

Characteristics and properties of stainless steel (1)

Eng. N.W. Buijs
Van Leeuwen Stainless B.V.

In spite of countless applications there are still too many misunderstandings about stainless steel. What is stainless steel and how can different forms of corrosion be fought against or prevented in a simple way. These are some aspects, that will be treated in three articles in order to better clarify the comprehension concerning stainless steel.

The question is what is understood with the notion stainless steel. In reality, it seems that the term stainless steel is used very often, but that this is a less lucky expression when it is taken as it is, because stainless steel has limitations as to corrosion performances. Due to these limitations corrosion, mostly linked to the oxidation process, can still occur and this is popularly also called rust. Therefore, the term rustproof should be used only for the highest precious metals, like gold and platinum.

Precious means that the metal is in a steady thermodynamic state so that it remains in this mode. Such a metal is also defined passive, because it does not react with its environment. The stability level of a metal in a certain watery environment is also dependent on factors like:

- Redox-potential
- pH (degree of acidity)
- temperature of the solution

In normal conditions stainless steel does not react with its environment so we can say that stainless steel is a passive metal. In those situations in which stainless steel may partially or totally react with its environment, the passivity disappears totally or locally, what has corrosion as consequence.

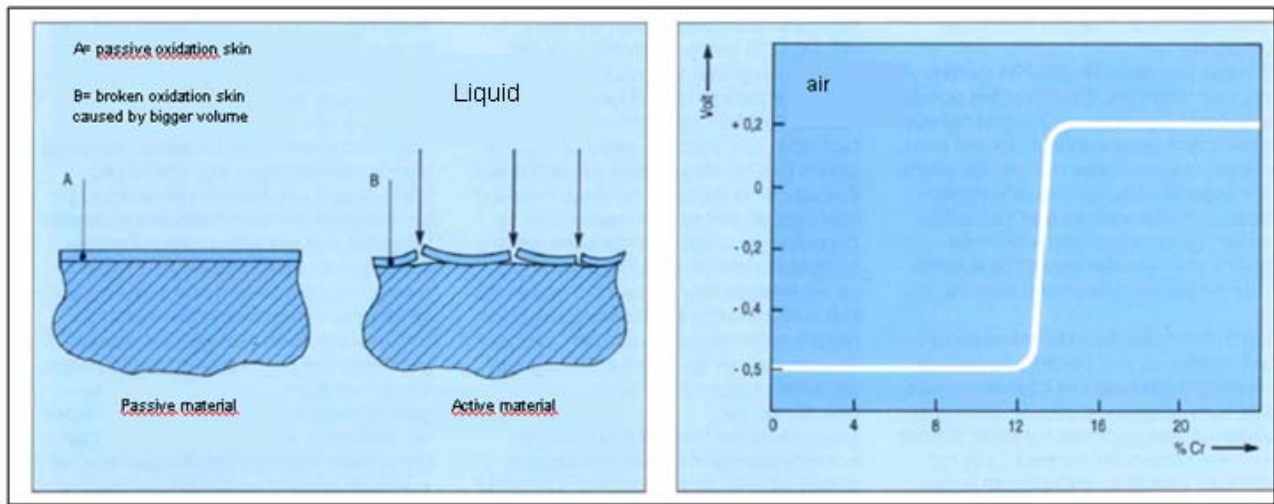
Corrosion is defined as deterioration of a metal because of a chemical or electrochemical reaction with a medium that stays in contact with that metal. Deterioration can be total or local. Therefore in this article besides the mechanism through which stainless steel does not rust, also several forms of corrosion, which can be easily treated or in many cases even prevented, will also be described.

What is stainless steel?

Before completing its definition, the concept of iron and steel will be



Vacuunit in stainless steel 316L for an oilrefinery



Schematic impression of passive and active metal

Influence of the chrome percentage in an iron-chrome alloy measured on the potential with respect to the H-electrode in water saturated with air

described closer. Iron (Fe) is an element, abundantly present in the earth crust, but never pure; usually it is found as iron ore which is a compound of iron and oxygen. Every system tends to the lowest energy state, thus that means, that the ore of ferrous oxide is a stable compound which will always stay in this state without any external activation. It is possible to break this powerful compound by means of an external action with the help of a chemical reaction, which costs relative much energy. Besides electrolysis this can be done by chemical reactions, which take place at high temperatures, like for example in a blast furnace. With the aid of carbon, which is added in the form of cokes, and energy an endothermic reaction takes place, in addition to which heat is needed so that the reaction can take place (frame1).

