Solving Corrosion Issues in the Chemical, Petrochemical and Refining Industries Through the Use of Space Age SuperAlloys.

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Abstract
As manufacturers in the chemical, petrochemical and refining industries strive to increase efficiencies and output in their process systems, operating temperatures, pressures and flow rates rise daily. As a result of these ever changing conditions, more aggressive strength and corrosion issues arise, often increasing concerns exponentially. To combat deterioration of system components (such as pipes, fittings and flanges), materials with greater heat and corrosion resistance are required for surface, subsea and downhole applications. NACE estimates the impact of corrosion results in an industry loss of over $300 billion per year throughout the aforementioned industries. Approximately $150 billion of these costs can be prevented by various forms of corrosion engineering and project planning.

Careful evaluation and selection of new super alloys and stainless steels, reliable operation can be achieved and all around costs controlled. With an understanding of the metallurgical properties of these products, engineers and designers can confidently select materials that offer the best balance of performance and cost without compromising safety or production.

Introduction
With the availability of new nickel, corrosion resistant and heat resistant alloys, engineers and metallurgists can select the appropriate alloy for their specific application whether it is an aqueous corrosive or corrosive media environment. The fabrication of these alloys has given the chemical, petrochemical and refining industries the ability to process and transport oil and gas products without compromising the environment and safety.

Production systems designed and constructed with the properly selected (based on established material properties, laboratory testing and previous field experience) corrosion resistant alloy (CRA) will provide a safe and leak free system for the full life of the project. Although material costs of these systems are significantly greater than the cost of standard carbon alloy systems, many wet corrosive environments exist that cannot safely be explored and developed without the use of CRA materials. Cost savings and safety can however, be realized with the use of CRA materials as corrosion inhibitor injection is not required and maintenance costs are greatly reduced compared to carbon steel production systems. When a lifetime cost analysis is conducted, CRA materials often demonstrate a viable economic option.

Selection Processes for Corrosion Resistant Alloys (CRA) and Heat Resistant Alloys
Corrosion and heat resistant alloys are selected by chemical, petrochemical and refining companies in a variety of ways. Two methodologies, however, are most commonly used.

In the first approach, a company will employ a pipe manufacturer/fabricator and select a wide range of alloys to test under laboratory conditions. This process is very expensive and not cost effective. Gathering results can take up to several years.

The second most commonly used approach to alloy selection is the review of all current literature containing corrosion, performance and field application data. Through this technique, companies can quickly eliminate alloys not recommended for their specific application. Once an alloy has been selected, the company will test the proposed alloy to address questions not answered by current available data sets within the industry. One must be very careful when using this methodology as temperature can play a critical role in an alloy’s corrosive resistance. The resistance of CRA’s at one temperature is not necessarily indicative of its corrosion resistance at other temperatures. Changes in environmental controls such as sulfur or H₂S will also have a profound impact on resistance to stress cracking. In this specific instance, Chrome is beneficial and Nickel is detrimental to high temperature sulfidation, not aqueous (stress corrosion cracking) SCC. Nickel is beneficial for resistance to SCC. The alloys listed are used in high temperature, sulfidizing environments, but not under aqueous SCC conditions (e.g., sour wells). An INCONEL 671, 690 or 693 should be selected or an INCOLOY 800HT or 803 (Figure 1).

The Use of Nickel-Based Alloys in an Aggressive Aqueous Environment Containing Acids
Although the number of environments encountered within the chemical, petrochemical and refining process industries is vast, the performance of Nickel-based, corrosion resistant
alloy materials is most often based on their resistance to a few aggressive inorganic aqueous solutions (predominantly hydrochloric acid, sulfuric acid, and hydrofluoric acid). These solutions can result in pitting, leaching, crevices, inter-granular and galvanic corrosion and stress induced erosion. Figures 2-4 display the effects of acids on these alloys.

