Increasing the corrosion resistance of stainless steel

It is common knowledge that stainless steel cannot be endlessly exposed to chemical or maritime environments without corrosion eventually occurring. For example grades such as AISI304 are not used near the coast and AISI316 has a limited application in chemical plants. New technologies have been developed that substantially increase the resistance of the oxide layer, significantly increasing corrosion resistance. This article will address this extensively after providing information regarding the condition of the surface.

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In addition to the natural, relatively high resistance that the passive oxide layer of stainless steel offers against all kinds of external influences, there is another important aspect and that is the roughness of the surface. The smoother the surface, the better the corrosion resistance and that is, among other things, related to dirt and dust settling into the pores of a rough surface. A rough surface has sometimes 2 to 3 times more surface area than a polished surface, translating into more interaction with the surroundings. A good example of this is stainless steel AISI316 parking posts along the coast. These posts are often ground with 240-grit material, but the top of the post is polished. Over time, the posts show heavy rusting, also called "tea stains" due to their relatively rough surfaces, while the polished tops seem to have no issue with this. However, the same material is used which means the surface topography plays a significant role. On a rougher surface, deeper deposits of dirt and dust can occur that pose a danger to the material. In many cases, this can lead to corrosion known as 'under-deposit attack'. Stainless steel must be able to 'breathe' because this material exists thanks to oxygen. In the event of dirt and debris deposits, the relatively large oxygen molecules have more difficulty reaching the material than the small chlorine ions that can 'creep' beneath the deposits. There, they can make contact with the material and result in rust products, contaminating a substantial portion of the stainless-steel surface. As explained before, this contamination results in 'tea stains'. For this reason, it is important that roughly sanded surfaces are never exposed to such environments in order to prevent this type of corrosion.

Wet blasting

For this reason increasing importance is being placed on the wet blasting of stainless steel, because this creates a surface that offers almost no opportunity for dirt and debris to attach to the surface. A well-known term is PureFinish, which was developed decades ago for treating the metals of aeroplane components and is now used for industrial purposes. However, such surfaces are still not as smooth as those that are polished. The advantage is that bacteria can be removed more easily than on a polished surface. That does sound contradictory and therefore requires some explanation. On a polished surface, vacuum and adhesion allow bacteria to bind particularly well. This is sometimes called the "leech effect". For this reason, wet blasting forms a great compromise between polished and ground surfaces. The roughness achieved with wet blasting lies on average between Ra = 0.3 en 0.6μm. The Soil Retention Index (SRI) value after wet blasting appears to be the most preferable when compared with all other surface treatments/ finishes. This concerns the value of the quantity of impurities that remain on a surface after a cleaning has taken place. Furthermore, something called a peening effect occurs and that means that a slight accumulation of pressure occurs in the surface. This also decreases the sensitivity to stress corrosion. An advantageous coincidence is that this wet blasting technique has almost no environmental impact. Image 1 shows a piping component that has been treated with this technique.

Image 1. Stainless steel piping component treated with PureFinish wet blasting (photo from Innomet b.v.)

However, it should be noted that no free-iron contamination occurs on the surface during situations such as the production of a stainless-steel component. Should this occur by accident, these areas must be pickled for the purposes of thoroughly removing this free iron.

The oxide layer

The passive oxide layer on stainless steel is also called the chromium oxide layer for the sake of convenience. However, upon closer inspection, this is much more complicated than it sounds. This layer, which is only about 15 nanometres thick, consists of 5 thinner layers, each with its own chemical composition (Image 2). To be thorough, it should be mentioned that 1 nanometre (nM) equals 10^{-9} metre and that is the thickness of just a few atomic layers. What stands out is that the bottom three layers contain iron bonds, in addition to chromium bonds. The top two layers contain no iron bonds, only chromium bonds and water caused

