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CORROSION ASPECTS FOR STAINLESS STEEL SURFACES IN THE BREWERY, DAIRY AND PHARMACEUTICAL SECTORS

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ABSTRACT

Based on practical cases, tests and available literature the paper reviews the relation between surface condition and corrosion properties of stainless steel used in breweries, dairies and pharmaceutical processing plants. Aspects related to specification, corrosion testing and post-treatment (e.g. pickling and passivation) are also discussed.

Keywords: Corrosion testing, CPT, pitting potential, standards, accept criteria, surface roughness, post-treatment, sensitization, brewery, dairy, pharmaceutical.

INTRODUCTION

Stainless steels for processing plants in the brewery, dairy and pharmaceutical sectors are normally specified as either AISI 304 or AISI 316L type material. When supplied from the steel mill, the material is documented with an inspection certificate (e.g. EN 10204-3.1), which ensures that the most crucial parameters affecting corrosion resistance are fulfilled. This implies spectral analysis of the chemical composition as well as intergranular corrosion testing of the heats to ensure that the microstructure is healthy. The main corrosion form in question for the product side is localized corrosion such as pitting and crevice corrosion, since the equipment is exposed to chloride-containing and potentially aggressive products and cleaning agents.

To a great extent the steel certificate ascertains that the basic corrosion properties of the stainless steel are met. For the brewery, dairy and pharmaceutical sectors a well documented surface condition of the supplied steels is required as well to meet the requirements for hygiene and cleanability as discussed in another paper /1/. The surface condition is as minimum characterised by the manufacturing route /2/ but normally implies additional requirements to the surface roughness (*Ra*).

The subsequent handling of the semi-finished products during fabrication always involves risks of compromising the corrosion resistance unless the basic guidelines for handling stainless steel are followed strictly. For instance, the surface finish may be contaminated or damaged during cold forming. Moreover, hot forming or subsequent heat treatments may alter the microstructure, and likewise heat tinting or geometrical defects may be introduced during welding. Although these issues are well-described in the relevant standards, disputes occur frequently where the consequences and measures for re-establishing the corrosion resistance are questioned.

The paper reviews the most common corrosion-related issues that are encountered during commissioning of processing plants for the brewery, dairy and pharmaceutical sectors. As a material testing institute, FORCE Technology is often involved in such cases, either as an independent third party or when contracted by one of the companies. Consequently, the following review is mainly based on our experience from practical cases, but tests and available literature are included as well. In cases where fabrication defects compromise the corrosion resistance, it is our intention to illustrate the consequences and discuss available methods for re-establishing the surface.

STANDARDS TO SPECIFY AND RE-ESTABLISH SURFACE REQUIREMENTS

Besides from choosing the correct stainless steel grade providing sufficient corrosion resistance, it is equally important to specify the right surface condition of materials used in brewery, dairy and pharmaceutical sectors. This parameter obviously influences the cleanability and hygienic properties of the equipment. Moreover, the surface condition affects the corrosion resistance to a certain extent, which means that requirements may possibly be met by specifying the proper finish rather than upgrading the chosen alloy.

Several standards are available for specifying the surface requirements of stainless steel equipment. The ASME-BPE standard /3/ and ISPE baseline guides are widely applied for pharmaceutical plants. For the dairy and brewery sector the 3A and EHEDG guidelines are commonly used but individual company standards are also frequently used. Along with these standards, international standards are available on specific items like tubes (e.g. DIN 11850 and DIN 11866).

Depending on the specific use of the equipment, the specified finish ranges from 2B/2D (pickled) to mechanically polished and electropolished finish. The typical minimum requirements for the equipment are listed below, but great care should always be taken when specifying and interpreting such criteria:

- Surface roughness, $Ra \leq 0.6$ µm
- Metallic bright and clean surface
- Surface defects are only acceptable to a specified level
- Final passivation

The interpretation of the surface roughness is thoroughly discussed in another paper /1/. Likewise, the allowable degree of local surface defects is often an issue for dispute. The ASME-BPE standard /3/ provides a fairly clear specification of this, whereas other standards often lack relevant details. One example is the DIN11850 standard concerning stainless steel tubes for the food industry. This standard refers to EN 10217-7 regarding technical delivery conditions, e.g. allowable surface imperfections. When read literally, this standard allows manufacturing-related surface imperfections up to a depth of the specified minimum wall thickness, which is 90 % of the nominal wall thickness. To avoid any subsequent discussions, it is recommended to make additional specifications for the allowable surface defects.

