Material Selection for Deepwater Gate Valves

By:
Mahmoudreza Dana Seresht

Supervisor:
Stein Ramberg

Examiner:
Rolf Sandström

Master Degree Project

School of Industrial Engineering and Management
Department of Materials Science and Engineering
Royal Institute of Technology (KTH)
SE-100 44 Stockholm, Sweden
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ABSTRACT

Material selection is an important step during the design process of an object. The goal is to produce an object to meet the requirement with minimum cost. During the recent years with discovery of oil and gas in deep water, oil and gas industry facing new challenges of handling corrosive material in seabed that gives more importance and criticality to material selection of equipment for this kind of application. Hydrogen sulfide (H2S), chloride and carbon dioxide (CO2) have made the big challenges for material that handle corrosive fluids in the seabed.

This report presents a brief review of material selection for two parts of deepwater gate valve, Body and Gate. It is mostly focused on mechanical properties and required corrosion resistance. Ferritic alloys with low PRE numbers and low mechanical properties and also austenitic alloys with low yield strength are not a proper option for this case. Alloy 2205 is the most common stainless steel which is used in deep water gate valve production. There are other alloys in duplex group that show better mechanical and chemical properties than alloy 2205 but because of their high expense are not used by industries.

Keywords: Gate Valve, Corrosion, Austenitic, Lean Duplex Steel, Duplex Stainless Steel
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1 INTRODUCTION

In recent years increasing of energy uses and consumption of existing oil and gas deposits, make it necessary to search for deeper oil and gas resources. In this field, equipment contact with environment containing salt water, hydrogen sulfide and carbon dioxide. Depend on composition and temperature these aggressive environments can cause different kind of corrosion so because of these condition, new material development, evaluation of materials are using in oil and gas industries is necessary. It should be also clear that how materials are chosen and which parameters influence the material selection. In this aggressive condition (high pressure, high temperature and high flow rate), carbon steel or low alloy steel has insufficient corrosion resistance. High alloy stainless steels probably are the best choice to be used in this kind of aggressive environment to prevent corrosion that caused by chloride ions, H2S and CO2 [1,2].

Duplex and super duplex stainless steels have equal amount of austenite and ferrite structure and are promising alloys in deep oil and gas services. Combination of these two phases cause some advantages, concentration of plastic deformation on ductile austenite phase results in better mechanical properties. These two phases also have electrochemical effect on each other, the ferrite phase as anode can protect austenite which behaves as cathode. These kind of stainless steels exhibit good resistance to corrosion at high carbon dioxide pressure, high concentration of chloride ions and limited amount of hydrogen sulfide [1,2].

Different companies use different individual ways for CRAs(Corrosion Resistant Alloys) selection. Some big companies with research facilities simulating the situation of a part with a initiated test program then according to the previous information in that field, a group of alloys is selected and finally information from tests result to elimination or acceptance of alloys. Another way is to find and review the literatures which are applicable in the field condition specially the literatures that containing corrosion data. Using this method gives limited number of candidate alloys, these selected alloys must be tested under specific field condition to select correct alloy. Using of other resources like NACE 175/ISO15156 which cover different alloys for different applications, literature review and using available data are the other and less expensive method for material selection but it should be considered that, for example the corrosion behavior of alloys is different when the parameters of aggressive containing environment change [8].
1.1 Gate Valve
“A subsea gate valve is used to control the flow of fluid from the reservoir through the X-mas tree and into the pipeline system”. Valve is opened or closed by moving stem that moves a round or rectangular disc in a linear direction. When the pressure drop through the valve is critical, gate valves are used to have minimized pressure drop and uninterrupted flow. The gate valve should be fully closed or open otherwise it produces turbulence and increase gate or seal’s tendency to erosion [3].

![Diagrams of Gate Valve Stages](image)

Figure 1: “Stages of Gate Valve”[3]

Operation of gate valve can be seen in figure 1, the fluid flow through the pipe and nothing stop it when the gate valve is fully open, figure 1a. The opening between the outer sealing and seat
allows fluid to flow into the valve cavity. It is seen in figure 1b that the flow stops when valve is closed. When valve is partly closed sealing mechanism as shown in figure 1c starts to work, it happens when seat is pushed into the valve due to high pressure between seat and gate. Figure 1d shows that sealing mechanism is completely working. High pressure in cavity helping to keep valve closed. Opening valve needs more work to overcome all the forces are shown in figure 1e [3].

### 1.2 Corrosion Mechanism in Sour Service

Crude oil and gas contain of hydrogen sulfide, chloride ions and water that provide an aggressive environment in contact with metals. Relevant to these kinds of production, different kinds of corrosion mechanisms may happen. A brief review of these kinds of corrosion mechanisms is given in this section.

#### 1.2.1 H2S Cracking Corrosion

In the sour environment which contain of H2S, two kind of H2S cracking corrosion can be happened.