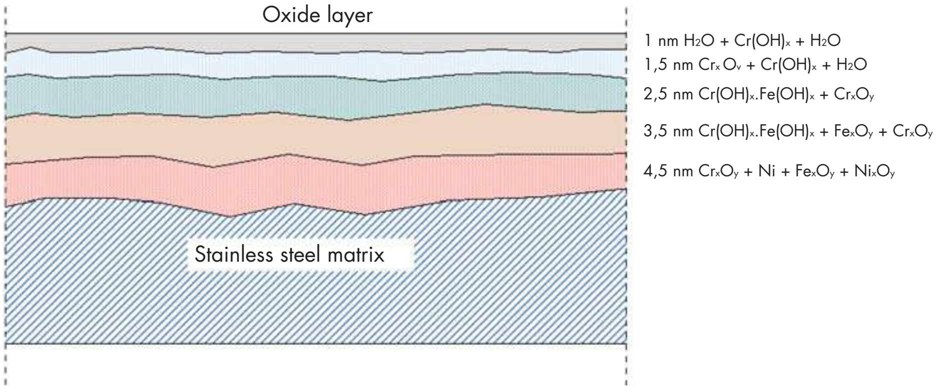

Image 2. Graphical representation of the complex oxide layer of stainless steel.

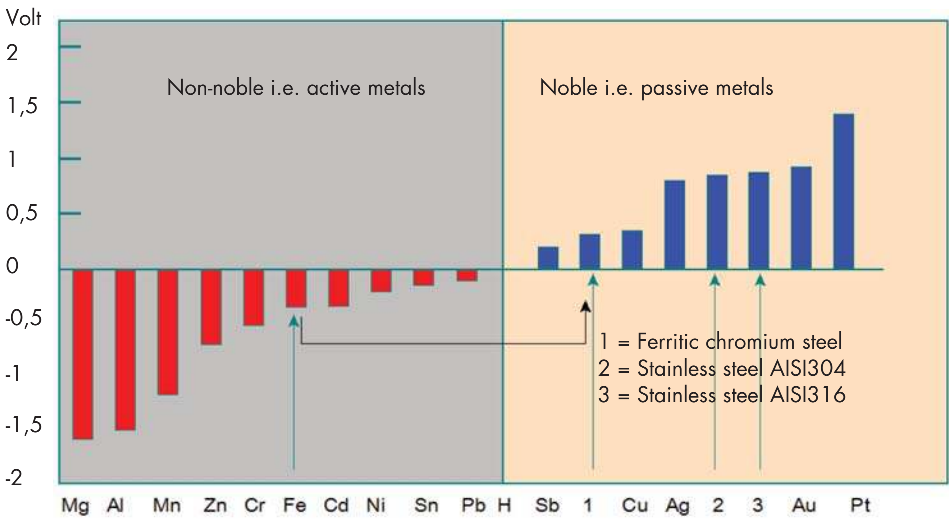

Image 3. The series of noble metals that is also called the potential series.

