HOW PRODUCTION TECHNOLOGIES INFLUENCE SURFACE QUALITY OF ULTRACLEAN GAS-SUPPLY EQUIPMENT: ASSESSMENT OF SURFACE TECHNOLOGIES

(Second of four parts)

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To meet the increased purity requirements of today's semiconductor industry, the surfaces of ultraclean gas-supply systems must be free of contaminants at both the micro and macro levels. The surface of such a system should neither retain nor generate particles, and its structure must be homogeneous and free from inner tensions so that component movement and corrosion stress do not result in particle generation. In addition, there must be no monomolecular layer of impurities, such as organic compounds (e.g., grease and oil) or residue from cleaning agents (e.g., phosphates and sulphates).[7,8,10,11,22–24]

The main aim of a surface treatment must thus be to achieve this ideal surface as nearly as possible. This article will describe several surface treatments, including both preliminary mechanical processes (e.g., turning and drilling) and cleaning processes (e.g., acid treatments, rinsing, and drying). To characterize the surface structures we have used original valve components from Ceodeux production as well as some specially manufactured sample pieces. The components were processed using CNC machine tools.

MECHANICAL-PROCESSING PROCEDURES

Mechanically processed surfaces show a wide statistical distribution of surface-roughness values (Table 1), independent of the procedure used (e.g., drilling, turning, reaming, roll finishing, or micropolishing). This extremely wide distribution is typical of such tough

Surface Processing	Ra (μm)	Rz (μm)
Drilling	0.34–7.20	7.20–38.00
Drilling and reaming	0.29–2.29	4.66–11.72
Drilling and reaming and roll finishing	0.20–1.16	1.26–11.98
Drilling and reaming and micropolishing	0.56–1.50	3.18–11.38
Drilling and reaming and roll finishing and micropolishing	0.12–0.86	0.56–7.42
Turning	0.24–1.60	1.32–10.00
Turning and micropolishing	0.20–2.00	1.56–8.86

Table I: Range of surface-roughness measurements, depending on type and order of mechanical-surface processing used on AISi 316L material.

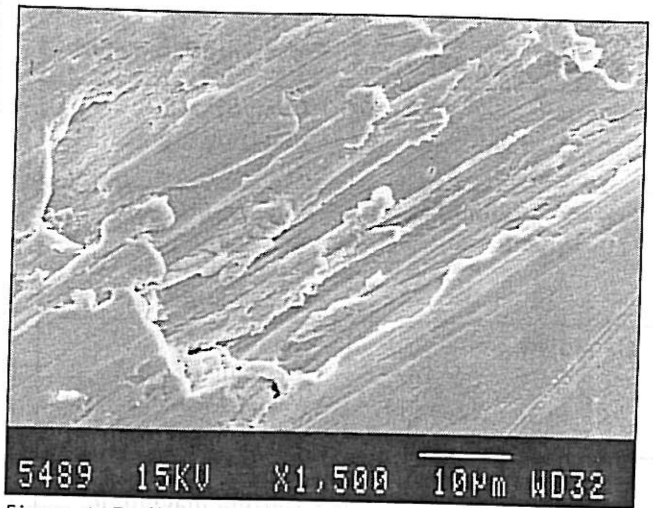

Figure 1: Drilling. *The SEM photograph shows a typical rough edge where a chip has been torn out during drilling carried out on AlSi 316L (1500×).*

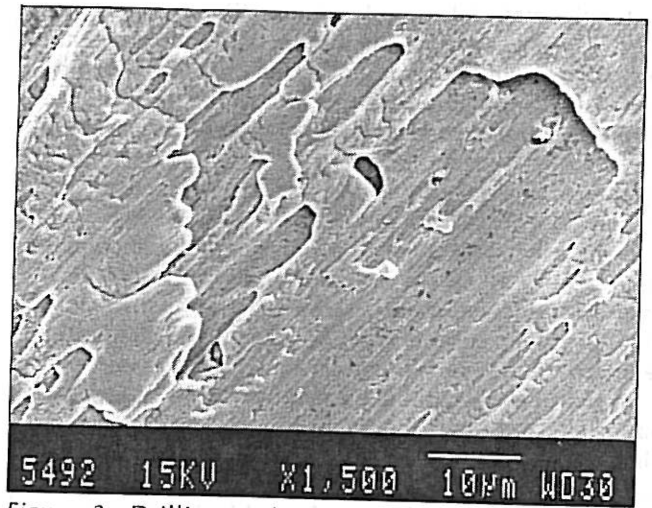

Figure 2: Drilling and reaming. *The deep fissuring cannot be removed by subsequent reaming treatment. The upper layers of the structure are simply reversed and "spread" over the surface (1500×).*

