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SURFACE OPTIMIZATION OF STAINLESS STEELS FOR APPARATUS AND VESSELS IN THE PHARMACEUTICAL, FOOD, AND PROCESS ENGINEERING INDUSTRIES

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Abstract

The relationship between manufacturing parameters and application conditions for equipment Stainless steel containers can be of significant importance for the products manufactured with them in the food and chemical industries. The component surface of the container is of particular relevance here, as it is in direct contact with the media. High demands are often placed on the surfaces regarding corrosion resistance, cleanability, and the lowest possible adhesion behavior of products. Existing regulations and guidelines generally specify the surface roughness to be achieved, the material to be used, and also final surface treatment processes, such as electropolishing. The research presented here aimed to demonstrate the possible variation in the properties of surfaces produced by grinding.

To focus on the influence of the different mechanical properties of the base material, a metastable austenitic steel AISI 304 with different grades of deformation and the austenitic steel AISI 316L were used for this purpose. The application of an alternative mechanical processing method based on a slide grinding process is also to be compared with the results of conventionally processed surfaces and its applicability is discussed, particularly for the pharmaceutical industry.

In addition to the surface roughness achieved, the resulting corrosion resistance achieved is compared in particular based on the critical pitting potential between the different surface conditions. The adhesion behavior of foreign particles was determined by ISO 12103-1. Further characterization of the surfaces produced was carried out using light and electron microscopy as well as 3D surface characterization using high-resolution focus variation.

The results show that, depending on the process parameters used, but also depending on the mechanical properties of the base material, there is a clear influence on the surface produced. It can be seen that the interaction between the grinding process and the base material can have a very differentiated effect on the final component properties achieved. By adapting the process parameters in the form of a modification of the mechanical processing, a reduction in the adhesion behavior of foreign substances can be achieved.

Key words*: Cleanability, Particle adhesion, Stainless steel, Surface treatment, Corrosion resistance.*

1. Introduction

The manufacture of machinery and equipment in the areas of plant and container construction always requires mechanical and thermomechanical processing methods. Stainless steels are particularly necessary for sensitive applications in the chemical industry, in the manufacture of pharmaceutical products, and in food processing. The steels used there are predominantly austenitic stainless-steel alloys, which have a high corrosion resistance and a high elongation at break, which is equivalent to good formability. The surface quality requirements are to be regarded as particularly high under the specifications of hygienic design (cf. EHEDG) [1, 2].

Good formability leads to a high degree of design freedom in the manufacture of components or equipment and at the same time to challenges in surface finishing. During processing, it must be considered that chip formation during grinding or other mechanical surface treatments changes considerably depending on the base material ductility. It should also be noted that plastic deformation of the material can lead to hardening, which also affects the mechanical processing of the surface. In addition, the number of available or required surface treatments for stainless steel is very diverse [1].

Responsible for the characteristic that gives stainless steel its name is the passive layer that forms itself under ideal ambient conditions. The thickness of a stable passive layer on a stainless steel is very small, 5 to 10 nm. The main factor responsible for the formation of a stable passive layer is the chemical composition of the base material, primarily the chromium content. The homogeneity and the achieved Cr/Fe ratio of these uppermost atomic layers of a component are decisive for the resistance achieved. Here, processes such as pickling, passivation, and in particular electropolishing offer a very helpful supplement to processes such as grinding and brushing. These mechanical processes are mostly necessary for manufacturing reasons and are primarily used to achieve defined surface roughness or to remove unwanted residues on the surface, such as those resulting from hot rolling or forming processes, but also from thermal joining like welding [1, 3].

For sensitive applications, such as in pharmaceutical plant engineering, food technology, the chemical industry, or medical technology, further requirements are often placed on the surfaces in addition to the corrosion resistance of the materials used. In general, it can be summarized for these areas that the surfaces must be easy to clean, and the adhesion of processed products or residues should be avoided as far as possible. The challenge is that the surface must optimally be adapted to the respective application so that the adhesion of the product can be avoided. General statements regarding the cleaning behavior of surfaces with different types of contamination can therefore not be made. However, industry-specific specifications based on empirical values, but also on scientific findings, can certainly be found. An example of this is the specifications of the Basel Chemical Industry (BCI), which give instructions for the use of chemical pickling, passivation, and electropolishing for piping, apparatus, and other components made of stainless steel in the Basel standard BN94 [4] [1, 3 and 5].

