

Characteristics and properties of stainless steel (3)

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The types of stainless steel can not only be attacked by threats from the outside but also from the material itself. A professional selection of the materials is a first demand and also its processing needs the due attention.

Besides the threats from the outside (MK 3) there are also threats from the inside which can be very active and dangerous. A lot of people do not realize that there are also threats for the resistance to corrosion because of undesired effects from the stainless steel itself. The biggest danger which can arise is the formation of chrome carbides, which are bonds between chrome and carbon.

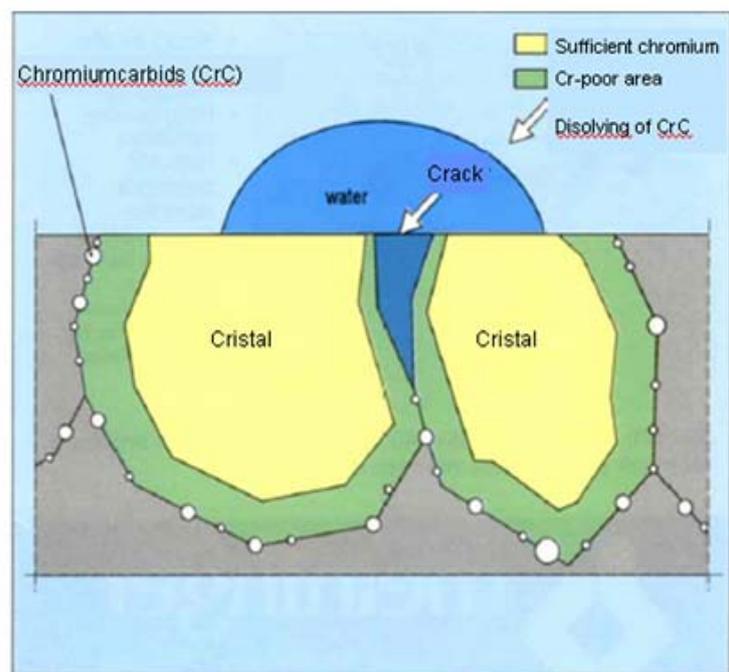
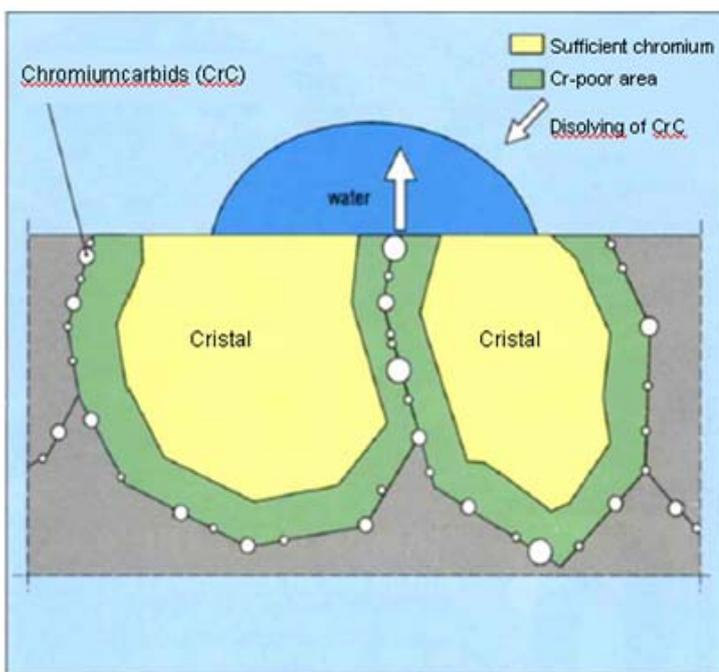
Threats from the inside

Carbon has always the tendency to form carbides with the chrome which is present and these have a very negative potential in an electrolyte. This means that similar anodic spots always dissolve in an electrolyte. Chrome forms a thick tenacious chrome-dioxide hide, which protects stainless steel from corrosion, but if carbon gets in its vicinity than it can happen that chrome is alloyed carbon (frame). Chrome, which is not alloyed to oxygen, can also alloy with carbon, from which develop thin secretions

(precipitates) of chrome carbides. Usually these precipitates separate on the grain-border. Chrome, which is locally alloyed to carbon, sees to it that there is too little chrome left locally to the matrix to stay passive. This spot, which is poor in chrome, becomes active and the consequence is pit corrosion.