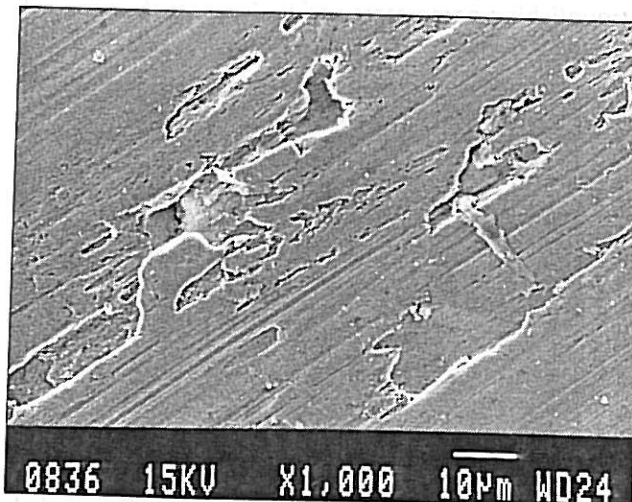

Figure 3: Drilling and reaming and roll finishing. *Although a roll-finishing treatment carried out after reaming smooths the surface considerably, it does not eliminate the surface defects (1000×).*

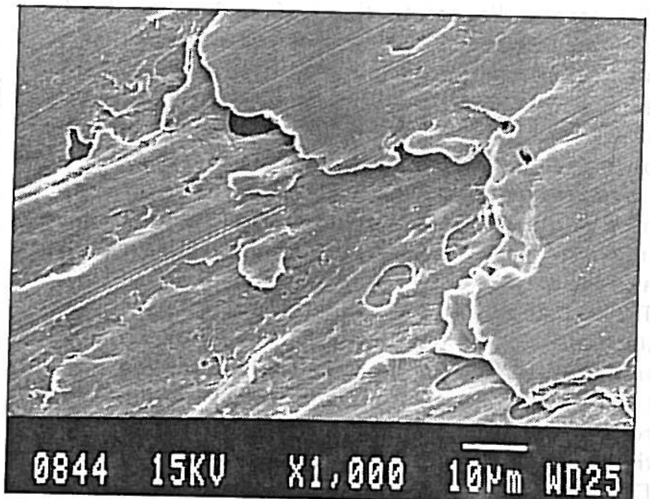

Figure 4: Drilling and reaming and roll finishing and micropolishing. *Even this expensive and complicated series of treatments has not resulted in a noticeable improvement in the surface. The torn edge of the chip formed during drilling is still clearly visible (1000×).*

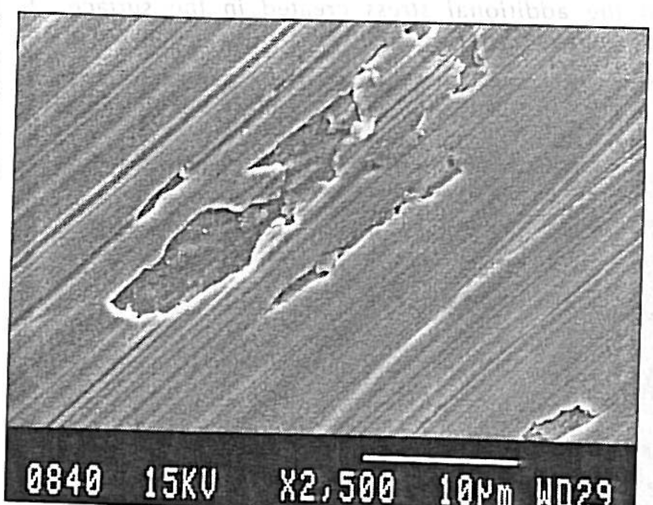

Figure 5: Turning. *Turned surfaces show a more homogeneous structure than drilled surfaces (2500×).*