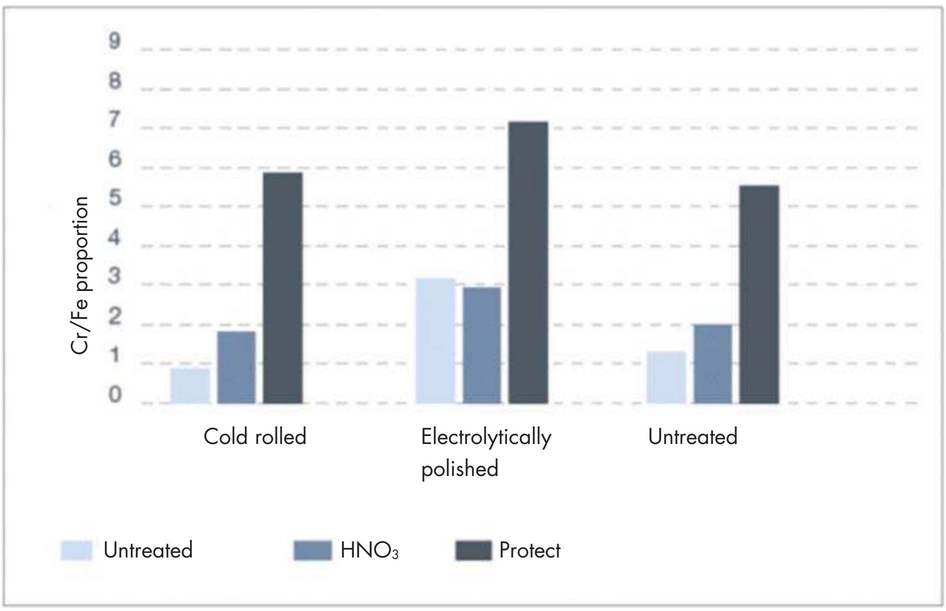

Image 4. The ratio of chrome to iron in the oxide layer after various treatments (source: Poligrat GmbH).

by crystallization. An immersion technique has been developed for making the bottom three layers as iron-free as possible using special organic acids. This is called the Polinox Protect treatment that was developed by the German company Poligrat. It will be clear that lowering the iron content of the oxide layer will make a highly positive contribution to the final corrosion resistance. An additional treatment has been developed to complement this surface technique that will increase the positive potential of the stainless steel even further which is called thermochemical treatment (TC). Attention will be given to this treatment in this article as well.

In the series of noble elements, one can see that iron is not a noble metal, with a negative potential of -0.44 Volts. Once an alloy is created of iron and 12% chromium, this material shifts into the passive zone, somewhere between antimony (Sb) and copper (Cu). As soon as the chrome content is further increased and nickel is added as well, then these types shift further to the right and settle between silver and gold.

This is shown in image 3. However, it should not be assumed that stainless steel belongs to the noble metals, because this only applies to the oxide layer. If this oxide layer collapses due to something like excessive chemical stress, which renders it irreparable, this exposed area will react to oxygen in the same way as non-alloy iron or steel.

Image 4 shows the ratio between the elements chromium and iron, which are contained within the oxide layer.

In the untreated state, this ratio appears to be more or less 1 and that means that both elements are equally present quantitatively. As soon as the surface is passivated with nitric acid (HNO_3), the ratio between elements becomes more favourable, since there is almost twice as much chromium present as iron. With the Polinox Protect treatment, this ratio becomes even more favourable towards chromium which has a positive influence on corrosion resistance. Image 4 shows the ratio for untreated, electrolytically polished, and 240-grit ground stainless steel.

AISI304 type stainless steel is never used near seawater, but as soon as the ratio between chromium and iron content in the oxide layer becomes favourable, good potential applications appear. Image 5 shows the pitting potential in sea water per different type of surface treatment. Here, it is assumed that the seawater is at ambient temperature. Therefore, the pitting potential indicates the electrical potential at which pitting corrosion begins.

There are various assumed conditions for these measurements, specifically 2b and 3d finishing, a surface ground with 240-grit. A shot-peened and pickled surface and an electrolytically polished surface are assumed as well. The red bars indicate the pitting potential of the common condition that