Regarding the term passivation, reference is normally made to the ASTM A380 and A967 standards. For electropolished surfaces, the ASTM B912 has recently become available. According to these standards, it is no longer compulsory to perform a strong nitric acid passivation that actively builds up the protective oxide film and improves the Cr/Fe ratio of the outer layers. Today, the passivation treatment may be performed with milder non-oxidizing acids like citric acid as long as it leaves the surface perfectly free from inclusions and metallic contaminants (like iron) that otherwise might hinder the spontaneous passivation process of the stainless steel.

Although the mentioned standards provide a good basis for obtaining the desired corrosion resistance, they seldom provide specific methods or acceptance criteria for assessing the corrosion resistance of the finished product.

METHODS TO CHARACTERISE CORROSION RESISTANCE

The possibility of on-site non-destructive testing methods is limited for directly measuring the obtained corrosion resistance of the finished equipment. Assessment of the pitting resistance of stainless generally requires a semi-destructive test that generates pits in the material either by electrochemical polarisation or a temperature ramp test. Consequently, this testing approach has never found wide use for on-site evaluation, since it would require subsequent repair of the tested area.

Simpler and non-destructive tests are available for obtaining an indicative measure of the corrosion resistance. The ASTM A380 and ASTM A967standards describe several test methods for this purpose, including the water wetting and high-humidity tests for detecting highly susceptible areas as well as the ferroxyle and copper sulphate tests for detecting free iron. Short-term salt spray testing (2 hours) may also be used to evaluate the condition. Such tests will effectively reveal any iron contamination or local areas with equally low corrosion resistance that present a possible risk of initiation sites for pitting. However, the tests do not provide a sufficiently fine graduation to reveal defects that are related to geometrical surface issues or sensitization of the metal.

Another non-destructive approach is to measure the corrosion potential of the surface in a well-defined test solution. This method is available as commercial instruments under the names Oxilyser or Passivation Tester. A micro electrochemical cell (ec-pen) for measuring pitting potentials in very small areas (1.5 mm^2) is also available as a commercial instrument. Although both techniques can provide valuable data, a thorough basis for establishing clear acceptance criteria with these methods is still desirable.

In extreme cases, where sensitization is suspected as a result of improper heat treatment (e.g. during welding) there is a range of test methods available for evaluating the risk of intergranular corrosion. The oxalic acid etch test according to ASTM A262 can be made on-site with portable polishing and etching equipment. The polished and etched microstructure is either evaluated on-site with microscope or, alternatively, a replica cast is taken for later examination in the laboratory.

Another way of quantifying the degree of sensitization can be obtained using the ASTM G108 standard test method based on Electrochemical Reactivation (EPR). This technique has also been adapted to provide on-site evaluation /4/.

The simplest approach to evaluate the presence of sensitized areas (e.g. in HAZ) is to perform a mild pickling treatment of the welds or suspected surface. Any sensitization will be revealed as severely etched areas that can easily be detected by a specialist.

We have experience with most of the above methods from practical cases in the brewery, dairy and pharmaceutical sectors. To evaluate how fabrication-related surface issues affect pitting resistance we have applied two main approaches.

Provided the fabrication procedures and surface treatments are well documented, a reasonable estimate of the obtained corrosion resistance can be based on surface characterisation and corrosion data (see next section). Non-destructive assessments may be applied to characterise the surface topography better, e.g. by surface roughness measurements or replica castings of the surface for subsequent examination in a scanning electron microscope. When this information is combined with the known effects of surface finish and chemical post-treatment, a fairly good estimate of the resulting corrosion resistance can be established.

When disputes get stuck and harder evidence is needed, we have occasionally tested samples cut from the plant to verify the corrosion resistance. This approach may seem as a last resort but on the other hand it provides the answers quickly without too much delay in the project. As an example, such disputes may arise from various discolouring phenomena (possible heat tinting) that represent borderline cases according to common standards.

In order to test against well-accepted criteria, we apply standard methods whenever possible. The ASTM G150 CPT method is perhaps the only standardized electrochemical method that allows comparison of pitting data between testing laboratories, Figure 1. As the standard contains extensive statistical data for grades AISI 316L and better, it is clear what to expect from a healthy stainless steel. However, the harsh testing conditions of the G150 method (1 M NaCl and -700 mV SCE) do not allow testing of the AISI 304 material, which is frequently used for dairies and breweries.