So originates pig iron, which gathers in a fluid state at the bottom of the blast furnace and that is occasionally tapped. The pig iron that has been originated, goes to the factory in order to bring up the mark the right analysis. The presence of some tenths percent of carbon makes this iron to be steel, like we daily meet in all kind of forms. Steel is thus an alloy of iron with a controlled quantity of carbon. By additionally alloying a relative small quantity of elements like nickel, chrome, vanadium, molybdenum, and so on, it is possible to especially increase the mechanical values, and this is partially due to the several thermal treatments which can be applied on this kind of steel. In this article we will not go into details on this respect.

All steels which are not alloyed or slightly alloyed have one common aspect and that is, that they all have an active condition or, with other words, all these kind of steels will react especially with oxygen, if an electrolyte is present (for example water). This will result in the fact, that the surface will oxidize (burning), so

that a corrosion product will originate which is also called rust.

In order to contrast the forming of rust it is possible to treat the surface, by coating (protecting varnish), by galvanizing (zinc protective layer), greasing, rubbering etc. All these protective layers prevent the electrolyte from coming in contact with the steel and as far as no imperfections come into being in these protective layers, everything goes well.

However, as soon as a small hole arises in the protective layer for example because of a damage, corrosion starts attacking this small spot very intensively, therefore it is also commonly called local corrosion. Of course this can only happen if an electrolyte is present. This is also the reason why the maintenance teams inspect the several steel constructions very carefully in order to prevent this kind of very undesired corrosions. Rust is thus a chemical conversion from iron to ferrous oxide, so that basically the previous formula develops itself in inverse direction. We can imagine the rust process as reported in the frame1. This is an exothermic reaction, because heat is released.

For completeness it has to be underlined, that there are also other reactions which could take place so that for example Fe_2O_2 is also formed, but this is not relevant for this article. From the two previous reactions we can gather that the energy is not lost, because the energy needed to release the iron ore is released again during the oxidation of the iron into its original form.

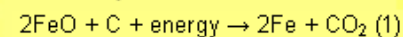
Since every system strives to the lowest energy state it is clear that the rust process cannot be prevented without any action. It is possible to compare it to a trunk which has been rolled up a slope with many difficulties. If you let it go than it will automatically roll back. If you put a small stick in front of it the trunk will stay at the higher level, even if this has received potential energy.

It is thus the sake, that we continuously put a small stick before the oxidation process so that this will not take place. Besides the above described protective layers, it is also possible to reach the objective by alloying the steel at a higher level, through which it becomes stainless steel. In principle this can be reached only with the element chrome.

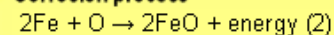
Reduction and oxidation process

Frame 1

Reduction process

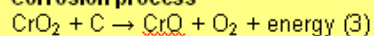


Corrosion process



Binding of carbon to chrome

Corrosion process



Chrome alloyed steel

The passivity of pure steel is relatively small. In spite of this, from the preciousness diagram it appears that iron is more precious than for example aluminium and chrome, whereas these metals behave so passive in an electrolyte. This is because the formed oxidation skin (rust layer) on the steel has a bigger volume with respect to the underlying mother material (also called matrix) (See picture 1.).

This is also the reason why the oxidation product swells, wherefore it breaks itself with the pressure. In this way the corrosion product does not form a unity with the mother material and so it becomes porous. This in antithesis to the corrosion products which form themselves on the surface of, for

example, aluminium and chrome which due to the same volume as the matrix, show a well closed characteristic. The chromium-plated bicycle handlebar represents a good example. Thanks to the perfect fitting of the chrome dioxide oxidation skin on the underlying chromium, the handlebar remains beautifully shining until cracks appear on the surface, which quickly changes the handlebar in something which is not presentable. In other words, even if aluminium and chrome are less precious than iron, they show themselves more precious than iron, because these elements have the 'privilege' to have a well fitting oxide skin which seals the material in such a way, that no electrolyte is anymore able to reach the mother material. Aluminium and chrome passivate themselves with the air, whereas this is not done by iron, because the iron oxide skin brings about more porosity due to its bigger volume, and this makes it possible for the electrolyte to continuously reach the mother material. For this reason an iron or steel object will eventually rust completely, so that at the end it totally disappears and turns back to its original status (ore).

Also the well-known rusting of a steel bolt is a consequence of the oxide skin swelling process. Fortunately, metal experts have found out something to change the steel condition from active to passive, so that it becomes stainless. This has been achieved by them by alloying it more with the element chrome. If the chrome percentage in iron becomes 12% till 13%, then the passivation is so good, that the alloy will not rust in normal water and air. In picture 2 we can clearly see the sharp turn from a negative potential to a positive one or, in other words, a sharp turn from an active behaviour to a passive behaviour of the steel.