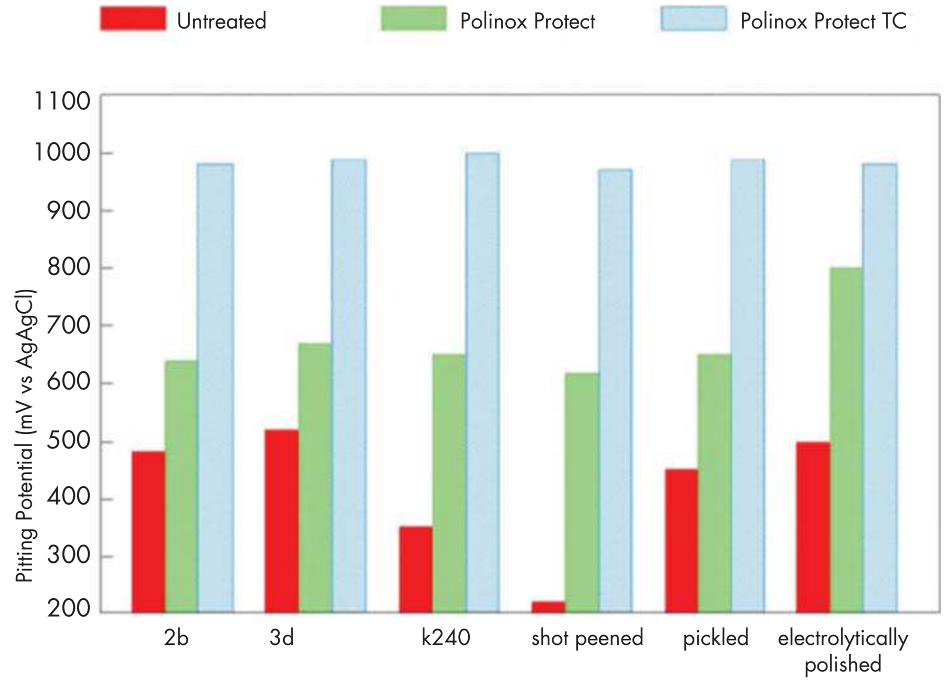

Image 5. Pitting potential of AISI304 stainless steel in seawater (source: Poligrat Gmbh).

is typically encountered in practice.
It is worth noting that the pitting potential substantially declines as soon as the material is sanded with 240 grain or shot peened. That is entirely in line with the previous statement in this article that a rougher surface offers less corrosion resistance than a smooth surface.
The green bars represent the pitting potential of AISI304 that has been submerged for a number of hours in Polinox Protect. The blue bars indicate this potential after the additional thermochemical treatment (TC) has been done. Organic acids are natural acids that can simply be disposed of into the regular sewage system.Further elaboration on this subject is not entered into in this article.
The minimum corrosion potentials of stainless steel that are necessary to prevent corrosion in various environments are:

- Rural environment: 150 – 200 mV
- City environment: 350 – 450 mV
- Coastal region: > 650 mV

The last value explains why stainless steel corrodes so quickly in coastal environments. For this reason, the removal of iron bonds is important to significantly increase the potentials. Following are recommendations for the use of AISI304 stainless steel in exterior applications, depending on the various surface treatments.

- Electrolytically polished: this makes AISI304 resistant in rural and urban areas;
- Pickling: this makes AISI304 resistant in rural environments, but not resistant enough for urban areas and coastal regions—this is why at least AISI316 is recommended in these cases;

Image 6. AISI304 motor cap treated with Polinox Protect after four years of use. Photo Poligrat.

- Polinox Protect treatment: it makes AISI304 sufficiently resistant for rural and urban environments; this goes for coastal regions as well, but in that case, it is preferable to use AISI316 instead;
- Polinox Protect + TC: makes AISI304 resistant in all environments, including coastal regions and maritime environments.

Car manufacturer Rolls Royce has developed car types with AISI304 motor caps that have been treated with Polinox Protect. After four years of testing in corrosive environments, from tropical maritime environments to winter conditions with heavy road salt, it turned out that this stainless-steel type worked out well in combination with the Polinox Protect treatment, both externally and internally (image 6).
Intensive testing has also been performed in an environment containing chlorides with 240-grit ground, stainless steel of the chromium steel qualities EN 1.4016 (AISI 430), EN 1.4301 (AISI 304), and EN 1.4571 (AISI 316Ti). The samples were exposed in the untreated and passivated condition, as well as with a Polinox Protect treatment, and furthermore, with an additional thermochemical treatment (image 7). One sees that the simple chromium steel acquires a potential after the Polinox Protect treatment that is somewhat higher than that of the AISI316Ti in the untreated condition. The pitting potential of AISI304 (1.4306) is even 60 mV higher than that of the 316Ti (1.4571) in the untreated state. The thermochemical treatment sets the bar higher again—significantly so—before pitting corrosion will occur. The rest will be further explained in this graphic.