The state-of-the-art is a multi-stage processing of the component surface. The decisive factor here is a step-by-step procedure so that deformed or impaired edge areas of the surface are removed in stages. When grinding stainless steel surfaces, for example, the roughness is usually reduced in stages by gradually increasing the grain size of the abrasive used [1 and 6].

Despite all efforts, the final achievable properties of a component surface are not exclusively dependent on the final mechanical finishing of the component. It is necessary to consider influencing factors along the entire value chain. This includes first of all the melting of the stainless steel and the associated adjustment of the chemical composition, which is kept within clearly defined limits by the usual material numbers. Despite high standards in steel production, variations are possible. It is generally up to the steel manufacturer to decide which manufacturing process and which production steps are selected in detail to arrive at the respective delivery format. Typically, a limited amount of typical non-metallic inclusions remains in the steel. Although it is possible to reduce these inclusions to the lowest possible level during the manufacturing process by applying appropriate procedures, they cannot be completely avoided in industrial processes. Consequently, corresponding impurities are still possible and permissible to a limited extent when grades are supplied from electro-slag re-melting furnaces or from vacuum processes. Here, too, the current standards allow for corresponding tolerance ranges [2, 6, and 7].

In addition to rolling and the corresponding heat treatments, which are common to produce coils, the final surface treatment of the flat material by the steel manufacturer or specialized processors is also important. Particularly for ground material, it should be noted that a specification regarding the selected grain size of the abrasive must not be equated with a defined surface roughness of the processed material. Depending on the parameters selected, corresponding variations are possible. For example, a significant change in the achieved roughness of the sheet metal can be achieved by varying the contact pressure, by the degree of abrasive wear, or by combining different abrasive belts connected in series. According to the international standards EN 10088-2 [6] and EN 10088-3 [8], the final design and technical properties of ground surfaces can vary considerably. Agreement between the steel supplier and the user on the available properties and the desired roughness of the products thus manufactured is also recommended in the above-mentioned standards [6 and 8].

The delivery format produced in this way usually represents the starting product for pharmaceutical apparatus and plant engineering. The relatively good formability of austenitic steels offers a high degree of geometrical design freedom. Care must be taken to ensure that high degrees of forming also lead to a change in the surface topography. Special attention must also be paid to thermal joining techniques. Welding of stainless steels can be regarded as state of the art today, but it must be carried out with specialist knowledge and care. The mechanical and also chemical post-treatment of welds or comparable joints should be considered mandatory for this application. In apparatus engineering, the overgrinding of the weld seams produced is also frequently required, for example, to enable uniform cleaning of component surfaces. The topography and, above all, the defect adhesion of the surface (finest cracks and fissures, distortions, lattice defects, etc.) are determined by the quality of the grinding process. These defects can be minimized by electrochemical finishing, but a negative "footprint" of the grinding process remains [1 and 3].

How different surface finishes of stainless steels affect their corrosion resistance, but also, for example, the adhesion of foreign particles or cleanability, is the subject of a large number of scientific studies. Exemplary for a multitude of investigations are the results of Faller and Gümpel [9]. In this paper, the influence of mechanical processing on the corrosion behavior of stainless steel is presented for different processes [9]. Further investigations additionally show an influence of the grain material used on the corrosion resistance achieved for ground surfaces [10, 11, 12, and 13]. For the cleaning of stainless steel surfaces, Frank *et al.*, [14], show for different surface finishes that it is not the averaged surface roughness, but rather the number and characteristics of local irregularities that determine the amount of residues remaining.

Although these specifications already provide a comprehensive and sensible limitation of the processes to be used and the final surface treatment, many variable factors remain in the production of stainless steel components. This article aims to use selected parameters to demonstrate the possible range of variation in the properties achieved. For industrial applications, manufacturing parameters can be derived from this which can lead to an improvement in the desired surface properties.

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Having all of this in mind, this research aimed to demonstrate the possible variation in the properties of surfaces produced by grinding.

2. Materials and Methods

Two alloys, AISI 304 and AISI 316L, were used for the tests. Both alloys were available as cold-rolled sheets. The chemical composition is listed below in Table 1.