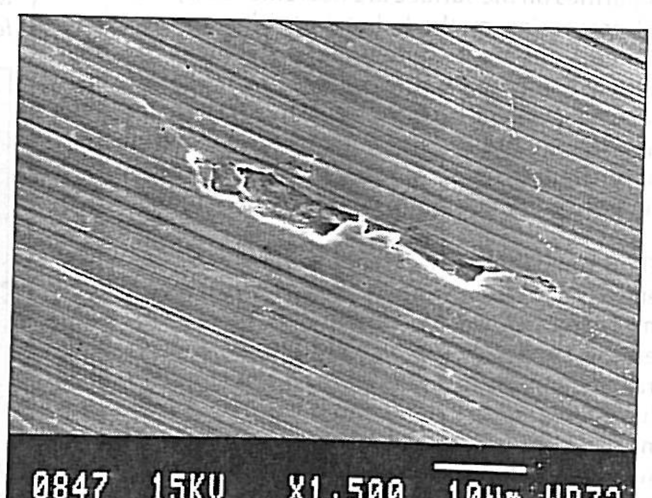

Figure 6: Turning and micropolishing. *Micropolishing of a turned surface results only in an optically improved degree of brilliance; the surface structure is not improved (1500×).*

austenitic materials as aluminum-silicon 316L. The deep fissuring caused by machining is directly attributable to the tough character of the material. During processing, long chips are torn out of the surface; the blunter the tool used, the worse the effect. The narrowly specified limits of surface-roughness levels demanded by ultraclean gas technology cannot be met by using the mechanical-processing methods listed in Table I.

In the electronic microscan photographs shown in Figures 1–6, all of the surfaces show a more or less fissured surface structure. The photographs also show that once deep defects have occurred, they cannot be removed by the mechanical treatments illustrated.

Mechanical Smoothing as an Alternative to Electropolishing. Although highly brilliant surfaces can be obtained by using mechanical smoothing treatments (i.e., reaming, roll finishing, and micropolishing), these procedures are not adequate for achieving the proper surface quality. A number of hidden defects will result from such treatments, the most serious of which are as follows:

- The areas adjacent to the surface become badly deformed during reaming and roll-finishing treatments. This cold deformation can cause severe hardening and brittleness of the material, and thus material stress, such that the hardened upper layer may split open (Figure 7). These surface alterations are reflected in Vickers hardness measurements (a VH-1 measurement in the zones adjacent to the surface showed an increase in hardness from 235 at the outset to an average of 362 following roll finishing).
- The surface deformation caused by roll finishing and the associated hardening and brittleness of the material near the surface results in less corrosion resistance. Both the brittleness and the loss of corrosion resistance can lead to increased particulation when the component is in use.
- Deep cracks already in the material (caused, for example, by drilling) are not adequately evened out by reaming and roll-finishing treatments, which merely cover the cracks by stretching the top layer of material over them (Figures 2–4, Figure 7). Particles and other contaminants are thus locked in.
- Impurities on the surface are not removed by mechanical-processing methods but instead are pressed, or "rolled," into the surface by such methods (Figure 8).
- Although micropolishing provides an apparently brilliant surface, the stresses caused in the material by production and surface-processing procedures remain (Bailby layer), and deep defects and surface impurities are not removed (Figures 4 and 6).

Electropolishing. Electropolishing has become the preferred final treatment for the inner surfaces of such components as valves, filters, and tubes.[7,8,11] However, the results of electropolishing depend on many parameters (Table II), and a divergence of just one single value among them can lead to a worsening in the propensity of the surface to generate particles or other contaminants. Critical parameters include the preliminary treatment of the surface, the purity of the material, and the surface-finishing treatments.

Preliminary Treatment of the Surface. The smoother and more homogeneous the surface is before electropolishing, the better the result will be.[25,26] Electro-

Parameters Influencing the Polishing Result	Processing Parameters
Material	• Composition. • Inclusion rate. • Structure.
Surface (preliminary treatment)	• Microstructure/ macrostructure. • Contamination. • Accessibility.
Electrolyte	• Composition. • Cationic content. • Water content. • Contamination.
Process technology	• Temperature. • Current magnitude. • Charge density. • Cathode arrangement. • Finishing treatment.

Table II: Summary of the most important electropolishing parameters and their respective processing parameters.[26–30]

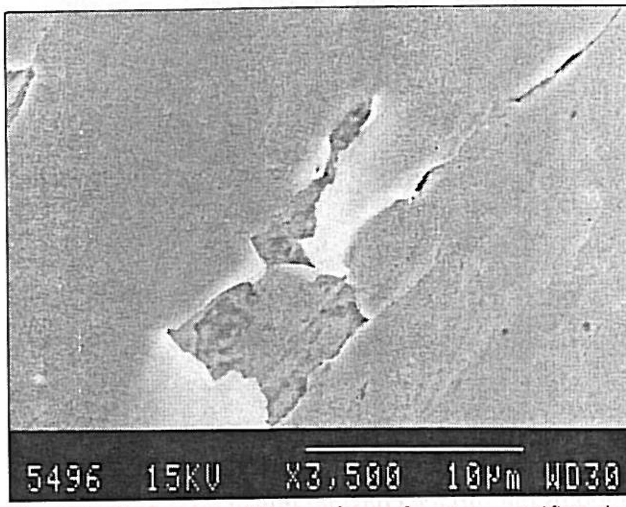

Figure 7: Structure of the surface of an inner orifice that has been smoothed by reaming followed by roll finishing. The severe brittleness of the surface zones, combined with the additional stress created in the surface, leads to flaky blistering (3500×).