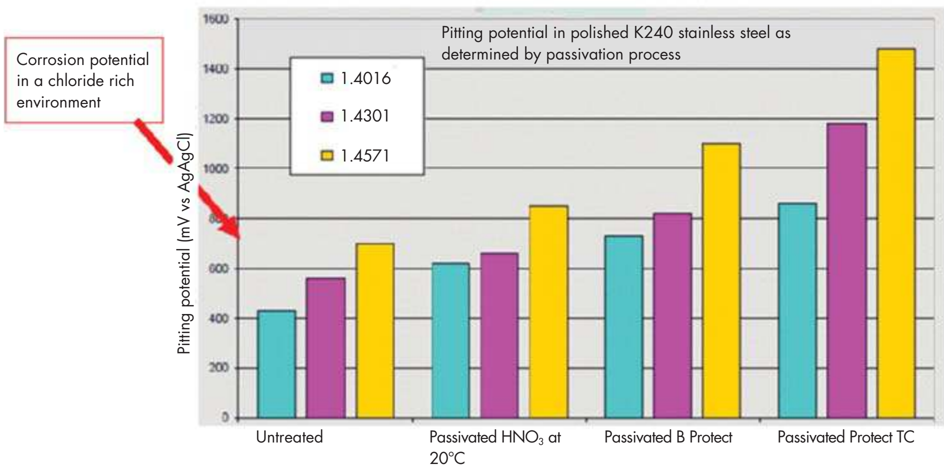

Image 7. Pitting potentials of various stainless-steel types, depending on the passivation (source Poligrat Gmbh).

Image 9. The right half is nearly free of iron bonds which makes it look as if it has been pickled (photo: Poligrat).

Image 10. Untreated AISI430 fish hooks, treated fish hooks on the right (source: Poligrat)

Image 8 shows the pitting potential of various stainless-steel types, specifically AISI 430 (1.4016), 304 (1.4301) and 316Ti (1.4571). The red bars represent the potentials of 240-grit ground surfaces. The green bars represent the potentials of a Polinox Protect treatment and the blue ones represent an additional TC treatment. Here, it is also evident to what extent stainless steel can be improved for optimal resistance to corrosion. Even the resistance to stress corrosion is enormously increased with this.
During the welding of stainless steel, temperature colours often appear caused by, amongst others, the presence of iron in the oxide layer. For this reason, testing is done on a comparable sample. The right half of this has been immersed in a bath of organic acids (50°C) and the results can be seen in image 9. The whole creates the impression that this half has been pickled, but that is not the case.
If, during the production of stainless steel, some free iron accidentally reaches the surface, this will not be removed through wet blasting, however it will after the Polinox Protect treatment. It is important to remember that prevention is better than having to fix it.
Fish hooks are typically made of ferritic chromium steel, because this material possesses better mechanical properties. Surgical tools are mostly made from martensitic stainless steel, because it is more wear resistant and therefore, remains sharper. Both alloys have a highly limited corrosion resistance, but with the removal of the iron bonds from the surface, there is much better corrosion resistance. Fish hooks made of 430 ferritic chromium steel rust fairly quickly in seawater, but with a treatment in a Polinox Protect bath of 60°C, followed by a TC treatment at 140°C, these products can last for 500 hours without issue (image 10). This applies for martensitic components as well.
In short, it can be proposed that removing iron as much as possible from the oxide later will lead to the following results:

- Substantially increasing the resistance to pitting corrosion;
- Lasting nearly twice as long before stress corrosion occurs;
- More resistance to the occurrence of temperature colours during welding;
- Removing rust, free iron, contaminants, and corrosion products;
- Restoring the corrosion resistance of welding seams and heat-influenced areas;
- Keeping the surface in optimum condition;
- Restoring mechanically damaged areas;
- Combats roughening.