The AISI 304 material was further formed in multi-stage cold rolling steps so that it was available in three degrees of deformation. The initial state without additional cold forming also had no forming martensite. A forming degree of $\varphi = 0.3$ with approx. 12% forming martensite was selected as the second condition. The third state was the degree of deformation $\varphi = 0.6$ with approx. 50% deformation martensite. The degree of deformation listed here was determined using electromagnetic measurement.

The surface treatment of the metastable austenitic samples of the material AISI 304 was carried out by path-controlled grinding to achieve the most reproducible machining process possible. Silicon carbide (SiC) and corundum (Al_2O_3) were used as abrasives. The samples made of the austenitic material AISI 316 were machined once using manual multi-stage grinding, as is common in the manufacture of containers for the pharmaceutical industry (cf. [4]), and on the other by a modified slide grinding process. In both cases, corundum was used as the abrasive. Following the requirements of BN94 [4], the surfaces produced in this way were additionally electropolished afterward.

Corrosion resistance was determined using electrochemical tests, including re-passivation after a defined current density had been reached. On this basis, the pitting susceptibility factor (PSF) was determined in addition to the critical pitting potential.

Table 1. Chemical composition of the stainless steel used

Material	Chemical composition in mass fractions in %									Pitting resistance equivalent number (PREN)
	C	Cr	Ni	Mo	Mn	N	Si	P	S	
AISI 304	0.034	18.08	8.02	0.12	1.23	0.065	0.34	0.029	0.001	20.43
AISI 316L	0.022	18.22	10.45	1.86	1.63	0.061	0.62	0.028	0.003	26.19

The surfaces produced in this way were evaluated using light microscopy, scanning electron microscopy, and tactile and optical determination of the surface roughness. To compare the cleaning behavior of the surfaces produced in this way, selected states were examined by ISO 12103-1 concerning the adhesion behavior of particles of different sizes.

3. Results and Discussion

As a result of the increase in the degree of deformation and thus also the increase in the proportion of martensite in the microstructure, there was a considerable change in the mechanical properties. This can be seen as an example in the stress-strain diagram for the degrees of deformation investigated here (Figure 1). As a result of the cold forming process, there is a significant reduction in elongation at break at the two forming degrees φ = 0.3 and φ = 0.6 with a simultaneous increase in yield strength and tensile strength.

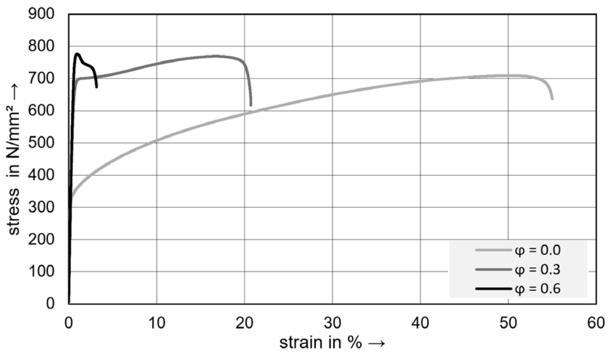

Figure 1. Stress-strain curve for stainless steel AISI 304 with different degrees of deformation

Various methods were used to assess the surfaces produced. Local characterization using scanning electron microscopy primarily allows a subjective comparison. Regardless of the process parameters used, there are recognizable preferred directions for all states except for the slide-ground surfaces. These can still be seen after electropolishing. It is also very clear to see that these surfaces very often have local gaps or overlaps in the surface profile (shown in Figure 2 and Figure 3).

Subjectively, a difference can be seen here between the surfaces of the AISI 304 material ground with silicon carbide (SiC) and those ground with corundum (Al_2O_3). The number of these surface defects is lower on the surfaces ground with silicon carbide (SiC).

