

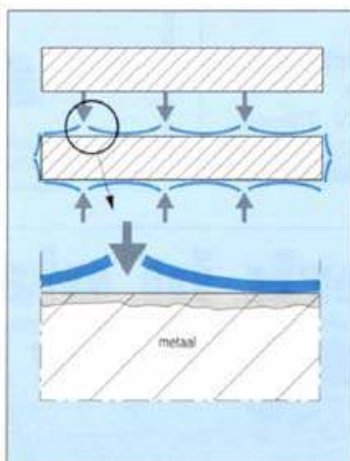
Risks with the welding of stainless steel (1)

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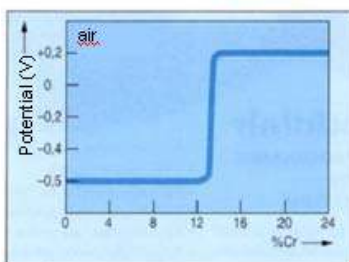
Concerning the processing of stainless steel there is still a lot of incomprehension and even lack of knowledge. Especially concerning the combination of components with the help of the thermal welding process there seems to be much ignorance, because of which there regularly arises unnecessary corrosion damage. In three articles it has been tried to give more clarity to everybody that is involved in the process of stainless steel. Next to the possibilities and the dangers that involve the welding process, there is, in a limited way, going into the metallurgical aspect of the phenomenon stainless steel.

Unalloyed and lightly alloyed carbon steels are active metals, because they react with the environment if there is an electrolyte (water). The element iron, freed with a lot of effort and energy from its form of ferrous oxide, with the help of carbon reduction that has taken place in a blast furnace, would love to go back to its original condition, i.e.: iron ore. This iron ore owns the lowest energy state and the laws of thermodynamics teach us that each system strives for it. In other words: iron would love to oxidize again and that happens faster if there is an electrolyte such as water, under delivery of energy. The majority of metals show this need to oxidize, with the exception of precious metals such as platinum and gold. These last metals are therefore by definition to be regarded as rust-proof. The term 'rustproof steel' is in itself an incorrect name.

Therefore the experts use the term stainless steel. Metals such as aluminum, titanium and chromium also react very intensely with oxygen, but the formed layer of oxide immediately seals off the metal, so that oxidation stops. These metals therefore have the property or ability to passivate themselves. Ferrous oxide does not have this property, because ferrous oxide has a larger volume than iron matrix. This is also the reason why



1. If the oxideskin is bigger than the matrix, it destructs itself. Result : corrosion

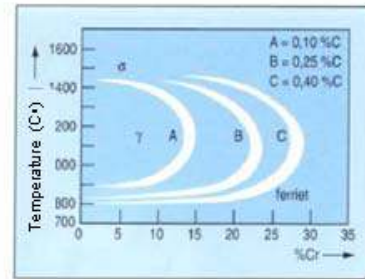
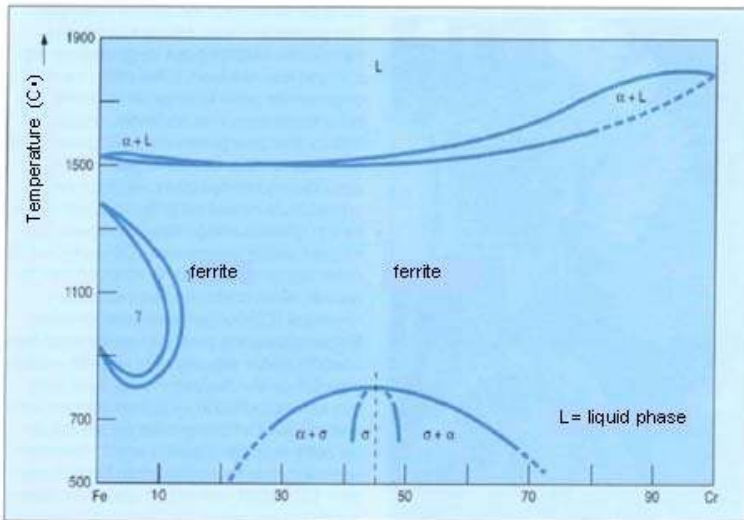


2. Potential turning point at 12% chromium iron goes on oxidizing, until it has completely returned to its original state. The reason for this is that the layer of oxide crushes itself, because of the larger volume, through which the electrolyte can penetrate further to new metal

layers, in order to corrode those too (figure 1).