Nickel alloys used today can be categorized and grouped according to their primary alloying elements:
- **Nickel**: caustic solutions
- **Nickel-copper**: mild, reducing solutions, especially hydrofluoric acid
- **Nickel-molybdenum**: strong reducing media
- **Nickel-iron-chromium**: oxidizing solutions
- **Nickel-chromium-silicon**: super-oxidizing media
- **Nickel-chromium-molybdenum**: versatile alloys for all environments

It is well documented that chromium is the key element in the resistance of a nickel alloy to sulfidation. Nickel alloys containing 20-80% chromium are shown to outperform pure nickel, containing 20-80% chromium, have shown to outperform pure nickel. Nickel alloys used today can be categorized and grouped according to their primary alloying elements:

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Stainless Steel vs Corrosion

Stainless steel is separated from other steels by the use of a minimum chromium content of 10.5% making stainless steels more resistant to corrosive media environments and oxidation. Corrosion resistant stainless steel grades are grouped into families based on their microstructures (martensitic, austenitic or duplex).

Martensitics are resistant to moderate atmospheric corrosion and mild organic media corrosion. Their corrosion resistance is lower than that of more highly alloyed grades, limiting their use in process environments. Their strength and tempering resistance are improved by molybdenum.

Austenitic grades are not magnetic. The most common austenitic alloys are iron chromium-nickel steels. Iron chromium-nickel steels are widely used. Due to their high chromium and nickel content, austenitic grades are the most corrosion resistant of the stainless steel group.

Duplex stainless steels are the newest of the stainless steels. This material is a combination of austenitic and ferritic material. Duplex stainless steels have higher strength and superior resistance to stress corrosion cracking. General characteristics of each stainless steel family and grades are easily obtained throughout industry publications.

Stainless steel can be classified as “corrosion resistant” when used in aqueous environments and vapors below 1200°F (650°C) and “heat resistant” when used above this temperature. The usual distinction between heat and corrosion resistant grades is carbon content. For a stainless steel to perform well in a corrosive environment, carbon content must be low. Heat resistant grades of stainless steel have higher carbon content to improve elevated temperature strength.

Much like Nickel-based alloys, stainless steels can suffer from galvanic pitting and crevice corrosion and inter-granular stress related cracking (Figures 6, 7 and 8). When alloying elements such as Nickel, Chromium and Molybdenum are added, each alloying element improves the stainless steels resistance to pitting, crevice and oxidation corrosion.

Localized Corrosion

Various corrosive media and conditions induce different types of attack. General corrosion is a general thinning of a component. Its advance can often be monitored over time and the life of a component accurately predicted. Other types of attack can be more troublesome. Localized attack (pitting and crevice corrosion) can result in rapid deterioration of a product in a very specific area. While a component may show very little general attack, it may be perforated by pitting or crevice attack. Such attack is often encountered under acid-halide conditions. The presence of a tight crevice (e.g., under a fastener) can greatly accelerate the rate of localized attack. Stainless steels and alloys with higher contents of chromium, molybdenum and nitrogen are generally found to be most resistant.

Pitting Corrosion

Under certain conditions, particularly involving high concentrations of chlorides (such as sodium chloride in sea water) (Figure 5), moderately high temperatures and exacerbated by low pH (i.e., acidic conditions), very localized corrosion can occur leading to perforation of pipes and fittings, etc. Steel grades high in chromium, and particularly molybdenum and nitrogen, are more resistant to pitting corrosion.

