Properties and optimum manufacturing process for functional stainless steel surfaces

Functional surfaces

One of the most demanding markets when it comes to valve manufacture is the pharmaceutical sector. Valves that are suitable for the most demanding applications are required for the complex construction of pharmaceutical systems in order to guarantee sterile processes. Valves made from stainless chromium nickel steel are particularly important here; among other things, they should exhibit optimum cleaning behaviour as well as maximum corrosion resistance. To satisfy these requirements, the focus is not only on the Hygienic Design of these valves but primarily on the functional surface of media-wetted areas. The manufacture of these surfaces in the valve body is therefore closely tied in with a demanding and valid process that brings together all areas of production, from machining through to wet chemical finishing. Innovative manufacturing processes, compliance with qualitative specifications and in-depth manufacturer expertise in all areas also play an essential role here.

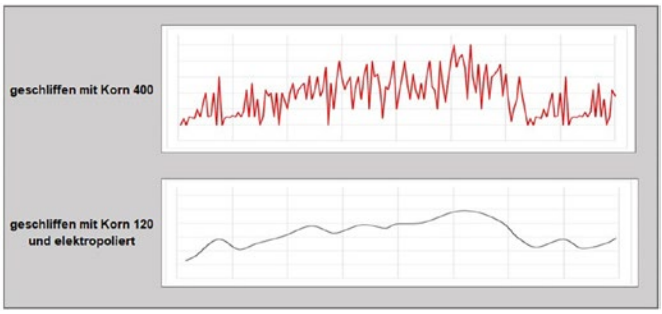
What are functional surfaces?

The requirements for functional surfaces are directly related to hygiene safety in pharmaceutical production systems. In the media-wetted area, it is essential that the valves used exhibit optimum cleaning behaviour and maximum corrosion resistance. On a macroscopic level, this is implemented by means of a design that meets the Hygienic Design criteria. The specifications and provisions for this are stipulated by various directives such as the Good Manufacturing Practice (GMP), Food and Drug Administration (FDA) and European Hygienic Engineering and Design Group (EHEDG). Materials are selected according to the resistance criteria for the media and processes used. Lists containing specifications regarding media and materials are referred to during the selection process. Regulation (EC) No. 1935/2004 must also be observed. On a microscopic level, the focus for this functional surface is on an appropriate topography and morphology. Although commonly used in practice, it is not sufficient to define the surface specification based on the trivial application of an average surface finish of Ra.

An Ra value can cover the most diverse range of topographies. Component manufacturers are therefore required to provide further definitions here based on the influential factors for the manufacturing process. The following criteria can be defined, for example:

- Flaws such as cracks, scratches, scores or shrinkage holes are not permitted or are only permitted within the specified tolerance limits in line with DIN 11866 or ASME BPE-2016
- Inclusions of foreign matter such as abrasive grain residues or abrasive paste that may be produced during the pharmaceutical production process must be avoided
- Glossy – without intense tempering colours that cause corrosion
- Presence of a complete passive layer (chromium oxide layer) for corrosion resistance to prevent any interaction with the media
- Homogeneous structural constitution of the base material
- Smooth and therefore small „true“ surface without peaks for good cleanability. Figure 1 clearly shows the reduced „true extension“ of the electropolished surface with an assumed geometric projection onto an ideal smooth surface based on the more pronounced smoothing curve after the electropolishing process.
- Low surface tension as proof of the complete removal of a polished surface, for example by means of electropolishing

Precise specifications and quality features can be found in the manuals and works standards from the respective component manufacturers. Ideally, the manufacturers should have the maximum possible production depth in order to combine all processes in-house and thereby meet the highest quality standards.



Comparison of a mechanically polished and an electropolished surface

How are functional surfaces produced?

Producing a functional surface involves all manufacturing processes (Figure 2). All mechanical machining measures from grinding through to electropolishing are precisely synchronized with each other.

The requirement for a defined surface must be taken into account as early as the machining of the valve bodies with a geometrically defined cutting edge, for example during milling or turning. The maximum surface roughness must be specified in work instructions. The use of selected cooling lubricants and the avoidance of organic markings such as fingerprints or greases that would affect subsequent electrochemical processes must also be taken into account. Measures to minimize the risk of transmission from BSE/TSE pathogens of animal origin must also be implemented in accordance with the official journal of the European Union and the 2004/C 24/03 guideline (BSE/TSE free).