Passivation

As it has already been stated, chromium has the wonderful property of making itself passive by the use of a good sealing layer of chromic oxide. The chromium wraps itself up, as it were, through which the electrolyte can not penetrate further, therefore stopping the oxidation process. Active chromium therefore passivates itself, through which the metal behaves almost as precious as platinum and gold. If chromium is alloyed in steel, then it appears that a content of 12% of chromium is enough to form this layer of chromic oxide on the steel surface, through which the same passivation appears. The active steel has then become suddenly passive, because in principle it cannot react anymore with its environment thanks to this perfectly fitting layer of oxide. From this moment on the so called chromium steel is formed. In figure 2 it is clearly visible how a negative potential at about 12 % turns to a positive one. In addition, it has to be reported that metals such as copper, silver, gold and platinum also have such a positive potential. Chromium has a potential of -0.56 V, but chromic oxide has a potential



4. Influence of the carbon content on the size of the austenitic area

3. Equilibrium – diagram according Hansen (Constitution of binary alloys)

of + 0.8 V with regard to the so called hydrogen potential. In principle stainless steel can be divided in four groups:

- ferrite chrome steel;
- martensite chrome steel;
- ferrite/austenite chrome nickel steel (duplex);
- austenite chrome nickel steel.

The metallurgical and physical properties of these main groups differ considerably from each other, which has consequences for welding.

Chrome steel

The corrosion resistance of chrome steel is more or less exactly proportionate to the percentage of chromium. Chrome steels can be subdivided in two main groups i.e. in the martensite and in the ferrite structure. The chromium

percentage of the groups is respectively +/- 12% to 14 % and 14% to 27 %.

The state/condition/situation diagram for iron and chromium is reproduced in figure 3. The amount of carbon largely determines the size of the austenite area. The situation diagram in figure 3 is then only applicable at 2 carbon percentages of 0,03 % carbon. Figure 4 again gives the influence of the percentage of carbon on the size of the austenite area. If a chrome steel goes through the austenite area during the cooling down phase, than at room temperature there is a martensitic structure. This is in contrast to a ferrite quality, which does not undergo a transformation in structure when cooling down. It will also be clear that these ferrite qualities will not undergo a

transformation in structure through specific heat treatments. The mechanical properties of martensitic chrome steels are strongly dependent on the percentage of carbon. In iron chrome systems, at about 45% chromium, the well known sigma-phase arises (fig. 3). The sigma-phase is a hard and brittle connection of iron and chromium, which undermines both the non-corrosive and the mechanical properties. This connection is therefore highly undesired. Between the sigma- and the ferrite area there also exists a transitional area where both structures appear next to each other. As the chrome percentage increases in the alloys the chance for sigma-phase-formation rises, although, even with chrome steels with 12 % chrome this undesired sigma-phase is found.

Both ferrite- and martensite-chrome steels especially tend to brittle during welding. The most important reasons for this brittling are:

- grain/granule growth at raised temperatures;
- foundation of a sigma-phase;
- precipitation of carbides.

Granule growth

Ferrite chrome steels are especially sensitive to the situation in which a very rough crystalline structure can form in a heated area, leading to considerable brittling. Of course for those areas this causes a small amount of toughness. Martensitic qualities are less sensitive for that.



5. Precipitation of chromecarbids in stainless

Sigma phase

The formation of the sigma phase does not only lead to brittling as described above, but it also affects corrosion resistance, because this phase withdraws the chromium from the matrix which was so extremely necessary for passivation. Especially during this phase, if in direct contact with the environment, the chrome can come under the critical percentage of 12% and then such a location will immediately turn to an active area, through which there will arise strong local corrosion. Ferrite qualities in general have a higher inclination to the formation of sigma phase because the chrome percentage happens to be higher.

Precipitation of calcium carbides

As with the formation of the sigma phase there will be brittling at the formation of chromium carbides (fig.5). In this case there is a big danger that the formation of such calcium carbides gets "consumed" off the matrix, through which the local chromium amount can become too low. Inter-crystalline corrosion is then mostly the consequence, since such calcium carbides precipitate on the granule boundaries because of the favourable nucleus chance. If chromium calcium carbides are formed at lower temperatures, the diffusion speed of chromium is too low to divide itself homogeneously as precipitate. Therefore, there the notorious 475°C – brittle can arise. Moreover, such calcium carbides are richer in chromium than when they originate at higher temperatures, through which the danger of corrosion increases further.

Properties

In general, we can state that physical chromium steels appear to have much in common with unalloyed carbon steel. Chromium steels are for example magnetic and the coefficient of expansion is almost the same as the one of carbon steel. This means that transformations that can originate during welding are often as large as the ones with carbon steels. Heat conductivity however, is about twice as small as the one of carbon steel and as a consequence, under similar welding situations, the base material immediately next to the welding area cools down less quickly than with normal steel. The big disadvantage with this is that



GMAW weld of a stainless steel cover

the chance for granule growth and the sigma phase considerably changes.

