MATERIALS

ROUGING AND SERVICE PERFORMANCE OF ELECTROPOLISHED 316L SS FOR HYGENIC SERVICES

Type 316L stainless steel is the most widely used alloy for hygienic equipment for the biopharm industries. In high-purity water systems such as Water for Injection (WFI), rouge often forms, requiring periodic removal treatments. There is also a need for smooth product-contact surfaces that can be readily cleaned. Electropolishing (EP) is a most effective method of providing a smooth surface, free of contaminants such as abrasive compounds, free iron, and other foreign substances. This article includes information on practical experiences involving improved service performance through electropolishing.

How Electropolishing Works

The simplest description of electropolishing is that it is the opposite of electroplating a metal. Rather than depositing a metallic layer as is done in electroplating, metal is removed from the surface. The part to be electropolished is made the anode by connecting to the positive side of a DC power circuit while the cathode, usually copper, is connected to the negative side of the DC power source. An electrical circuit is completed through an acid blend electrolyte removing metal ions from the anode, producing the bright, shiny surface associated with an electropolished surface. A simple electropolishing setup is shown in Figure 1 where the component to be polished is placed in a tank. This is the common method used for smaller items that can easily fit into a tank.

For larger components such as vessels, a partial filling and rolling technique is often employed. With this technique, the cathode may be fastened in a stationary location and the surface to be electropolishing is moved (rotated). For *in situ* (in place) electropolishing, the cathode is hand held and manually moved over the surface to be electropolished. Figure 2 is an illustration of a typical hand-held cathode applied to a work piece. Using proper procedures, manual electropolishing produces the same quality results as obtained by tank electropolishing.

For further information on the principles of electropolishing, the reader is encouraged to refer to articles by Faust (1).

Procedure and Specification

It is good practice for organizations doing electropolishing to have an Electropolishing Procedure Specification describing elements of their process control. There are a number of process parameters critical in an electropolishing procedure that must be controlled to produce a quality surface. These parameters are identified as “essential variables” and a change in any essential variable affects the outcome of the process. The essential variables are described here:

- Amperage/time as defined in ampere-minutes per square inch. This determines metal removal, allows for removal calculation, and establishes a repeatable process on a variety of part shapes and sizes.
- The temperature range of the bath during operation. This variable affects current distribution that in turn controls uniformity of surface metal removal. Good practice includes maintaining the bath temperature within a specific range, for example ± 10°F (± 5°C).
- Bath monitoring. The electrolyte must be maintained to a controlled composition. Factors of greatest concern are metal pick-up and the water content, both of which if not controlled can affect electropolishing quality. During use, metal salts increase in the electrolyte and are

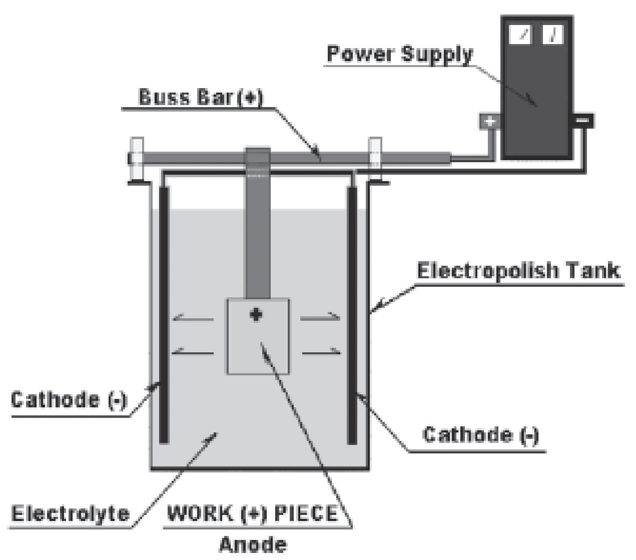

Figure 1. A simple electropolishing set-up for items that can be processed in a tank.

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controlled by decanting and adding new electrolyte. Also the electrolyte is hygroscopic and takes on water or loses water, depending upon the operating environment. The water content can be controlled by increasing bath temperature to "cooking off" excess water or by adding water as required. Both variables can be controlled by using periodic analysis and specific gravity monitoring to determine when corrective action is needed.

Requiring an electropolishing procedure specification with proper control of essential variables is a major step in assuring quality electropolishing workmanship.

