MORPHOLOGY AND PRODUCING OF TIO_2 PARTICLES

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Abstract. Paper deals by problems of nanoparticles and nanomaterials applicated in technical practice. Description of nanostructures and their physical, chemical and mechanical properties is in the article. There are mentioned embodiments of production TiO_2 nanoparticles which are carry out by fine grinding processes. Realization of functional tests related to the physical properties of the resulting particles and subsequent application in practical activities in the field of engineering practice. Today, we are seeking and examination ways they can make best use of the properties of the material. When applied on the base material (metal, plastic, glass, etc.) of very thin layer of another material, the base material can produce very different properties. Most of the thus obtained characteristic is very advantageous and improves mechanical properties. Mechanical properties and physical properties such corrosion resistance, hydrophobicity, surface detachment of dust and the like. To obtain these properties, it is necessary to apply this layer of fine nanoparticles, which are produced by means of technology of fine grinding processes.

Keywords: nanoparticles, engineering practice, grinding processes.

Introduction

Titanium dioxide (TiO_2) is widespread and the comonly used substance. It is known as titanium dioxide and is used for example as a colorant. It has many useful features such as UV rezistentnost (use sunscreen), a high refractive index, etc [1]. Nowadays we are looking for an exploring ways how to make best use of the properties of the material.

When applied on the base material (metal, plastic, glass) of a very thin layer of a different material, will obtain this base material very different properties. Most of the thus obtained properties is very advantageous and improves mechanical properties such as corrosion resistance, hydrophobicity, non-attachment of dust on the surface and the like. To obtain these properties, it is necessary to apply this layer of fine nanoparticles (units of nanometers to hundreds of) [2].

This research is focuses on the method for obtaining nanoparticles of TiO_2, which are needed for coating of other thus treated materials.

1. The methodology and used instruments

By the process of mechanical milling we can obtain a very wide range of particle sizes. The best suited for coating are the smallest grain sizes. As small as possible. On the distribution of the sample according to the size of grains we use analytical sieving machine AS 200 from Retsch. It contains several screens with graded mesh sizes. Sieving process is based on the principle of mechanical (vibration) when sample falls progressively finer sieves. In the first phase of research, we looked at the factors influencing the milling process itself. These variables that can affect the process itself is several. We examined how changing a variable effect on the resultant sample [3].

To obtain nanoparticles of TiO_2 we used methods of mechanical milling in a planetary ball mill. Ball mill comprises of a grinding station (grinding vessel). The speed is adjustable in the choosed range. The grinding container has a volume of 250 ml and its material is zirconia ZrO_2. Furthermore, we can set the time interval between the milling.

Mechanical grinding of obtaining powders is a time consuming method . The sample preparation length can reach even several days.

The next step is the division of the fractions according to grain size. We obtain a very wide range of particle sizes by mechanical milling. On dividing the sample according to the size of the grains we use analytical screening machine. It contains several screens with graded mesh sizes (20μm-25mm). Sieving process is based the principle of vibration and the sample falls progressively to finer screens.

2. Grinding affecting factors

Changing of the grinding process conditions has significant effect on the quality of the sample. Such variables that can affect the grinding process are:

- total grinding time – total time, which leads to the crushing of the sample;
- grinding interval – the time between partial grinding;
- pause – time interval cooling of the sample;
- revolution speed.

It was found that coarse grinding (Fig. 1) best fits values given in table 1.

Table 1

Revolution and coarse grinding time

Coarse grinding	
Total time	4 min
revolution	400 min^{-1}

These values are set as a reference values for gross grinding each new sample preparing.

It is necessary to find the optimal ratio of variables for fine grinding so as to prevent aggregation of particles and adherence to vessel walls.

Table 2

Sample sieving data and the weighting of individual fractions

Testing sample						
1st grinding				2th grinding		
Mass		100.55 g		Mass		94.31 g
Total grinding time		10 min		Total grinding time		60 min
Revolution speed		450 min^{-1}		Grinding interval		30 min
-	-	-		Pause		4 h
-	-	-		Revolution speed		450 min^{-1}
Mass distribution after 1st grinding				Mass distribution after 2th grinding		
Particle size, µm	Mass, g	Utilization, %		Particle size, µm	Mass, g	Utilization, %
$x>400$	0.00	0.0		$x>400$	0.00	0.0
$x<400 \wedge x>125$	3.16	3.3		$x<400 \wedge x>125$	50.09	55.6
$x<125 \wedge x>40$	19.49	20.5		$x<125 \wedge x>40$	38.01	42.2
$x<40 \wedge x>20$	63.91	67.1		$x<40 \wedge x>20$	2.00	2.2
$x<20$	8.71	9.1		$x<20$	0.00	0.0

Preliminarily grinding process indicates that already after 10 minutes of the first grinding is 67.1 % of the particles in the size range of x < 40 microns x > 20 microns and particles x<400 microns x>125 microns is only 3.3 %. With further screening we use only the finest three screens.