This unwished thermal reaction works in the best of ways under a thermal constraint, like for example the welding process. These separations (i.e. chrome carbides) happen mainly in the area influenced by the heat. In practice, sometimes a very sharp corrosion can be seen near the welded spot (knifeline attack). In order to solve this problem an option would be to glow the welded spot so that all the carbides will dissolve again into the main material. After the thermal shock this dissolved situation will stay under control and no pit corrosion problems should be expected. In practice, however, this doesn't seem to be so easy, because this dissolving glowing not always possible. For this

reason two mechanisms have been elaborated which can resolve the problem. The first mechanism can be found in the quality AISI 304L/316L (low carbon) where the content of carbon is made so low that the chrome carbides cannot or can hardly originate. In this case it is, however, important that products containing carbon will be kept away from this stainless steel, mainly while welding. The carbon content is namely so unnaturally low that the material has an urge to absorb it (thermodynamic law). Another mechanism can be found with stainless steel AISI321/316Ti. Some titanium has been added to these qualities in order to 'capture' this carbon. The affinity (in other words the power of attraction) of carbon and titanium is bigger than the affinity with chrome. For this reason titanium will 'marry' carbon quicker than chrome. In this way, it is not chrome carbides which originate but titanium carbides which are scattered finely and disperse. These small titanium carbides precipitates are



Schematical impression how chromiumcarbids arise on the grainboundaries.

Schematical impression how chromiumcarbids dissolve

therefore not an obstacle for stainless steel. The addition of some niobium is also known as a way to achieve the same effects as with the titanium element. Actually, the undesired chrome carbides form the greatest threat from the inside. With some attention it can be avoided that problems arise from there. Other threats, like the formation of other complex precipitates and inside stresses which can cause stress corrosion, are not treated in this article.

Inter-crystalline corrosion

The term inter-crystalline corrosion comes from the fact that the undesired chrome carbides nestle on the grain border, because such a crystal border is a perfect sprouting place for similar precipitates. The means dissolves the base carbides (picture. 3) and corrodes the area which is around these chrome carbides because locally the content of chrome is under the required 12%. In this way, the metal crystals will lie loose and this will cause an inter-crystalline crack (picture 4) . A little pulling stress in the material facilitates the formation of a crack, enormously. Austenitic stainless steels are usually supplied in the melting glowing condition, i.e. heating (dissolving glowing) at +/- 1.050 °C and afterwards quenched in water or pressed air. In this way, all carbon will basically remain dissolved in the material so that it will not have any negative impact on the resistance to corrosion. If the material is heated again to the temperature range of +/- 550 °C to +/- 850 °C (for example by welding or low stress heating) carbon has a big tendency to combine with chrome and so chrome carbides will originate on the grain border. A heat treatment of a stainless steel in this critical temperature area is called sensitizing. Experience teaches us that a carbon content of less than 0.05 % in most cases is enough to sufficiently prevent inter-crystalline corrosion after welding. In some cases, however, in case the medium leads to it it is important that the carbon content is lower than 0.03% in

order to prevent inter-crystalline corrosion. These kind of environments are amongst others concentrated nitric acid or mixtures which contain hydrogen fluoride. Because of the employment of a protective gas during welding and also because of welding of very thick-walled boards, the requirement is to have an even lower

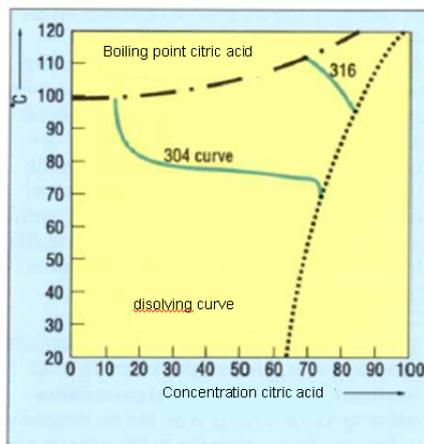
Elements of impact

Impact of elements possibly present in stainless steel:

- **Natrium (N)** : Natrium increases the strength of austenitic stainless steels and influences the structure in the same way as nickel. Until a certain level, it can even replace nickel as long as the structure is austenitic.
- **Copper (Cu)**: copper improves the resistance to corrosion in certain acids. Sometimes, addition of copper can lead to precipitation hardening.
- **Titanium (Ti) and Niobium (Nb)**: these elements stabilize the stainless steels because they bind carbon whereby the risk of inter-crystalline corrosion decreases strongly. The affinity of carbon with titanium is higher than the affinity with chrome, whereby there is a low risk of formation of undesired chrome carbides which usually set themselves on the grain border what can lead to inter-crystalline corrosion. Titanium- and niobium carbides will distribute themselves on the matrix in a disperse way and in this way the risk of inter-crystalline corrosion can be neglected.
- **Manganese (Mn)** accelerates the deformation characteristics of stainless steel at high temperatures and besides this the mechanical characteristics are improved. Manganese is an austenite former and therefore can be used as a substitute of nickel, as it is the case with AISI200 stainless steels.
- **Phosphorus (P) and Sulfur (S)**: in principle phosphorus and sulphur are always undesired elements and will always have to be avoided for their polluting effect.

content of carbon. Inter-crystalline corrosion takes mainly place in acid

environments, but the experience has taught that also seawater can be a cause, wherefore it can be said that neutral media do not have to be totally harmless in this connection. The explanation can be the local pH reductions caused by crack or pit corrosion.



Isocorrosion 0,1 mm/year for stainless steel in citric acid

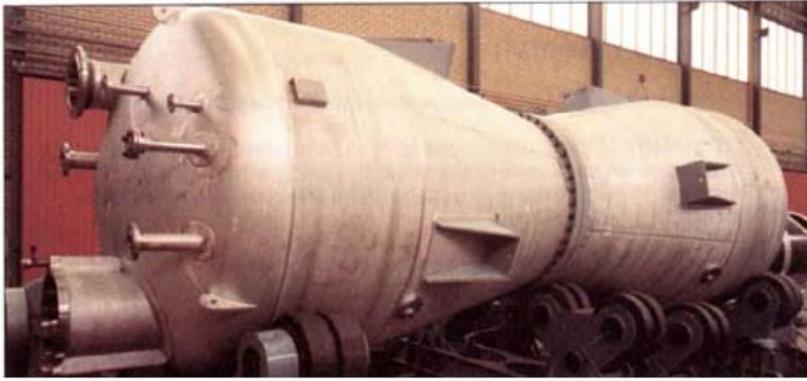
Tests

The most common methods to test the resistance of stainless steel against inter-crystalline corrosion are:

- the Strauss test
- the Huey test

When doing the Strauss test (DIN 50914, ASTM A262 practice E) the samples are immersed in a boiling solution of copper sulfate and sulfuric acid with small particles of copper in it, during 15,20 or 24 hours (depending on the norm). The evaluation consists of the samples being bent in a certain way and after this the surface is inspected.

With the Huey test (ASTM A262) the samples are immersed for five periods of 48 hours in boiling nitric acid of 65%. The corrosion speed is defined per period as function of the loss in weight. It has, however, to be highlighted that the results of this test are mainly applicable to strongly oxidizing situations and therefore can mislead on other environments. Reading it in the right way, it can be said that the results will indicate whether the material has been welded correctly. The Huey test may not be used to compare the resistance to corrosion of the various stainless steels or to predict the resistance to other types of corrosion.