Other EP Requirements

There are other important steps needed to obtain a quality product in addition to those relating to the actual electropolishing operation. To meet a specified roughness average (Ra) after electropolishing, it is usually necessary to mechanically polish (MP), or grind to an Ra near that of the specified surface finish prior to electropolishing.

Before electropolishing, the surfaces must be cleaned of foreign material such as oil, grease, dirt, or any substance that could prevent making a good electrical circuit. The cleaning may include use of detergents, solvents, or acids. The proper cleaning is dependent on the type and degree of contamination.

After the electropolishing, any electrolyte remaining on the surface must be completely removed, ending in a final rinse using deionized (DI) water. One check to assure a complete rinse is by measuring the conductivity (or resistivity) of the final DI rinse water.

Many high-purity endusers require passivation to be performed following electropolishing. Some studies have shown heavy metal hydroxides and/or chemical residues may precipitate during the initial water rinse subsequent to electropolishing. These contaminants can be removed using passivation procedures (with nitric acid, phosphoric acid, or citric acid-based chelants or alternates) followed by a DI water rinse. Other studies demonstrate passivation may enhance the corrosion resistance of an electropolished surface of 316L stainless steel. The authors believe that the case for passivation has gained favor primarily because the quality of the electropolishing and subsequent rinsing has been unpredictable due to lack of controlling the electropolishing process. If properly performed (see EP Procedure Specification), including rinsing with DI water to a matching resistivity, electropolishing is able to deliver optimum cleanliness and corrosion resistance without further passivation.

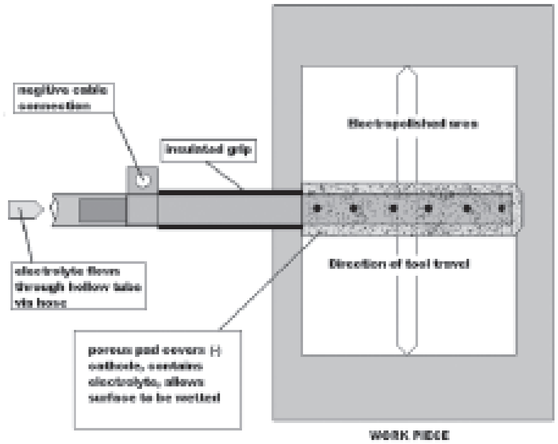

Figure 2. Illustration of tool used for manual electropolishing (in situ electropolishing).

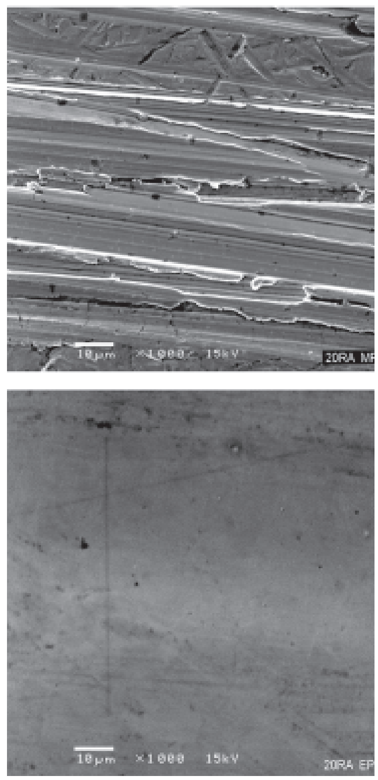

Figure 3. Mechanically polished surface, 20 Ra µin (top). Electropolished surface, 20 Ra µin (bottom). Surfaces shown at 1,000 X with same Ra µin.

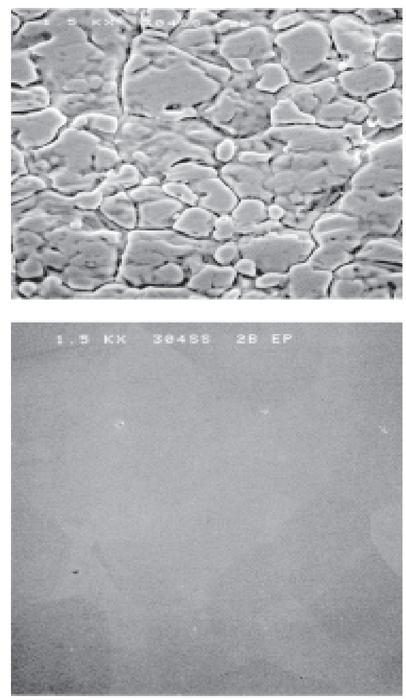
Figure 4. 2B sheet, mill finish, 10 Ra µin (top). 2B sheet after electropolishing, 7 Ra µin (bottom). Both surface at 1,500 X. Electropolishing leaves little or no grain boundaries or surface imperfections.