One reason pitting corrosion is so dangerous is due to the fact that once a pit is initiated, there is a tendency for it to continue to grow, although the majority of the surrounding steel is intact (Figure 8). The tendency for a particular steel to be attacked by pitting corrosion can be evaluated in the laboratory under many different conditions. This is achieved using the Pitting Resistance Equivalent Number (PRE). The PRE has been found to give a good indication of the pitting resistance of stainless steels. A number of other standard tests have been developed, but the most common is that given in ASTM G48. The PRE can be calculated as:

\[
PRE = \%Cr + 3.3 \times \%Mo + 16 \times \%N
\]
Crevice Corrosion

The corrosion resistance of a stainless steel is dependent on the presence of a protective oxide layer on its surface. It is possible under certain conditions for this oxide layer to break down in reducing acids, or in some types of combustion where the atmosphere is reducing. For example, areas susceptible to crevice corrosion where the oxide layer can break down include under gaskets, in incomplete weld penetrations and in sharp re-entrant corners or overlapping surfaces. These conditions can all form crevices that can promote corrosion.

For a corrosion site to develop, a crevice has to be of sufficient width to permit the entry of the corrosive media, but sufficiently narrow to ensure that the corrosive media remains stagnant. Crevice corrosion usually occurs in gaps a few micrometers wide, and is not commonly found in grooves or slots in which circulation of the corrosive media is possible. This problem can often be overcome by paying attention to the design of the component, in particular avoiding formation of crevices or at least keeping them as open as possible. Crevice corrosion is very similar to pitting corrosion; alloys resistant to one are generally resistant to both. Crevice corrosion can be viewed as a more severe form of pitting corrosion as it will occur at significantly lower temperatures than does pitting (Figure 8).

Galvanic Corrosion

Galvanic corrosion is an electrochemical process involving the flow of an electric current that can be generated by a galvanic effect that arises from the contact of dissimilar metals in an electrolyte (an electrolyte is an electrically conductive liquid). Three specific conditions are required for galvanic corrosion to thrive: 1) two metals must be widely separated on the galvanic series (Figure 10), 2) they must be in electrical contact, and 3) their surfaces must be bridged by an electrically conducting fluid. Removal of any of these three conditions will prevent galvanic corrosion.

Stress Corrosion Cracking (SCC)

Stress corrosion cracking (SCC) is induced from the combined influence of tensile stress and/or corrosive environments. The impact of SCC on an alloy usually falls between dry cracking and the fatigue threshold of that alloy. Required tensile stresses may be in the form of directly applied stresses or residual stresses. The problem of SCC can be quite complex. Buried pipelines are an example of such complexity. The impact of SCC is commonly known as a catastrophic form of corrosion.

Cold deformation and forming, welding, heat treatment, machining and grinding can introduce residual stresses. The magnitude and importance of such stresses is often underestimated in these industries. Residual stresses set up as a result of welding operations tend to approach the yield strength. The build-up of corrosion products in confined spaces can also generate significant stresses and should not be overlooked. SCC usually occurs in certain specific alloy-environment-stress combinations.

Usually, most of the alloy surface remains unaffected, but fine cracks penetrate into the material (Figure 9). In the microstructure, these cracks can have an inter-granular or a trans-granular morphology. Macroscopically, SCC fractures have a brittle appearance. SCC is classified as a catastrophic form of corrosion, due to the fact that the detection of such fine cracks can be very difficult and the damage not easily seen or predicted. A disastrous failure may occur unexpectedly, with minimal overall material loss (Figure 12).

In some instances, it has been found possible to improve resistance to SCC by applying a compressive stress to the component at risk. This can be done by shot peening the surface for example. Another alternative is to ensure the product is free of tensile stresses by annealing as a final operation. Stress relieving (different from annealing) is a lower temperature heat treatment that accomplishes this result and is often employed. These solutions to the problem have been successful in some cases, but need to be very carefully evaluated both in field and laboratory settings.

It can be difficult to guarantee the absence of residual or applied tensile stresses in an alloy. Thus, nickel-based products alloyed with chromium and molybdenum and stabilized by either titanium or niobium are widely applied in refining and petrochemical operations to improve their resistance to inter-granular corrosion, but not in downhole applications. Examples of such materials are alloys 825 (UNS N08825) and 625 (UNS N06625).

