FERRITIC STAINLESS STEELS

Ferritic stainless steels are iron-chromium (Fe-Cr) based alloys that are used for their anticorrosion properties rather than for their mechanical properties (strength, ductility or toughness). However, these properties are still considered when Stress Corrosion Cracking (SCC) is taken into account and for which ferritic grades are considered superior to austenitic grades.

Formerly, ferritic stainless steels were used in non-welded constructions (riveted and bolted assemblies, etc.). The first generation (those with high chromium) were supposed to be non weldable, particularly for thicker sections that have a high propensity to cold cracking and to a drastic drop in ductility in the as-welded condition. The low weldability of these alloys is mainly due to a high chromium content and to the difficulty related in obtaining alloys with a low level of impurities. The invention of the AOD (Argon Oxygen Decarburization) process in the 1960's has enabled the development of high purity Fe-Cr alloys containing negligible traces of carbon. Since then the development of refined grades in thinner sections has led both to a significant gain in weight and structures maintaining their good integrity during the welding process.

Typical Uses

Ferritic stainless steels are used in many fields and applications such as elements and accessories for kitchens and bathrooms, roofs, architectural objects, appliances, safeguards, metallic doors, elevators, storage tanks, etc. Because of their good thermal conductivity and low thermal expansion these alloys are also used in the manufacturing of chimneys, mufflers, exhaust systems, fasteners, as well as heating elements used in molten salt baths for heat treatments, etc.

Compared to austenitic stainless steels, the low coefficient of thermal expansion (CTE) of the ferritic metal explains the low tendency to scaling of the refractory oxide layer formed at the surface. This feature ensures the good thermal stability of these alloys. However, it is important to outline that ferritic stainless steels have a designed temperature generally limited to 400°C (750°F) maximum in order to prevent the fragilisation of the ferritic microstructure which occurs roughly at 475°C (890°F), mainly in the high chromium grades.

Classes (generations) of ferritic alloys

The evolution of ferritic stainless steels has been through three main steps or generations. This progress has aimed at the development of a fully ferritic single-phase microstructure that has a significant corrosion resistance and a good weld integrity in the as-welded condition. The development of these properties has been achieved through :
- A gradual increase of chromium content.
- The addition of elements such as niobium, titanium and aluminum (Nb, Ti and Al) that have a high chemical affinity for the residual interstitial elements such as carbon, nitrogen or oxygen (C, N or O).
- The addition of other ferrite stabilizing elements such as molybdenum and silicon (Mo and Si).

The first generation includes mainly the following grades: 430, 434, 436, 442 and 446. Besides their high chromium content, those containing 0.12% to 0.20% of carbon are vulnerable to a drop in ductility and to corrosion due to the formation of martensite (quenched structure) and intermetallic precipitates in the ferritic phase in the as-welded condition.

The second generation includes low carbon alloys developed from the modification of first generation grades. They contain other ferrite forming elements like titanium, niobium and aluminum. In addition to promoting the ferritic microstructure, aluminum also improves the oxidation resistance at high temperatures by stabilizing the chromium oxide layer. This generation includes the 405, 409, 409Cb, 439, etc. The weldability of these alloys is noticeably better than the one of the first generation grades.

The third generation is that of the recent alloys called super-ferritic. The forming process of these alloys experiences some difficulties related to the elevated chromium levels. These are used for applications subjected to severe corrosion conditions such as in chloride environments. The grades 444, 29-4, 29-4-2 are the most typical ones in this class. These consist of high purity alloys where the interstitial elements, carbon and nitrogen in particular, are reduced to a minimum in order to improve the ductility of the alloy. Among the alloying elements is molybdenum which increases the localized corrosion resistance in addition to its ferritizing effect.

Microstructure

Ferritic stainless steels have a ferritic single-phase structure that is stable at any temperature. Chromium remains the main alloying element which ensures the stainless character to these ferritic alloys. The content of other elements such as nickel and manganese must remain marginal while carbon and nitrogen traces must be reduced as much as possible.

The Delta ferrite phase (δ) forms at high temperatures from the liquid, once crystallized, it does no longer transform upon cooling. This fully ferritic microstructure is therefore not hardenable by any heat treatment. This lack of phase transformation explains the tendency of these alloys to grain coarsening of the microstructure upon heating.

Weldability

The various problems inherent to the welding of ferritic stainless steels are mainly summarized in the following: cold cracking and loss of ductility, hot embrittlement and hot cracking, deterioration of corrosion resistance.