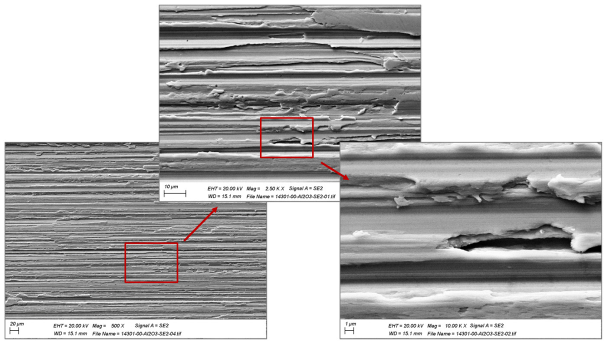

Figure 2. SEM image of a surface of material AISI 304 industrially ground with corundum showing a micro-gap in the surface at different magnifications [18]

When it comes to the large-scale and statistically correct determination of these irregularities and surface imperfections, which play a major role in terms of both durability and the adhesion of particles and microorganisms, conventional evaluation methods very quickly reach their limits. Local defects in the microtopography of the surface, as exemplified by the scanning electron micrographs in Figure 2, are not detected by tactile methods for roughness measurement.

The use of measurement methods for determining surface roughness values according to ISO 25178 [15], represents a possible alternative here. However, since in industrial practice, grinding is always a two-dimensional process in which a large number of abrasive grains generate the surface topography, there is a correlation between the classic surface roughness and the possible number and characteristics of local surface imperfections.

Figure 4 shows that with an increase in the tactile measured roughness, the susceptibility to pitting, determined by the pitting susceptibility factor (PSF),

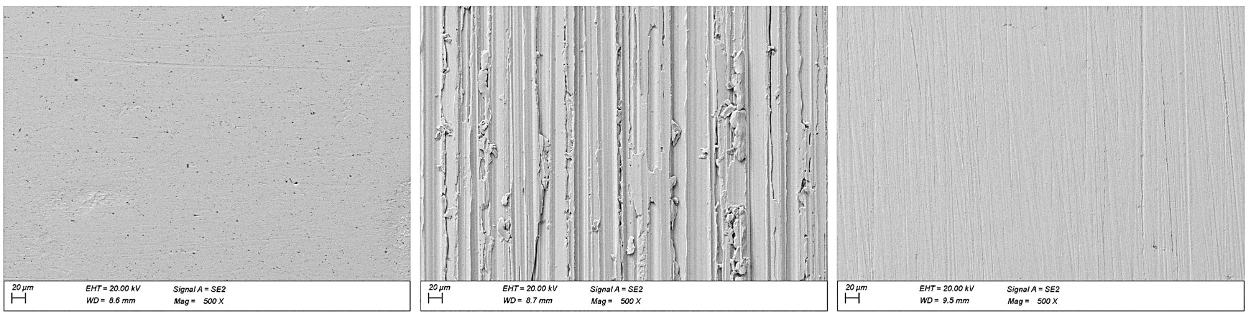

Figure 3. SEM image of a surface of material AISI 316L. Left: vibratory grinding with subsequent electropolishing; Center: manual grinding with 40 grit; Right: manual grinding with 400 grit

also increases. The PSF according to Klapper *et al*., [16], is used as a method for evaluating the susceptibility of a surface to pitting. The calculation is carried out by including different parameters of the electrochemical corrosion measurement. By including resting potential and re-passivation potential, in addition to the classic pitting potential, in the calculation, the ability to heal a surface attack is taken into account [16, 17, and 18]. The different degrees of deformation were used to produce a different surface roughness with comparable grinding parameters. The direct influence of the degree of deformation on the corrosion resistance achieved was also investigated but is not addressed further in this paper [18].

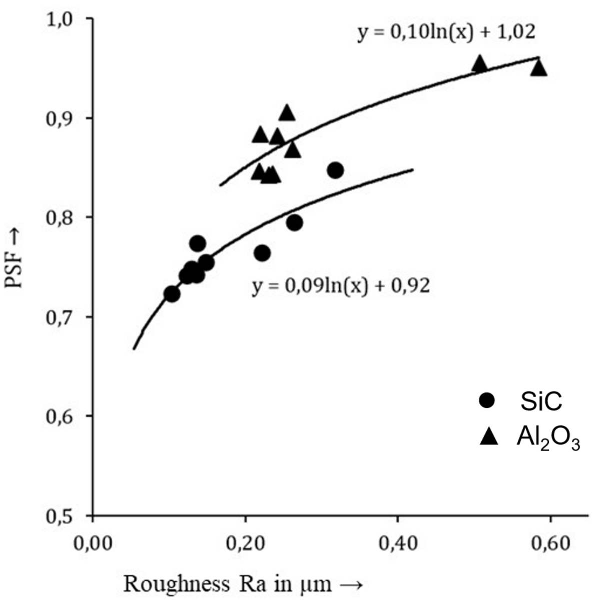

Figure 4. Calculated PSF (pitting susceptibility factor) according to Klapper *et al.*, [16, 17], *via* the tactile measured surface roughness Ra for industrially ground surface finishes with calculated logarithmic trend line material 1.4301/AISI304 [18]