The conditions of the G150 test are furthermore far from the typical service conditions in food and pharmaceutical processing plants. In order to test under conditions closer to this level, the pitting potential is determined by using cyclic polarisation in milder chloride solutions. Based on ASTM G61 standard, this technique has been further improved to allow testing of plate and tube sections without cut-faces and with "crevice-free" mounting /5,6/. This ensures a high degree of reproducibility. The previously published work has formed a good basis for evaluating the corrosion resistance of AISI 304 and AISI 316L materials in practical cases where the quality was questioned.

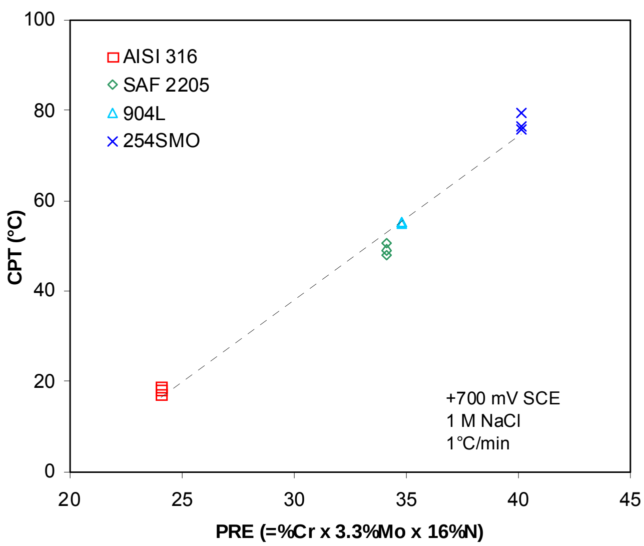

FIGURE 1 – Relationship between alloying and CPT determined with ASTM G150 (1 M NaCl, +700 mV SCE).

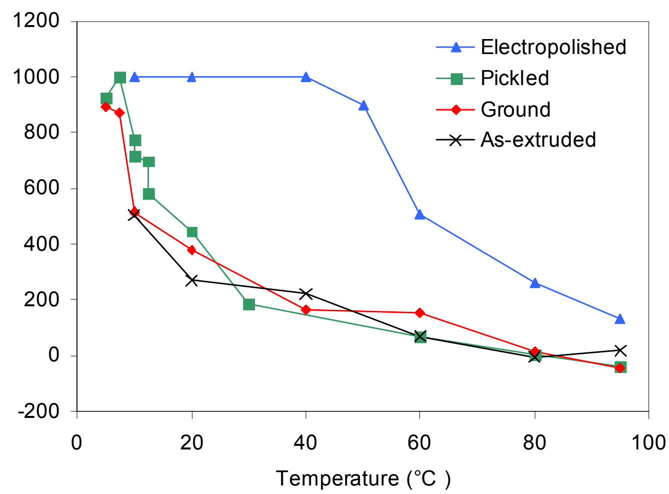

FIGURE 2 - Relationship between pitting potential and temperature of different surface conditions in 5 % chloride solution /5,6/.

DEPENDENCE BETWEEN SURFACE CONDITION AND CORROSION RESISTANCE

The literature provides several data about mechanical and chemical surface treatments in respect to corrosion resistance. However, the way data is obtained varies due to the lack of standardized testing techniques as discussed above. This makes direct comparison of different datasets difficult.

The results of a project on the influence of various surface conditions on pitting resistance have previously been published /5,6/. Despite the very different surface topographies, tubes with ground, extruded and pickled finish came out with nearly the same pitting resistance when tested in passivated condition, Table 1. As expected, the electropolished finish showed superior pitting resistance in comparison to this. The study included both pitting potential determination at various chloride levels (Figure 2) and CPT-testing according to ASTM G150.

TABLE 1.
Comparison of critical pitting temperatures (CPT, °C) of AISI 316L tubes (ø60-ø63 mm) obtained by using either polarization technique or ASTM G150 /5,6/.