Downhole Oil and Gas Applications Using CRA’s

Over the past 35 plus years, there has been considerable laboratory and field experience attained when drilling and completing deep oil and gas wells that contain hydrogen sulfide (H2S) and carbon dioxide (CO2). A significant amount of literature is available detailing material selection for these environments as well as environments that produce acid by-products that further add to the severe corrosive environment for downhole tubulars. Corrosion resistant alloys have significantly better corrosion resistance than that of traditional carbon alloy steels that are utilized when drilling in sweeter and more benign downhole environments. Material selection for corrosion resistant alloys in the oil and gas industry is well documented.

In sour wells, environmental cracking can occur by two different mechanisms: 1) hydrogen embrittlement, and 2) stress corrosion. Hydrogen embrittlement involves a cathodic reaction in which hydrogen ions are reduced to elemental hydrogen. Hydrogen ions may result from galvanic corrosion of connected dissimilar metals or from acidizing operations performed on the reservoir. In sour well environments, the major source of hydrogen embrittlement is usually dissolved H2S in wellbore and reservoir fluids. Elemental hydrogen absorbed by a metal can lower ductility to the point where the metal becomes embrittled. If the metal is under sufficient stress, cracking can result. Such cracking in H2S environments is termed sulfide stress cracking (SSC).

Hydrogen embrittlement and SSC are essentially low-temperature phenomena with maximum severity occurring in the ambient range. Stress corrosion involves an anodic
Mechanically Lined Tubulars

Over the years, mechanically lined corrosive resistant tubulars have gained widespread acceptance industry-wide. This methodology is the most economic for manufacturing CRA lined pipe when using carbon steel outer pipe, however, internally lining carbon steel tubulars does have its problems. One such problem has to do with the fact that there is not a metallurgical bond between the two tubes for structural integrity. If bending is necessary for serviceability, this method will result in buckling of the liner. An advantage to using this type of lined tubular is for inspection purposes. Quality control features are better because both the outer pipe and liner can be inspected using traditional inspection techniques offered throughout the industry.

Metallurgically Bonded Tubulars

Several different techniques exist for the manufacturing of metallurgically bonded tubulars (MBT). During manufacturing, a bond is created between the structural outer pipe and the corrosion resistant inner pipe. It is not uncommon to achieve bonding of 98% of the surface area being joined using this method16. Other metallurgically bonded techniques include: roll and weld roll-clad or explosive-clad alloy steel plate to make tubes for such things as sour oil service.

To assure an adequate bond has been obtained, specific tests have been developed (ASTM A26322) and (ASTM A26423). Testing of this pipe also involves ultrasonic inspection of the carbon steel alloy and the inner corrosion resistant liner. This currently is the preferred methodology among manufacturers (e.g., alloy 825 clad steel plate rolled and welded with INCONEL filler metal 625 with the alloy 825 on the ID to carry sour oil or gas).

Extrusion Method

This method seems to be a favorite option for companies at the forefront of clad development. This process involves taking a combination billet of carbon steel and a corrosion resistant alloy and hot extruding the hollow to longer lengths. A carbon steel tubular is machined to very tight tolerances and then a corrosion resistant alloy tubular is inserted into the bore. The corrosion resistant alloy tubular shell is also machined to exacting tolerances.

Several techniques can be used to produce the combination billet depending on the manufacturer. One technique involves taking the heating of the outer carbon steel billet so it expands, and then the CRA billet is inserted into the bore. A second technique is to cool the inner CRA billet to extremely cold temperatures and then insert it into the carbon steel outer billet. When using both techniques, the temperatures of the two components reach equilibrium at room temperature and a tight mechanical fit is produced. This mechanical fit prevents the CRA inner billet from moving within the carbon steel wall. The ends of the combination billet are commonly seal welded prior to extruding to prevent the intrusion of air, oxygen and other contaminants into the interface. This practice varies based on the specific producer. The primary objective is to
facilitate a higher percentage of bonding between the two tubular surfaces. This heavy walled tubular billet is then extruded. Extrusion is performed at temperatures in excess of 1260°C (2300°F) which results in a metallurgical bond between the carbon steel outer pipe and the CRA material on the ID surface.