**Sulfide Stress Cracking (SSC):**

This kind of corrosion develops cracking in the present of surface tensile stress, corrosion and water. Cracking produces at stress levels below tensile strength of material. In SSC, corrosion produces hydrogen ions that pick up electrons and form hydrogen molecules at the base material[4]. Hydrogen has different solubility and diffusivity into the different metal structure and also can affect their mechanical properties differently. For example, Hydrogen reduces the ductility of ferritic structure but does not have any influence on austenitic structure. Hydrogen can pronounce embrittlement in both ferritic and austenitic structure but their yield and tensile strength are unaffected. Hardness and tensile strength of steel increase by influence of hydrogen. It was found by investigation that before hydrogen charging, the hardness of ferrite is more than austenite but it reverse after hydrogen charging. Hydrogen is important in wet corrosion which is controlled by electrochemical reactions, containing anode and cathode reactions [5].
Anode Reaction:

\[ Me \rightarrow Me^{x+} + xe^- \quad (1) \]

Cathode Reaction:

\[ 2H^+ +2e^- \rightarrow H_2 \quad (2) \]
\[ O_2 +4H^+ +4e^- \rightarrow 2H_2O \quad (3) \]
\[ O_2 +2H_2O +4e^- \rightarrow 4OH^- \quad (4) \]

Uniform corrosion for stainless steel often accrue in acidic environment and the common way
of hydrogen formation is equation 2.

Hydrogen embrittlement is a problem that metallic material can suffer at presence of hydrogen
even at ambient temperature. Ferritic, martensitic and duplex steel show more susceptibility to
hydrogen embrittlement than pure austenite. It is well known that materials with higher strength
are more susceptible to hydrogen embrittlement than the same materials with lower strength.

HISC (Hydrogen Induced Stress Cracking) is a kind of failure that is caused by hydrogen in
industries. The mechanism of HISC in duplex steel is not clear, a crack propagates from ferrite to
austenite and induces localized microcracking of the austenite grains. The hydrogen enhances
dislocation movement; an obstacle is produced by accumulation of dislocations in front of the
diffusion zone. At a critical level of dislocation emission, crack propagates into the austenite[5].

Hydrogen atoms can diffuse into the metal and cause crystalline embitterment, H2S can promote
the diffusion of hydrogen atoms [4].

**Hydrogen Induced Cracking (HIC):**

Atomic hydrogen diffuses into the crystal structure of steel, in the steel microstructure, there are
sensitive locations that can trap diffused hydrogen atoms and cause hydrogen embrittlement. In
HIC, hydrogen accumulates in for example segregation bands and with increasing hydrogen
atoms, hydrogen pressure increase and can deform the surrounding steel. For corrosion resistance
alloy (CRA) NACE MR0175/ISO 15156 and NORSOK M-001 has established different limiting
operating and environment parameters (Temperature, Partial Pressure of H2S, PH). Table 1 can
be used to avoid SSC [4].
1.2.2 Chloride Induced Pitting and Stress Corrosion Cracking (CSCC).
Duplex, super duplex, austenitic and super austenitic stainless steel are resistant to CO2 corrosion but susceptible to CSCC and pitting. In pitting corrosion small holes are created and localized in metal surface area where the remind surface is un-corroded. In CSCC there are two steps, first the passive film should be broke down which calls Initiation and depends on Cr and Mo content. The second step is Propagation which is depends on microstructural and the area around precipitates that are lack of chromium [4].
PRE(%Cr + 3.3%Mo + 16%N) shows the material resistance to pitting. There are also CPT(Critical Pitting Temperature) and CCT(Critical Crevice Temperature) which are used for comparison of different steel, see table 2 [4].

Table 2
‘Typical PRE, CPT and CCT number for Stainless Steel”[4]

<table>
<thead>
<tr>
<th>Materials</th>
<th>Typical PRE</th>
<th>CPT (°C)</th>
<th>CCT (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>304L</td>
<td>19</td>
<td>2.5-4</td>
<td>-</td>
</tr>
<tr>
<td>316L</td>
<td>24-28</td>
<td>5-15</td>
<td>&lt;5</td>
</tr>
<tr>
<td>904L</td>
<td>36</td>
<td>40-45</td>
<td>15-25</td>
</tr>
<tr>
<td>254 SMO (6% Mo)</td>
<td>46</td>
<td>65-80</td>
<td>30-60</td>
</tr>
<tr>
<td>Duplex (22% Cr)</td>
<td>35</td>
<td>20-42</td>
<td>17.5-25</td>
</tr>
<tr>
<td>Super Duplex (25% Cr)</td>
<td>42</td>
<td>55-88</td>
<td>35-43</td>
</tr>
</tbody>
</table>

1.2.3 Corrosion from Dissolved Oxygen
In hydrocarbon service, oxygen present must be avoided. Only alloys with PRE>40 can show resistance to crevice corrosion to ambient temperature [4].

1.2.4 Galvanic Corrosion
Galvanic corrosion occurs when two different metals contact each others. These two different metals with different potential should be in electrical contact and exposed to an electrolyte environment [4].

1.3 Influence of Alloying Elements
Figure 3. shows that Cr and Ni have a great effect on corrosion resistance of alloys. To achieve a good corrosion resistance at least 21% Cr and 4% Ni are required. However increasing of Cr and Ni amount improves corrosion resistance differently [2].
Figure 3: “Effect of the Cr and Ni on resistance to pitting corrosion.

