Nickel alloys in offshore oil & gas; metallurgy and welding considerations

Nickel-based Corrosion Resistant Alloy(s) (CRAs) are essential for providing long term resistance to corrosion for many components exposed to oil & gas production environments. The selection of materials for sour environments is governed by a complex set of factors and, if not properly carried out, can lead to mistakes in application and misunderstanding about the performance of CRAs in a specific service environment. Good welding, fabrication and post-weld heat treatment practices are essential. This article takes a broad based look at popular nickel alloys used in offshore oil and gas; welding and metallurgy problems and design code and specification requirements.

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Nickel-based alloys are used for a broad range of applications in oil & gas production and marine engineering. Excellent corrosion resistance, good mechanical properties, versatility and reliability make them the first choice in construction of process vessels, piping systems, pumps, and valves etc. designed for service in aqueous and high-temperature environments.

1. Material strength and mechanical properties, whether produced by cold working or precipitation hardening (aging) treatments and the resultant mechanical properties
2. Corrosion resistance in the corrosive environment of an oil or gas field.
3. 300 series austenitic stainless steels have a tendency to crack in sulfide environments.

“The selection of nickel-based CRAs for producing and transporting corrosive oil and gas can be a complex procedure.”

Many variables influence the performance of a material in a specific environment. These include concentration, temperature, aeration, liquid or gaseous flow rates, impurities, abrasives and cycling process conditions.

Material selection philosophy
The selection of metallic materials for use in oil and gas production is extremely important for design and project integrity. In today’s deep sea wells high temperatures, high pressures and corrosive media are encountered and repair is extremely expensive or impossible so careful screening and expansive tests are important. Factors determining selection of a material include:

- and chloride-containing environments, hence application of super austenitic stainless steels which are highly alloyed to give a better performance against stress corrosion cracking and localized corrosion are advised. The nickel content of an alloy is responsible for its behavior against stress corrosion cracking.
- Selection of materials for sour wells is governed by a complex set of factors. Operating temperatures can be as high as 800°C (1470°F). The hot gas is corrosive, and the marine atmosphere aggressive. High-temperature strength, corrosion-resistance, ease of fabrication and readily available welding products to match the base materials are important considerations. The goal is to use a material that performs successfully while providing optimum economy.
- elements including copper, niobium, tungsten, aluminum and titanium may have significant effects on corrosion-resistance or mechanical strength.

Corrosion in oil and gas environments
The corrosion behavior of CRAs in oil and gas environments depends on several parameters: temperature, chloride concentration, CO₂ partial pressure, H₂S partial pressure, water composition (formation water/condensation water), pH and flow rate. In sour environments, different corrosion phenomena have to be considered: general corrosion, localized corrosion or environmental assisted cracking (Sulphide Stress Cracking (SSC) or Stress Corrosion Cracking (SCC)). In Table 1,
the possible influence of the different parameters on the different forms of corrosion is summarized. However, these parameters are not independent. For example, the pH depends on the water composition and on the CO₂ and H₂S partial pressures. High chloride content can be found in formation water, while no chloride or very low content is present in condensation water. While condensation water can present a low pH (4), formation water is generally present at higher pH values (>4) due to the presence of bicarbonate. When considering environmental assisted cracking, the cracking mechanisms depend on the materials. For austenitic alloys such as nickel-based alloys, the SCC resistance is superior compared to many steels; however, SCC sensitivity increases with the temperature.

Corrosion issues

CO₂ Corrosion (Sweet Corrosion): CO₂ is a main corroding agent in oil and gas production systems. CO₂ will mix with the water forming carbonic acid making the fluid acidic (reducing the pH value). CO₂ corrosion is influenced by temperature and an increase in pH value. At elevated temperatures, iron carbide (siderite) will form on the material as a protective scale, and the corrosion rate is reduced. CO₂ corrosion is enhanced in the presence of oxygen and organic acids which dissolve the protective iron carbide scale and prevent further scale formation.

Hydrogen Sulfide Corrosion (Hydrogen Attack and Sour Corrosion): Though the presence of hydrogen sulfide corrosion is less significant, the primary concern with hydrogen sulfide is the hydrogen attack on metal causing embrittlement. Fluids with high levels of H₂S are termed ‘sour’, and NACE defines the H₂S levels above 0.05 psi of partial pressure as sour condition.