Cold cracking and loss of ductility

These are largely related to the formation of martensite, a hard and brittle phase, between the ferritic grains upon cooling. The phenomenon of cold cracking depends on numerous factors: content of interstitial elements (C, N) present in the alloy, heat or welding conditions and also of the post-weld heat treatment (PWHT). Indeed, the reduction of the interstitial elements aims both to the improvement of the intergranular corrosion resistance and to the prevention of the martensite formation upon cooling.

When considering the stress exerted on the welded joint, its effects are relatively low due to the low coefficient of thermal expansion of the ferritic structure on one hand and to the fact that the base metal is generally shaped into thin sections on the other hand.

Concerning the effect of hydrogen, its high diffusivity in the ferritic structure imply a preheat and a post-

heat treatment (PWHT). Taking this into account, sometimes the use of some austenitic filler materials is recommended for welding thick or critical joints to prevent them from cold cracking.

Hot cracking

This phenomenon depends particularly on the purity of the alloy and the size of microstructures grains. The purity is related to the content of undesirable residual elements sulphur, phosphorus, carbon, etc. (S, P, C, etc.) which segregate at the last stage of solidification to form low melting eutectic compounds (an eutectic compound has a specific analysis and the lowest melting point for a mixture these elements). Furthermore, the presence of these compounds will serve as starters for hot tearing, which will occur mainly during the alloy contraction at the last stage of solidification. However due to their primary ferritic solidification mode, hot cracking is less critical in the ferritic stainless steels than in the austenitic stainless steel because the predominant phase, Delta ferrite (δ), is less sensitive to the effect of impurities since it may, among others, dissolve sulphur up to a limit of 0.14%.

The other controlling factor is the sensitivity of ferritic grains to coarsening under the effect of heat. The more the microstructure is coarse, the less are the number of grain boundaries and the longer they are. The segregation of residual impurities at grain boundaries render them in a liquid or a pasty state at the final stage of solidification. As a consequence of that, the already solidified grains will be prone to slide on each other from the weak plans before causing internal tearing in the microstructure. So, overheating and maintaining the structure of the alloy at high temperatures must be avoided as much as possible. In this regards, a moderate preheat at 150-200°C (300-400°F) helps to reduce the heat input and the holding time at high temperatures during the arc time. In addition, the good thermal conductivity of ferritic alloys is another advantageous factor which accelerates the cooling rate, refines the microstructure and reduces the risk of hot cracking.

Hot embrittlement

Various embrittlement modes (loss of ductility) are associated to ferritic stainless steels whose three main forms are listed below:

Embrittlement at 475°C

This phenomenon is proportional to the chromium content and occurs in the temperature range of 425-550°C (800-1025°F). It is the result of the decomposition of the ferrite into two phases: a rich-chromium phase (α') and a rich-iron phase (α). The more the alloy is rich in chromium and ferritizing elements (Mo, Nb), as in the alloys of the 3rd generation, the faster will be the reaction. The consequences of this reaction consist essentially in a selective corrosion of the rich-iron phase. In order to prevent this form of embrittlement, the service temperatures of the part must always be limited to 400°C (750°F) max.

Precipitation of embrittling phases and intergranular corrosion

Sigma Phase: like for the embrittlement at 475°C, Sigma phase (a chromium-rich and very brittle phase) is the product of transformation of the ferritic Delta phase occurring when the microstructure is subject to a long exposure time in the temperature range of 540-870°C (1000-1600°F). This new phase forms rapidly in high chromium grades and molybdenum is also a promoting element for that transformation. The presence of this new phase alters both the corrosion resistance and the ductility of weld joints. Dissolving this phase requires a solutionizing heat treatment at a temperature of

around 870°C (1575°F) followed by water quenching.

Chi Phase: it forms predominantly in molybdenum bearing grades, mainly those of the 3rd generation such as 29-4 (29Cr-4Mo) or 29-4-2 (29Cr-4Mo2Ni). This phase, stable up to 900°C (1650°F), forms mutually with Sigma phase.

High temperature embrittlement: this embrittlement is due to the precipitation of intermetallic phases (carbides, nitrides) at the grain boundaries at temperatures of roughly of 0.7 Tm (melting temperature of the alloy). Influential factors consist of residual elements or impurities (C, N, O), grain size and the chromium content. For this matter, cast alloys that often contain high levels of carbon are not recommended. Titanium or niobium stabilized grades or aluminum bearing grades (denitrifying element) inhibit both the grains coarsening and the intergranular precipitation. Intergranular precipitation embrittles locally the grain boundaries and alters the ductility of the whole structure. In order to restore the ductility and the corrosion resistance of the weld, one must dissolve these precipitates by a solutionizing heat treatment to 750-950°C (1380-1740°F) followed by rapid water cooling.