CPT in °C		**Polarization Cl^-, mg/l**			**ASTM G150 Cl^-, mg/l**
Surface condition	***Ra*, µm**	**500**	**5,000**	**50,000**	**35,500**
Ground,	**0.19**	**14**	**9**	**6**	**7 ± 2**
Extruded	**5.4**	**13**	**<10**	**<10**	**11 ± 4**
Pickled	**0.48**	**17**	**14**	**9**	**14 ± 5**
Electropolished	**0.12**	**65**	**45**	**45**	**57 ± 13**

In comparison to the surface finish, the weld quality is more decisive for the corrosion resistance. It has earlier been shown that the oxygen content of the shielding gas strongly influences the pitting resistance of standard stainless steel grades, Figure 3. At 20-30 ppm oxygen in the shielding gas the pitting resistance of AISI 304 is significantly impaired, whereas AISI 316L and UNS 08904 tolerate slightly higher oxygen levels. These results have formed the basis for our colour reference atlas for welds /8/ that is widely used to specify weld accept criteria in the brewery, dairy and pharmaceutical sectors.

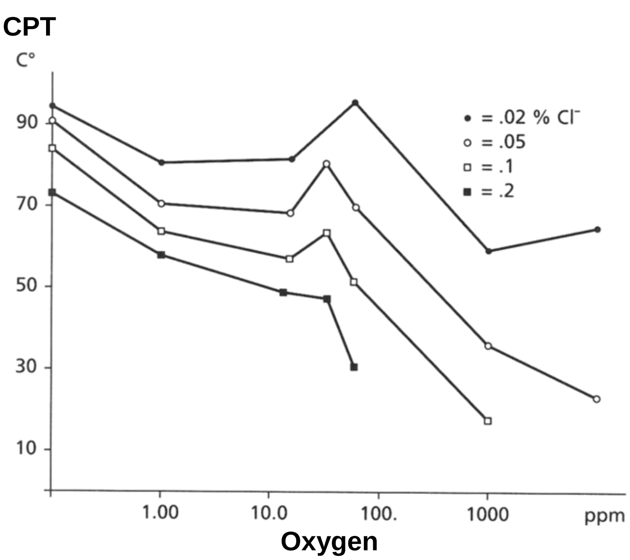

FIGURE 3 - Relationship between oxygen content in shielding gas and pitting temperature of TIG welded AISI 304 /7/.

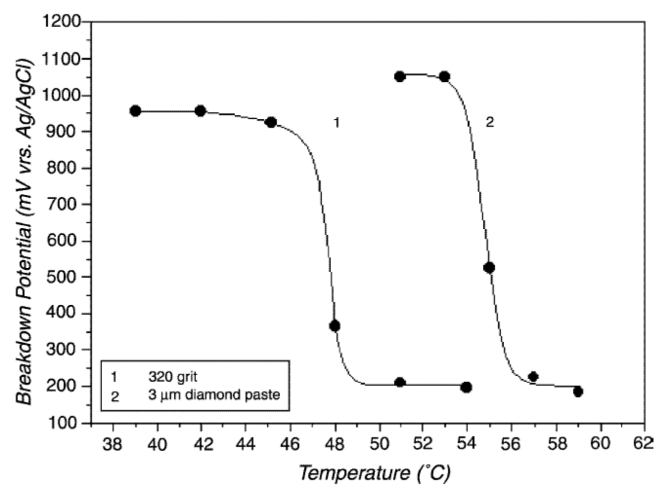

FIGURE 4 – Breakdown potentials as function of temperature of 904L with two different surface finishes in 1 M NaCl /11/.

Several papers in the literature support the above statements. Ericsson et al have published pitting potential data for AISI 316 that emphasizes the importance of pickling subsequent to abrasive treatment in order to improve resistance /10/.

Moayed et al have shown that the critical pitting temperature (CPT) of 904L increases with increasing surface smoothness obtained by abrasive treatment, Figure 4.

Data based on exposure in ferric chloride (ASTM G48) show a similar tendency, Figure 5. The beneficial effect of decreasing surface roughness has furthermore been proven by quantifying the nucleation rate of metastable pitting and electrochemical noise measurements /13,14,15/.

Another approach has been to characterize the dependence between chemical composition of the passive layer (i.e. Cr/Fe ratio) and abrasive and chemical surface treatment /16,17/. It is shown that common passivation treatments provide only temporary improvement of the passive film. In few days the passive film adjusts itself and reaches an equilibrium state that mostly depends on the environment /17/.

Based on the literature as a whole, it is commonly accepted that electropolished finish provides better resistance than pickled finish, whereas mechanically ground or polished finishes fall in the least corrosion resistant group. Presumably, this ranking can be related to the resulting amount of free inclusions and surface roughness related to the different surface treatments.