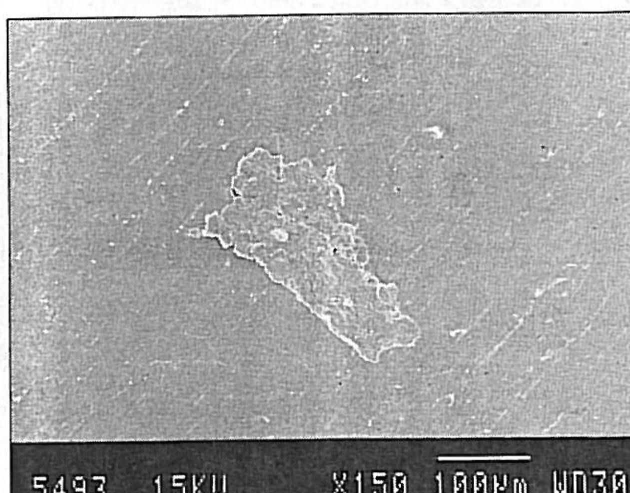

Figure 8: A foreign particle pressed into the surface by reaming and roll finishing (150×).

polishing can reduce the surface-roughness values by a factor of between 1.5 and 3 (Figure 9). This should be taken into account during mechanical finishing of components. Where necessary, additional measures must be taken to reduce the original roughness prior to electropolishing.

Table III gives the Ra values before and after electropolishing for surfaces with different pretreatments. The very wide statistical distribution of roughness values caused by the various types of prior mechanical treatments is narrowed only slightly by electropolishing. If sufficient material is removed (limit values 30–50 μm), all microimperfections and roughness will be eliminated, regardless of the type of prior treatment. Deep-lying defects, however, remain (Figures 10 and 11). Such defects could be reduced or even completely avoided by using sharp cutting tools or by performing multistep finishing with abrasive mechanical treatments (e.g., grinding), using progressively finer grain sizes.

Chemical treatment prior to electropolishing can crucially influence the result. It can generally be said that all nonconductive contaminants—e.g., organic contaminants, salts (especially halogenide), and metal oxide—will have a visibly detrimental effect.

Material Purity. The purity of the material is very important to the electropolishing result, since electropolishing exposes impurities in the material. Nonmetallic inclusions and segregations result from such additive elements as manganese, sulfur, titanium, copper, aluminum, zirconium, calcium, and silicon, which may be present in austenitic steel. These elements are not necessarily added to the steel as alloys but represent impurities typical of steel. Their property of forming a low-melting eutectic leads to the formation of nonmetallic inclusions during cooling (Figures 12 and 13). Depending on the types of impurities and on the conditions that produced them, the inclusions may be oxides, sulfates, carbides, nitrides, phosphates, carbonitrides, silicates, and the like. Their nonconductive properties lead to disturbances in the electropolishing process; these become apparent through, for example, aggression on the material surrounding the inclusion particles. This exposure leads to the increased release of particles from the surface.

Surface-Finishing Treatments. Polishing electrolytes consist mainly of sulphuric/phosphoric acid mixtures. If the electropolished surface finishing is not carried out according to specifications, residual phosphates, which are difficult to dissolve, can be produced (Figures 14 and 15).[7,8,31] These layers can be removed by using a finishing treatment with nitrous or sulphuric acid as well as a final deionized (DI) water rinse. The material's typical inclusion rate must be considered (Figures 16 and 17), and all precautions should be taken to prevent contamination of the surface through handling by the human operator (Figure 18).