Grain coarsening

The grains of a ferritic structure start to grow from 1000-1100°C (1830-2010°F) since the microstructure does not undergo any phase transformation. The phenomenon speeds up when the metal is in the cold hardened condition and it favors concurrently the sensitization to intergranular corrosion of the microstructure. The grain size and the content in interstitial elements have a combined effect in the loss of ductility. Stabilized grades (Ti or Nb) show a better resistance to grains coarsening than the non-stabilized grades.

Welding processes and influential parameters

On the microstructural point of view, a free martensite and a free precipitates ferretic microstructure is sought in a welded joint in order to achieve a good toughness in the as-welded condition. For that, several considerations inherent to the ferritic microstructure must therefore be taken in account during the welding of ferritic stainless steel.

The ferritic phase, in the weld joint and the heat affected zone, is sensitive to interstitial elements such as carbon and nitrogen which could alter locally this phase by diffusion and transform it to austenite at high temperatures. Then this austenite will tend to transform to martensite (brittle) along the ferritic grains of the microstructure upon cooling.

The semi-automatic welding process of these steels excludes the use of carbon dioxide CO_2 and nitrogen for shielding of the molten puddle, as a purge or as a back shielding. Gas used for the GMAW process consist of the mixture of Ar-(1-2%) O_2 mixture which must also be of a high purity, particularly when welding super ferritic stainless steel grades (3rd generation). If CO_2 gas is to be used instead of oxygen, its content must also not exceed 1-3%. The role of oxygen is to stabilize the arc and promote the wetting of the molten pool.

GTAW process uses high purity inert gases like pure argon or a mixture of Ar-30% He to increase the welding speed.

Welding must be performed with a low heat input (1 kJ/mm) to limit the grain growth. Similarly, the welding time must also be reduced especially for the case of high chromium and high purity grades. For the same holding time at high temperatures, it is rather the high chromium alloys that are more prone to the loss of their toughness. The role of preheating consists in limiting the holding time at

high temperatures and in reducing the tendency of the grain coarsening in the HAZ.

Among the questionable welding processes, SAW is not suitable for welding these grades especially for the case of thin gauge materials.

Filler metals

The ferritic filler metals available are very limited compared to austenitic filler metals. Base metals are welded with stabilized or low carbon filler metals in order to minimize the sensitization. The most common example consists of the welding of stainless steel 430 with E430Nb or 439 with ER439 (439Ti).

Low or medium chromium grades, 1st and 2nd generations, are generally welded with an equivalent filler metal: 430, 430Nb, 409, 409Cb, 439. Stabilized austenitic filler alloys, 347 or 309Cb, have the advantage to produce a "duplex" microstructure in the welded joints that results in an improved ductility in comparison to ferritic microstructures. However, because of the reduced resistance to stress corrosion cracking (SCC) of austenitic stainless steels in chlorides environments, filler metals of that series are not recommended for welding super ferritic alloys of the 3rd generation. Since most of these alloys have no equivalent filler metal, it should be then suggested to weld them using as a filler metal:
– small strips cut from of the same base metal, or
– nickel-based filler metals equivalent to alloy 625, C-276, C-22, C-59, etc. This is especially recommended for thick welded joints or even those which are exposed to temperature changes in service. The nickel alloys have a low thermal conductivity which will reduce heat transfer to the base metal and thus to narrow the extent of the HAZ while preventing the grain coarsening.

Preheat and post-weld heat treatment – PWHT

Preheat or post weld heat treatments are not necessary when the alloy is completely ferritic before welding and in the as-welded condition. Remember that excess of heat accumulation in the metal coarsens the grains and slows down the cooling. Furthermore, a slow cooling leads to the precipitation of intergranular phases.

In general, a preheat and an interpass temperature within 150-300°C (300-400°F) are recommended for ferritic microstructures that may contain some proportion of martensite.

The post weld heat treatment may compromise the corrosion resistance of rich-chromium 3rd generation alloys containing molybdenum such as 29-4 or 29-4-2 because of their very high susceptibility to the formation of brittle phases like Sigma and Chi at heating temperatures.

To restore the ductily to a ferritic structure containing martensite, one has to carry out a postweld heat treatment as soon as the welding operation is completed from the interpass temperature. This stress relieving treatment is done at a temperature of 750-800°C (1380-1470°F) maximum, which remains slightly below that corresponding to the local reformation of austenite in carbon-rich areas. This treatment aims to temper the martensite, to reduce residual stresses developed in the microstructure after welding and to improve toughness in the welded joint and the heat affected zone.

For joints welded with nickel filler metals, a post weld heat treatment at 620°C (1150°F) may be sufficient to temper the martensite and avoid the risk of cold cracking. In summary, this treatment prevents cold cracking phenomenon called hydrogen-induced cracking (HIC).

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