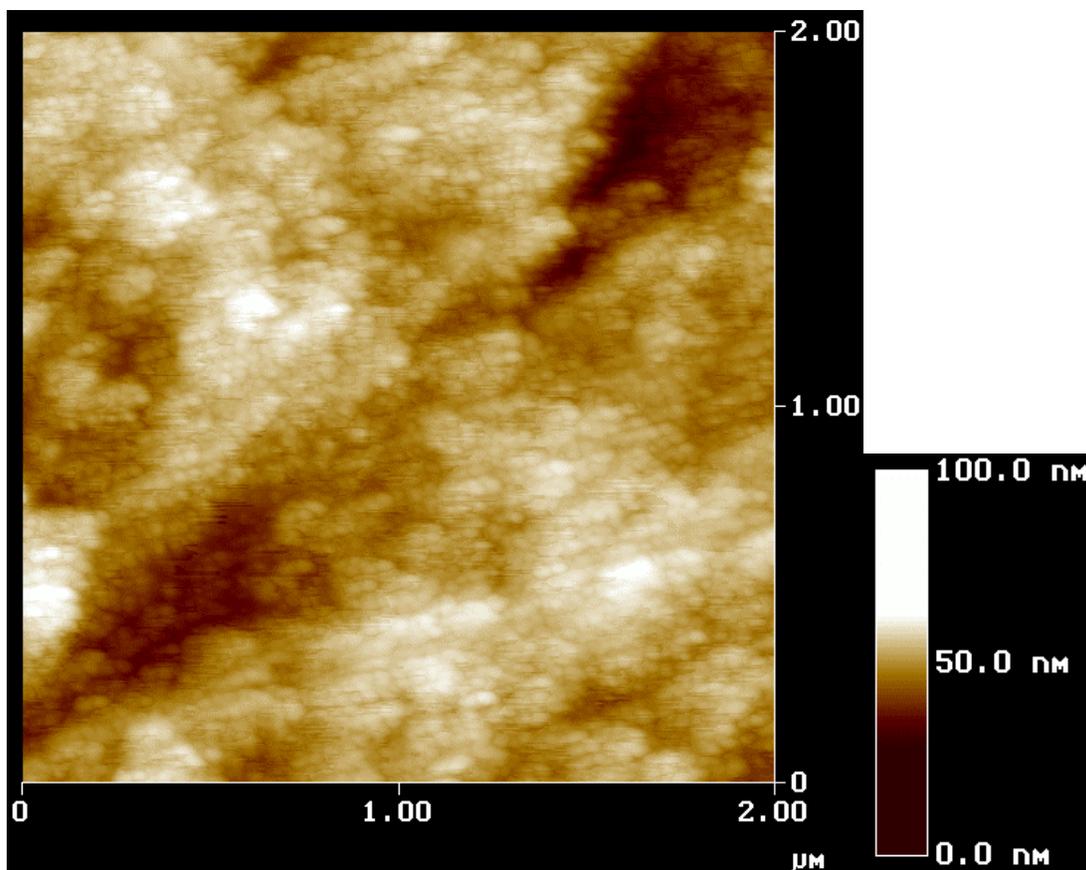


Fig. 5 AFM tapping mode image of Tioasp, HT @ 300° C, measured at ETHZ

3.3 Mechanical Properties

3.3.1 Heat treatment at 300° C

The results from the samples heat treated at 300° C show that nothing can be measured with this test. Thus only two samples were investigated, Tioasp and Tialasp. In Fig. 6a no change of slope can be observed and also the SEM pictures (Fig. 6b) show that the coating is penetrated by the tip right from the start. This means that the test is not sufficiently sensitive for such coatings.