This is because a thin though oxide skin of chrome dioxide, having the same volume as the underlying material, is formed on the steel surface. Therefore the metal becomes perfectly sealed, so that the electrolyte can not reach the active metal anymore. However, it is very important that oxygen is always present in order to form this oxide skin and to keep it intact. The passive chrome steel is, for example, also able to resist the diluted nitric acid at room temperature, because this acid reacts oxidizing. The alloy thus becomes rust-proof thanks to the fact that at least a minimum of 12% of chrome is present.

After chrome it is molybdenum which increases steel passivation mostly. It should be clear that the oxide film must be perfect, in order to avoid oxidation to originate in the pores. This oxide film, formed by chrome dioxide, arises very fast on a clean metallic surface in most of the oxidation environments and solutions like for example (diluted) nitric

acid. If the surface is dirty and/or contains residuals of weld sealing-wax or similar substances, then the creation of this oxide film is considerably hindered and the risk of corrosion increases rapidly.

If the oxide film (also called hide) is chemically or mechanically damaged and the conditions are so that the hide is not able to restore itself (self-heating-effect), then local corrosion will take place, while the remaining part stays intact. In acid reducing environments usually the metal cannot build up a protective oxide hide because of lack of oxygen which is needed for doing this. Moreover, in such environments, an oxide skin which is already present can even dissociate (fall apart), through which the metal will behave as active and will so be diluted. The velocity with which this will take place, can be measured and expressed, for example, in mm/year. From this explanation it is clear, how relative is the notion of rust-proof.

Chrome steel

The main element of stainless steel is chrome and the minimum required quantity is 12%. The fact that stainless steel can resist to corrosion, is due to a simple passivation because of this relatively high level of chrome content. In general, we can say that the resistance to corrosion increases when the content of chrome increases. Moreover, chrome also gives a higher resistance to oxidation at high temperatures.

Chrome does not cause any change in the structure of pure iron that is ferritic. Therefore it is often also called ferritic stainless steel. The physical properties are also almost the same as ferritic steel. If there is enough carbon, it is also possible to temper chrome steel like carbon steel, through which also the tensile strength increases.

Several stainless steel types have chrome as the only alloy element, even if most of the qualities also have significant quantities of other alloy elements. The goal of these additions is to increase corrosion robustness and/or to change the structure. Incidentally it is possible to have as aim to increase the mechanical strength through this. Resuming, it is possible to say that, in general, chrome steel looks like the normal construction steel, even if with the big difference that it has become passive and that it will stay like this, if the corrosion load does not become too big. Due to the little resistance to corrosion the applications are also rather limited. Besides the use for kitchen utensils and home applications it is also gaining more importance in the coachwork, because the mechanical values are good and, moreover, it is easy to maintain. In this context we can think at the city- and regional buses' frame, which the

producers have to deliver with an always increasing and guaranteed lifetime. However, in chemical environments the limits of this alloy will be easily experienced and therefore at that time the so called 18/9 was introduced, which besides the even higher chrome content had also an addition of nickel.

Chrome nickel Steel

As stated before, the resistance to corrosion increases proportionally to the increase of the chrome content. In this quality the alloy has 18% of chrome and moreover almost 8% of nickel. This alloy is often indicated by the term '304' (AISI 304).

Nickel (Ni) influences the structure and the mechanical properties of stainless steel. If the nickel content is high enough, then stainless steel gets an austenitic structure. For convenience we can then speak about austenitic stainless steel. Compared to the pure chrome steel this leads to significant variations of the:

- mechanical properties
- better workability and toughness;
- higher temperature resistance;
- better welding properties;
- physical properties, like for example it does not become magnetic.

In some environments the corrosion resistance becomes higher due to the presence of nickel. The applicable fields of this alloy are, at the end, much wider than those of chrome steel due to its unique and often much better properties. It is possible to think about installations in the food- and dairy industry and in the mild chemical processes.

As stated before, the element molybdenum increases the passivity of stainless steel and it is evident that a significant improvement of the corrosion performances of chrome nickel steel takes place already with the presence of two percent of molybdenum (Mo). In this way we get chrome nickel molybdenum steels also called '316'.