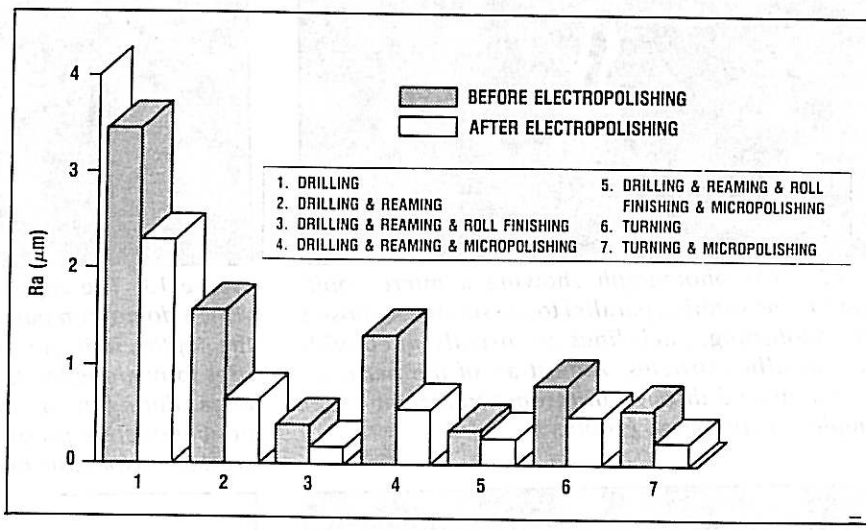

Figure 9: Comparison of surface roughnesses before and after electropolishing, depending on the mechanical processing method used. (Mean values from about 25 individual measurements taken from Ceodeux production.)

Type and Order of Treatment	Ra (μm) before Electropolishing	Ra (μm) after Electropolishing
Drilling	0.34–7.20	0.60–5.99
Drilling and reaming	0.29–2.29	0.22–1.82
Drilling and reaming and roll finishing	0.20–1.16	0.10–0.42
Drilling and reaming and micropolishing	0.56–1.50	0.30–0.96
Drilling and reaming and roll finishing and micropolishing	0.12–0.86	0.24–0.34
Turning	0.24–1.60	0.14–0.72
Turning and micropolishing	0.20–2.00	0.10–0.43

Table III: Range of surface-roughness measurements (Ra) before and after electropolishing, depending on prior mechanical treatment.

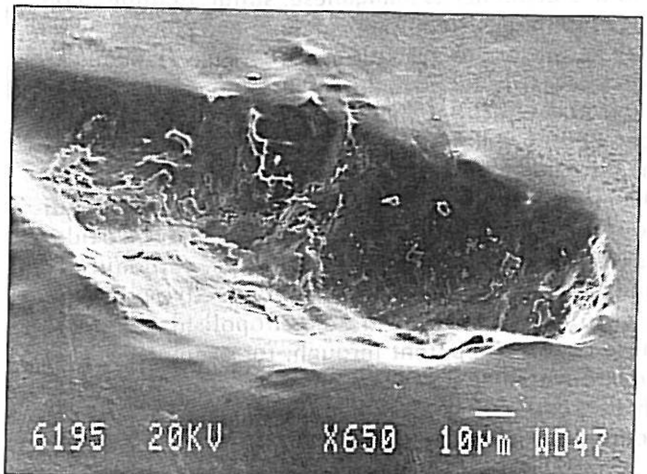

Figure 10: A macro disturbance in the surface, originally caused by drilling, that has not been completely polished out by electropolishing (650 ×).

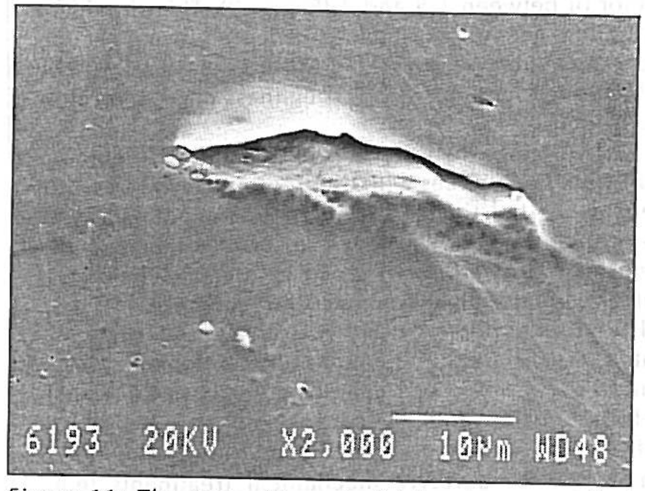

Figure 11: The austenitic material has been stretched like a thin layer over the defect site, and the leveling effect of electropolishing has been insufficient to eradicate the site (2000 ×).