10 pct FeCl$_3$·$6H_2$O, 50°C, 24h” [2]

Figure 4 shows the influence of Cr and Ni content on pitting corrosion resistance. It can be seen from figure (4a) that with increasing amount of Ni more Cr is needed to obtain satisfactory pitting resistance. It is seen from figure (4b) that 4 to 8 percent Ni are needed to achieve satisfactory results for alloy with 22% Cr and 25% Cr [2].

Figure 5. shows the relation between pitting corrosion rate and ferrite content. It is shown that in alloy with (5.5% Ni, 7% Ni) and (22% Cr, 25% Cr) at a constant ferrite content, changing in Cr and Ni percent do not affect pitting corrosion resistance [2].
Figure 5: ‘Effect of ferrite content on pitting resistance’[2]

Figure 6. It is seen how the general corrosion is affected by Cr and Ni contents. The results are similar to the results were shown in figure 1. The difference is that when Cr content increases more than 4%, the corrosion resistance only changes with Cr content [2].

Figure 6: “Effect of the Cr and Ni contents on resistance to general corrosion”[2]

Figure 7. shows the influence of Mo and N on pitting corrosion rate. With adding Mo up to 3%, almost completely pitting resistance is obtained. Nitrogen increasing has less effect on pitting
corrosion. To achieve optimum resistance to pitting and general corrosion a combination of 3% Mo and 0.1% to 0.15% N is recommended [2].

![Figure 7: “Effect of Mo and N content on pitting resistance, 25Cr-7Ni Alloy”[2]](image)

2 DISCUSSION

2.1 Preselection of Material

During pre-selection the material types which are possible to apply are identified. The purpose is to find suitable materials types at an early stage of the design process. In this way a basic understanding for which groups of candidate materials can be considered is created and the total effort is limited by eliminating many material types [6].

Subsea gate valves contain of different parts as explained before among them we investigate on Body and Gate part. These two parts can be made by casting or forging. Steels are normally used in valves manufacturing and also Aluminum has high capability to cast or forged. Now we are going to study these two groups and try to eliminate one of them.
Table 3 shows general requirements for deepwater gate valves, Table 4 gives mechanical requirements for body and gate and Table 5 gives mechanical properties for aluminum alloys.

**Table 3**

General requirements for deepwater gate valves

<table>
<thead>
<tr>
<th>Requirement</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Design life time</td>
<td>30 Years</td>
</tr>
<tr>
<td>Design water depth</td>
<td>2000-3000 m</td>
</tr>
<tr>
<td>Valve design temperature</td>
<td>-35 to +145 °C</td>
</tr>
<tr>
<td>Valve design pressure</td>
<td>500 to 700 Bar</td>
</tr>
</tbody>
</table>

**Table 4**

Minimum Mechanical requirements for body and gate

<table>
<thead>
<tr>
<th>Requirement</th>
<th>Body</th>
<th>Gate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength</td>
<td>500 Mpa</td>
<td>750 Mpa</td>
</tr>
<tr>
<td>Yield Strength</td>
<td>400 to 450 Mpa</td>
<td>450 to 500 Mpa</td>
</tr>
</tbody>
</table>

**Table 5**

Mechanical properties for aluminum alloys

<table>
<thead>
<tr>
<th>Requirement</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength</td>
<td>230-570 MPa</td>
</tr>
<tr>
<td>Yield Strength</td>
<td>215-505 MPa</td>
</tr>
</tbody>
</table>

With comparing values in the tables 4-5, it can be seen that aluminum alloy cannot fulfill the mechanical requirements. Also these parts are in contact with corrosive environment (containing H2S and NaCl) and according to NACE MR0175/ISO15156 they should not be used in direct
contact with H2S because of severe corrosion attack. On the other hand, there are different types of steel alloy that can achieve these values of mechanical properties.

2.2 Prerequisite

It is known that high performance stainless steels can be a good option with regard to mechanical requirement. In this section the chemical, mechanical properties and weldability of this group will be reviewed but it also should be noted that because of aggressive containing environment only the stainless steels with good corrosion resistance may meet the requirement so the focus will be on this group.

2.2.1 High Performance stainless Steel

The ‘high performance stainless steels’ are a group of stainless steel which in compare with standard stainless steel shows high corrosion resistance in different corrosive environment. High performance stainless steel classified into three groups: Austenitic, Ferritic and Duplex [7].

**Austenitic Stainless Steel**

These grades consist of face-centered cubic austenite. They have low yield strength and high tensile strength. At high temperature secondary phases form that damage the corrosion resistance and mechanical properties so these alloys are not allowed to use at temperature above 500°C[7]. Table 6. gives some example of this group.