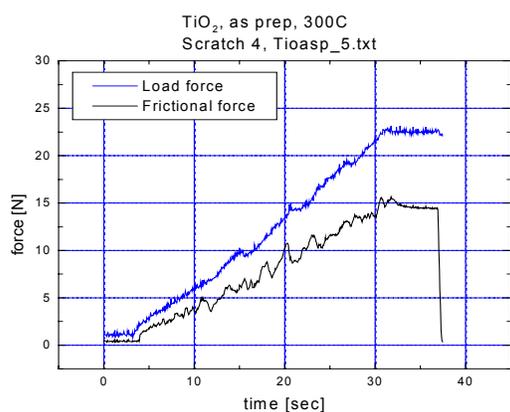


Fig. 6a Scratch result

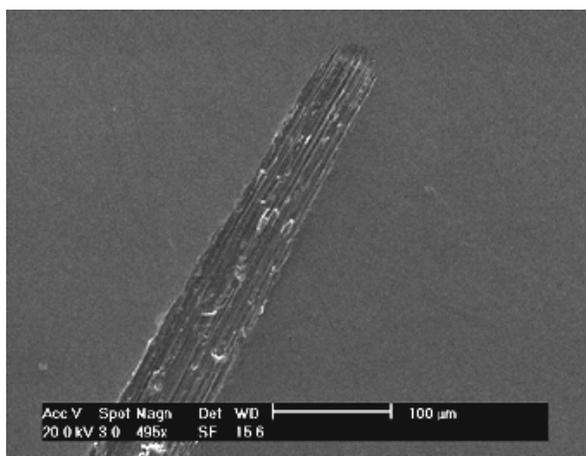


Fig. 6b SEM image of the start of the scratch

Fig. 6 Scratch test results, TiO₂ as prep., HT 300° C

3.3.2 Heat treatment at 600° C

These experiments showed the typical change of slope for a stronger coating. Thus F_c could be determined for all samples (Fig. 7). A polished sample without coating was also measured. All the scratch test results are shown in Appendix 2.

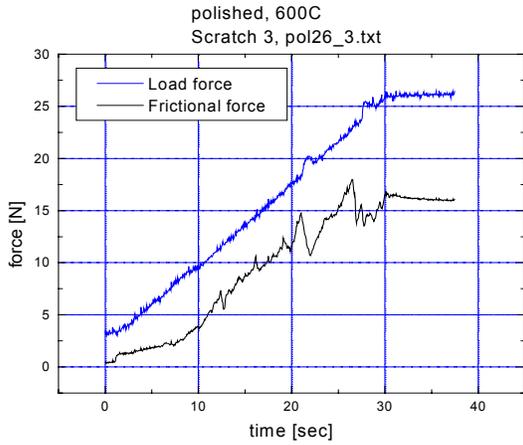


Fig. 7a Scratch result on a polished surface

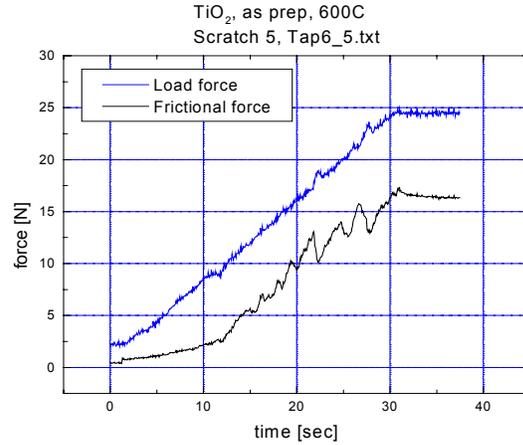


Fig. 7b Scratch result on TiO₂, as prepared

Fig. 7 Scratch test result, HT 600° C, comparison of coated and non coated surface

The results (Fig. 8) show no big difference in F_c between all coated samples and the uncoated one. This has been statistically analysed (Appendix 2), giving the result that the mean of population A (coated samples) shows no difference to the mean in population B (polished sample) on a 0.05 level of significance, using a t-test. This means that the critical force measured is not due to the coating, but due to a grown oxide layer of titania underneath it. Therefore, the influence of the coatings themselves could not be resolved with this test.

