

Chromium Steels*

If an unalloyed steel is exposed to high temperatures it oxidizes fairly rapidly. This is due to the relatively high affinity of iron for oxygen; the oxide layer formed does not provide the underlying steel with sufficient protection against further oxidation. When chromium is added to the steel, however, the oxide layer adheres far better to the metal and at the same time its structure is such that progressive oxidation is to a large extent suppressed.

Chromium has a high affinity for oxygen. This is one of the reasons why chromium steels are resistant to oxidation. Moreover, if the oxide layer is damaged or attacked in the presence of an oxidizing atmosphere, local formation of a fresh oxide layer takes place rapidly. It will be appreciated that the oxidation resistance of a particular steel is determined by the amount of chromium it contains. Steels which have a chromium content higher than about 11% are known as stainless steels.

On the basis of their structure the chromium steels can be divided into two main types, i.e. the martensitic chromium steels containing 11.5-18% Cr, and the ferritic chromium steels which contain 14-27% Cr.

Fig. 1 shows the equilibrium diagram for iron and chromium. The extent of the austenite region is largely determined by the carbon content of the material. The diagram shown applies to a carbon content of 0.03%. Fig. 2 illustrates the effect of carbon content on the extent of the austenite region.

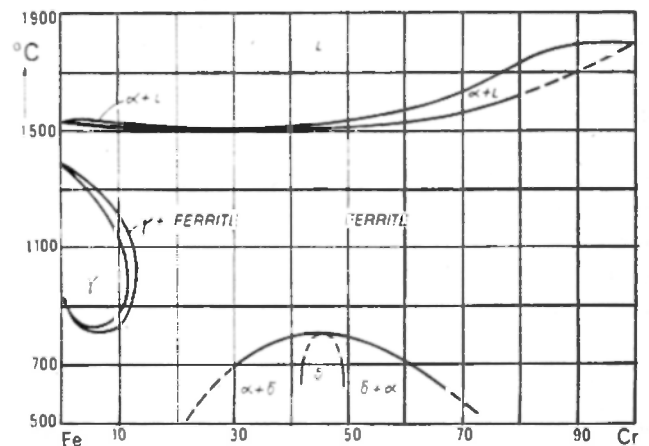


Fig. 1 Equilibrium diagram for iron-chromium according to Hansen (constitution of binary alloys)

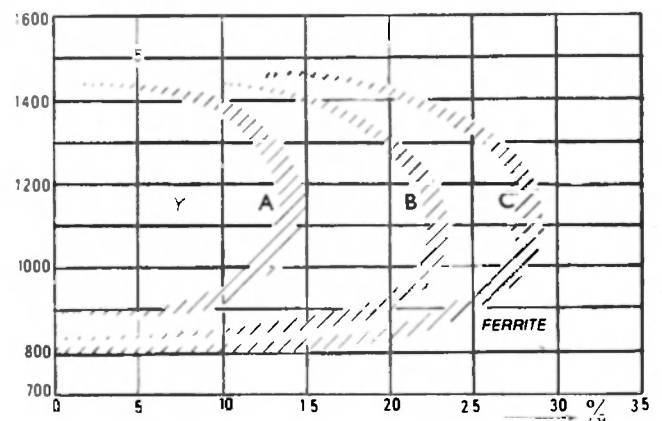


Fig. 2 Effect of carbon content on the extent of the austenite region : A : 0.10% C; B : 0.25% C and C : 0.40% C.

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Steels of a composition such that they pass through the austenite region on cooling have a martensitic structure at room temperature. In contrast, the ferritic chromium steels do not undergo transformation during cooling ; it is therefore not possible to produce desirable structural changes in these steels by a heat treatment.

The martensitic chromium steels must be tempered after being quenched from austenitising temperature in order to obtain mechanical properties suitable for practical applications.

In the iron-chromium diagram the sigma phase appears at about 45% chromium. Sigma is a very hard and brittle compound of iron and chromium, which from the points of view of both corrosion resistance and mechanical properties must be considered as extremely undesirable.

The sigma region and the ferrite region in the iron-chromium equilibrium diagram are separated by a transition region, in which both the sigma and the ferrite phases are present. It is not completely known how far this transition region extends at low temperatures. The low chromium of the martensitic stainless steels generally ensures that sigma phase does not form during elevated temperature exposure.

It is clear that steels with a high chromium content are more prone to the formation of sigma than the low-alloy steels.