<table>
<thead>
<tr>
<th>Name</th>
<th>UNS Number</th>
<th>Sub Group</th>
<th>C</th>
<th>N</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Cu</th>
<th>PRE Number</th>
<th>Tensile Strength (Mpa)</th>
<th>Yield Strength (Mpa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>316L</td>
<td>S31603</td>
<td></td>
<td>0.03</td>
<td>0.10</td>
<td>16.0-18.0</td>
<td>10.0-14.0</td>
<td>2.0-3.0</td>
<td>-</td>
<td>23</td>
<td>485</td>
<td>170</td>
</tr>
<tr>
<td>Alloy 825</td>
<td>N08825</td>
<td>A-1</td>
<td>0.05</td>
<td>-</td>
<td>19.5-23.5</td>
<td>38.0-46.0</td>
<td>2.5-3.5</td>
<td>1.50-3.50</td>
<td>28</td>
<td>586</td>
<td>241</td>
</tr>
<tr>
<td>317LN</td>
<td>S31753</td>
<td>A-2</td>
<td>0.03</td>
<td>0.10-0.22</td>
<td>16.0-20.0</td>
<td>11.0-15.0</td>
<td>3.0-4.0</td>
<td>-</td>
<td>30</td>
<td>570</td>
<td>270</td>
</tr>
<tr>
<td>904L</td>
<td>N08904</td>
<td>A-3</td>
<td>0.02</td>
<td>-</td>
<td>19.0-23.0</td>
<td>23.0-28.0</td>
<td>4.0-5.0</td>
<td>1.00-2.00</td>
<td>32</td>
<td>530</td>
<td>220</td>
</tr>
<tr>
<td>Alloy 28</td>
<td>N08028</td>
<td>A-3</td>
<td>0.02</td>
<td>-</td>
<td>26.0-28.0</td>
<td>29.5-32.5</td>
<td>3.0-4.0</td>
<td>0.60-1.40</td>
<td>36</td>
<td>517</td>
<td>213</td>
</tr>
<tr>
<td>254SMO</td>
<td>S31254</td>
<td>A-4</td>
<td>0.02</td>
<td>0.18-0.22</td>
<td>19.5-20.5</td>
<td>17.5-18.5</td>
<td>6.0-6.5</td>
<td>0.50-1.00</td>
<td>42</td>
<td>650</td>
<td>300</td>
</tr>
<tr>
<td>4565S</td>
<td>S34565</td>
<td>A-5</td>
<td>0.03</td>
<td>0.40-0.60</td>
<td>23-25</td>
<td>16-18</td>
<td>3.5-5.0</td>
<td>-</td>
<td>41</td>
<td>650-880</td>
<td>350-550</td>
</tr>
<tr>
<td>654SMO</td>
<td>S32654</td>
<td>A-6</td>
<td>0.02</td>
<td>0.45-0.55</td>
<td>24.0-26.0</td>
<td>21.0-23.0</td>
<td>7.0-8.0</td>
<td>0.30-0.60</td>
<td>54</td>
<td>750</td>
<td>430</td>
</tr>
</tbody>
</table>

(PRE=Pitting Resistance Equivalent= %Cr + 3.3%Mo + 16%N)
There are six different subgroups

*Subgroup A-1*

Alloys in this group can be used in strong sulphuric acid solutions because of high nickel content, this high level of nickel also increase resistance to chloride stress corrosion cracking[7].

*Subgroup A-2*

Compare with type 316L and 317L, this group shows good resistance to corrosion in halide environment. Adding nitrogen stabilizes austenite phase, increase corrosion resistance and decrease nickel consumption [7].

*Subgroup A-3*

%10 more nickel improves corrosion resistance in acid and chloride environment [7].

*Subgroup A-4*

With high amount of nitrogen, chromium and molybdenum, these alloys can reach to PRE number around 40 to 43 and show good resistance to acid and chloride stress corrosion cracking[7].

*Subgroup A-5*

High strength and low resistance to chloride stress corrosion cracking because of low nickel content[7].

*Subgroup A-6*

These grades achieve a combination of high strength and resistance to chloride stress corrosion cracking[7].

![Alloy 316](image)

Figure 8:”The corrosion resistance of Alloy 316/316L stainless steel in CO2/NaCl environments in the absence of oxygen and H2S. Corrosion rates of ≤0.05 mm/yr (2 mpy) and no SSC or SCC”[8].
Resistance of 316L to non-H2S containing environment can be seen in figure 8. This alloy is sensitive to presence of oxygen (cause pitting corrosion)[8].

Figure 9 shows results of corrosion test of alloy 28 in H2S containing environment. Alloy 28 shows more resistance to H2S containing environment than other stainless steel but it is susceptible to SCC in environment containing H2S and chloride which needs more evaluation[8].

Figure 9: "The corrosion resistance of Alloy 28 in H2S/CO2 environments in the absence of elemental sulphur. Corrosion rates of ≤0.05 mm/yr (2 mpy) and no SSC or SCC"[8].

Alloy 825 is immune to all CO2 concentration and only is sensitive to H2S, temperature and high level of chloride concentration, figure 10[8].

Figure 10: "The corrosion resistance of Alloy 825 in H2S/CO2 environments in the absence of elemental sulphur. Corrosion rates of ≤0.05 mm/yr (2 mpy) and no SSC or SCC"[8].
Alloys in this group show good resistance to corrosion (with PREN > 30) but most of them cannot fulfill the mechanical requirements and are expensive.

