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AOD Metal Refining...

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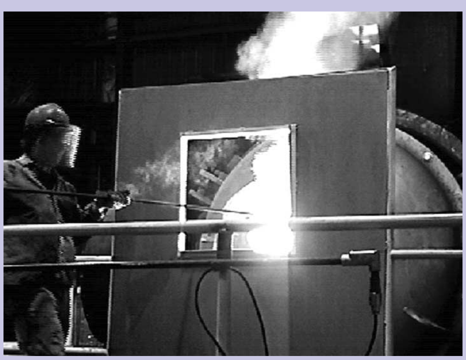
flexible from the standpoint of the quenching media. Water, as well as forced air can be used. 2205 is the least prone of the duplex alloys to form sigma ferrite. Proper heat-treatments, and metal chemistry controls will provide the optimum cast material for the shop to process.

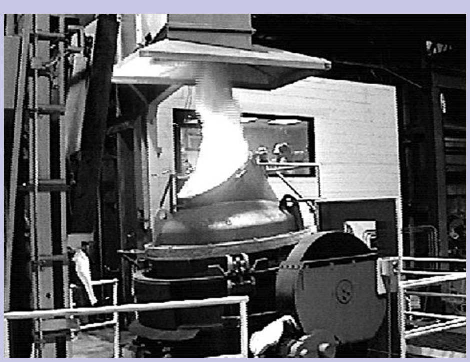
Conclusion

Since the AOD's startup on February 10th, 2000, we have processed over 1000 tons. The system has already shown us many benefits in this short period of time. The "in-house" return scrap inventory has been dramatically reduced. Rework and scrap has been lowered by 22-34% over previous years. In addition, our weld rod expenditures are 43% below budget year to date. The AOD also allows us to purchase lower cost grades of raw materials to produce our steels. Thus we have lower raw material costs from a purchasing stand-point.

The AOD System has met our highest expectations. This investment has allowed us to position ourselves with the elite foundries in the marketplace, and will keep our costs and our customers costs as low as possible.



AOD vessel, Argon-Oxygen blowing.



Checking bath temperature.

How to Pick the Right Nickel Alloy for Corrosive Services

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Why the interest in Nickel alloys?

Chemical and other process industries utilize some of the widest range of materials, confronting many forms of corrosion. Successful operation and performance often depends upon nickel-base alloys, which are extensively used in pumps to resist the severe effects of corrosion, and provide trouble free service. Nickel alloys offer a combination of excellent corrosion resistance, heat resistance and mechanical properties; making them well suited for many aggressive applications.

Proper selection of materials is a critical engineering function. Advances in metallurgical knowledge and processing technologies have resulted in the development of many nickel alloys offering broad application. The difficulty lies in determining which alloy is best suited for what service.

The key to successful application of nickel alloys is understanding the materials chemistry; corrosion mechanisms; and taking adequate measures to minimize risk of degradation through appropriate materials selection. However, making the proper nickel alloy selection is sometimes difficult, and often seems complicated or confusing.

This article should help familiarize engineers with the common nickel alloys utilized within the pump industry, review their typical use, and provide guidelines for selection by characterizing them in terms of chemistry and performance. General guidelines for selecting which nickel alloy is best suited for what service shall be given.

Nickel Alloy Metallurgy

One of the most significant attributes of nickel with respect to the formation of corrosion resistant alloys is its metallurgical compatibility with many other metals, such as copper, chromium, molybdenum, iron, and others. Nickel is resistant to a variety of corrosive media, and can readily alloy with most metals to form specific alloys for wide application.

Complete solid-solubility exists between nickel and copper, as well as nickel and molybdenum, resulting in binary alloys. Wide solubility with iron and chromium allows for many additional alloy combinations.

Nickel alloys are generally face-centered cubic fully austenitic alloys, however many can be precipitation hardened. For corrosion applications the precipitation of secondary phases usually reduces the corrosion resistance of the alloy, and as a result, is generally avoided.

To optimize performance, developers of nickel alloys have taken advantage of the fact those large quantities of other elements forms solid solution alloys in this face-centered cubic structure, without forming brittle phases. Common alloying additions for enhanced corrosion resistance are copper, molybdenum and chromium. The common groups of nickel alloys utilized in pumps can thus be classified according to their principal alloying constituents as follows:

- commercially pure Nickel
- binary alloys such as Nickel-Copper
- binary alloys such as Nickel-Molybdenum
- ternary alloys such as Nickel-Chromium-Iron
- ternary alloys such as Nickel-Chromium-Molybdenum
- complex alloys such as Nickel-Chromium-Iron-Molybdenum-Copper

Improved melting and processing technologies, as well as an improved understanding of the role of various alloying elements on the physical metallurgy have played a key role in the development of nickel-base alloys. The effect of various elements may be favorable or detrimental, depending upon the specific service application conditions.