How Smooth is "Smooth"?

In spite of recognized limitations, the most widely used measurement of surface roughness is the Ra value. A mechanically polished surface typically has contour of sharp peaks and valleys as well as torn metal at the top of peaks as shown in Figure 3 (top). The stylus probe used in Ra measuring is not pointed enough to accurately record the depth of the narrow valleys or grooves. However, the Ra measurement does factor in the surface waviness such as may be present on an electropolished surface where the peaks and valleys

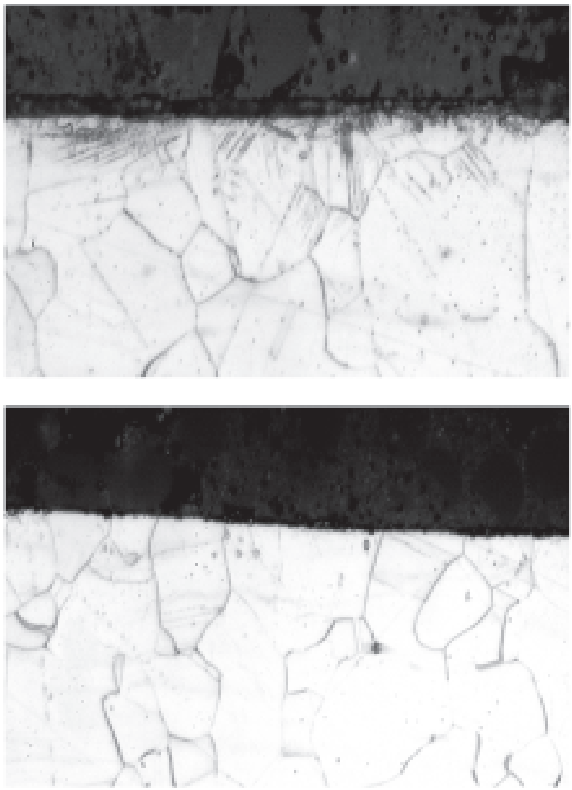

Figure 5. Mechanically polished surface showing a cold-worked surface approximately 0.0003-in deep (top). Surface layer with cold-worked surface layer removed after electropolishing (bottom). Illustration of cold-worked surface layer resulting from mechanically polishing and removal by electropolishing.

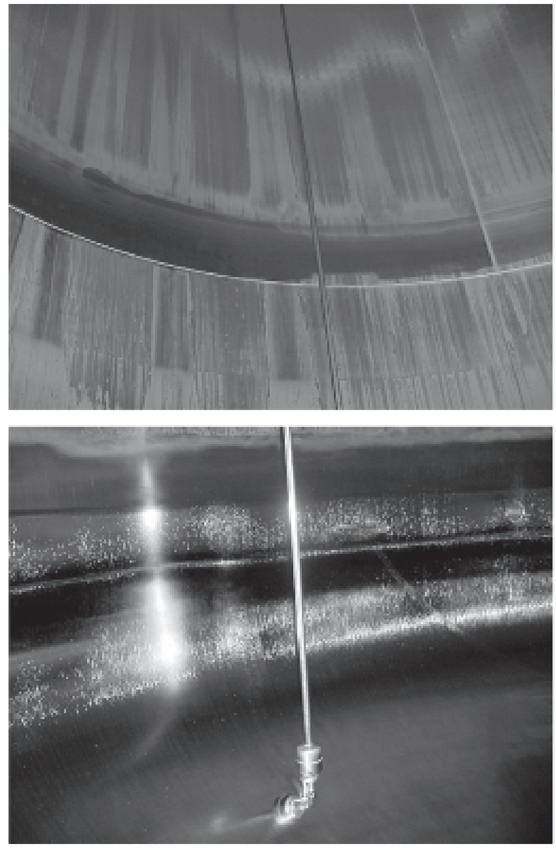

Figure 6. Electropolished band remained rouge free while mechanically polished surfaces developed rouge (top), as while as the bottom head that was electropolished remained free of rouge (bottom).

have been removed as shown in Figure 3 (bottom). As a result the two surfaces with a completely different profile can have the same Ra in this case 20 micro-inch (µin). The MP surface Figure 3 (top) is typical of a Number 4 polish on a Type 316 stainless steel plate obtained with a 180 grit abrasive while the electropolishing of Figure 3 (bottom) was obtained by electropolishing over a 120-grit finish.