In addition to the influence of surface roughness, Figure 4 clearly shows that the grain material used can have a significant effect on the corrosion resistance and the pitting susceptibility achieved. The actual electrochemically determined resistance to pitting, represented by the PSF, shows a correlation with the surface roughness present. However, it can also be seen that, in addition to the roughness, the grain material used also has a significant effect. That this influence is due to the topography present is made clear by Figure 5. Both images shown are microscopic images of pitting that has occurred on ground surfaces. While the surface ground with silicon (a) shows a round corrosion attack, the pitting on the surface ground with corundum is very uneven [18].

Comparative observations with manually ground, polished, or electropolished surfaces of the same alloys show that a lower surface roughness does not automatically lead to a further increase in corrosion resistance. The particular manufacturing process, as well as the selected process parameters, play a dominant role. The Abbott-Firestone curve in Figure 6 is used to compare the generated surface topography of different ground samples.

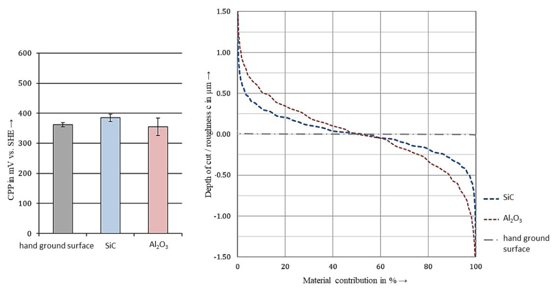

Figure 6. Comparison of different ground surfaces based on the critical pitting potential and the optically detected surface topography based on the Abbott-Firestone curve [18]

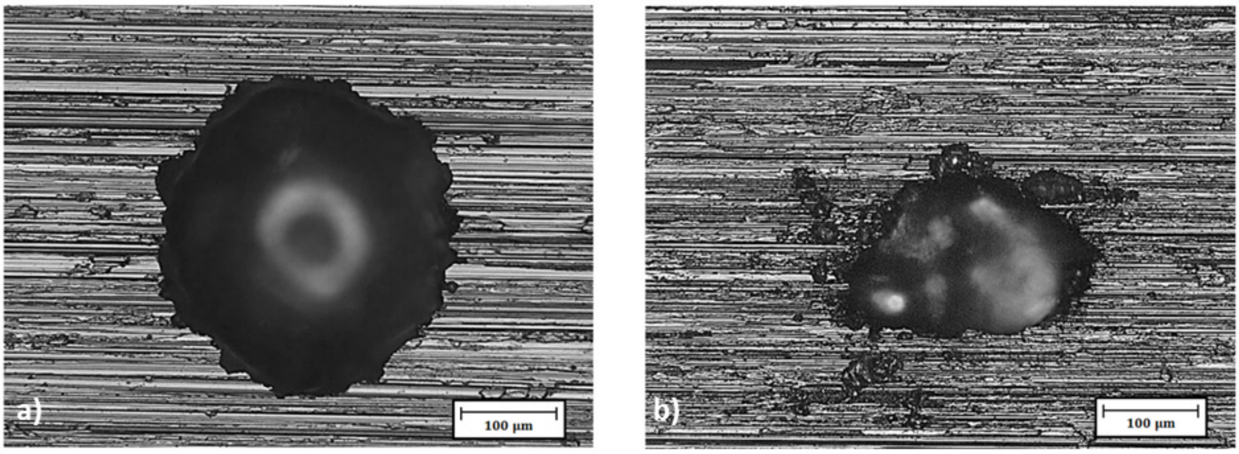

Figure 5. Comparison of the geometric characteristics of pitting using the example of material 1.4310/AISI 301: a) ground with silicon carbide, b) ground with corundum [18]

While the manual laboratory grinding, grit 1200 (silicon carbide), shows a very homogeneous surface, the two machine-ground surfaces with silicon carbide and corundum, respectively, grit 54, have a much more irregular topography with a significantly higher depth of cut c. Nevertheless, it can be seen from the measured electrochemical pitting potential (CCP) that the hand-ground surface does not have a higher corrosion resistance [18].