**Ferritic Stainless Steel**

With ferritic microstructure, they show high resistance to chloride stress corrosion cracking but their toughness can be reduced by increasing grain size (have limited toughness)[7]. Table 7 gives some examples of this group.

<table>
<thead>
<tr>
<th>Table 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanical and Chemical Properties of Ferritic Stainless Steel</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Name</th>
<th>UNS Number</th>
<th>C</th>
<th>N</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>PRE Number</th>
<th>Tensile Strength (Mpa)</th>
<th>Yield Strength (Mpa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>409</td>
<td>S40977</td>
<td>0.02</td>
<td></td>
<td>11.5</td>
<td>0.5</td>
<td></td>
<td>12</td>
<td>450</td>
<td>320</td>
</tr>
<tr>
<td>430</td>
<td>430</td>
<td>0.04</td>
<td></td>
<td>16.5</td>
<td></td>
<td></td>
<td>17</td>
<td>450-600</td>
<td>280</td>
</tr>
<tr>
<td>444</td>
<td>444</td>
<td>0.02</td>
<td>0.01</td>
<td>17.8</td>
<td></td>
<td>2.1</td>
<td>25</td>
<td>420-640</td>
<td>275-300</td>
</tr>
</tbody>
</table>

This group of steels shows good resistance to oxidation at high temperature up to 700-950. At low temperature compared to the austenitic group, ferritic stainless steels have lower toughness and ductility also their resistance to corrosion is lower than austenitics but high content of Cr and Mo can improve their corrosion resistance similar to austenitic grade. Grain growth in heat affected zone and weld metal decrease the weldability of ferritic grades[14]. Because of low PRE number and mechanical properties of alloys in this group, ferritic alloys do not cover the requirement for fabrication of deep water gate valves and it is not allowed to be used for this purpose.

**Duplex Stainless Steel**

They have equal portions of ferrite and austenite in their microstructure. This group shows high strength, resistance to general corrosion and SCC[7].
Subgroup D-1
Alloy 2304: no better corrosion resistance than standard austenitic grades but higher strength and resistance to SCC than 316L and 317L[7].

Subgroup D-2
Alloy like 2205, combination of corrosion performance and low cost make it useful alloy in duplex group[7].

Subgroup D-3
These alloys need higher nickel to balance their higher chromium

Subgroup D-4
Best corrosion resistance because of high content of chromium, molybdenum, nickel and nitrogen. They also achieve strength higher than high-performance stainless steel[7].

Table 8 gives some example of this group.

<table>
<thead>
<tr>
<th>Name</th>
<th>UNS Number</th>
<th>Sub Group</th>
<th>C</th>
<th>N</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Cu</th>
<th>PRE Number</th>
<th>Tensile Strength (Mpa)</th>
<th>Yield Strength (Mpa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2304</td>
<td>S32304</td>
<td>D-1</td>
<td>0.03</td>
<td>0.05-0.20</td>
<td>21.5-24.5</td>
<td>3.0-5.5</td>
<td>0.05-0.60</td>
<td>-</td>
<td>22</td>
<td>600</td>
<td>400</td>
</tr>
<tr>
<td>2205</td>
<td>S32205</td>
<td>D-2</td>
<td>0.03</td>
<td>0.14-0.20</td>
<td>22.0-23.0</td>
<td>4.5-6.5</td>
<td>3.0-3.5</td>
<td>-</td>
<td>34</td>
<td>760</td>
<td>450</td>
</tr>
<tr>
<td>2550</td>
<td>S32550</td>
<td>D-3</td>
<td>0.04</td>
<td>0.10-0.25</td>
<td>24.0-27.0</td>
<td>4.5-6.5</td>
<td>2.9-3.9</td>
<td>1.5-2.50</td>
<td>35</td>
<td>790</td>
<td>600</td>
</tr>
<tr>
<td>2507</td>
<td>S32750</td>
<td>D-4</td>
<td>0.03</td>
<td>0.24-0.32</td>
<td>14.0-26.0</td>
<td>6.0-8.0</td>
<td>3.0-5.0</td>
<td>0.50</td>
<td>38</td>
<td>930</td>
<td>530</td>
</tr>
</tbody>
</table>

It is seen in figures 11 and 12 that alloy 22Cr in non-H2S containing environment has greater resistance than alloy 316L and even alloy 25Cr can reach to a higher pitting resistance than alloy 22Cr but both alloy 22Cr and 25Cr are sensitive to high concentration of chloride ions and show susceptibility to SCC at 140°C in the absence of oxygen[8].
Figure 11: “The corrosion resistance of 22Cr duplex stainless steel in CO2/NaCl environments in the absence of oxygen and H2S, Corrosion rates of ≤0.05 mm/yr (2 mpy) and no SSC or SCC”[8].

Figure 12: “The corrosion resistance of Alloy 2550 in H2S/CO2 environments in the absence of elemental sulphur. Corrosion rates of ≤0.05 mm/yr (2 mpy) and no SSC or SCC”[8].