Both the ferritic and the martensitic steels tend, generally speaking, very readily to brittleness, and this is a particular problem during welding. The most important causes of this brittleness are :

- Grain growth at high temperatures. As a result of welding, a very-coarse crystalline structure can occur in the heat affected zone, as a result of which the material develops a limited, local toughness. The ferritic chromium steels are exceptionally prone to this, the martensitic chromium steels hardly.

- The formation of sigma phase. This not only causes the material to become brittle but can also lead to a serious deterioration in the corrosion resistance due to the extraction of chromium from the material in the immediate vicinity of the sigma phase. The ferritic chromium steels, due to their higher chromium content,

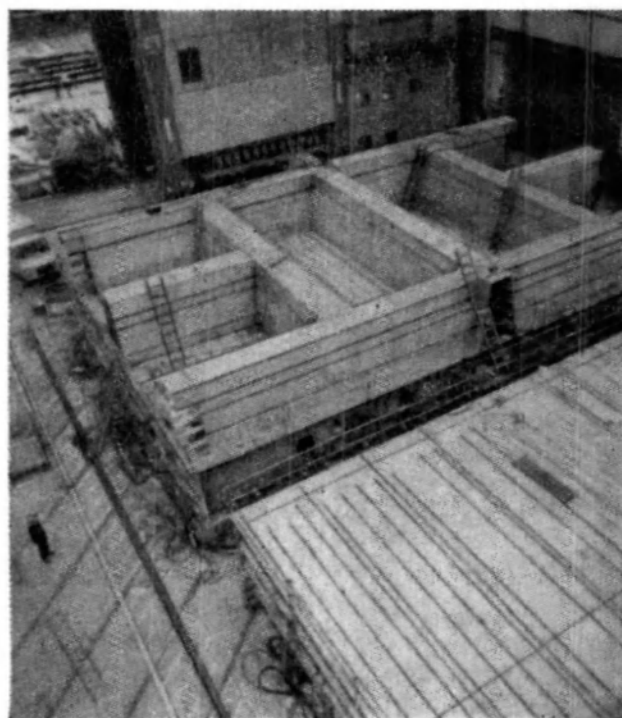


Fig 3. Bottom of a stainless steel tank for bulk Chemical tanker under construction at Kockum's Shipyards, Sweden.

tend more strongly towards the formation of sigma phase than do martensitic chromium steels.

- Carbide precipitation. As is the case with the formation of sigma phase, the result of carbide precipitation is a brittle material, with severe local loss of chromium leading to an adverse effect on corrosion resistance. This is particularly so when the carbides are formed at lower temperatures, when the diffusion rate of chromium is not high enough to restore the homogeneous distribution in the matrix ; what is known as "475° brittleness" is a form of such carbide precipitation. In addition, the carbides which form at lower temperatures are richer in chromium than those formed at higher temperatures.

The coefficient of linear expansion of chromium steels is practically the same as that of unalloyed steel. The distortion which may arise during welding is, therefore, comparable with that of unalloyed steel. The thermal conductivity, however, is about half that of unalloyed steel. As a result, under comparable welding conditions the parent metal directly adjacent to the weld cools less rapidly than is the case with unalloyed steel. Because of this, the chance of grain growth and the formation of sigma phase is increased.

Table I. Martensitic chromium steels

AISI-code	C h e m i c a l c o m p o s i t i o n						
	C	Cr	Mn	Si	P	S	other
403	≤ 0,15	11,5-13,5	≤ 1,0	≤ 0,5	≤ 0,04	0,03	—
410	≤ 0,15	11,5-13,5	≤ 1,0	≤ 1,0	≤ 0,04	0,03	—
414	≤ 0,15	11,5-13,5	≤ 1,0	≤ 1,0	≤ 0,04	0,03	Ni 1,25-2,5
416	≤ 0,15	12,0-14,0	≤ 1,25	≤ 1,0	≤ 0,06	0,15	—
416Se	≤ 0,15	12,0-14,0	≤ 1,25	≤ 1,0	≤ 0,06	0,06	≥ 0,15Se
420	≤ 0,15	12,0-14,0	≤ 1,0	≤ 1,0	≤ 0,04	0,03	—
431	≤ 0,20	15,0-17,0	≤ 1,0	≤ 1,0	≤ 0,04	0,03	Ni 1,25-2,5

Martensitic chromium steels

The most important of the martensitic chromium steels are summarized by AISI specification in Table I. These types are airhardening. A good combination of strength and toughness has to be obtained by a suitable heat treatment.

The hardness of the martensite is governed mainly by the amounts of carbon and chromium in the steel. When the chromium content is high, the carbon content must also be high in order to give the steel a martensitic structure (see fig. 2 and AISI 431). The martensite hardness will then be relatively high.