Martensitic qualities

Some martensitic chromium steels following the German Raw Material Numbers are mentioned in table n.1. After this number the AISI regulation is mentioned, that more or less matches as for the analysis. The qualities mentioned in table 1 become hard in contact with the air, and through the right heat treatment an optimum combination of strength and toughness can be reached. The quality of hardness is decided by the amount of chromium and carbon. If the amount of chromium is high, also the amount of carbon should be high, in order to get a martensitic-structure. Something good can be seen on the basis of the quality 1,4057 and figure 4. Nickel is sometimes added in small quantities in order to stimulate the formation of martensite. The mechanical properties of the weld and the weld environment with martensitic qualities cannot really be called good because of the undesired formation of carbides. In the temperature range between 475°C and 550°C these carbides can precipitate, through which the so-called '475°C –brittle' can originate. It is, therefore, important that the parts that need to be welded stay as short as possible in this temperature range. This implies, among the other things, that it should not be pre-heated. This is again in contrast with the possibility that cold cracks can originate (also called hydrogen cracks), because the martensite

structure happens to be predisposed for it. Therefore, it would be wise, with thicker (6 mm) pieces of work, to preheat at a temperature close to about 200°C. Attention should be paid to the fact that, during the welding process, hydrogen absorption will not take place. Welding processes which are poor in hydrogen, such as MIG and TIG-welding, lend themselves in an excellent way to the welding of stainless steel, in connection with the sensitivity of hydrogen cracks.

Using electrodes, it should be made sure that especially the protecting coating is dried out, even if this is still not a guarantee that with this the crystallization of water is removed. It is also recommended to weld martensitic types of stainless steel with additional austenite welding materials, in order to give the weld an acceptable toughness. Both of these do not go well in a highly sulphurous environment because in austenite nickel can start reacting with sulphur, through which an undesired corrosion can occur.

Ferrite chromium steels

With ferrite chromium steels the structure remains completely ferritic from the solidification till the room temperature. Even if with longer temperature stress the feared sigma-phase can arise, the effect of an undesired large granule growth in a heat-influenced area is much more harmful, because this leads to a very bad brittling exactly next to the welded joint. Since a structure change cannot arise, this rough structure can not be removed by heating the material. On the

contrary, the granules will go on growing. This is also the reason why the mechanical values of ferrite stainless steel, which is influenced by heat, are far from being satisfactory. Adding some austenite material will give a little improvement, which, however, cannot prevent increased granule growth in the heat-influenced area, and brittling can occur. This however, causes the weld itself to become considerably more ductile, through which stresses can be absorbed better. Care should also be taken of that the welded joint is not completely austenite, in view of the possible heat-cracks.

In view of brittling through granule growth, it is better that ferrite chromium steels be not pre-heated. But in view of the inadmissible stresses that arise with welding thick sheets, brief preheating to about 200°C is recommended. Care should also be taken of that the heat-input remains as small as possible, and the welding speed as high as possible. Both can be particularly well attained with the help of the MIG-welding process. In principle, a heat treatment after welding can be omitted. Also, finishing of the weld is recommended, because peak voltages as a consequence of milling can be very disadvantageous (notch effect). Certain alloy elements such as nitrogen, nickel, titanium and vanadium also have an inhibiting influence on granule growth. Some of the ferrite qualities are reported in table 2. Also here the German Material Number is leading. The AISI-standard corresponds approximately with the German definition.

Applications of chromium steel

In welding constructions martensitic chromium steels never or almost never appear. Such qualities are found especially where, next to a certain corrosion resistance, there is also a demand for good resistance to wear. For example, moulds, turbine-components, knives and medical instruments. Ferrite chromium steel is found in oven construction (especially the aluminium containing types used, for example, in baskets and racks), as turbine-components, in cracking installations for the use of petrochemistry, but also in car frames (buses) and also in large kitchen equipment.

Table 1: Chemical composition of martensitic stainless steel

Werkstoff.Nr	AISI-type	C[%]	Cr[%]	Si	Mn	S	Ni
1.4000	403	0,08	12-14	≤1	≤1	≤0,03	--
1.4006	410	0,08-0,12	12-14	≤1	≤1	≤0,03	--
1.4005	416	0,15	12-13	≤1	≤1	0,25	--
1.4021	420a	0,17-0,25	12-14	≤1	≤1	≤0,03	--
1.4057	431	0,14-0,23	15,5-17,5	≤1	≤1	≤0,03	1,5-2,5