This group is the most promised group for this specific application because of high PRE number and mechanical properties. Using of alloy 2205 is the best option. Alloys 2507 and 2550 have better chemical and mechanical properties than alloy 2205 but their high cost make them uneven for producing deep water gate valves.
2.2.2 Weldability

Weldability of Austenitic Stainless Steel

A completely austenitic weld structure can cause problems of weldability. Hot cracking during solidification of molten metal is one of the problems, if these cracks reach the surface and broke it, the crevice corrosion also can initiated. There is also a difference between wrought material with homogeneous structure and weld structure with associated segregating because of rapid solidification[9].

The chemical composition can also change the solidification modes. Figure 13 shows possible solidification modes for 316L. As it can be seen, molten metal may solidify in ferritic, austenitic, austenitic –ferritic and ferritic-austenitic. When the weld is austenitic, the melt will solidify to austenite and no more transformation occurs. In the austenitic –ferritic weld, first austenite solid forms and the retained melt between the austenite dendrite solidify as δ-ferrite but for ferritic-austenitic weld, this is the ferrite which solidify first and then austenite solidify between ferrite dendrites and the growth of austenite reduce the volume fraction of ferrite[10].

Figure 13: “Solidification Modes in AISI 316L, A = austenitic; AF = austenitic-ferritic; FA =ferritic-austenitic; F = ferritic”[10]

Figure 14 shows a slag rejected by the solidification front which has completely different chemical composition compared with the weld. Slag elements like calcium, silicon,
aluminum, etc have a higher solubility in ferrite than austenite so the ferritic-austenitic solidification mode is preferred to eliminate slag formation[10].

![Figure 14: SE and BE images of weld slag][10]

For austenitic stainless steel, Hammar and Svensson developed an equation which gives the correlation between chemical composition and solidification modes [10].

\[
\text{Cr eq} = \text{Cr} + 1.37 \text{ Mo} + 1.5 \text{ Si} + 2 \text{ Nb} + 3 \text{ Ti} \\
\text{Ni eq} = \text{Ni} + 0.31 \text{ Mn} + 22 \text{ C} + 14.2 \text{ N} + \text{Cu}
\]

\(\text{Cr eq}\) and \(\text{Ni eq}\) are contain of elements that promote ferrite and austenite formation.

\(\frac{\text{Cr eq}}{\text{Ni eq}} < 1.5 \rightarrow \text{austenitice or austenitic-ferritic solidification mode}\)

\(1.5 < \frac{\text{Cr eq}}{\text{Ni eq}} < 2.0 \rightarrow \text{ferritic-austenitic solidification mode}\)

\(\frac{\text{Cr eq}}{\text{Ni eq}} > 2.0 \rightarrow \text{ferritic solidification mode}\)

It can be seen that tendency for ferrite formation increase when \(\frac{\text{Cr eq}}{\text{Ni eq}}\) increase [10].

Segregation is another phenomenon happens during weld solidification which can influence weld corrosion characteristic of structure. During the first stage of solidification of austenite stainless steel, N and Ni which promoting austenite formation retain within the dendrite, while Cr and Mo which promote ferrite formation reject to the liquid phase. This segregation cause composition differences between the interdendritic region and dendrite center so the region with lower PRE
value (areas containing with lower Cr and Mo) can be attacked by corrosion environment. The results from chloride corrosion test of weld metal type 254 SMO shows (Figure 15) that with increasing heat input during welding the resistance to corrosion decrease. The explanation is that with increasing heat input the dendrite space and elements segregation increase. Figure 15 shows effect of heat input on dendrite space and CPT(Critical Pitting Temperature)[9].

![Graph showing the effect of heat input on dendrite space and CPT.](image)

Figure 15: “Effect of heat input on corrosion resistance of type 254 SMO weld metal” [9]

**Weldability of Ferritic Stainless Steel**

“Ferritic stainless steels are very much less weldable than austenitic stainless steel”. One of the problems in ferritic stainless steel welding is grain growth which occurs at high temperature. This grain growth in both weld metal and HAZ decrease weld area toughness. Ferritic stainless steel are more sensitive to intergranular corrosion than austenite stainless steel because of the lower solubility for interstitial elements in ferrite, also σ-phase may form when welding methods
with high heat input are used. Formation of σ-phase reduces corrosion and toughness properties [9].

**Weldability of Duplex Stainless Steel**

Duplex stainless steel first solidifies to single phase ferrite and then transform to austenite. “During welding, the high temperature regions of HAZ transform to ferritic structure and grain growth occurs”, this phase change to austenite on cooling. Corrosion and toughness of HAZ depends on austenite reformation, the high content of ferrite can affects these properties.

Welding duplex stainless steel with high energy beam can stop austenite formation, on the other hand welding with low heat input results in a coarse grain ferritic structure in HAZ area and decrease corrosion resistance due to localized Cr depletion (less time for diffusion). For controlling weld metal structure, it is a common way to use filler material with high Ni content which promotes austenite formation but for the HAZ area the low heat input welding methods should be avoided [9].

Summary of welding problems and precautions for these three high stainless steel groups can be found in table 9.