A thermochemical treatment (TC) is performed at high temperatures, which thermally enhances the oxide layer, resulting in a further increase of the potential of the already "purified" oxide layer. TC involves a short treatment of 5 to 10 minutes at 140°C – 200°C, depending on the alloy and the structure. A thin layer of haematite that is extremely corrosion resistant will appear on the surface. This will further increase the electrical potential and, in turn, the corrosion resistance as well.
The combination of PureFinish and the above treatment will lead to an extraordinary resistance to corrosion. Not to mention, these processes can also be used individually. If this unique combination is used, the condition applies that the PureFinish treatment must be performed first. The complete improvement of corrosion resistance can be explained by the fact that the surface offers little room for dirt and debris to settle or for damaging deposits and furthermore, a higher potential is achieved on the surface as well. For this reason, it is expected that this unique combination will lead to a greater range of applications for the well-known AISI304 and 316 qualities. However, the ferritic and martensitic qualities will also perform much better thanks to these techniques and that will appeal primarily to medical professionals, who have to work with such materials the most. The company that has exclusive access to this combination of techniques in the Netherlands is the Metalfinishgroup in Joure. This service will be available beginning in November 2017.

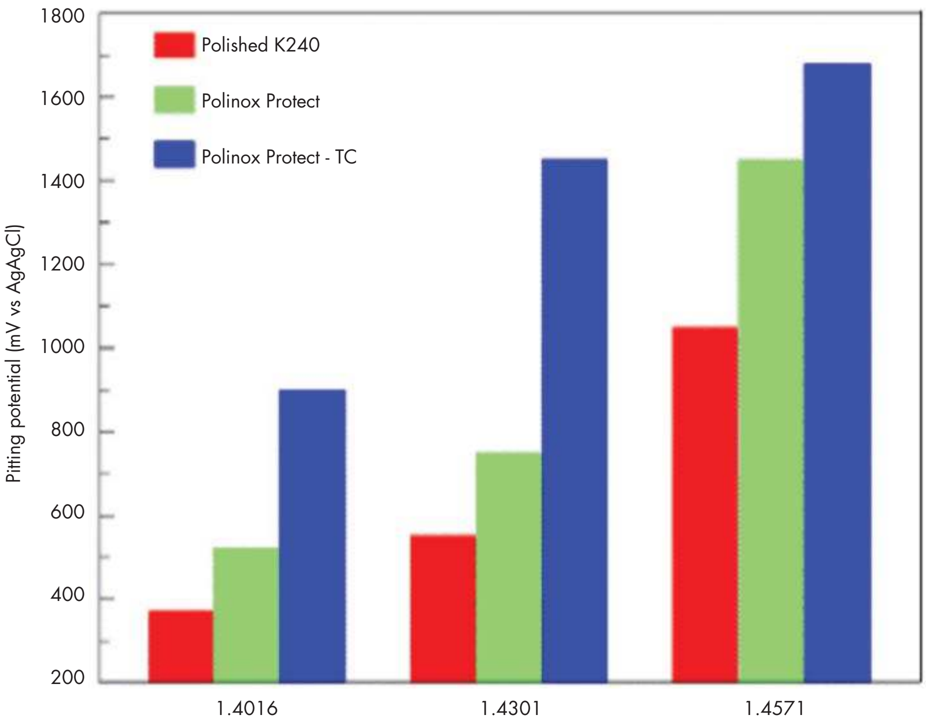

Image 8. Pitting potential of chromium steel, stainless steel, and a nickel layer in seawater with 20,000 ppm chlorides (source: Poligrat Gmbh).

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