There are various techniques being used and developed to improve the bonding efficiency between the outer carbon steel pipe and the inner CRA liner. It can be difficult to anticipate corrosion using this method because it is difficult to determine how evenly the alloy layer is distributed inside the carbon host pipe.

Fabrication of CRA's

Austenitic and super-austenitic stainless steels and nickel alloys generally exhibit excellent ductility, thus, they are readily formed. They tend to be stronger than mild carbon steels so more power is required for forming. To avoid ferrous contamination (embedded iron) of the CRA’s, forming dies and rolls used to form carbon steel are often wrapped or lined with stainless steel (Figure 11). As previously noted, residual stresses from forming may induce stress cracking in some materials in some environments. Such materials should be stress relieved or annealed after final forming to alleviate residual stresses.

Welding CRA's

Fabrication procedures for corrosion-resistant stainless steels and alloys are well established. Joining procedures for austenitic and super-austenitic stainless steels and solid solution nickel alloys normally employ conventional processes and products. It is generally advisable to use over-matching composition welding products for joining CRA’s. Due to their cast structure, weldments suffer from elemental segregation during solidification. This results in some portions of the weld being depleted of some alloying elements, while other parts of the weld are enriched. Depleted zones tend to exhibit reduced corrosion resistance compared to the wrought base metal. To counter this effect, welding products with higher contents of alloying elements are recommended for joining CRA’s. For example, 316 and 317 stainless steel and 6% molybdenum grades of super-austenitic stainless steels are often joined with alloy 625 welding products. In a similar manner, INCO-WELD 686 welding products, arguably the highest alloyed welding products available, are used for joining.

Summary

Stainless steels and nickel-based corrosion-resistant alloys are especially effective in mitigating corrosion problems in the refining and process industries. The products, however, must be properly processed to be effectively deployed and the correct steel or alloy must be used for the application. Although a product offers good resistance in one environment, it does not guarantee the same resistance in another. There is no universally resistant material currently available. With proper care and preparation, however, corrosion-resistant components and systems can be built that offer long, reliable service. With that long reliable service, alloy products may prove to offer exceptional value despite their high initial cost.
Nomenclature
ASTM = American Society for Testing and Materials
API = American Petroleum Institute
CRA = Corrosion Resistant Alloys
MBT = Metallurgically Bonded Tubulars
NACE = National Association of Corrosion Engineers
PRE = Pitting Resistance Equivalent Number
SCC = Stress Corrosion Cracking
SSC = Sulfide Stress Cracking
UNS = Unified Numbering System

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References
Figure 1

Conditions for Possible Sulfidation. Based upon H₂S Concentrations in H₂ - H₂S Gases and Temperatures Above the FeS/Fe Line for Carbon/Low Alloy (5% Cr) Steels and Above the Cr₆S/Cr Line for Alloys with > 5% Cr. 400-1,200°F = 204-648°C.

Figure 2

Ni-Cr-Mo Alloys in Sulfuric Acid

Figure 3

Ni-Cr-Mo Alloys in Hydrochloric Acid

Figure 4

Corrosion in a Simulated FGD Medium

Figure 5

Corrosion in Flowing Seawater 150 ft/sec. (45.7 m/sec.)

<table>
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<th>Corrosion/Erosion Rate</th>
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<tbody>
<tr>
<td></td>
<td>mpy</td>
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<tr>
<td>NiCrMo alloy 625</td>
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<tr>
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Figure 6

Galvanic Corrosion from low velocity seawater

Figure 7

Pitting Corrosion
Figure 8
Crevice Corrosion

Figure 9
Stress Related Cracking

Figure 10
Coppson Diagram: Nickel vs. Stress Corrosion Cracking

Figure 11
“Roll Bonding” Clad Packet Assembly