Effects of major alloying elements

To overcome the obstacles of more corrosive environments, nickel alloys offering higher levels of corrosion resistance were developed. Some have specifically added or deleted certain alloying elements to achieve specific characteristics. The alloy content determines the corrosion resistance.

As previously stated, **Nickel** provides a matrix that is metallurgically compatible, and forms a solid-solution with many other elements. This element

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has some of its own unique electrochemical properties, which make it important as an alloying base. Under most conditions nickel readily forms a passive film, and exhibits good corrosion resistance to some oxidizing environments. However, the passive film that forms is not very stable and will suffer localized corrosion when exposed to strong oxidizing environments. Nickel improves corrosion resistance to mild reducing or alkali media.

Copper additions provide resistance to reducing media such as sulfuric, hydrofluoric and other halogen acids, but are sensitive to aeration and the presence of oxidizers. This element also improves resistance to seawater and more concentrated brines.

Molybdenum, like copper, provides resistance to reducing corrosive media, and enhances localized corrosion resistance against chloride damage in seawater, brines, and other chloride environments. This element also provides solid-solution strengthening and enhanced resistance against stress-corrosion-cracking (SCC).

Chromium benefits nickel by promoting and preserving passivity. It enhances the passive surface film formation in the presence of oxidizers. Chromium provides resistance to oxidizing media, and enhances the localized corrosion resistance. Chromium is by far the most important element for increasing high temperature oxidation and hot sulfidation resistance. Stable chromium oxide scales not only retard oxidation but also act as effective protective barriers against other forms of attack.

As mentioned earlier, nickel alloys are generally classified according to their alloying constituents. The commercial forms of nickel alloys utilized in the pump industry can be briefly characterized as follows:

Commercially pure nickel
This family is represented by wrought Nickel 200 and 201, as well as the cast alloy ASTM A494 Grade CZ-100.

These alloys are important in handling cold or hot concentrated caustic alkali solutions and dry chlorine. Caustic is a key chemical in the aluminum and paper industries where nickel pumps are widely utilized.

Nickel offers good resistance to corrosion in natural waters, and mild deaerated reducing acids. In reducing acid environments nickel often reaches an open-circuit potential equal to the platinum potential. However it does not readily liberate hydrogen during corrosion and therefore has some utility in dilute acids like sulfuric, hydrochloric, and phosphoric. When contaminated with oxidizers, nickel alloys containing chromium and iron offer superior resistance.

One area where nickel receives wide usage is as a material of construction for high temperature chlorination or fluorination reactions. The pure metal appears to offer superior corrosion resistance than any of its alloys because it forms a passive nickel chloride or fluoride on the surface, which controls the corrosion reaction.

The most significant attribute of pure nickel is unexcelled resistance to uncontaminated caustic alkalis.

Nickel-Copper (Monel) Alloys
Wrought Alloy 400 and K-500, as well as the cast alloy ASTM A494 Grade M-35-1 represent this family.

Monel alloys posses excellent corrosion resistance in seawater and deaerated reducing environments. However, they can pit in stagnant seawater. Aeration and oxidizing agents greatly increase corrosion rates. The Monel alloys offer good resistance to halogen acids and compounds, particularly hydrofluoric acid.

Again, other nickel alloys containing chromium and molybdenum offer superior resistance to localized corrosion in stagnant seawater, or when oxidizers are present.

Nickel-Molybdenum Type "B" Alloys
Wrought Alloy "B" types, as well as the cast alloy ASTM A494 Grade N-12MV or N-7M represent this family.

The addition of molybdenum greatly increases resistance in strong reducing environments such as hot hydrochloric acid. This group offers superior resistance to sulfuric, phosphoric, hydrofluoric, and hydrochloric acids under reducing conditions. Because of the high molybdenum content, these alloys are resistant to localized corrosion (pitting and crevice) in most acidic chloride (non-oxidizing) environments.

However, because these alloys lack chromium they are not suitable for oxidizing conditions. When oxidizing agents such as air, cupric (Cu^{2+}), ferric (Fe^{3+}), or chromate (CrO_4^{2-}) ions, or others are present as impurities, corrosion rates will increase rapidly. These alloys offer little corrosion resistance to oxidizing acids such as nitric or chromic, or oxidizing salts such as cupric or ferric chlorides. Under these conditions nickel alloys containing both chromium and molybdenum are required, since they can passivate under the influence of oxidizing agents.

Nickel-Chromium-Iron Alloys
Wrought Alloy 600, as well as the cast alloy ASTM A494 Grade CY-40 represents this family.

The addition of chromium greatly increases resistance to mildly oxidizing media, but the absence of molybdenum limits usefulness in reducing acid media. Though suitable for organic acids, they offer minimal resistance in strong mineral acids due to the absence of molybdenum. The use of these alloys is generally for oxidizing corrosive and elevated temperature services.