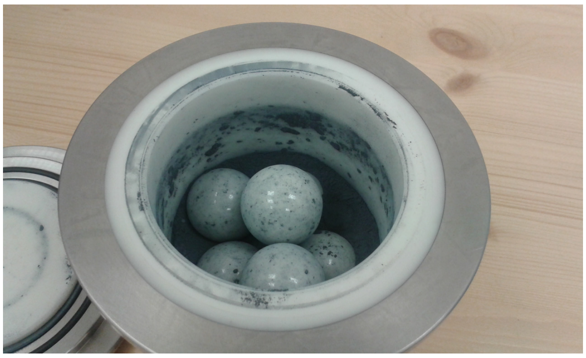

Fig. 1. **Coarse grinding**

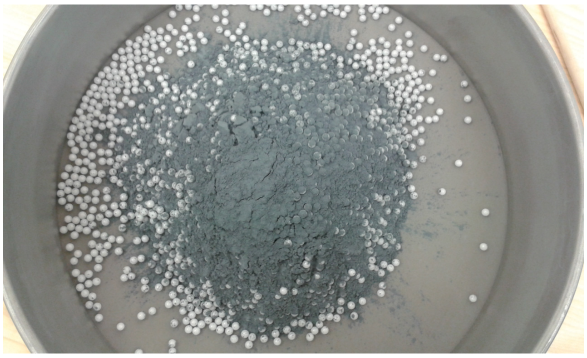

Fig. 2. **Sieving process**

Amount of heat arise during milling process. After 120 minutes of the milling process is the vessel very warm. Approximate temperature measurements of the vessel showed temperature. 127 ºC. The powder was compressed on the bottom of the vessel. It was impossible to remove the powder and the sample could not be sieved. High speeds and long grinding interval combination is not suitable in this case. Long milling time without pause is the cause of a large amount of heat to the sample. It has got a negative consequence for final powder production.

From the above it is clear the need to speed reduce to shorten the interval of grinding and extend break to the accumulated heat dissipation from the sample. The powder can easily get out of the container after the first grinding and sift. There is no apparent particle aggregation, (Fig. 2).

Table 3

Sample 1 grinding

Sample 1						
1st grinding				2 th grinding		
Mass		100.98 g		Mass		97.32 g
Total grinding time		60 min		Total grinding time		60 min
Grinding interval		10 min		Grinding interval		10 min
Pause		50 min		Pause		50 min
Revolution speed		250 min^{-1}		Revolution speed		250 min^{-1}
Mass distribution after 1st grinding				Mass distribution after 2 th grinding		
Particle size, µm	Mass, g	Utilization, %		Particle size, µm	Mass, g	Utilization, %
$x<125 \wedge x>40$	1.55	1.6		$x<125 \wedge x>40$	-	-
$x<40 \wedge x>20$	87.34	88.3		$x<40 \wedge x>20$	-	-
$x<20$	10.00	10.1		$x<20$	-	-

Table 4

Sample 2 grinding

Sample 2						
1st grinding				2 th grinding		
Mass		100.56 g		Mass		83.68 g
Total grinding time		120 min		Total grinding time		120 min
Grinding interval		10 min		Grinding interval		10 min
Pause		50 min		Pause		50 min
Revolution speed		250 min^{-1}		Revolution speed		250 min^{-1}
Mass distribution after 1st grinding				Mass distribution after 2 th grinding		
Particle size, µm	Mass, g	Utilization, %		Particle size, µm	Mass, g	Utilization, %
$x<125 \wedge x>40$	32.62	34.8		$x<125 \wedge x>40$	50.60	64.5
$x<40 \wedge x>20$	50.94	54.4		$x<40 \wedge x>20$	26.96	34.4
$x<20$	10.12	10.8		$x<20$	0.90	1.1

For other samples, to influence heating, was shortened grinding interval to 5 minutes. Furthermore, we have focused on yield relative onto the total grinding time. From each sample was taken away finest fraction for further analysis and ensuing particle – coating research.

3. Evaluation of grinding process and grain morphology

From the ground sample is taken a proportion from only the finest fraction. Grain morphology is analyzed by electron microscope.