**Table 9**

Summary of Weldability properties of Austenitic, Ferritic and Duplex Stainless Steel[9]

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Problems</th>
<th>precautions</th>
</tr>
</thead>
</table>
| Austenitic Stainless Steel | Alloy segregation in weld metal  
Solidification cracking  
Crevices                                      | Overalloyed, high nickel alloy filler materials  
Low heat input  
Low interpass temperature(100°C max.)                      |
| Ferritic Stainless Steel   | Grain growth in HAZ  
Coarse grained weld metal  
Reduced impact strength  
Reduced corrosion resistance                        | TIG welding procedure with good shielding and backing  
Extreme cleanness of weld preparation  
Autogenous welding or matching filler  
Low heat input to minimize grain growth                  |
| Duplex Stainless Steel    | Grain growth in HAZ  
High ferrite levels  
Reduced toughness  
Reduced corrosion resistance (high temperature precipitates, σ-phase) | Overallloyed filler (higher Ni)  
Controlled heat input  
Controlled interpass (200°C max.)                      |
3 CONCLUSION

Austenitic stainless steels generally show good weldability and corrosion resistance. High alloyed austenitics due to the high contents of Cr, Ni, Mo and N₂ show better resistance to SCC and pitting than conventional austenitic grades [14]. The lower yield strength than what is required and the cost of high alloyed austenitic grades are common reasons why they are not use for this application. Ferritic stainless steel with low PRE numbers and lower corrosion resistance and mechanical properties than austenitics and duplex groups are not allowed to use for deep water gate valves.

The resistance of duplex stainless steels to corrosion is generally similar to austenitic stainless steel also they show better resistance to stress corrosion cracking (SCC) than austenitic stainless steel. Higher tensile and yield strength of duplex stainless steel than austenitic stainless steel (See Figure 16) make it suitable to use in different parts of deep water valves that carries high pressure fluids with aggressive characteristic. Duplex stainless steel with lower nickel content is cheaper than austenitic stainless steel [13].

Filler material is required to be added during the welding of duplex steel when autogenous weld is often used for austenitic grades. It is important to use over alloyed consumable to balance both ferrite and austenite phase in duplex weld metal [14]. These good characteristics of duplex stainless steel compare to other high performance stainless steel make it a promised group for oil and gas industry especially for deep water valves.

Figure 16: Positioning of Duplex grades [12]
4 FURTHER STUDIES

Duplex stainless steels are widely use in oil and gas industries because of their good corrosion resistance, weldability and high strength. One of alloy in this group is LDX2101 which has low nickel content. Austenite and ferrite are balanced in its structure by using Mn and N. Using of high nitrogen content and a structure with equal amount of austenite and ferrite result to a high mechanical strength in this alloy. On the other hand this high mechanical strength is combined with good corrosion resistance compared with standard austenitic stainless steel and even better resistance to SCC (Stress corrosion Cracking)[11]. Lean duplex stainless steel(LDX 2101) With 1.5% nickel and 0.22% nitrogen can achieve austenite formation in heat affected zone(HAZ) and weld metal with lower price[14].

Table 10 shows the mechanical properties, chemical composition and PREN value of some duplex, lean duplex and austenitic stainless steel, it is shown that LDX 2101 with high tensile and yield strength can fulfill mechanical requirement.

Table 10

Typical chemical composition, mechanical properties and PREN value of duplex and standard austenitic grades[11]

<table>
<thead>
<tr>
<th>Name</th>
<th>ASTM/ UNS</th>
<th>Typical chemical composition[wt%]</th>
<th>Mechanical properties</th>
<th>PREN</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cr 1Cr Ni Mo Mn N</td>
<td>$R_{p,0.2}$ [MPa]</td>
<td>$R_{m}$ [MPa]</td>
</tr>
<tr>
<td>LDX 2101</td>
<td>S32101</td>
<td>21.5 1.5 0.3 5.0 0.22</td>
<td>480</td>
<td>700</td>
</tr>
<tr>
<td>2304</td>
<td>S32304</td>
<td>23.0 4.8 0.3 - 0.10</td>
<td>450</td>
<td>670</td>
</tr>
<tr>
<td>2205</td>
<td>S32205</td>
<td>22.0 5.0 3.1 - 0.17</td>
<td>510</td>
<td>750</td>
</tr>
<tr>
<td>3407</td>
<td>304L</td>
<td>18.1 8.1 - - -</td>
<td>280</td>
<td>580</td>
</tr>
<tr>
<td>4404</td>
<td>316L</td>
<td>17.2 10.1 2.1 -</td>
<td>280</td>
<td>570</td>
</tr>
</tbody>
</table>
From pitting corrosion test, figure 17 shows the CPT (Critical Pitting Temperature) of LDX 2101 that is greater than alloy 3407. SCC (Stress Corrosion Cracking) test was done on this group and the results summarized in table 11. It can be seen that LDX 2101 shows a higher resistance to SCC than standard austenitic stainless steel and equal to duplex steel 2205 also LDX 2101 was tested in H2S containing environment and no evidence of cracking was found [11].