A wide range of data is also available for stainless steel surfaces exposed to atmospheric conditions /18,19,20/. Generally the same ranking is reported as for the fully immersed exposure conditions above. However, other parameters are more decisive here, such as wetting properties and the ability to collect dirt.

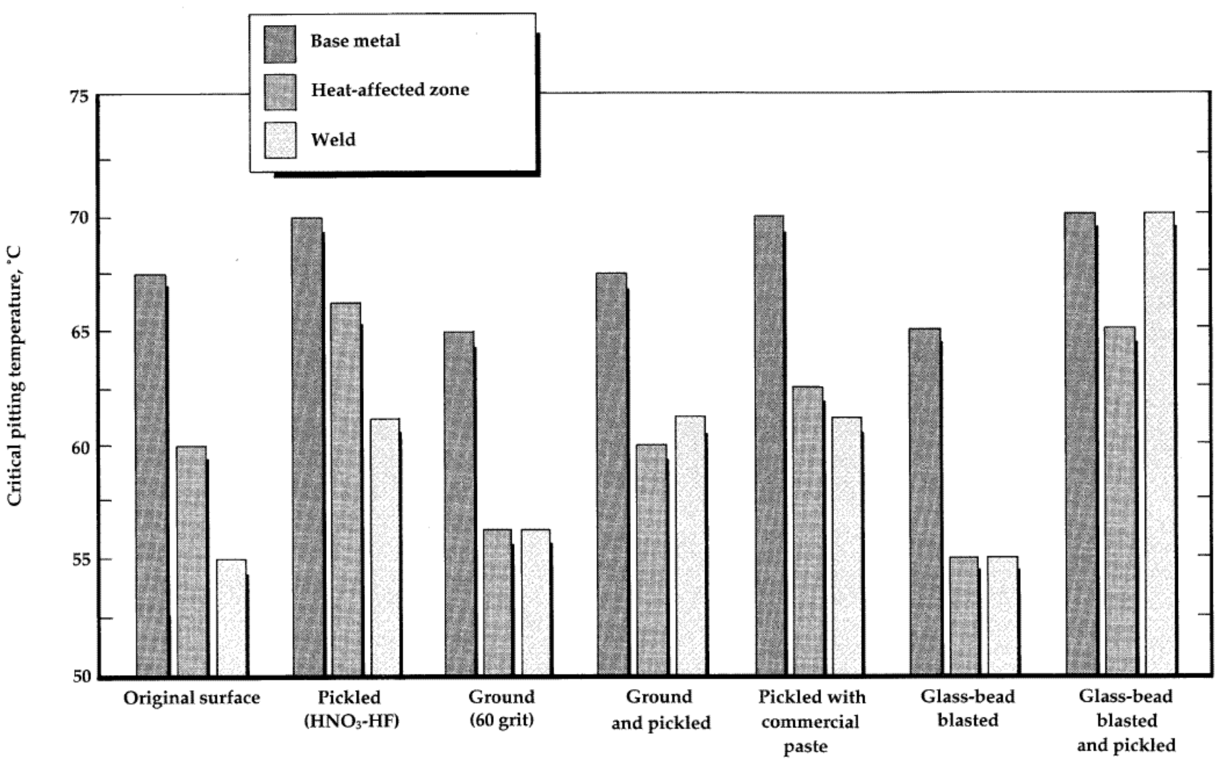

FIGURE 5 – Critical pitting temperature in ferric chloride (per ASTM G48) in base metal, HAZ and weld areas of UNS N08926 with different surface finishes /12/

CORROSION RELATED DEFECTS ENCOUNTERED DURING COMMISSIONING

As a material testing and consulting institute we often see the worst cases when it comes to fabrication defects that are observed during final commissioning. The key questions are possible consequences and remedies to re-establish the surface.

A typical defect type is mechanical scratches or tool marks like those shown in Figure 6. Since this kind of defect often involves micro crevices it is unacceptable in an industry where cleanliness is a key issue. Besides from compromising the cleanability, the crevice significantly lowers the resistance against chloride-induced corrosion. Depending on the severity of the micro cavities and the accessibility the surface, different methods may be considered for re-establishing the surface. Mechanical grinding to remove the defect is the first choice. However, on-site grinding should always be carefully planned to ensure complete removal of the grinding dust, since this could otherwise introduce a secondary problem.