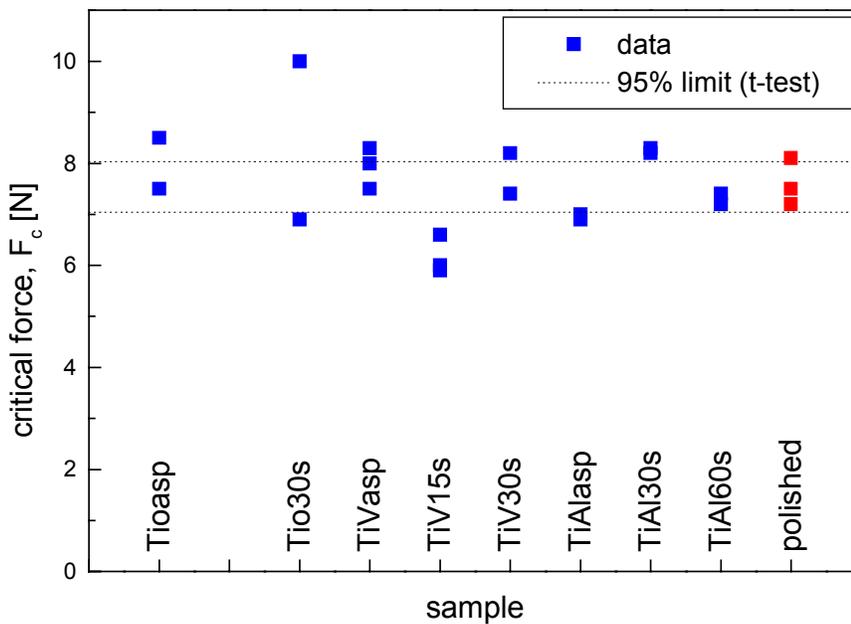


Fig. 8 Combined results from scratch test, HT 600° C

3.3.3 Oxide Layer Growth

It turned out that an oxide layer grows beneath the coating, as seen in the scratch tests. And that this affects the topography as well. Thus the increase in roughness from samples heat treated at 300° to those at 600° C is not due to any changes in the coating, but to the oxide layer grown from the titanium substrate. This could also be seen in the non coated polished samples shown in Fig. 3. This means that the coating does not act as an oxygen diffusion barrier.

Because of the importance of the oxide layer growth, it needs further investigation. According to Zwickler, ref. 14, the following growth ratios occur in c.p titanium. Zwickler also provides laws for the oxide layer growth in different temperature regimes. These ratios are for an oxygen atmosphere, but it is also mentioned that up to 1000° C the behaviour is very similar in air.

Table 4 Oxide layer growth ratios according to ref. 13

	100 min		1000 min (~18 h)	
temperature	weight gain	growth law	weight gain	thickness
HT @ 300° C	0.0045 mg/cm ²	logarithmic	0.0065 mg/cm ²	0.038 µm
HT @ 600° C	0.11 mg/cm ²	cubic	0.21 mg/cm ²	1.24 µm

The estimated thicknesses of the resulting oxide layers are inaccurate, because it was assumed that the weight gain is only due to the oxygen consumed in the formed oxide layer and that there is no solubility of oxygen in the metal. It was also assumed that the formed oxide layer reaches the theoretical density of rutile, 4.25 g/cm³.

Of course, these results are for uncoated samples, but they are still very reasonable for the system used in this study and explain the results obtained in the experiments mentioned above.

4 Conclusions

The nanocrystalline particles obtained in the sols could easily be deagglomerated with the process investigated. It was possible to obtain an almost monomodal particle size distribution. It was shown that with only a short processing time the particles could be reduced in size down to an average of 40 nm. This provides a method to improve the sols stability against sedimentation, according to Stoke's law. Considering the crystallite size of 4-6 nm, the particles still consist of an agglomerate of the crystals. Thus, it might be possible to reduce their size further by a longer processing time or by improving other parameters in the process.

By changing the particle size distribution, the sol's viscosity can also be tailored, according to ref 13. And by doing this, the thickness of the spin coated layers might be adjusted, because it is mainly dependant on the sol's viscosity¹⁵.

The effects of the particle size distribution and the chemistry in the sols on the topography, could not be clearly resolved due to the major role the oxide layer growth played during the heat treatment. Although some systems showed large agglomerated particles, their presence could not be observed by AFM, not in the images and not in the roughness values. Thus, the influence of the particle size distribution needs further investigation. The sensitivity of the AFM in contact mode, due to bad quality of the probes, can be improved by using tapping mode. In which case only the lowest point of the probe measures the surface and the problem of imaging the blunt probe itself can be reduced.

For further investigation of the structure of the coated gel on the surface other techniques could be more conclusive. For example, high-resolution FE-SEM or even TEM. The latter could also give good information about the pore structure.

The mechanical properties of the coatings could not be measured. On one hand because of the oxide layer growth on the titanium surface at high temperatures and on the other hand because of the insensitivity of the scratch test used, rendering it unsuitable for coatings as thin and weak as the one in this system. Other tests might include a micro-hardness test with very small forces.

The problem of the oxide layer growth can be reduced by different approaches. The coatings could be heat treated in a neutral atmosphere, for example. According to ref. 13, this is still very hard to achieve, because of the reactivity of the titanium, which oxidises even at very low partial pressures of oxygen. Thus, to investigate the structure of the coatings, it would easiest to change the substrate material. Of course, by changing the substrate, e.g. to silica glass, the interface properties, like adhesion, would completely change.

Further experiments that are urgently needed include ellipsometry, to get information about the thickness of the coated layer.

In general, the aqueous sol-gel route investigated seems to be a very promising technique to get a reproducible TiO₂ coating for biological applications and research. It also has a high potential in other fields of sol-gel materials, due to its very small crystallite size and its ability to adjust chemistry in a very exact and homogeneous way. These fields include photovoltaic applications or catalysts¹⁶⁻¹⁷.

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