The hydrogen attack mechanism is complex and caused by absorption of atomic hydrogen in steel depending upon certain pressure, temperature and the pH value of the fluid. Corrosion in oil and gas production facilities may occur by one or more of the following:

1. Chloride-induced localized corrosion (e.g. seawater)
2. CO₂ partial pressure
3. H₂S partial pressure
4. Presence of elemental sulfur
5. Chemicals (e.g. completion brines, acidizing compounds)
6. Products of reaction of these components [3]
7. pH value
8. Temperature (bottom hole temperature and top temperature)

A critical corrosion effect in H₂S containing sour gas environment is SSC, which may cause sudden brittle fracture. Factors affecting the cracking resistance of CRAs in sour gas are:

1. Chemical composition, strength, heat treatment, microstructure, manufacturing method and finished condition of the material
2. H₂S partial pressure or equivalent dissolved concentration in the water phase
3. Acidity (in situ pH) of the water phase
4. Chloride or other halide ion concentration
5. Presence of oxygen, elemental sulfur or carbon dioxide
6. Other oxidants
7. Temperature
8. Pitting resistance of the material in the service environment
9. Galvanic effects
10. Total tensile stress (applied and residual stress)
11. Exposure time

Susceptibility to SSC increases with higher hardness and strength. Other factors in the microstructure such as grain size, phase precipitation, chemical composition variations (due to the presence of different phases) also influence corrosion characteristics. The susceptibility for SSC also depends on the level of stress, imposed or residual. The higher the stress in the component (direct tensile loading or residual tensile

Table 1: Influence of different parameters on corrosion of CRA in oil and gas environments [1]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Influence</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>Promotes general and localized corrosion</td>
</tr>
<tr>
<td>pH</td>
<td>Decreases pH value</td>
</tr>
<tr>
<td>H₂S</td>
<td>Promotes EAC</td>
</tr>
<tr>
<td>Temperature</td>
<td>Low pH promotes corrosion and EAC</td>
</tr>
<tr>
<td>pH</td>
<td>Influence on EAC depends on material</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>Promotes localized corrosion and EAC</td>
</tr>
</tbody>
</table>

Corrosion resistance philosophy

Chlorides are common in oil and gas production which may cause a breakdown of the protective passive layer of alloys, causing pitting corrosion, crevice corrosion and/or SCC. Pitting corrosion is localized and causes pinholes and crater shaped pits. The pit starts on the surface and goes deep into the material. It often appears in materials which show a capacity for passivation. If the protective layer is partly destroyed, pitting corrosion will occur. Many process and cooling media contain chlorides so this kind of corrosion is very common. The possibility of pitting corrosion rises with the content of chloride, temperature and acidity of the media.

Crevice corrosion occurs in gaps, such as at flanges, expanded tube ends or other mechanical joints. It results from galvanic corrosion cells which form due to differences in concentration of the corrosive medium, for instance, due to differing aeration. It may also occur under deposits. The factors which influence crevice and pitting corrosion are similar. If these types of corrosion mechanisms occur, no prediction can be made regarding how long it will take for complete material failure.
stresses from the fabrication process), the higher the susceptibility to SSC. Another corrosion effect is caused by the presence of CO₂, but nickel alloys are generally not affected by presence of CO₂ in the sour gas environment. Normally, sour gas wells have more than one corrosive species, such as carbon dioxide, hydrogen sulfide and chlorides. However, the corrosion rates expected from one component acting alone cannot be merely added to obtain some estimated corrosion rate of the combination of the other species. There is a synergistic effect where small additions of one corrosive species may drastically affect the total severity of the environment.

Metallurgical considerations

**Exposure to high temperatures during fabrication:** Nickel alloys are selected primarily for corrosion resistance. Heat treatments (e.g.: improper annealing, stress relief, etc.) and welding can cause corrosion of the alloy in some process environments. Corrosion may be due to sensitization of the base metal in heat-affected zones, formation of secondary phases, and segregation in the weld metal or residual stress. All these heating types may result in intergranular attack, pitting, crevice corrosion or SCC in some materials.