Grinding should preferably be followed by pickling and passivation in order to dissolve any micro slag particles uncovered by the grinding process. Pickling without prior grinding might be considered if it can be demonstrated (e.g. by corrosion testing) that the cavities are "opened", and thereby made less susceptible to corrosion as a result of the chemical treatment.

Iron contamination is another frequent issue that may occur as a result of tool marks or grinding dust in the fabrication area, Figure 7. Except from the formation of rust, the stainless surface is usually unaffected unless the environment is simultaneously highly contaminated with aggressive compounds like chloride. In that case micro pits may be observed in the surface. In most cases an acidic decontamination is sufficient for removal of the iron and rust products.

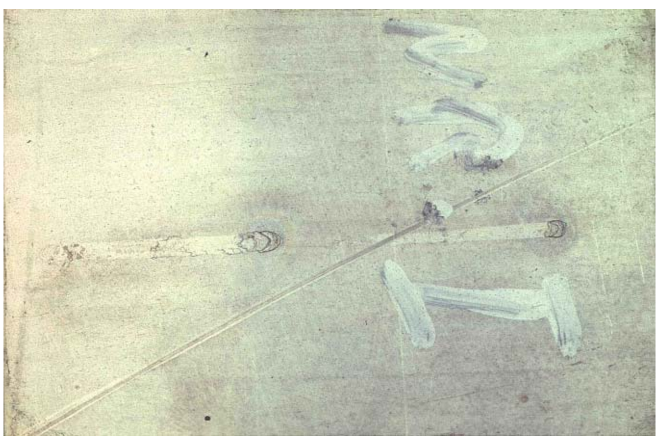

FIGURE 6 – Mechanical scratches on stainless steel surface.

FIGURE 7 – Iron contamination from airborne grinding dust on the exterior of tubing.

It has been shown that severe heat tints from welding have a negative influence on the pitting resistance of stainless steel, Figure 8. This is further confirmed by numerous corrosion failures where through-wall pitting developed in heat tinted welds or HAZs after a short exposure period. For this reason it is common practice to specify maximum allowable heat tint levels of welds according to colour reference atlases /8,9/. When proper shield gas protection has been applied during welding, there is usually no need for additional post-treatment. In cases where severe heat tinting occurs and the welds are free from geometrical defects (like incomplete root penetration) pickling may be applied. However, a quality level that obviates pickling should always be aimed at, since this treatment affects the surface roughness and may be quite complicated to perform in a fully completed plant.

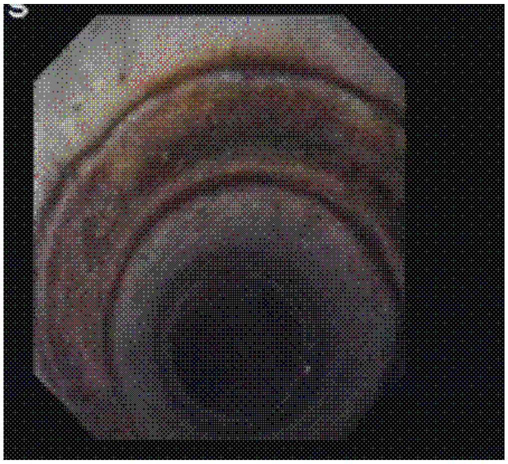

FIGURE 8 – Severe heat tinting in circumferential weld as seen with endoscope.

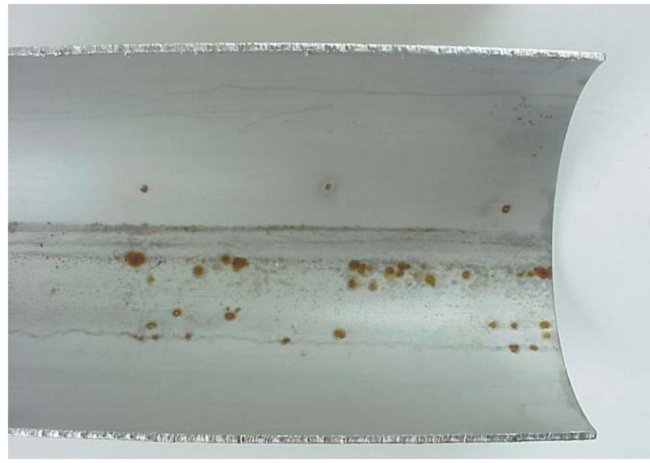

FIGURE 9 – Rust spot on the inside of a sensitized tube.