Chrome nickel molybdenum steel

Molybdenum has the same effect on the structure as chrome has and mostly it increases the corrosion resistance both of ferritic and austenitic stainless steel. In some countries this stainless steel with molybdenum (AISI 316) is also called 'acid-free', because this quality has such a striking corrosion resistance to aggressive watery sulphur compounds. Indeed the term 'acid-free' has to be avoided within the stainless steel terminology. This, in general, is very useful in many chemical processes and in seawater-applications. Over the last years there has been a tendency to increase the content of molybdenum even more, so that a super rust-proof

steel type could be created like 245SMO. In this article this will not be analyzed deeper because it would lead too far. Indeed, it is a development that has not to be neglected because the corrosion resistance in the more aggressive seawater is quite good. Also the increasing demand for the so called duplex structures (ferritic/austenitic) is not anymore a development which can be thought away, because here we are facing a unique combination of relative high level mechanical properties and a high corrosion resistance.

Table 1: Relation between structure, composition, hardability and magnetism of stainless steel groups

RVS type	%C	%Cr	%Ni	hardable	magnetic
ferritic	0.08	12-14	-	No	Yes
	0.10	16-19	-	No	Yes
	0.25	24-28	-	No	Yes
martensitic	0.09	12-14	-	Yes	Yes
	0.17	16-18	1,25-2,5	Yes	Yes
ferritic – austenitic	0,10	24-27	4,5-7	No	Yes
austenitic	0,10	16-26	7-26	No	No

Table 3: Mechanical properties of different types of stainless steel

AISI type	0.2% yield strength	Tensile strength	Elongation	Constriction	Impact value
304	185	500-700	50	60	85
304L	175	450-700	50	60	85
316	205	500-700	45	60	85
316L	195	450-700	45	60	85
321	205	500-750	40	50	85
410	300 or 450*	550-750	20 of 18*	-	85 or 70
630	1000	1100	1-15	-	-

* depends of heat treatment

Table 2: Chemical composition of different types of stainless steel

AISI type	C% max	Si% max	Mn% max	Cr	Mo	Ni	other
304	0,08	0,75	2,0	18-20	-	8-11	-
304L	0,03	0,75	2,0	18-20	-	8-13	-
310	0,15	0,75	2,0	24-26	-	19-22	-
316	0,06	0,75	2,0	16-18	2-3	11-14	-
316L	0,03	0,75	2,0	16-18	2-3	10-15	-
316Ti	0,08	0,75	2,0	16-18	2-3	10-14	Ti=5xC
321	0,08	0,75	2,0	17-20	-	9-13	Ti=5xC
410	0,15	1,0	1,0	11,5-13	-	-	-
430	0,12	1,0	1,0	16-18	-	-	-
630	0,04	0,6	0,28	16	-	4,25	3Cu, 3Cb, 0,27Ta

Table 4: Equivalents of different types of stainless steel

AISI USA	DIN D.	AFNOR Fr.	JIS JAPAN	SIS SW	BS UK
304	1.4301	Z5CN1809	SUS 304	2332	304S15
304L	1.4306	Z2CN1810	SUS 304L	2352	304S12
316	1.4401	Z6CND1711	SUS 316	2347	316S16
316L	1.4404	Z2CND1712	SUS 316L	2348	316S12
316Ti	1.4571	Z6CNDT1712	-	2350	320S17
321	1.4541	Z6CNT1810	SUS 321	2337	321S31
410	1.4006	Z12C13	SUS 410	2302	410S21
630	1.4542	Z6CNU1704	SUS 630	-	-

Head groups

Depending on the structure it is possible to divide stainless steel in four groups, namely:

- ferritic stainless steel;
- martensitic stainless steel;
- austenitic/ferritic stainless steel;
- austenitic stainless steel.

Some characteristics like toughness and magnetism are directly related to the structure. To have a glance of the various parameters of the stainless steel types, see table 1.

Before examining more deeply the various corrosion aspects and properties of these four head groups, an overview of other possible elements present in stainless steel will follow (frame 3).

For an overview of the chemical composition of the many available types of stainless steels see table 2. All the values in the table are indicators which give a reasonable average value of the different regulations that can be marginally different one from the other. The mechanical values are reported in table 3.

Terms like AISI 304 and AISI 316 come from the American norm. In many industrialized countries there are local norms; so Germany has its own so called raw material numbers that are often used in our country too. Finally, in order to have a clearer view of all these types there are definitions of all the equivalents in table 4. Here it applies too, that, broadly speaking, the types in general fit in one with the other. These general links, at the end, lead to a satisfactory interchangeability. As can be seen from the tables, besides 304 and 316 it is also spoken about 304L and 316L, where wrongly it is said that the L indicates the welding quality. This is a big misunderstanding because it is only related to a lower carbon content (low carbon), as can be seen from table 2. The reason why these modified qualities have been developed will be clarified in section 2.

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.