Figure 2: Simple overview of the typical manufacturing steps for a stainless steel valve body

Tempering colours during welding

During welding procedures that are part of a standard routine in valve body production, both the weld and the heat-affected zone must be assessed and taken into consideration. The welding procedure involves the significant manipulation of the structure and surface. The tempering colours that can appear during the welding procedure are used as an indicator of increased pitting potential. The tempering or discolouration of a metal surface as the consequence of corrosion is defined in accordance with DIN EN ISO 8044 and occurs as a reaction to the mixing of alloying elements with oxygen to form metal oxides. The discolouration of stainless steel alloys from a golden yellow colour gradation is critical. Pickling or pickling followed by electropolishing has proven to be a very effective method of removing tempering colours (Figure 3)

Figure 3: Untreated weld – pickled weld – pickled and electropolished weld

Grinding process

Machining with a defined cutting edge is followed by machining with a geometrically undefined cutting edge by means of grinding and polishing. This machining stage has a significant impact on the quality of the surfaces. The heat produced while hand-polishing surfaces can have a negative effect on the structural conditions; possible effects include microstructural changes down to a depth of several micrometers. Furthermore, the machining marks on the surface are ordered, which results in a more inhomogeneous surface finish than irregular machining marks from a chaotic grinding process such as slide grinding. The abrasive products involved in manual grinding can also produce deposits that are not bonded to the surface and can subsequently come loose. It is therefore essential to ensure that the grinding process is carried out in accordance with individual production specifications. The sanding quality differs depending on the type of abrasive material and the desired Ra value. Generally speaking, a relatively coarse abrasive material is used initially, then a finer abrasive material.

In order to make the demanding grinding and polishing processes reproducible and to achieve a consistently high level of quality, complex, automated grinding processes such as robot, flow or slide grinding processes are sometimes used. The slide grinding process is described in more detail below by way of example.

Automated grinding processes: Slide grinding

Slide grinding or slide machining is a reproducible and fully capable alternative to the manual grinding process. During this automated grinding process, the abrasive products, together with the workpieces, are placed in an oscillating drum with aqueous solution (compound). All exterior burrs and other exposed areas of the components are processed at the same time during the grinding process without experiencing the unwanted side-effect of secondary burr formation as can be the case, for example, during the manual grinding and polishing process. An Ra value of <0.2 µm can be achieved. Due to the micro-roughness that is produced as well as the pickling process that must follow, the diffuse refraction initially gives the components a matt surface structure, which does not, however, represent a qualitative defect. During the subsequent electropolishing process, the homogeneous and non-reflective surface is then transformed into a more aesthetic surface with a higher degree of shininess and reflection. The surface is classified based on the metal release test in accordance with the European guideline on „Metals and alloys used in food contact materials and articles“ as well as sensor-based tests (DIN 10955) in line with the requirements of 1935/2004 EC. The surface tension can be determined in the same way as hand-polished valve bodies by means of a drop angle measurement. The deformation depth of the slide-ground bodies, which are in no way of a lower quality than hand-polished valve bodies, is also checked by creating a micro-section followed by subsequent analysis under a microscope (REM or light microscope).

Electropolishing

Electropolishing, electrolytic polishing or e-polishing for short are designations for an electrochemical procedure for levelling a surface with an irregular texture. Electropolishing is normally carried out after mechanical polishing, which already ensures a largely even surface.

Electropolishing represents the reverse of a galvanic process; it involves electrochemical removal from the surface of the workpiece. The workpiece to be processed is immersed in an electrolyte bath and connected to a DC circuit as an anode. The current causes metal ions to be removed from the surface of the workpiece and these are dissolved in the electrolyte solution. As iron and nickel are removed more readily from the alloy group, the chrome-iron ratio of the layers of material near to the surface shifts in favour of chrome during electropolishing treatment.

Mixtures of sulphuric acid (H_2SO_4) and phosphoric acid (H_3PO_4) which do not attack the material when de-energized are normally used as electrolytes. Additives such as surfactants and inhibitors that have a positive impact on the wetting and removal behaviour are also present.

As material is more readily removed from edges and surface elevations, electropolishing results in a largely even surface. Ra values in the range of 0.2–0.4 µm can be achieved here.

In contrast to mechanical treatment methods, electrochemical removal of the uppermost material layers results in

a surface that is free from tension. In addition, the workpiece exhibits a completely austenitic macrostructure up to the surface.

During electropolishing, material is removed by anodic oxidation of the metal atoms, which depends on the processing time, current density, electrolyte composition and bath temperature. Following this removal of material, the „true“ surface of an electropolished material is reduced by approximately 80% in comparison to a surface mechanically polished (with 220-grit). Electropolishing therefore has an extremely positive effect on cleaning behaviour in comparison with a mechanically polished surface.

The following specifications must be observed during electropolishing:

- The deformed layer that can be produced during mechanical surface processing through grinding and polishing should be completely removed
- Removal rates must be defined in accordance with standards and the thickness of the deformed layer, which will be different depending on the type of mechanical machining
- Following electropolishing, the workpiece surface must exhibit the agreed surface roughness, for example Ra ≤ 0.8 µm, as it cannot be reworked once electropolishing is complete
- The quality of the electrolyte used must be ensured by means of continuous verification of the metal and acid content. The effectiveness of the electropolishing process must be verified on a regular basis, for example by means of X-ray photoelectron spectroscopy (XPS) and based on the removal rate. The ferroxyl test, which is used to detect ferritic impurities on the surface using an indicator solution and colour change, is also used as the basis for qualification.
- It should be possible to verify the removal based on recorded process data (current strength, time, area and bath yield)

Due to the complex profile of requirements, it is not only innovative but also logical for component manufacturers to integrate the electropolishing process into their own businesses in order to combine chemical and electrochemical machining steps into the internal material flow in addition to the mechanical machining processes. To guarantee the reproducibility of the surface finish and meet specific customer requirements, the processes must be flexible. This is where a multifunctional and fully automated system for cleaning, pickling, electropolishing and passivation can help (Figure 4).