When sensitization is observed, it is usually a result of inadequate degreasing prior to welding. However, in few cases this phenomenon has also been ascribed to improper procedures during casting or fabrication of e.g. tubes from semi-finished plate products. Figures 9 and 10 show extreme examples of longitudinally welded tubes that were severely sensitized, possibly due to incomplete lubricant removal prior to annealing during tube fabrication. The problem was recognised as rust and soot contamination during the final endoscopy of the circumferential tube welds. Metallographic cross sections and corrosion testing according to ASTM A262 revealed sensitization to a depth of 50-100 µm along the inner tube surface, Figure 11. On this basis, there was no other possibility than replacing all the tubes in order to avoid the possibility of intergranular corrosion. Pickling was not an option given the depth of the affected material.

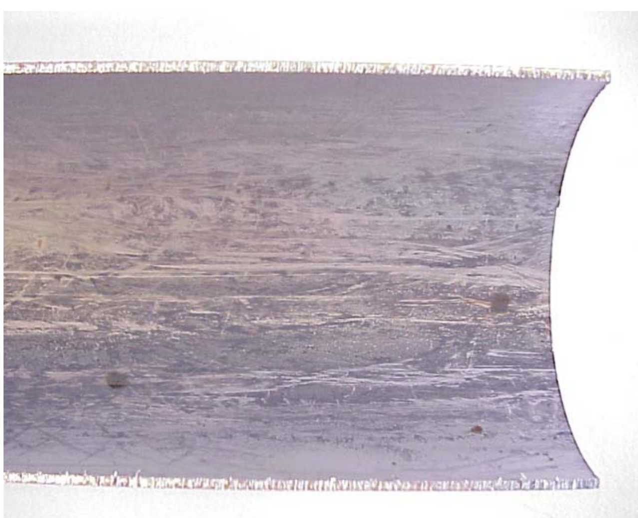

FIGURE 10 – Soot contamination on the inside of a sensitized tube.

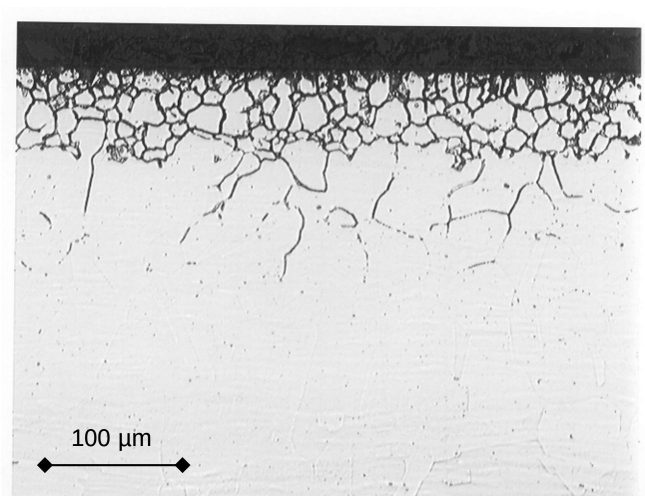

FIGURE 11 – Cross section along inner side of sensitized tube. El. oxalic acid etched.

The above examples of fabrication defects undoubtedly have a negative influence on the corrosion resistance if not dealt with before final commissioning. However, we seldom observe such defects as the prime cause for corrosion failures in systems operating at the nominal service conditions. In most cases failures are either related to improper conditions during hydrotesting or unforeseen changes towards more aggressive service conditions, e.g. higher temperature. Although some of the mentioned defect types may appear insignificant in this respect, there is no doubt that such defects lower the tolerance against corrosion and compromise the hygienic requirements.

CONCLUSIONS

Stainless steels for processing plants in brewery, dairy and pharmaceutical sectors are normally specified as either AISI 304 or AISI 316L type material. When supplied from the steel mill, the material is documented with a certificate. This certificate ensures the fulfilment of the most crucial parameters affecting corrosion resistance, such as chemical composition, microstructure and surface condition. During subsequent fabrication of the equipment there are several risks of compromising the corrosion resistance unless the basic guidelines for stainless steel are strictly followed. The paper has reviewed the most common aspects that might impair the corrosion resistance of the final equipment. On this basis, a number of important issues to ensure optimum corrosion resistance have been summarised below:

- Carefully specify the requirements for weld and surface quality according to common standards such as ASME-BPE. Ensure that the standards include possible defect types or alternatively specify additional requirements.
- Preserve the original surface as far as possible during fabrication.
- Plan the fabrication process to minimize the amount of subsequent mechanical grinding.
- Specify a maximum allowable heat tint level of welds in order to minimize or avoid the need for post-treatments like grinding and pickling.
- Ensure complete draining after hydrotesting or, alternatively, use high purity water for this purpose.
- Always perform a final decontamination (or passivation) to remove particulate contaminants, but do not rely on this treatment as a measure that removes coarse defects related to surface finishing and welding, or provides a permanent improvement of the corrosion resistance.