Table 2: Analysis of ferritic stainless steel

Werkstoff nr.	analyse in %					
	C	Si	P	S	Cr	andere
1.4002 (405)	0,08	1	0,04	0,03	12-14	Al 0,1-0,3
1.4016 (430)	0,08	1	0,04	0,03	15,5-17,5	
1.4104 (430F)	0,17	1	0,06	0,35	15,5-17,5	Mo 0,2-0,6
1.4762 (446)	0,12	0,7-1,4	0,04	0,03	23-26	Al 1,2-1,7
1.4935 (442)	0,17-0,25	0,1-0,5	0,04	0,03	11-12,5	Mo 0,8-1,2 Ni 0,3-0,8 V 0,2-0,4 W 0,4-0,6

Table 3: Analysis of ferritic/austenitic stainless steel

Werkstoff nr.	analyse in %						
	C *)	Si *)	Mn *)	Cr	Mo	Ni	andere
1.4460	0,05	1	2	25-28	1,3-2	4,5-6	N 0,05-0,2
1.4462 (AISI 318LN)	0,03	1	2	21-23	2,5-3,5	4,5-6,5	N 0,08-0,2
AISI 329	0,20	0,75	1	23-28	1-2	2,5-5	N 0,08-0,2

Table 4: Analysis of austenitic stainless steel

Werkstoffnr:	analyse in %		Mn *)	Cr	Mo	Ni	andere
	C *)	Si *)					
1.4300 (302)	0,12	1	2	17-19	--	8-10	
1.4301 (304)	0,07	1	2	17-19	--	8,5-10,5	
1.4306 (304L)	0,03	1	2	18-20	--	10-12,5	
1.4310 (301)	0,12	1,5	2	16-18	0,8	6-9	Mo≤0,8
1.4828 (309)	0,2	1,5-2,5	2	19-21	--	11-13	
1.4841 (310)	0,2	1,5-2,5	2	24-26	--	19-22	
1.4401 (316)	0,07	1	2	16,5-18,5	2-2,5	10,5-13,5	
1.4404 (316L)	0,03	1	2	16,5-18,5	2-2,5	11-14	
1.4449 (317)	0,07	1	2	16-18	4-5	12,5-14,5	
1.4571 (318)	0,08	1	2	16,5-18	2-2,5	10,5-13,5	Ti≤5xC
1.4541 (321)	0,08	1	2	17-19	--	9-12	Ti≤5xC
1.4550 (347)	0,08	1	2	17-19	--	9-12	Nb≤10xC

Ferrite/austenite chromium nickel steel

These duplex-qualities are magnetic, but do not become hard. Because of the large chromium percentage the alloy has an excellent durability against all forms of corrosion such as stress-and

well corrosion, while the mechanical properties are significantly better than the ones of austenite types. Regarding welding it is not necessary to heat, unless the material is very thick. Just like with ferrite chromium steels, attention should be paid with

regards to granule growth and the formation of the feared sigma-phase. Furthermore, the welding process does not differ from the welding of other qualities of stainless steel. Of course, a duplex weld additional material ought to be used. A well known quality is the Raw Material Number 1.4462, a composition which among other things, is reported in table 3. A commonly used welding additional material for this, has 22% chromium, 9% nickel and 3% molybdenum. If still higher mechanical demands are set the quality 1.4460 can be used.

Austenite stainless steel

In order to be able to belong to this category, the sum of the chromium and nickel percentage has to contain at least 26%. The well known chrome nickel steel 18/8 (AISI 304) belongs to this group. Austenite stainless steel has a homogeneous non-magnetizable structure, which however, is soft and transformable. Because of the nickel percentage, the austenite area spreads till under room temperature. In many cases molybdenum is added in order to improve the durability in chlorine and fluorine containing environments.

Cold deformation can locally produce a little martensite, through which it becomes locally a little magnetic. It speaks for itself that on those places the mechanical properties will diverge strongly from the matrix. If these effects want to be eliminated, than it should be heated at a temperature between 1000 to 1065°C. The big advantage of this heat activity is that the high inner stresses disappear, through which the ability to transform becomes better. This heating is also to the benefit of corrosion resistance. Austenite stainless steel cannot be made hard, it welds very easily and has little sensitivity for granule growth. One of the most well known disadvantages is the sensitivity to heat cracks during welding. This can be reduced during welding by the presence of ferrite, that already has to be present during solidification. A part of this ferrite will be converted again during the cooling phase into austenite, even if a part remains ferrite. The disadvantage of this rust ferrite is that it causes selective corrosion, but in practice it shows that a

certain percentage of ferrite is acceptable.

Some commonly occurring austenite qualities are reported in table 4. Also here the German Material Numbers have been chosen and the comparable AISI-normation, which has been put between brackets. Austenite stainless steel has a relatively low elastic limit; which can be considerably raised by adding nitrogen, through which the so called 'LN'-qualities arise. Nitrogen does not have influence on the final weld quality. Furthermore, this stainless steel type has a high coefficient of expansion, a low heat conductivity and a high electrical resistance.