Another illustration of surface improvement by electropolishing is shown comparing a 2B mill finish sheet surface at 1,500X having an Ra of 10 µin in Figure 4 (top) and the same surface after electropolishing at 1,500X in Figure 4 (bottom) and having an Ra of 7 µin. The Ra measurements were made by a conventional contact instrument and do not reflect the obvious surface smoothing shown in Figure 4 (bottom).

Using the same specimens, the 2B mill finish before and after electropolishing were compared using a white light vertical scanning interferometric surface texture analysis (VSI). The VSI employs a non-contact technique using a laser beam to measure the surface contour. The VSI examination showed there was considerable surface roughness even though the Ra is 7.4 µin, which is normally considered quite a smooth surface. Similarly, the electropolishing surface point profile is free of crevices and is Ra 2.3 µin. The VSI better illustrates the surface improvement obtainable by electropolishing over the conventional contact Ra measurements.

Figures 4 and 5 illustrate that electropolishing has essentially removed all grain boundary ditching and surface imperfections while leveling out the surface. In addition impurities, such as abrasive materials, free iron embedded during fabrication and other contaminants are removed by electropolishing. Grinding or any operation that imparts a cold worked or smeared surface layer creates what may be referred to as an "altered layer".

What is this "Altered Layer"?

Cold working operations such as machining, grinding, mechanically polished, and buffing create a cold-worked surface layer. This altered layer usually does not have the full corrosion resistance of the undisturbed base metal. The layer varies in thickness from a very thin layer below a polished surface to over a 0.005-in. distorted layer found in an investigation of rough machined counter-bores in heavy wall stainless steel pipe for a nuclear application. A study made some years ago by Wulff (2) identified six distinct layers of oxides and deformed austenite and ferrite extending to a depth of about 0.0012 in on a ground surface to 0.0002 in on a polished (honed) surface. This cold-worked layer is shown in Figure 5 (top) extending about 0.0003 in below the surface of a 180-grit sanded surface and the removal of the altered layer by electropolishing in the bottom of Figure 5.

The detrimental affect of this altered layer to service performance varies, depending upon factors such as the thickness and degree of cold work in the layer, the service environment, and the particular stainless alloy. Tuthill (3)

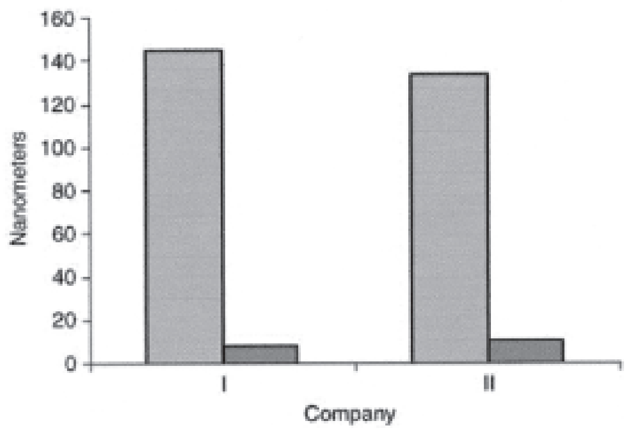

Figure 7. Comparison of surface roughness on stainless steel samples from two manufacturers. The average roughness for the electropolished samples (dark bars) was reduced from the control samples (light bars).

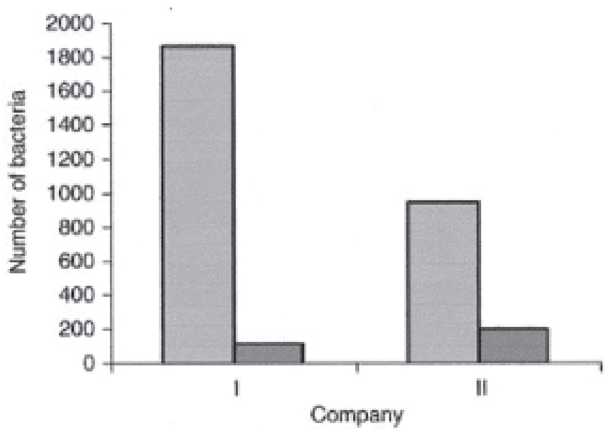

Figure 8. Comparison of bacterial attachment with stainless steel samples from two manufacturers. The numbers of attached bacteria on electropolished samples (dark bars) were significantly reduced from the control samples (light bars).

in a number of presentations has also emphasized the detrimental affect of the altered layer and the need to remove the layer in order to provide the most corrosion resistant surface and one most resistant to rouging.