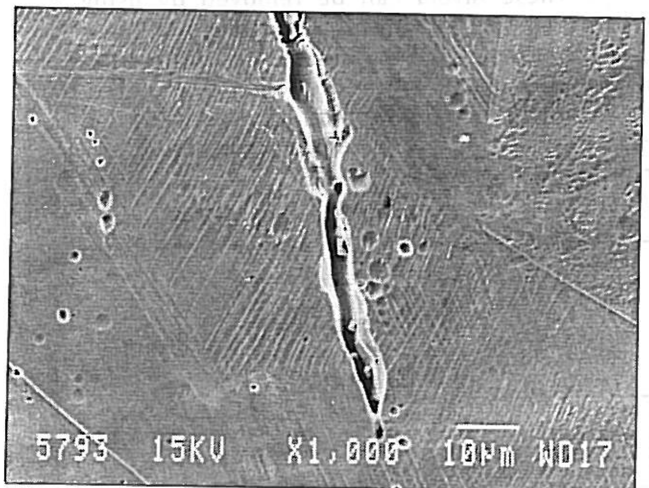

Figure 12: SEM photograph showing a microscopic segregation line running parallel to the surface, exposed by electropolishing. Such lines are usually filled with tiny, nonmetallic particles. Almost all of the particles had been removed through ultrasonic treatment when the sample was prepared (1000 ×).

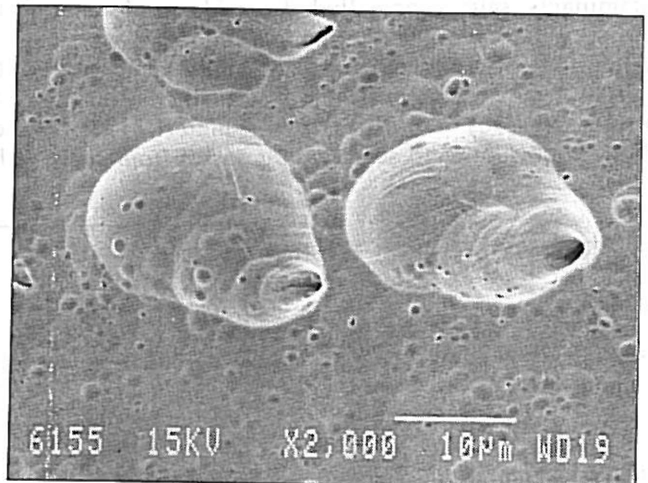

Figure 13: The appearance of these segregation lines, which do not run parallel to the material but rather into the depths, indicates nonmetallic inclusions. Deep cavities form along the lines, and the intense development of gas during the dissolving process combined with the nonconductive properties of the inclusions leads to a weakening for basic material in the aperture area (2000 ×).

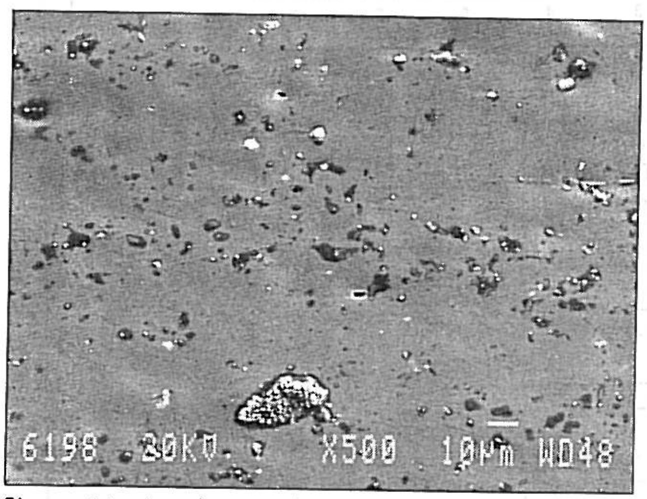

Figure 14: An electropolished surface that has been unsatisfactorily finished. The white spots are exposed nonmetallic inclusions (in this case, AlSi compounds), and the dark spots are phosphorus and sulphur compounds (residual matter from the electrolytes) (500 ×).

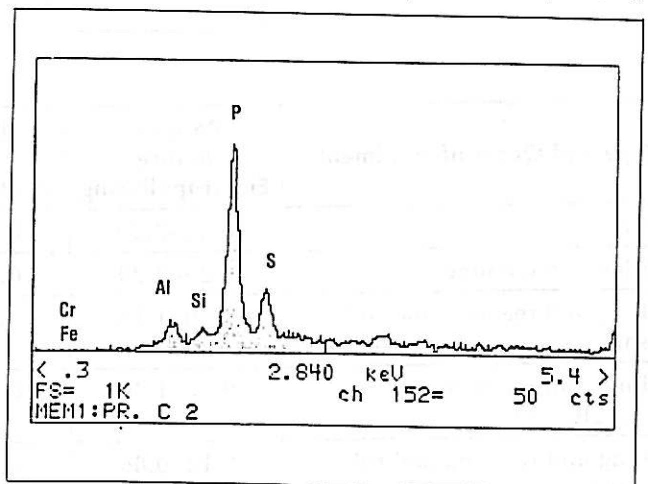

Figure 15: Energy-dispersive analysis of surface layer shown in Figure 14. The high phosphorus and sulphur contents can be easily seen.