In some cases a little nickel is added to the steel to promote the formation of martensite (AISI 414 and AISI 431).

Types AISI 416 and AISI 416 Se are alloyed with sulphur and selenium respectively, with the object of achieving good machinability. The weldability of these types is poor since serious porosity can easily occur.

Great care must be exercised in the welding of these martensitic stainless steels in view of their hardenability.

Because of increased hardness, and accompanying loss of ductility special care must be taken to prevent cracking.

To obviate fast local cooling subsequent to welding, the workpiece must be preheated and the interpass temperature accurately controlled. The usual preheat and interpass temperature range is 200-320°C; the carbon content and material thickness is used to judge whether or not preheating is necessary; e.g. plate thickness less than 6 mm and the carbon percentage

below 0.10% does not require a preheat. The martensitic structure which may arise is also very sensitive to hydrogen cracking. It is for this reason that low-hydrogen electrodes have always to be used; rebaking electrodes before use is always recommendable.

Both the MIG and the TIG processes are very suitable for welding these materials, since both processes are inherently very low in hydrogen.

Welding of the martensitic chrome steels is preferably done with consumables of which the deposited weld metal matches that of the base material. After welding a stress relief heat treatment of 720-780°C for a period of at least 30 minutes or a quench and temper heat treatment as prescribed for the base metal is necessary to improve the ductility of welded joints and heat affected zone. If stress relieving is applied the material must first be slowly cooled to room temperature to allow any remaining traces of austenite to be transformed into martensite. If this is omitted the residual austenite may transform into martensite after stress relieving which may cause new stress contractions.

When it is not possible to carry out a heat treatment after welding a filler metal on basis 25 Cr/12 Ni (E 309) or 25 Cr/20 Ni (E 310) has to be preferred.

The use of austenitic chrome-nickel steel as the filler metal is undesirable, for instance when the corrosive environment contains much sulphur. Due to the formation of nickel sulphide the material may lose its resistance to corrosion.

Again, if rapid and repeated temperature changes are involved the use of austenitic chrome-nickel steel as a filler is less suitable, since the coefficient of expansion of chrome-nickel steel is significantly higher than that of chromium steel. In such cases, it is always desirable

Table II Welding processes and weld filler materials for martensitic chromium steels.

Welding process	Filler material						Heat treatment	
	Nominal C	chemical composition Cr	Ni	Mo	Mn	Si	preheat * *	post weld
Coated electrodes	≤ 0,08	11,0-13,5	—	—	≤ 1,0	≤ 0,90	200-320°C	720-780°C
	≠ 0,03	24	13	—	1,5	0,8	20-250°C	—
	≠ 0,15	26	21	0,5	1,5	0,3	20-250°C	—
	* ≠ 0,08	25	5	1,5	1,0	0,8	20-250°C	720-780°C
MIG-solid wire	≤ 0,12	22	11	—	1,2	0,8	20-250°C	—
	≠ 0,12	26	21	—	1,5	0,5	20-250°C	—
	* ≠ 0,08	15	—	—	1,0	0,8	20-250°C	720-780°C
MIG-cored wire	≤ 0,08	24	13	—	1,5	0,8	20-250°C	—
TIG-rod	≤ 0,12	22	11	—	1,2	0,8	20-250°C	—
	≠ 0,12	26	21	—	1,5	0,5	20-250°C	—
	* ≠ 0,08	15	—	—	1,0	0,8	20-250°C	720-780°C

* These filler materials are for use only when the corrosive environment is high in sulphur. For thick plate use only for the final run.

* * The preheat temperature must be higher when the carbon content is higher and the plate is thicker. As a rule plates thinner than 6 mm are not preheated.

to choose a filler metal which approximates the composition of the parent metal. The selection of a filler material for the welding of martensitic chromium steel is illustrated in Table II. Preference is given to the material first listed.

Ferritic chromium steels :

This group of steels has a chromium content of 14 to 27%. Their chemical composition is such that austenite formation does not occur at high temperature. From the solidification point to room temperature the structure of the steel remains ferritic. The high-chromium types in particular are prone to form sigma phase when exposed to high temperature for long periods. However, the most serious problem in the welding of the ferritic chromium steels is not the risk of sigma phase formation ; it is very much more the risk of grain growth in the heat affected zone. As a result of this grain growth the material acquires a local, coarse-grained structure which can make it very brittle. This brittleness cannot be removed by heat treatment, since no structural changes take place on heating ; on the contrary, the process of grain growth would only continue further. A welded joint in ferritic chromium steel will therefore always be accompanied by a more or less coarse-grained transition zone, which will in general possess poor mechanical properties, particularly notch toughness.