The investigations carried out and listed as examples of the influence of grinding surface processing point to the complexity and interaction of different manipulated variables. Under idealized conditions on a laboratory scale or during the automated processing of flat products, the most ideal processing parameters can be found and set. Achieving a homogeneous and reproducible surface by manually guiding a grinding machine is not a matter of course and is determined by the skills of the personnel. An even greater technological challenge exists in the manufacture of components for pharmaceutical plants with complex geometries. Although austenitic steels can be formed very well, weld seams are usually unavoidable. To subject these to mechanical finishing, for example for containers on the media side, a high level of skill and experience on the part of qualified personnel is essential.

This work is particularly demanding when the machined area cannot be seen. If this involves components with requirements for minimum wall thickness, there is a risk that this will be undercut by the grinding of the weld seam. Reworking in this condition, shortly before the completion of the product, is not technically feasible.

As a possible alternative, the application of a vibratory grinding process was used as part of the present investigation. In contrast to mechanical grinding, this is usually time-controlled. The investigation of the surface using the example of 3D surface characterization using focus variation in Figure 7 shows that in the case of the automated mass finishing process, there is no preferred direction on the component surface. This is consistent with the SEM images in Figure 3. It should be noted here that no local discontinuities or distortions can be detected.

The surfaces machined in this way using mass finishing also achieve a lower surface roughness, which can have a positive effect on any subsequent treatments using electropolishing. Comparative measurements regarding the critical pitting potential or the pitting susceptibility factor (PSF) do not reveal any significant differences between the different machining processes.