Fig. 3 shows a detail of the grain fraction x<20 micron from sample 2, after the first fine grinding (120 minutes). From the geometry of the grains is obvious that we are in the nanometer range. The shape of the grains is irregular with sharp edges. This is typical for the mechanical ball mills grinding. That is probably reason of a large grain aggregation. Aggregation is also caused by charge on the grain surface.

With grain size decreasing are growing relatively surface forces. They impede to the classical gravity (vibration) screening. From visualization apparently, that even these methods can produce a nanometers sort of particle range.

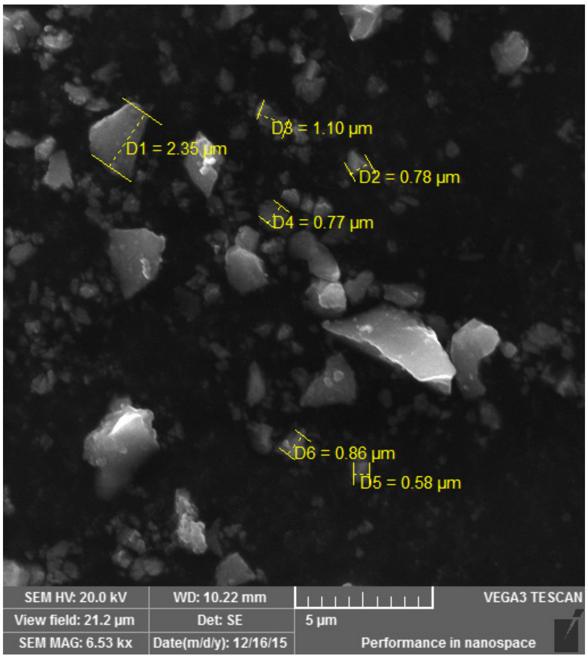

Fig. 3. **Detail of the grain fraction *x*<20 micron of sample 1**

Fig. 4 shows detail of grains of the sample 2 (60 minutes). And here we are in the nanometer range. Compared to sample 1, is there relatively more small particles. Although in sample 1 in Fig. 3 was total grinding time 120 minutes compared to the previous, where the grinding time was of only 60 minutes, but the grinding interval of the sample 1 was 10 minutes and in the sample 2 was 5 minutes.

This confirms the theory, that short time intervals of the individual milling, is preferable. By this procedure is the greatest percentage of the smallest particles.

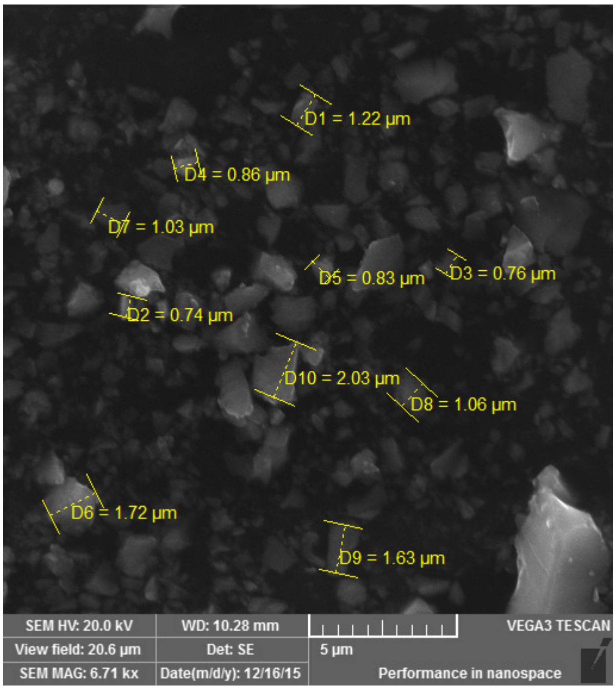

Fig. 4. **Detail of the grain fraction *x*<20 micron of sample 2**

3.1. Optimum milling yield evaluation

Final way of our research activity was focused on maximum of obtained yield of particles x <20 microns depending on the grinding time with conditions maintaining.

Given these data, an obtained optimum:

- total grinding time – 240 minutes;
- grinding interval – 5 minutes;
- pause – 55 minutes ;
- revolution speed – 250 min^{-1}.

From the graph in Fig. 4 we can see proportion of the finest fraction increasing with the time. The smallest particles after four hours of grinding are not increasing. Probably here are its limits of used grinding method.