Table III gives the chemical compositions of a number of important ferritic chromium steels.

The object of the small addition of aluminium to AISI 430 is to suppress martensite formation. Since the steel contains only 14% chromium, a partially martensitic structure would not be impossible if the aluminium was omitted.

Types AISI 430F and AISI 430FSe contain fairly appreciable quantities of sulphur and selenium respectively, with the object of improving machinability. This results, however, in a clearly negative effect on weldability ; neither type can be welded without the appearance of porosity.

Type AISI 446 contains a small addition of nitrogen, the purpose of which is to restrict grain growth at high temperature by means of nitride formation.

From the foregoing it follows that the weldability of the ferritic chromium steels leaves something to be desired.

Depending on the welding process used, there will always be a more or less serious embrittlement of the heat affected zone. The filler material used is almost always an austenitic chrome-nickel steel, preferably Type E 309. Use is sometimes made of Type E 310, but the weld metal then deposited is completely austenitic, which is undesirable in view of the susceptibility to solidification cracking.

Table III Ferritic chromium steels

AISI-code	Chemical composition						
	C	Cr	Mn	Si	P	S	other
405	≤ 0,08	11,5-14,5	≤ 1,0	≤ 1,0	≤ 0,04	≤ 0,03	—
430	≤ 0,12	14,0-18,0	≤ 1,0	≤ 1,0	≤ 0,04	≤ 0,03	Al 0,1-0,3
430F	≤ 0,12	14,0-18,0	≤ 1,0	≤ 1,0	≤ 0,04	≤ 0,15	—
430FSe	≤ 0,12	14,0-18,0	≤ 1,0	≤ 1,0	≤ 0,06	≤ 0,06	Se ≥ 0,15
442	≤ 0,20	18,0-23,0	≤ 1,0	≤ 1,0	≤ 0,04	≤ 0,035	—
443	≤ 0,20	18,0-23,0	≤ 1,0	≤ 1,0	≤ 0,04	≤ 0,03	Cu 0,90-1,25
446	≤ 0,20	23,0-27,0	≤ 1,0	≤ 1,0	≤ 0,04	≤ 0,03	N < 0,25

When an austenitic chrome-nickel steel is used as a filler material the problem of embrittlement in the transition zone naturally remains. The weld itself obtains a certain measure of ductility, however, and as a result any stresses arising can be better absorbed.

Ferritic chrome steels may have a high notch sensitivity at room temperature ; the transition from tough to brittle behaviour lies above room temperature, and therefore reheating is recommendable.

In order to keep stresses caused by welding low, preheating will also be beneficial. As a result of preheating, however, the heat affected zone will remain longer at high temperature, causing the problem of grain growth to appear to a correspondingly severe degree. Therefore only in cases involving plates thicker than 6 mm and stiff structures, in which high welding stresses can arise, is preheating to a maximum of 280°C employed.

During welding a high heat input should of course be avoided as far as possible. For this reason preference is given to a high welding speed and a relatively low welding current. In this respect MIG welding is a very attractive process, alongside welding with coated electrodes. As a rule, post-weld heat treatments, such as stress relieving, are not given.

In view of the embrittlement of the heat affected zone, local high stresses must be avoided by every possible means. Welds must be really smoothly finished. Undercutting, always undesirable in a weld, is absolutely impermissible with ferritic chromium steels. The same applies to defects such as imperfect root runs, excessive non-alignment of the plates, excessive root runs, etc.

Table IV contains information on filler materials for ferritic chromium steels.

Table IV Welding processes and weld filler materials for ferritic chromium steels.

Welding process	Filler material						Heat treatment	
	Nominal		Chemical composition				preheat	postweld
	C	Cr	Ni	Mo	Mn	Si		
Coated electrodes	≤ 0,08	15-18	—	—	≤ 1,0	≤ 0,9	200-320°C	—
	≤ 0,03	24	13	—	1,5	0,8	20-280°C	—
	≤ 0,15	26	21	0,5	5,0	0,3	20-280°C	—
MIG (solid wire)	≤ 0,12	22	11	—	1,2	0,8	20-280°C	—
	≤ 0,12	26	21	—	1,5	0,5	20-280°C	—
MIG (fluxcored wire)	≤ 0,08	24	13	—	1,5	0,8	20-280°C	—
TIG (rod)	≤ 0,12	22	11	—	1,2	0,8	20-280°C	—
	≤ 0,12	26	21	—	1,5	0,5	20-280°C	—