REFERENCES

1. Jan Elkjaer Frantsen, Troels Mathiesen, Specifying Stainless Steel Surfaces for the Brewery, Dairy and Pharmaceutical Sectors; Paper 095373, NACE Corrosion 2009.
2. ASTM A 480 / A 480M - 01; “Standard Specification for General Requirements for Flat-Rolled Stainless and Heat-Resisting Steel Plate, Sheet, and Strip”.
3. ASME Bioprocessing Equipment, ASME BPE-2007.
4. Jargelius R. F. A. et al.; Evaluation of the EPR technique for measuring sensitization in type 304 stainless steel; Corrosion, 1991, vol. 47, no 6, pp. 429-435.
5. Troels Mathiesen, Torben S. Nielsen, Jan Elkjaer Frantsen, Influence of various surface conditions on pitting corrosion resistance of stainless steel tubes type EN 1.4404, Paper 06095, NACE Corrosion 2006.

6. Torben S. Nielsen, Troels Mathiesen, Jan Elkjaer Frantsen, Pitting corrosion resistance of electropolished seamless stainless steel tubes type EN 1.4404, Paper 07194, NACE Corrosion 2007.
7. J.V. Hansen, E. Maahn, The effect of oxygen level in the shielding gas on the root side corrosion resistance of welded stainless steels; Proc. 11th Scandinavian Corrosion Congress NKM 11, Stavanger 1989.
8. Reference colour charts - for purity of purging gas in stainless steel tubes, FORCE Technology report 94.34.
9. Specification for welding of austenitic stainless steel tube and pipe systems in sanitary (hygienic) applications, American Welding Society, AWS D18.1:1999
10. Ericsson, R.; Schön, L. og Wallén, B.; Effect of some oxide removal treatments on the corrosion resistance of 316 stainless steel; 8th Scandinavian Corrosion Congress. Proceedings, Vol. 1 pp. 321-329; 1978.
11. Moayed M.H.; Laycock N.J.1; Newman R.C.; Dependence of the Critical Pitting Temperature on surface roughness; Corrosion Science, Vol. 45, No. 6, June 2003, pp. 1203-1216(14).
12. Tuthill, A.H. og Avery, R.E.; Specifying stainless steel surface treatment; NIDI Technical Series No. 10068; 1992.
13. Yu Zuo, , Haitao Wang and Jinping Xiong; The aspect ratio of surface grooves and metastable pitting of stainless steel; Corrosion Science, Vol. 44, Issue 1, January 2002, pp. 25-35.
14. G.T. Burstein and P.C. Pistorius, Surface Roughness and the Metastable Pitting of Stainless Steel in Chloride Solutions; Corrosion, May 1995, pp. 380.
15. A. Burkert, K. Schilling, A. Heyn; Einfluss der Schleifbehandlung auf das Korrosionsverhalten von Chrom-Nickel-Stählen; Materials and Corrosion, Volume 55, Issue 10, pp. 787 – 793.
16. JC Tverberg; Conditioning of stainless steel surfaces for better performance; Stainless Steel World, April 1999, pp. 36-41.
17. Lena Wegrelius and Birgitta Sjödén, Passivation Treatment of Stainless Steel; ACOM 4-2004, Outokumpu Stainless AB.
18. Karlsson, A. og Olsson, J.; Atmospheric corrosion of stainless steel; 7th Scandinavian Corrosion Congress, Trondheim, pp. 71-86, 1975.
19. D. Wallinder, I. Odnevall Wallinder, and C. Leygraf; Influence of Surface Treatment of Type 304L Stainless Steel on Atmospheric Corrosion Resistance in Urban and Marine Environments; Corrosion, vol. 59, nr. 3, pp. 220-228, 2003.
20. Houska, C.; Stainless Steels in Architecture, Building and Construction; Reference Book Series, No. 11024. Nickel Development Institute (NiDI), 2001.