Figure 4: Fully automatic electropolishing system

The following process steps must be carried out during wet chemical machining in order to produce a functional surface (Figure 5).

First, the valve body is degreased using alkaline cleaning agents in order to remove organic impurities, as these can have a negative effect on conductivity.
This is followed by flushing in a repeated cascade.
In the next process, the valve body is pickled. This chemically or electrochemically removes inorganic compounds such as metal oxides that have remained on the surface. These compounds are removed in an area of max. 2–5 µm so as not to place the crystal boundaries under heavy load.
Following further cascade flushing, the actual electropolishing process takes place. A high-quality surface is produced reliably using the anodic removal process.
The guide values for complete removal vary significantly and range from 5 µm with the ASME BPE 2016 to 30 µm with the BCI BN 94 (issue 2005-04-14), which would correspond to a bath time of approx. 30 minutes. Whether this removal rate corresponds to current production standards is questionable, however, particularly since over-polishing cannot be repaired; instead the surface has to be completely repolished and reconstructed.
To eliminate electrolyte residues on the electropolished surface, a further cascade flushing process follows, with a subsequent acid dip, whereby an oxide-corrosive solution activates the surface for further treatment.
During the passivation process that follows, the chromium-oxide protective layer is produced using diluted nitric acid (HNO_3).
The final step in this complex process is the drying of the components.

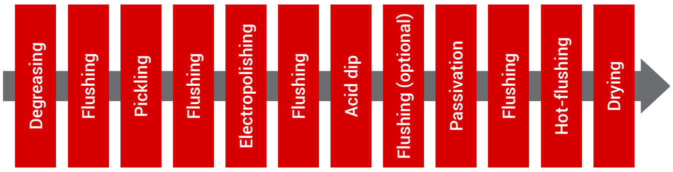


Figure 5: Process sequence for electropolishing. The individual process steps each involve one or more baths in the electropolishing system. With this complex process comes the difficulty of constructing the overall system including all its peripheral devices for fresh water treatment, preparation tanks, waste-water treatment as well as supply and exhaust air systems, which must take into account the fact that the sequences need to be flexible in order to meet customer requirements

Why is active passivation part of the process??

A self-passivation reaction takes place spontaneously as soon as a bright metallic surface is subjected to environmental influences whereby there is sufficient oxygen to form the chromium-rich oxide layer. This is not a validated process but is dependent on the specified influencing factors and requires a certain amount of time until a complete passive layer is formed. The formation of a passive layer requires certain proportions of chromium and carbon in the stainless steel, which must lie in a range of ≥ 10.5% Cr and ≤ 1.2% C. To actively form a passive layer, the reaction can also be activated using nitric acid. This guarantees that with material 1.4435, for example, an adequate and complete protective layer with a thickness of around 10 nm is present as soon as the manufacturing process is complete. A complete passive layer and therefore protection against corrosive attacks is present when, with material 316L SS, for example, the ratio of Cr/Fe is ≥ 1 at an information depth of 15Å in accordance with ASME BPE 2016. The Cr/Fe ratio is verified in accordance with ASME BPE by means of XPS analysis.

Acceptance criteria for electropolished, media-wetted surfaces

In addition to the aforementioned, ongoing process controls, the acceptance criteria specified in the standards in accordance with ASME BPE 2016 (Bioprocessing Equipment) and DIN 11866 (Stainless steel components for aseptic applications in the chemical and pharmaceutical industry – Tubes)
for mechanically polished and electropolished surfaces must also be observed. (Figure 6) Flaws are therefore only acceptable within the tolerance limits specified in these standards. There are also specific acceptance criteria that also need to be assessed following the electropolishing process. Manufacturers must produce a corresponding catalogue containing images of faults, which can be used as the basis for quality assurance evaluations. The surface roughness Ra is also measured in accordance with DIN EN ISO 4287. The measurement is carried out in accordance with DIN EN ISO 4288 and ASME B46.1.

Figure 6: Comparison: Hand-polished (left) and electropolished body (right)

Conclusion

In order to meet the requirement for a functional surface, the complex manufacturing processes for components in pharmaceutical production must be closely interlinked. This is the only way to ensure that products of the highest possible quality can be produced through the combination of state-of-the-art production systems and qualified employees and the interaction between all of the necessary processes. The more knowledge and the greater production depth component manufacturers have, the more efficiently they can both meet and respond to the special and demanding requirements of the pharmaceutical market.

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