**Welding of nickel alloys:** Nickel alloys are readily weldable and high-quality joints readily produced by conventional welding processes. However, some of the characteristics of nickel alloys necessitate the use of different techniques than those used for commonly encountered materials such as carbon and stainless steels. The choice of welding process depends on many factors. Base metal thickness, component design, joint design, position in which the joint is to be made, and the need for jigs or fixtures must all be considered. Service conditions and corrosive environments to which the joint will be exposed and any special shop or field-construction conditions and capabilities which might be required are also important.

**General considerations:** Welding procedures for nickel alloys are similar to those used for stainless steel. Thermal expansion characteristics of the alloys approximate those of carbon steel therefore essentially the same tendency for distortion can be expected during welding. All weld beads should have slightly convex contours. Flat or concave beads should be avoided. Preheating nickel alloys prior to welding is not normally required. However, if the base metal is cold (38°F (2°C) or less), metal within approximately 12 in. (300mm) of the weld location should be warmed to at least 10° above the ambient temperature to prevent the formation of condensate as moisture can cause weld porosity. The properties of similar composition weldments in nickel alloys are usually comparable to those of the base metal in the annealed condition. Chemical treatment (e.g.: passivation) is not normally required. Most solid solution nickel alloys are serviceable as welded. Precipitation hardenable alloys welded with hardenable welding products must be heat treated to develop full strength. It may also be desirable to stress relieve or anneal heavily stressed welded structures to be exposed to environments which can induce stress corrosion cracking. In most corrosive media, the resistance of the weld metal is similar to that of the base metal. Overmatching or non-matching weld metals may be required for some aggressive environments.

**Surface preparation:** Cleanliness is the single most important requirement for successfully welding nickel and nickel-based alloys. At high temperatures, nickel and its alloys are susceptible to embrittlement by sulphur, phosphorus, lead and other low-melting point substances. Such substances are often present in materials used in normal manufacturing processes. Examples are grease, oil, paint, cutting fluids, machine lubricants, and temperature-indicating sticks, pellets, or lacquers. It is often impractical to avoid the use of the above mentioned materials during processing and fabrication of the alloys. Hence it is mandatory that the metal be thoroughly cleaned prior to any welding operation or other high-temperature exposure.

For a welded joint in material that will not be reheated, a cleaned area extending 2 in. (50 mm) from the joint on each side will normally be sufficient. The cleaned area should include the edges of the work piece and the interiors of hollow or tubular shapes.

**Joint design considerations:** Weld bevels for joining nickel alloys always require wider root gap and wider angled Weld Edge Preparation (WEP) for better accessibility. As the side wall wetting behaviors of the alloys are not as good as carbon or stainless steels, the joint opening must be sufficient to permit the torch, electrode or filler metal to extend to the bottom of the joint. The operator must manipulate the weld puddle to direct the weld metal to the proper location in the joint.

**Recommendations of welding electrodes / filler metals**

CRAs are weldable with Shielded Metal Arc Welding (SMAW), Gas Tungsten Arc Welding (GTAW) and Gas Metal Arc Welding (GMAW). Metallurgical factors strongly influence procedures for welding dissimilar materials and precipitation-hardenable alloys. Welded joints can undergo metallurgical changes when subjected to cold work and heat treatment. By general sense of engineering, wrought alloys generally exhibit better weldability than castings. The dendritic structure of castings often exhibits severe elemental segregation. Also, castings often contain significant additions of silicon for fluidity. Silicon can compromise the hot-cracking resistance of some alloys and their weldability. Materials with a coarse grain structure (ASTM number 5 or coarser) are generally found to be less weldable than those with finer grain structures. Coarse-grain materials are particularly prone to base metal microfissuring. Grain size can restrict the use of processes having high energy input (e.g.: GMAW in the spray mode of transfer). Table 2 illustrates the effect of grain size on selection of welding processes for several alloys. Alloys are best welded in the annealed condition. Alloys with high levels of

| Table 2: Effect of grain size on recommended welding process for nickel-based alloys, (S) |
|---|---|---|---|---|
| Alloy | Grain Size | SMAW | GTAW | SMAW |
| 600 | Fine | x | x | x |
| 600 | Coarse | --- | --- | x |
| 601 | Fine | x | x | x |
| 601 | Coarse | --- | --- | x |
| 625 | Fine | x | x | x |
| 625 | Coarse | --- | --- | x |
| 706 | Fine | x | x | x |
| 706 | Coarse | --- | --- | x |
| 718 | Fine | x | x | x |
| 800 | Coarse | --- | --- | x |

Notes:
1. Processes marked X are recommended.
2. Fine grain size is ASTM No 5 or more.
3. Coarse grain size is ASTM No 5 or less.
4. SMAW is recommended in “spray transfer” mode.