Nickel-Chromium-Molybdenum Type "C" Alloys
Wrought Alloy 625, Alloy "C" Types C276, C4, C22; as well as the cast alloys ASTM A494 Grades CW-6MC, CW-12MW, CW-2M, and CX-2MW represents this family.

The addition of molybdenum to the Nickel-Chromium system broadens resistance to both oxidizing and reducing environments. Molybdenum greatly enhances resistance to localized (pitting and crevice) corrosion by aqueous chlorides, and provides resistance to reducing conditions. These alloys are compositionally balanced to resist both oxidizing and reducing conditions, and are best for mixtures of oxidizing/reducing acids, as well as acidic chloride environments. This group offers the widest range of resistance, and is heavily used in the chemical and other aggressive process industries.

The Alloy 625 (cast equivalent CW-6MC) is a lower molybdenum content alloy that offers

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How to Pick...

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less resistance to reducing media, but more resistance to oxidizing media than the Alloy "C" types.

Nickel-Chromium-Iron-Molybdenum-Copper Type "G" Alloys
Wrought Alloy "G" Types G, G3, G30, G50; as well as the cast alloy ASTM A494 Grade CU-5MCuC represents this family.

The composition balance of this family is more complex, offers broader resistance to complex environments containing highly oxidizing or mixed acids, and can withstand both reducing and oxidizing conditions. This group offers the highest chromium content of all nickel alloys, and is especially resistant to contaminated reducing acids such as phosphoric and sulfuric, containing oxidizing agents.

Corrosion Performance and Alloy Differences
It's not always easy to identify the differences among the various nickel alloys. For example, the Alloy "C" types are all close in chemical composition with subtle differences. The nickel base Alloy "B" types and Monel can be used for reducing environments but have low tolerance for oxidizing agents. On the other hand, nickel alloys such as the Alloy "C" types; require the presence of some oxidizing agents to form protective films, and are less resistant under pure reducing conditions.

When making an alloy selection, don't overlook the seemingly minor details that may dramatically alter the corrosion resistance of an alloy or alter the corrosive characteristics of the environment. For instance, sulfuric acid is generally considered a reducing acid, but in concentrations over 60 Wt.% the acid is considered oxidizing and shifts the behavior of the acid.

It's also important to know whether the medium contains contaminants such as chlorides or ferric ions. Their presence may greatly affect the ability to form or maintain protective surface films. The presence of oxidizers such as air, oxidizing ferric or cupric salts, chlorates, hypochlorites, and chlorides, or oxidizing acids such as nitric can significantly increase corrosion rates, and require alloys balanced with chromium to resist oxidizing conditions. Under these conditions, a nickel alloy with both chromium and molybdenum is superior. Alloys that contain chromium but are free of molybdenum are more appropriate for mildly oxidizing environments than for reducing ones.

Water is a critical component in aqueous corrosion; the presence of water may make non-aqueous or anhydrous media more corrosive. This is often why dilute acids behave more aggressively than concentrated pure acids. However, in other cases water provides the required oxygen needed to passivate materials like the chromium containing nickel alloys.

For this reason it's important to know all the details and all components in a process stream before selecting an alloy. In the world of corrosion, a minor detail can make all the difference. It pays to know the details.

General Selection Guidelines
Based on the knowledge of these elemental effects, alloys can generally be selected for service in environments with known behavior as an alkali, reducing, or oxidizing environment.

For caustic or alkali services resistance is determined primarily by nickel content. Nickel is a key element for these services. However, if the environment contains oxidizers that effect the behavior and corrosivity, alloys containing both nickel and chromium are superior.

Applications for commercially pure nickel and nickel castings are found primarily in caustic alkaline or dry chlorine services.

In reducing acids or reducing environments, molybdenum and copper additions are key and beneficial for resistance. The Alloy "B" types offer superior resistance under pure reducing or non-oxidizing conditions. The alloy with the greatest molybdenum content offers greatest resistance. For example, high molybdenum "B" Type nickel alloys offer the best resistance to hot hydrochloric acid environments. If oxidants are present, use of these alloys is significantly limited. More general purpose "C" Types containing equal portions of chromium and molybdenum are superior, offering a high degree of resistance to both oxidizing and reducing conditions.

Under oxidizing conditions high chromium is key and beneficial for resistance. The nickel-chromium-iron alloys are suitable for many oxidizing environments, while the "G" Types and "C" Types offer superior localized corrosion resistance where pitting corrosion is expected, such as in acidic-chloride or hypochlorite containing alkaline solutions. For pitting resistance, increased molybdenum and chromium are needed.

Simply stated, high nickel content is wanted when the service is an alkali or hot caustic; high molybdenum content and/or copper content is wanted for reducing conditions; while high chromium content is required for services that are oxidizing. When conditions are a mix of either reducing/oxidizing, or alkali/oxidizing the best materials are the Nickel-Chromium-Molybdenum alloys offering an optimized and balanced composition.

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