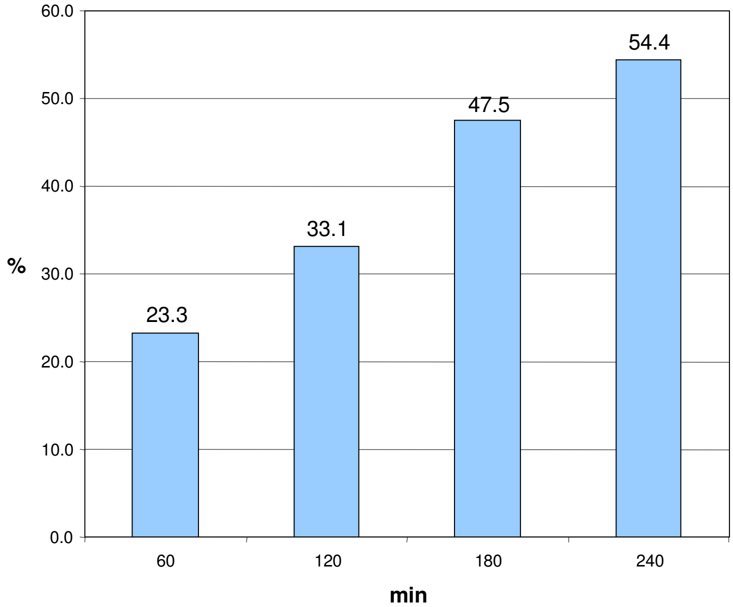

Fig. 4. **Mass share of the finest fraction depending on the grinding time**

From the graph in Fig. 4 we can see the average yield of the finest fraction per one hour of milling. It is perceptible, that the largest increase of the obtained material will be during the first hour of milling process. The yield of one hour gradually decreases with increasing milling time.

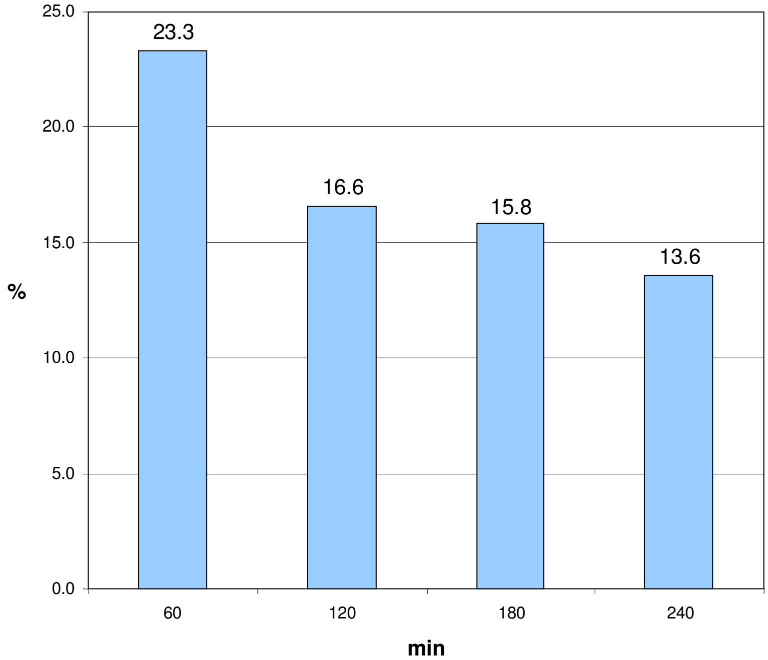

Fig. 5. **Mass utilization of the finest fraction of one milling hour**

Conclusions

The aim of the work was the preparation of titanium dioxide nanoparticles by mechanical milling. Next goal was to find optimum conditions and analysis of the grains resulting particles.

From the foregoing that we are able to achieve nanometer size fraction in grinding of TiO_2.

However very important are input parameters that affect subsequent grinding process. Even short periods of grinding can make a big difference in the final quality of the material.

The selected revolution speed 250 min^{-1}. appears to be ideal for titanium dioxide. The influence of the interval shortening of grinding time is a matter for further investigation. Already it is a time consuming operation. When for one sub-interval milling 5 minutes is necessary take 60 minutes of a time. If we have milling process for 180 minutes, it takes 36 hours of total time, when the milling machine runs. Further research phase of TiO_2 milling aims to reuse already milled powder size $x > 20$ microns, which is, after grinding sample of almost half of the former amount.

Under microscope observing shows irregular grain shape with sharp edges. Charge of particles on the surface of the particles, their small size and relative surface forces. These phenomena cause particle aggregation. It leads to problems during storage and sieving of the particles.

References

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