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residual stress due to rolling, drawing or forming can be prone to cracking. Alloy products annealed at lower temperatures (mill anneal) generally exhibit finer grain structures than those annealed at higher temperatures (solution anneal) and, thus, are found to offer a better welding response. Some alloys must be solution annealed prior to final heat treatment (e.g., precipitation hardenable alloys). If possible, such alloys should be welded after a mill anneal and prior to the solution anneal.

Effects of dilution
Dilution rate resulting from a set of welding conditions (welding process, technique, joint design, etc.) can be accurately determined by chemical analysis of a deposited bead. The elements normally of concern in considering dilution of nickel alloy welding products are copper, chromium and iron. The following dilution limits apply only to solid solution weld metal and wrought-based materials. The dilution of weld metal potentially detrimental elements (e.g.: Pb, Sn or Zn) shall always be avoided. The dilution rate can also be determined by an area comparison on a joint cross section. Nickel Welding Electrode 141 and Nickel Filler Metal 61 have high solubility limits for a variety of elements, and, from the standpoint of dilution tolerance, are excellent dissimilar-welding materials. Use of the products for dissimilar welding, however, is often limited by their lower strength in comparison with other nickel-alloy welding products. Nickel welding products have complete solubility for copper and can accept unlimited dilution by that element. Chromium dilution of Filler Metal 61 and Welding Electrode 141 should not exceed 30%. Nickel Welding Electrode 141 can tolerate up to approximately 40% iron dilution. Filler Metal 61, however, should not be diluted with more than 25% iron. The nickel-copper and copper-nickel welding products (MONEL Welding Electrodes 190 and 187, MONEL Filler Metals 60 and 67) can tolerate unlimited dilution by copper. Nickel-copper weld deposits can be diluted with up to approximately 8% chromium. Copper-nickel deposits (Filler Metal 67 and Welding Electrode 187) should not be diluted with more than 5% chromium. Iron dilution limits for deposits of MONEL Filler Metal 60 are influenced by the welding process used. Typical safe vales are GTAW/GMAW–15% and SMAW–30%.

INCONEL nickel-chromium welding products are the most widely used materials for dissimilar welding. They produce high-strength weld deposits, and the deposits can be diluted by a variety of dissimilar materials with no reduction of mechanical properties.

Welding of precipitation hardenable alloys
The ability of precipitation-hardenable alloys to be strengthened by heat treatment results from their complex chemical composition and intricate metallurgical reactions that must take place in a very exact manner. Joining such alloys must be done exactly according to complex welding and heat treating procedures. Cracking of welds and HAZ can occur when high residual welding stresses are present during the aging treatment as these areas have the highest residual stresses. Precipitation-hardenable alloys are best joined by processes which induce the least stresses in the weldment. Gas tungsten-arc welding is generally preferred. Ideally, matching composition welding products are used, however, if these are not available, a welding product of an alloy with properties similar to the alloy is used. When a dissimilar welding product must be used, it is critical that a product with similar aging constituents be chosen. Heat input during welding should be kept as low as practicable. For multiple-bead or multiple-layer welds, several small beads should be used instead of fewer large, heavy beads.

Aluminum-titanium-niobium hardened alloys such as INCONEL Alloys 706, 718, and 725 are best welded in the annealed or solution-treated condition. If complex units must be annealed in conjunction with welding or forming operations, the annealing temperature should be consistent with the specification and end-user requirements.

Conclusions
Due to excellent corrosion resistance and good mechanical properties, nickel-based alloys are used for a broad range of applications in offshore oil and gas engineering and production. The versatility and reliability of nickel based CRAs make them a prime material of choice for construction of process vessels, piping systems, pumps, valves and other applications designed for service in offshore applications. Many variables influence the performance of a specific material in a specific environment, including concentration, temperature, aeration, liquid or gaseous flow rates, impurities, abrasives and cycling process conditions. While every attempt has been made to present a broad base of information, more detailed data will often be needed for individual applications and environments. It is advisable to contact the manufacturers for more specific alloy properties and to share a wealth of experience on specific application environments for these alloy services.

References available on request

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