This altered layer can be removed by electropolishing or by a nitric-hydrofluoric acid pickle. While pickling is very effective in removing metal, the resulting surface will remain rougher than is desired for hygienic services where cleanability is important. Consequently, electropolishing is the most accepted procedure for biopharm services.

What about Rouge?

Rouge can form in high-purity water SS biopharm systems and is an industry concern. Rouge is receiving considerable attention by the American Society of Mechanical Engineers (ASME) BPE Subcommittee on Surface Finishes as well as some other organizations (4). However, a description of the three classifications of rouge and studies on rouge formation is beyond the scope of this article. Tverberg (5) has provided an excellent discussion on rouging.

The discussions to follow are limited to the authors' experiences and observations relating to rouging. A mechanically polished surface with the associated altered surface layer is much more prone to rouge formation and/or precipitation in systems using WFI compared to an electropolished surface. In the case studies that follow, electropolishing has slowed down or stopped the formation of rouge. It appears that iron release and subsequent rouge formation from a mechanically polished surface, even after it has been passivated, is much more prone to iron release than an electropolished surface. There have been limited (unpublished) studies on iron release from different stainless steel surfaces that tend to substantiate this theory and it is an area deserving of further investigation.

There is another surface condition associated with a mechanically polished surface that might contribute an increase in rouge and reduced service performance and that is a profile containing cracks, crevices and peaks bent over that contain trapped impurities from abrasive operations (see Figures 3 (top) and 4 (top) for examples of roughened surfaces). Certainly any embedded free iron on the surface could contribute to rouging and would be removed by electropolishing. It is less clear the role non-metallic abrasive materials or bonding agents used in the manufacture of abrasive might play regarding rouging, but they could be a detriment to cleanability.

Field Experiences

The following are field studies where electropolishing has been successfully used to significantly reduce rouging for extended periods of time. Comparisons between MP and electropolished surfaces in minimizing rouge formation are reported.

Case 1. A 10,000-gallon Type 316L vessel containing WFI had been in service for 10 years. This vessel had a history of rouging that required cleaning and passivation at every shutdown. The owner made the decision to mechanically polish (sand) the bottom head and electropolish.

When the electropolish crew entered the vessel, it was in the same rouged condition as it had been at every shutdown since installation. As instructed the electropolish vendor mechanically polished the bottom head to achieve the customers Ra requirement and then the bottom head was electropolished. While inside the vessel, the electropolish vendor also electropolished (no mechanically polishing) an 18-in band around the diameter of the vessel.

Following electropolishing, the owner had the complete WFI system, including the vessel de-rouged and citric acid passivated before returning the system to service. After 30 months, rouge had formed on all interior surfaces except where the electropolishing had been performed. The 18-in band remained rouge-free as shown in Figure 6 (top) and the bottom head shown in Figure 6 (bottom). At this 30-month inspection, the complete WFI system was again de-rouged and citric acid passivated. When opened after 48 months from the time of the electropolishing, the exact same result was observed (i.e., the electropolished bottom head and the 18-in band) and showed no sign of rouge formation. Since that time, the owner has had the vessel completely electropolished and it is expected that future rouge formation on the vessel surfaces will be retarded dramatically.

Case 2. Two Type 316L WFI vessels 36,000L and 20,000L both with a 180-grit factory interior finish and a history of rouging required to be chemically cleaned and (citric) passivated every 12 to 18 months. The owner had the vessels completely electropolished *in situ* over the original 180-grit factory finish followed by (citric) passivation. After 18 months in service, the owner reported that rouge had not returned and for the first time de-rouging and passivation was skipped.

Case 3. One large Type 316L "walk in" autoclave was electropolished to remove stubborn rouge that had built up with years of use. The customer reported that after 12 months of service the autoclave interior remains "clean and shiny," indicating that so far the rouge has not begun to return.