CHEMICAL POLISHING

Austenitic chrome-nickel steels generally have good chemical-polishing characteristics. As in electropolishing, the chromium becomes enriched in the layers adjacent to the surface, resulting in an enhancement of the surface's corrosion resistance.[7,8,10,23] However, chemical polishing cannot produce the same low levels of roughness as electropolishing, even when the original roughness level is the same,[23,32] because the material structure cannot be satisfactorily evened out by chemical polishing. If variously arranged crystal levels reach the surface, the result will be a rougher surface. The preconditions necessary for electropolishing must also exist for chemical polishing. In particular, the surface must have a low outset roughness (Table IV), since high roughness can be worsened by chemical polishing as a result of erosive procedures (Figure 19).

Most chemical-polishing procedures are faster than electropolishing. Note, however, that chemical polishing is not suitable for components with geometrically complicated forms (e.g., valves), since overpickling can occur as the chemical solutions continue to react after the component has been removed. In the case of smaller components with freely accessible surfaces, chemical polishing can be an alternative to electropolishing (although the possibility of nitrous-gas formation must be considered).

Unlike electrochemical shining processes, and due to a different electrolytic composition, chemical processes do not tend to form residual deposits on the surface. A final DI water rinse is sufficient.

FINAL CLEANING

In the finishing stage, all of the hidden defects caused by electropolishing should be removed. Such defects include exposed nonmetallic inclusions and segregations, electrolytic residues (e.g., phosphates and sulfates), and moisture. The final cleaning is a multistep procedure, selected according to the type of surface contamination. For example, in the case of surfaces with deep segregation lines, a normal acid dip followed by a deionizing rinse is not enough to eliminate the phosphate contamination. Electrolytic residues can be removed from the inclusion cavities only by means of diffusion procedures (Figure 17). These very slow procedures can be speeded up by varying the temperature and using ultrasonic treatments. Exposed nonmetallic inclusions are also not normally removed through acid

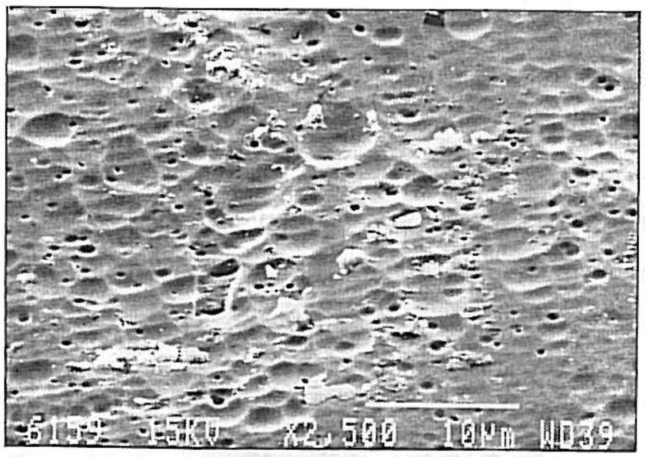

Figure 16: Frequency of particles in an electropolished AISi 316L sample. The usual acid-dipping/DI rinsing does not remove these particles from the surface (2500 ×).

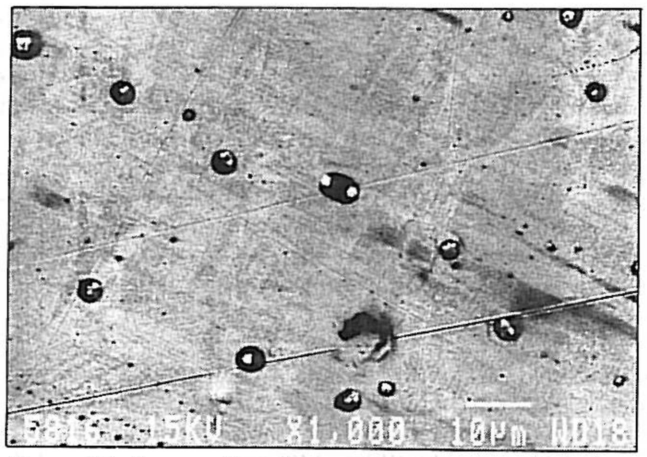

Figure 17: Segregation-line apertures exposed by electropolishing. The nonmetallic particles can be seen in the center of the apertures. The dark fields surrounding these particles are residual phosphates (1000 ×).