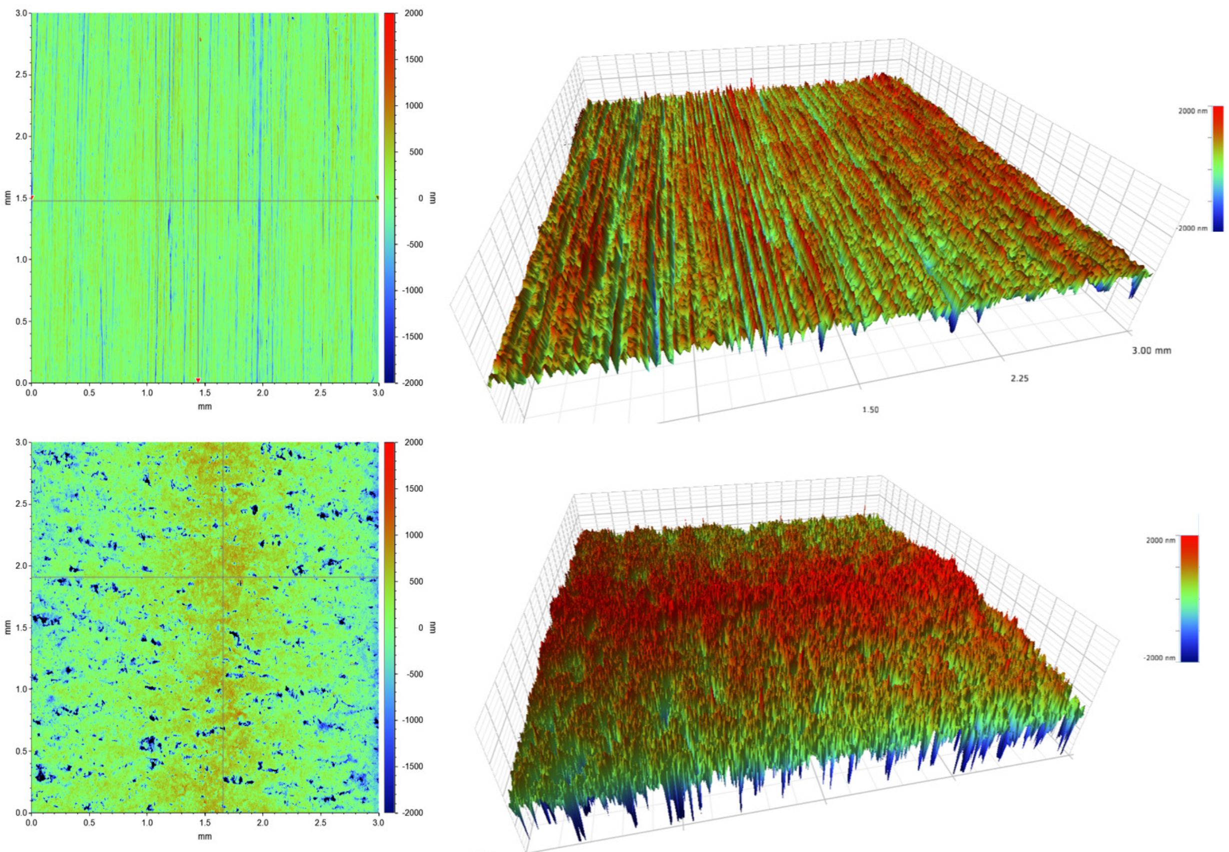

Figure 7. 3D representation of the finished surfaces on a container's inner wall. Above conventional, manually executed grinding technique, below automated process

The comparison of the adhesion behavior of foreign particles according to ISO 12103-1 [19] was carried out after electropolishing the surfaces. This was based on the specifications of BN94 [4] and also due to the comparable surface roughness after electropolishing. A measurement of the adhesion behavior with strongly differing roughness values would be further attributed to the dominant influence of the roughness [5]. The samples examined were taken from the inside of containers manufactured according to the usual specifications for pharmaceutical equipment. Electropolishing of the inside of the container was performed after grinding. The surface roughness obtained, determined by conventional tactile roughness measurement, is comparable for both containers after electropolishing. The significantly reduced number of remaining particles, however, indicates that automation can achieve a surface finish that is more favorable for cleaning. Since, as already mentioned above, the chemical resistance can be improved by the electropolishing step because of a higher Cr/Fe ratio in the passive layer, and the surface is generally more homogeneous, no improvement is to be expected in the comparison of the two surfaces regarding corrosion resistance.

Figure 8 shows the number of adhering particles on the measuring surface for samples with conventional manual grinding and subsequent electropolishing as well as for samples after automated time-controlled vibratory grinding with subsequent electropolishing. A clear adhesion behavior of particles can only be seen below a particle size of 100 µm. The number of adhering particles is significantly higher on the conventionally produced surface than on the surface after slide grinding.

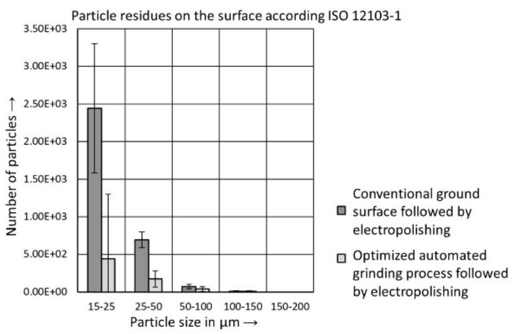

Figure 8. Comparison of measured particle residues, determined according to ISO 12103-1, as a function of particle size for conventionally ground and electropolished surfaces and for automatically ground and electropolished surfaces [19]

4. Conclusions

- Examining the ground surfaces, processed with different process parameters, shows that strong variations in the properties achieved are possible. The user should therefore focus more closely on the processing parameters used. In conjunction with the subjectively perceived differences in the severity of the surface defects in comparison between surfaces ground with silicon carbide and ground with corundum, this can be used as a possible cause. Depending on the localized nature of the surface imperfections, stable hole growth can occur on the surface at an earlier stage. Whereas the surfaces ground with SiC do not show stable pitting until later, resulting in different degrees of pitting.

- Based on the results presented here, the sliding grinding process use can be listed as a possible alternative. This grinding technique is ideal for the automated internal machining of rotationally symmetrical components/vessels. However, as the surface removal is significantly lower than with manual grinding due to the achievable and technically feasible contact forces/speeds for the common component sizes in pharmaceutical apparatus engineering, this leads to significantly longer processing times.

- The research work carried out indicates the general potential of adapting and optimizing process parameters concerning technical properties in container construction. Although the production costs were not taken into consideration, a reduction in the personnel costs incurred can be assumed. In addition, the results suggest a significantly more reproducible and homogeneous surface quality, which is particularly important for technologically advanced and sensitive applications.

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