Each of these field studies continues and it is possible that eventually the rouge may return. In each of these cases, rouge formation was enhanced by what could be the altered surface layer left behind during the manufacturing operations. In every case, when the factory finish was adequately electropolished, the rouge has not returned even while, as in Case 1, the remainder of the interior did re-form rouge adjacent to the electropolished surface.

Better Cleanability

Since the electropolished surface is essentially free of sharp "scratch" marks found on MP surfaces, the EP surface is much easier to clean and appears to result in reduced bacterial contamination. This was studied by Arnold, et al., of the USDA-ARS Russell Research Center (6). Two different surfaces were studied, a 2B (<10 µin Ra) mill finish and an electropolished surface, using one heat of material for the study. The surface morphology was measured by atomic force microscopy (AFM), which provided a comparison in the Z dimension as shown in Figure 7. Figure 8 compares the bacterial attachment between the 2B mill finish and the electropolished finish metal specimens processed by two different manufacturers. Although there is an appreciable difference in attachment between the two manufacturers, in both cases, the electropolished surface has a significantly lower level of bacterial attachment. It was also concluded that the AFM is very useful in performing studies involving surface roughness compared to contact instruments.

Discussion

Electropolishing provides an optimum product contact surface for Type 316L components to be used in biopharm services. Benefits realized include:

- Rouge formation is significantly delayed in actual operating systems.
- Providing a smooth, microscopic-featureless surface beyond that possible by mechanically polishing.
- Removal of any embedded foreign material deposited during the manufacturing process.
- Removal of the altered layer created by MP and offering the most corrosion-resistant surface to the environment.
- A more cleanable surface resulting in reduced bacterial contamination.

The addendum of article highlights criteria in the use of electropolished stainless steel.

Acknowledgement

The authors would like to thank the following persons for their helpful review comments. They are; G.E. Coates, Nickel Institute; P. Eilar, UltraClean Electropolish; Dr. T.H. Meltzer, consultant; J. Rau, Dockweiler; and D. Roll, Astropak.■

Addendum

Electroplished surface acceptance criteria. The importance of having each electropolished processor establish and follow their individual Electropolishing Procedure Specification was emphasized in the article. A less than full electropolishing (or "flash" EP) can produce a misleading shiny surface, but one that has not removed surface defects such as ditched grain boundaries, scratches, the altered surface layer, and other defects.

In practice, current electropolishing acceptance criteria is largely based on meeting a specified Ra value and a visual inspection for various surface conditions. Acceptance criteria commonly used follows.

Buffing (following electropolishing). Buffing is mechanically polishing to a high luster using very fine grit abrasives in a grease-bonding material. It may incorrectly be used to blend electropolishing defects areas and can be very difficult to detect visually. Furthermore, the embedded abrasives and entrapped compounds can be detrimental in service.

Blistering, cloudiness, haze—none acceptable. These defects most often are the result of failure to follow proven electropolishing procedures, or can be problems related to the unique geometry of the surfaces being electropolished. There are no industry visual standards to quantify acceptable/non-acceptable levels of, for example cloudiness, so all conditions are judged unacceptable.

End grain effect, orange peel, stringer indications, weld whitening— acceptable if Ra maximum is met.

In addition to the above criteria, specifically for EP surfaces, it is normal practice to employ limits for surface indications and physical anomalies for both mechanically polished and electropolished surfaces. The criteria may vary with various standards, but would typically include features such as: pits, dents, nicks, scratches, surface cracks, porosity, and inclusions.

Surface replicas. One challenge in work involving metallic surface analysis is monitoring any surface changes resulting from service use. Scanning electron microscope (SEM) can be used in some instances, but it is not easily adoptable for use in the field. A useful technique for recording and evaluating a surface is the use of metallographic replicas (7). Replication is a non-destructive sampling procedure that records and preserves the topography of a metal surface as a negative relief on a plastic film or compound. The microstructural replica can be examined in a light microscope, SEM, or by using white light Vertical Scanning Interferometric surface texture analysis. Often the fragile replica is vacuum metallized prior to observation, which provides contrast, conductivity, and a more durable sample of the surface.

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Key words: MATERIALS OF CONSTRUCTION, PHARMACEUTICALS, STAINLESS STEEL, WATER FOR INJECTION