HIGH NITROGEN CONTAINING DUPLEX STAINLESS STEEL HAVING HIGH CORROSION RESISTANCE AND GOOD STRUCTURE STABILITY

The present invention relates to a ferrite-austenitic Cr—Ni—Mo—N steel with high corrosion resistance and good structure stability. Duplex (ferrite-austenitic) stainless steels have several interesting properties, such as high strength and good resistance to stress corrosion. An increase of the alloying content will also give good resistance to pitting and crevice corrosion. High contents of the active alloying elements chromium, molybdenum and tungsten, however, increase the tendency for precipitation of intermetallic phases so strongly that problems can be obtained in the manufacturing and in connection with welding. Nitrogen stabilizes the alloy against precipitation of intermetallic phases at the same time as an increase of the resistance to pitting and crevice corrosion will be obtained. Thus a high content of N is desirable but is confined because of a limited solubility of nitrogen in the melt, which gives rise to porosity, and because of the solubility of nitrogen in the solid phase, which causes precipitation of chromium nitrides.

If the composition in the two phases is not the same with respect to active components, one phase will be more sensitive to pitting and crevice corrosion, which reduces the resistance of the alloy.

The optimizing of a duplex stainless steel with high corrosion resistance and good structure stability is thus very complex. Systematic development work has, however, resulted in a duplex stainless steel which in a surprising way combines a number of good properties, and this will be shown in the following. The composition of the alloy is not the most important factor, but more important is the balance between various alloying components and structure factors.

The alloying composition and the microstructure of the alloy according to the invention are as follows:

C—max 0.05%
Si—max 0.8%
Mn—max 1.2%
Cr—23-27%
Ni—5.5-9.0%
Mo—3.5-4.9%
Cu—max 0.5%
W—max 0.5%
V—max 0.5%
N—0.25-0.40%
S—max 0.010%
Ce—max 0.18%

and the remainder Fe besides normally present impurities, at which the alloying contents are so adjusted that the content of ferrite, α, is 30-55%.

Chromium is one of the most active elements in the alloy. Chromium increases the resistance to pitting and crevice corrosion and increases the solubility of nitrogen in melt as well as in solid solution. A high chromium content, >23%, is therefore desirable, preferably higher than 24.5%.

Chromium increases, however, in combination with molybdenum, tungsten, silicon and manganese, the tendency for precipitation of intermetallic phases. The sum of chromium, molybdenum, tungsten, silicon and manganese in the alloy has therefore to be limited. Nitrogen reduces the content of chromium in the ferrite phase and will therefore reduce the tendency for precipitation of intermetallic phases. The amount of ferrite in the alloy is also important through the influence on the phase composition. A decreased content of ferrite favors intermetallic phases. The chromium content should not exceed 27%.

Molybdenum is also a very active alloying element. Molybdenum increases the resistance to pitting and crevice corrosion. It has also been found that molybdenum in combination with a high content of austenite and high solubility in the austenite phase decreases the tendency for nitride precipitation in solid phase. A high content of molybdenum, >3.5%, is therefore necessary in the alloy, suitably higher than 3.8% and preferably higher than 4.05%.

But similar to chromium, molybdenum increases the tendency for precipitation of intermetallic phases and the content of molybdenum has therefore to be limited to max 4.9%.

Tungsten is an alloying element related to molybdenum and has a similar influence on the resistance to pitting and crevice corrosion as well as on the structure stability. Tungsten has, however, twice as high an atomic weight as molybdenum, it costs twice as much per weight unit as molybdenum, and increases the handling difficulties in the steel manufacturing. Tests and calculations of alloying with tungsten have shown that the manufacturing costs are considerably increased. The content of tungsten is therefore limited to 0.5 percent by weight.

Nitrogen is the most important alloying element in this new alloy. Nitrogen has a great number of effects on properties, microstructure and manufacturing cost. Nitrogen influences the distribution coefficient of chromium and molybdenum so that a higher content of nitrogen increases the content of chromium and molybdenum in the austenite. This has the following effects:

The contents of chromium and molybdenum in the ferrite decrease which reduces the tendency for precipitation of intermetallic phases which are precipitated in the ferrite or in the phase boundary ferrite-austenite.

The most frequently present intermetallic phases in this kind of alloy are σ-and χ-phase. None of these phases has any considerable solubility of nitrogen. A higher content of nitrogen will therefore delay the precipitation of σ- and χ-phase.

In welding operations nitrogen facilitates the re-precipitation of austenite which drastically improves the toughness and corrosion resistance of the welding joint. The rapid re-precipitation of austenite caused by nitrogen also decreases the tendency to precipitation of intermetallic phases. At the rapid precipitation the ferrite-stabilizing elements, among others chromium and molybdenum, are frozen in the austenite phase. The diffusion rate of the alloying elements in the austenite phase is considerably lower than in the ferrite phase. In other words there is obtained in the welding material and the heat-influenced zone a state of non-equilibrium, which lowers the contents of chromium and molybdenum in the ferrite phase, obstructing the precipitation of intermetallic phases.

Systematic examinations showed that the measure of the corrosion resistance (PCCR)* is given by (in percent of weight):

$$PCCR = \%\ Cr + 3.3\%\ Mo + 16\%\ N - 1.6\%\ Mn - 122\%\ S \quad (1)$$

* (i.e. Pitting and Crevice Corrosion Resistance)