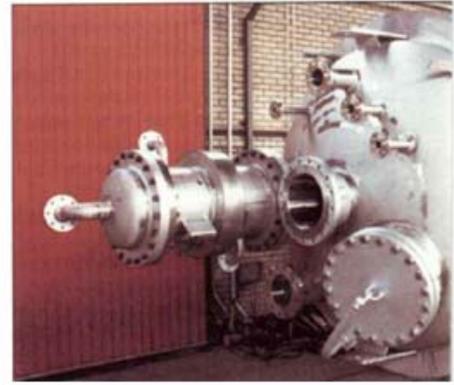
Composed reactors of 316L for the plastic industry

For certain corrosive media iso corrosion diagrams can be set up for stainless steel. In such diagrams the horizontal axis represents the concentration and the vertical axis the temperature of the medium. Very many diagrams have been created during the years and in picture 5 only one example is given. In the area under the curve the thickness corrosion for the specific type of stainless steel is less than 0.1 mm a year, wherefore it can be said that the material is suitable to be used in that specific situation.

Weldability

The various types of stainless steels which have been treated have also different welding characteristics. They all have in common one thing: the surfaces need to be perfectly cleaned before welding in order to obtain a good resistance to corrosion after welding. This is also the reason wherefore, if the welding does not occur under a sufficiently inert gas, the surface needs to be treated afterwards through, for example, staining, grinding, brushing or sand-blasting. Mainly with sand-blasting one should make sure that new sand is taken, because used sand in practice usually contains particles of steel, which are 'bombed' in the steel surface while blasting. It is not needed to prove that the surface would rust because of this. The weldability of ferritic stainless steel is tightly linked to its chemical composition and especially to the proportion between carbon and the quantity of chrome. For this reason, when welding ferritic stainless steel a distinction has to be made between old and new types. When welding the old types there is a risk of brittling, because of the high carbon/chrome proportion, since martensite can be formed in the zone influenced by the heat. The precipitation of chrome carbides on the grain border is also possible and this leads to a higher risk for inter-crystalline corrosion. In order to bring

the resistance to corrosion at level, it is required that the material undergoes a heat treatment. Due to the low C/Cr proportion in the new types of ferritic stainless steel, the structure remains totally ferritic at all temperatures. Because of the very low components of carbon and nitrogen and because of the presence of stabilizing elements, there is no risk of precipitation of chrome carbides. This means that there is no risk for inter-crystalline corrosion to arise after welding. When welding a board thinner than 3 mm there is no need of practicing a heat treatment; with thicker boards, on the contrary, it is advisable in connection with the better toughness and the processability of the material. All ferritic qualities are sensitive to grain growth in hot treated areas and for this reason the hot load will have to be kept as low as possible while welding. The welding material may be both austenitic and ferritic. Austenitic materials give a much tougher welding and this is mainly an advantage for heavier welding joints. The ferritic-austenitic stainless steel qualities, in general, have better welding characteristics than the pure ferritic ones. There is, though, a certain tendency to brittleness in the welding joint and for this reason it is advisable to use austenitic welding materials. Ferritic-austenitic qualities have also a tendency to grain growing which leads to brittling and to reduction of the resistance to corrosion in the area which is influenced by the heat. This unwished phenomenon, which arises because of the austenitic formation, can be prevented by quickly chilling after welding. In this way, even the area surrounding the weld can become completely ferritic. In this area the crystals are relatively big and there are even precipitates on the grain borders. The piece of work has therefore to be hot worked in order to have satisfying results. The tendency to grain growth in the area influenced by the heat decreases if



Reactor with heat exchanger

the proportion austenite/ferrite decreases. In general, austenitic stainless steel is easily weldable and it is not needed to preheat the metals which have to be welded or to give it a heat treatment after welding. However, the highest alloyed types have a certain risk of heat cracks tendency in the weld and for this reason similar qualities have to be welded with a minimum of heat contribution. If manifold welds have to be set one after the other, every single joint should be given the possibility to chill off. The sensitiveness to heat cracks decreases if a small percentage of ferrite is present in the weld. For this reason often welding materials containing some ferrite are used. To be noted that the presence of ferrite decreases the resistance to corrosion, but in such a way that in most cases it is still acceptable. In certain applications like in urea- and acetic acid production, the resistance to corrosion is considerably lower if the weld contains ferrite. In these cases the corrosion will be selective and therefore the ferrite phase will follow. For this reason, in similar environments, completely austenitic welds have to be set using austenitic welding materials. Because of welding, in a certain area the temperature will increase along the weld to a degree where the carbide precipitation will originate (500°C-850°C). Thanks to the fact that modern melting technologies for producing stainless steel can be controlled so easily that the carbon content stays low, after welding there will not be an increased risk of inter-crystalline corrosion anymore. It is suggested to use the qualities of a very low carbon content only at very heavy corrosive conditions and when welding with a high heat contribution because of certain welding processes.



