General facts about the processing of stainless steel

Ko Buijs, Van Leeuwen Stainless, The Netherlands

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, regularly resulting in unnecessary corrosion damage. This article attempts to shed light on the processing of stainless steel and deals with the possibilities and the risks involved in the welding process. It also covers some of the metallurgical aspects of stainless steel.

Introduction

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 this article it has been tried to give more clarity to everybody that is involved in the processing of stainless steel. Next to the possibilities and the risks 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. 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 prefer 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 prefer to oxidize again and that happens faster if there is an electrolyte such as water, under delivery of energy.

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

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 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.

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, than 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 than 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 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 of roughly +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/austenitic chrome nickel steel (duplex);
- austenitic chrome nickel steel.

The metallurgical and physical properties of these main groups differ considerably from each other.

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 amount of carbon largely determines the size of the austenitic area.

If a chrome steel goes through the austenitic 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. 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-phase 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 embrittlement are grain growth at raised temperatures, foundation of a sigma-phase and precipitation of carbides.

Martensitic qualities

Some martensitic chromium steels following the German Werkstoff Numbers are mentioned in table nr.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. 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 embrittlement' 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 preheated.

Table 1. composition martensitic stainless steels

Werkstoff Nr.	AISI	C%	Cr%	Si%	Mn%	S%	Ni%
14.000	403	0.08	dec-14	<=1	<=1	<0.03	–
14.006	410	0.08-0.12	dec-14	<=1	<=1	<0.03	–
14.005	416	0.15	dec-13	<=1	<=1	0.25	–
14.021	420A	0.17-0.25	dec-14	<=1	<=1	<0.03	–
14.057	431	0.14-0.23	15.5-17.5	<=1	<=1	<0.03	1.5-2.5

Table 2. composition ferritic stainless steels

Werkstoff Nr.	AISI	C%	Cr%	Si%	S%	Others %
14.002	405	0.08	12.0-14.0	<=1	0.03	Al 0.1-0.3
14.016	430	0.08	15.5-17.5	<=1	0.03	–
14.104	430F	0.17	15.5-17.5	<=1	0.35	Mo 0.2-0.6
14.762	446	0.12	23.0-26.0	0.7-1.4	0.03	Al 1.2-1.7
14.935	442	0.17-0.25	11.0-12.5	0.1-0.5	0.03	Mo 0.8-1.2 Ni 0.3-0.8 V 0.2-0.4 W 0.4-0.6

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 embrittlement 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 austenitic material will give a little improvement, which, however, cannot prevent increased granule growth in the heat-influenced area, and embrittlement 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 austenitic, in view of the possible heat-cracks. In view of embrittlement through granule growth, it is better that ferrite chromium steels be not pre-heated. 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.

If chromium is alloyed in steel, than it appears that a content of 12% of chromium is enough to form a layer of chromic oxide on the steel surface, through which passivation appears.

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 and also in buses frames.

Ferrite/austenitic chromium nickel steel

These duplex qualities are magnetic, but do not become hard. Because of the large chromium percentage and the presence of molybdenum the alloy has an excellent durability against all forms of corrosion such as stress corrosion cracking, while the mechanical properties are significantly better than the ones of austenitic 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 1.4462, a composition which among other things, is reported in table 3.

Austenitic 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. Austenitic stainless steel has a homogeneous non-magnetic structure, which however, is soft and transformable. Because of the nickel percentage, the austenitic 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. This stands for the so called solution annealing. 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. Austenitic stainless steel cannot be made hard, it welds very easily

Chromium has the wonderful property of making itself passive by the use of a good sealing layer of chromic oxide.

Table 3. composition ferritic/austenitic stainless steels

Type	UNS	C%	Cr%	Ni%	Mo%	N%
14.460	S32304	<=0,03	23,5-24,5	3,0-5,5	0,6	0,05-0,2
14.462	S31803	<=0,03	21,0-23,0	4,5-6,5	2,5-3,5	0,08-0,2
Superduplex*)	S32760	<=0,03	24,0-26,0	6,0-8,0	2,5-3,5	0,08-0,2

*) Cu 0,5-1% and W 0,5-1%

Table 4. composition austenitic stainless steels (manganese 2% maximum) S max 0.03% and P max 0.045%

Werkstoff Nr.	AISI	C%	Cr%	Si%	Ni%	Mo%	Others%
14.300	302	0.12	17-19	1	08-10	–	–
14.301	304	0.07	17-19	1	8.5-10.5	–	–
14.306	304L	0.03	18-20	1	10-12.5	–	–
14.310	301	0.12	16-18	1.5	06-9	0.8	–
14.828	309	0.20	19-21	1.5-2.5	11-13	–	–
14.841	310	0.20	24-26	1.5-2.5	19-22	–	–
14.401	316	0.07	16.5-18.5	1	10.5-13.5	2-2.5	–
14.404	316L	0.03	16.5-18.5	1	11-14	2-2.5	–
14.449	317	0.07	16-18	1	12.5-14.5	4-5	–
14.571	318	0.08	16.5-18	1	10.5-13.5	2-2.5	Ti<=5C
14.541	321	0.08	17-19	1	09-12	–	Ti<=5C
14.550	347	0.08	17-19	1	09-12	–	Nb<=10C

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 austenitic, even if a part remains ferrite. Some commonly occurring austenitic qualities are reported in table 4. Also here the German Werkstoff Numbers have been chosen and the comparable AISI-standards, which has been put between brackets. Austenitic stainless steel has relatively low elastic modules; 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, low heat conductivity and a high electrical resistance.

About the author

Ko Buijs is a recognized metallurgical / corrosion specialist on stainless steels as well as special metals. He works for Van Leeuwen Stainless. In addition, Mr Buijs is a lecturer for various organisations such as steel associations, technical high schools and innovation centres. He has published over 100 papers in a number of technical magazines. In close co-operation with Barsukoff Software Mr Buijs has developed the computer programme Corrosion Wizard 2.0.
Info www.corrosionwizard.com