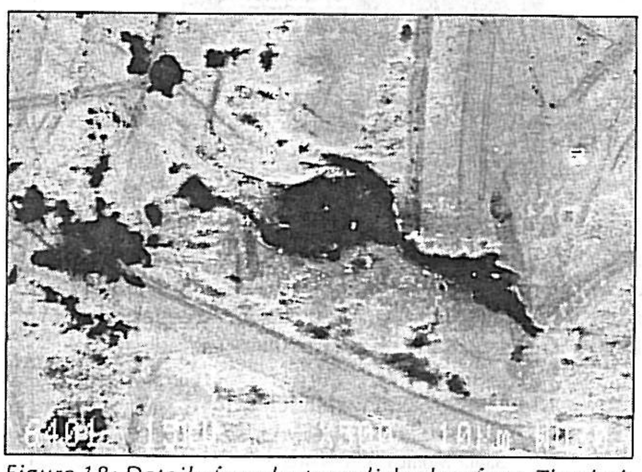

Figure 18: Detail of an electropolished surface. The dark layers are organic pollutants. This photograph clearly shows how a surface contaminated in this way, often through mishandling by a human operator, tends to release particles (500 ×).

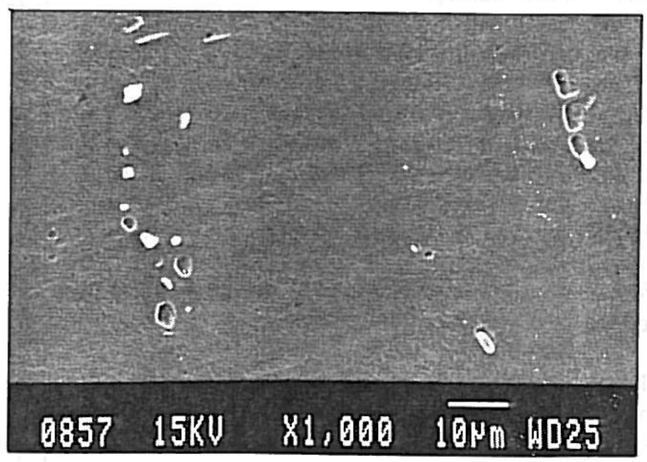

Figure 19: Turned and micropolished surface of AISi 316L material following additional chemical-polishing treatment. The white particles are nonmetallic inclusions exposed by the polishing (1000 ×).

Sequence of Treatments	Before Chemical Polishing	After Chemical Polishing
Drilling	2.1–7.2	5.4–7.1
Drilling and reaming and micropolishing	0.6–1.9	0.7–1.1
Drilling and micropolishing	0.3–0.7	0.3–0.4

Table IV: Influence of outset roughness on the chemical-polishing results for AISi 316L.

dipping/DI water rinsing alone (Figure 15); in this case, an ultrasonic treatment must also be carried out.

Final drying and surface protection are also part of the finishing operation. During operational gas-purging procedures, the moisture adhering to the surface (i.e., the monolayers) can only be eliminated very slowly.[33] Drying media as well as thermal processes (warm drying air) are used to remove the moisture.[34,35] It is, of course, crucial that particle-free media be used.

To avoid further moisture deposits from the air, the parts must be sealed into a protective film beneath a dry inert-gas shield. Note that such films can provide protection from vapor diffusion for only a limited time; for long-term protection, Al/Pe confound foils should be utilized.

CONCLUSION

The saying that any chain is only as strong as its weakest link is especially valid in semiconductor technology. Every single parameter with the potential to influence purity must be considered. For the inner surfaces of ultraclean gas-supply systems, two particularly important parameters are the choice of material and the surface quality. The following essential points must be considered:

- Nonstabilized, austenitic chrome-nickel steels in extra-low carbon (ELC) grades should be used.
- As purity requirements increase, the use of electroslag-refining material will be obligatory.
- Mechanical surface-treatment processes are not suitable finishing measures.
- The use of chemically or electrochemically polished surfaces is mandatory.
- The specification term *electropolished* alone does not suffice. The preliminary treatment, polishing parameters, and finishing treatment are all crucial elements and must be specified.
- The required surface quality cannot be achieved with only an acid-dipping treatment and a rinse in DI water after electropolishing.
- The final cleaning must be carried out under ultraclean conditions.
- Before the component is packed, the parts must be dried using drying agents.

In Part III of this series, specifications and inspection techniques for evaluating surface quality of ultraclean gas-supply equipment will be discussed.

(The reference listing will appear in a future installment of this series.)

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