Pipelines in 316L

Suggestions

In many cases damage from corrosion arises because of unsuitable or even wrong designing. Similar damages are completely unnecessary and in principle can be prevented by individuating the corrosion risk while designing. Other general reasons of corrosion damage are unpredicted operational situations. It is, therefore, very important to consider every possible deflection from the planned operational situations when designing and to take the corrective actions which arise from these defects. An installation which is subject to a serious corroding danger, if possible, will be designed in such a way that it can be inspected and cleaned very easily. It is also important that sufficient moisture draining is taken care of, mainly to prevent corrosive media being in the system for a longer period of time. This is even more important if the system is put out of action for a certain time. If a material is only subject to general corrosion it is not difficult to determine the eventual lifetime. The actual corrosion pace can also be measured by regularly determining the wall thickness. Local corrosion (pit-, split- and stress-corrosion) usually happens unexpectedly and therefore can lead to a total collapsing of the system in a relatively short time. When designing in stainless steel, it should always be striven to prevent narrow moisture filled splits because, mainly in environments containing chloride, these can cause split corrosion. Thus, mainly the kind of seal and sealing pressures have to be chosen in such a way that the electrolyte cannot come in between the metal and the sealing. Porous and chloride containing sealings may indeed not be used, and neither can graphite packings, because with stainless steel these can lead to galvanic corrosion. During welding of stainless steel constructions it is important that no pores or splits can be formed and that the welded metal penetrates completely in the weld cavity. Oxidized areas which arise when

welding, will come to a lower resistance to corrosion, especially to chloride corrosion. Therefore, it is so important that similar oxides are eliminated.

In order to bring the corrosion completely at level the surface needs to be radiated or abraded and afterwards to be washed with 20% diluted nitric acid. Through this the surface passivates in an optimum way in a very short time. The risk of having pit corrosion is much higher in still chloride solutions than in streaming ones. For this reason, systems have to be designed in such a way that no still standing waters can come into being, anywhere. If a medium continues flowing, it will also promote that no deposits will arise in the system on the metal surface. In unfavourable situations this precipitation can even lead to deposit corrosion, which is a form of split corrosion. In pipelines for seawater a biological growth can be possible which can lead to corrosion damage. This phenomenon can be fought against by making the stream speed high enough.

Selection of materials

If there are any doubts about which material should be chosen, it is always advisable to check with a material specialist of the supplier. For this reason it is very important to provide the supplier with all the conditions which can play a role, like for example:

- 1 the corrosion medium (also the chemical formula if possible)
- 2 concentration of the medium (if possible also the pH)
- 3 the quantity of pollution
- 4 the temperature

It is also very valuable to provide information related to the kind of installation (possibly with drafts and drawings), description of processes, materials already used, stream speed, temperature oscillation, demands regarding lifetime etc. Basically the more information is provided the bigger the chance that the right

material is chosen!

Conclusion

It goes without saying that there is much more to be said about stainless steel. Development carries on and the offer of many qualities, with their specific advantages and disadvantages, becomes always broader. What should be done is, therefore, selecting correctly the materials together with the expert of the producer/supplier. Correct, in this relation, also means that an expensive solution will not unnecessarily be chosen. In practice it appears that a certain material is chosen in order to be in any case sure that no corrosion will arise. This can be compared with the heavy steam locomotives which were built in former times because there was not enough knowledge about the strength theory, in other words make it so heavy that it will not break. In this way it will not be possible to work in an economic responsible way by 'redesigning' depending on the metal choice. Besides the technical lifetime also the economical duration of an apparatus has to be considered and this is mostly decisive.