Figure 17: “CPT values determined according to ASTM G150 in 1 M NaCl and ASTM G48 Method E in 6% FeCl$_3$ + 1% HCl” [11].

Table 11
“Summary of stress corrosion cracking testing (number of cracked samples with number of tested samples in parenthesis)”[11].

<table>
<thead>
<tr>
<th>Test method</th>
<th>4301</th>
<th>4404</th>
<th>LDX 2101</th>
<th>2304</th>
<th>2205</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wick</td>
<td>5 (5)</td>
<td>4 (4)</td>
<td>0 (6)</td>
<td>0 (6)</td>
<td>1 (6)</td>
</tr>
<tr>
<td>40% CaCl$_2$</td>
<td>6 (6)</td>
<td>—</td>
<td>0 (6)</td>
<td>0 (6)</td>
<td>0 (6)</td>
</tr>
<tr>
<td>25% NaCl</td>
<td>—</td>
<td>2 (4)</td>
<td>0 (4)</td>
<td>—</td>
<td>0 (4)</td>
</tr>
<tr>
<td>ASTM G123</td>
<td>4 (4)</td>
<td>4 (4)</td>
<td>0 (4)</td>
<td>—</td>
<td>0 (4)</td>
</tr>
</tbody>
</table>

$^{1)}$ Test terminated after 96 hours (4 days)

$^{2)}$ Test terminated after 165 hours (1 week)
4.1 Effect of Nitrogen on Corrosion Resistance

Weldability of duplex stainless steel (DSS) improves with using nitrogen as an alloy element. The reason is that nitrogen promotes austenite formation at higher temperature. The sensitivity of microstructure to low heat input welding decrease with using high amount of nitrogen. After welding, since the amount of austenite increases during the cooling, the size of ferrite grains decrease and the resistance to pitting corrosion on the heat affected zone (HAZ) and weld area increase. These results are well known by industries for welding of different DSS. It is important that the weld pool be protected from losing nitrogen because losing nitrogen increase ferrite content and participation of chromium nitride which means that the resistance to pitting corrosion decreases. Figure 18 shows that the formation of austenite increases significantly by adding nitrogen to shielding gas [14].

![Graph showing the effect of weld metal nitrogen content on the austenite formation (weld metal)](image)

Figure 18. “The effect of weld metal nitrogen content on the austenite formation (weld metal)”[14].

Nitrogen loss can have negative effect on pitting corrosion resistance but as it is shown in figure 19 using of higher content of nitrogen does not improve pitting corrosion resistance so much[14].
It should also be considered that using of high amount of nitrogen can promote nitride participation.

In figure 20 and 21 the effect of adding nitrogen to the shielding gas can be seen.

Figure 20. “(a) Nitrogen balance when welding with pure argon, (b) resulting LDX 2101 weld metal microstructure with (c) high ferrite content at the surface indicating nitrogen loss”[14].
Figure 21. (a) “Nitrogen balance when welding with nitrogen addition to shielding and backing gas, (b) resulting LDX 2101 weld metal microstructure with (c) high austenite content at the surface”[14].

Figure 20 shows the ferritic microstructure of LDX 2101 on the surface, using of pure Ar as shielding gas cause nitrogen loss due to the tendency of system to reach equilibrium. In figure 21, by using 90% $N_2 + 10% H_2$ as backing gas and $Ar + 2% N_2$ as shielding gas results in improvement of austenite formation on the surface and resistance to pitting corrosion[14].

### 4.2 Effect of Low and High Heat Input

The composition and cooling rate (which depends on material thickness and heat input) are two parameters that control the austenite reformation in the heat affected zone (HAZ). With low heat input and high material thickness, the microstructure will be highly ferritic with precipitation of chromium nitride within the ferrite grains both in heat affected zone and weld metal. Post weld heat treatment (PWHT) can annihilate nitrides and improve austenite formation[14].

Cooling rate decreases with increasing heat input. The low cooling rate increase nucleation and growth of austenite phase within both weld metal and heat affected zone which increases localized corrosion resistance. With low cooling rate elements like Cr and Mo that are ferrite stabilizer have enough time to diffuse into the ferrite and reach the equilibrium and increase resistance to corrosion but it should be noted that very high heat input cause extreme growth of ferrite grains and also participation of $\sigma$ phase in the weld metal[14].
4.3 General Principle

NACE MR0175/ISO15156-3 doesn't cover LDX2101 for sour service system in oil and gas industries because its PREN value is lower than 30. Standards have their procedure to qualified and accept a new material. For example in the NACE qualification is based upon field experience or laboratory testing. In the field experience qualification the experience shall be documented at least for two years and meet the metallurgical properties such as: chemical composition, product form, manufacturing method, strength, heat treatment condition, amount of cold work and microstructure\[15]\.

Standards are interested more in new materials which have field experience (maybe because of expensive laboratory test) but on the other hand, industries do not have much interest to use new materials which have not been qualified by standards since it can cost a lot regarding new manufacturing methods, new welding procedures and training course.

The availability of new materials is also a risk for industries. They have to be sure that these new materials are supplied by different supplier and with the same specific parameters and properties.
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