TECHNICAL LETTER

Alloy C72200 - A Cost-Effective Alternative to C71640 and Titanium

Copper-nickel alloys are used extensively in seawater applications because of their excellent corrosion resistance and reasonable cost. The most widely used copper-nickel alloy is 90-10 copper-nickel (alloy C70600), but its susceptibility to erosion-corrosion at high flow rates and in areas of localized high turbulence has led to the increased specification and use of titanium and alloy C71640 (an iron-manganese modified 70-30 copper-nickel). In the late 1960s, the International Nickel Company developed what has now become known as alloy C72200, a chromium-modified copper-nickel alloy with significantly superior resistance to inlet-end erosion and blockage erosion as compared to 90-10 copper-nickel. This alloy was commercialized in the mid 1970s and, shortly thereafter, was installed in the steam surface condensers of numerous coastal power plants in the United States. Examination of tubes pulled from these plants since their installation has confirmed alloy C72200's superior resistance to inlet-end erosion and blockage erosion. With ever-increasing raw material costs, alloy C72200 truly represents a cost effective alternative to alloy C71640 or titanium where these alloys are utilized to avoid erosion-corrosion problems.

Composition

Chemical composition requirements for the copper-nickel alloys discussed below are per ASTM B-543 and are shown in Table 1. Titanium references are for commercially pure titanium per ASTM B-338, Grade 2.

Table 1. Chemical requirements for selected copper-nickel alloys per ASTM B-543.

| Alloy | Cu | Ni | Pb, max | Fe | Zn, max | Mn | Cr |
|--------|------|-----------|---------|----------|---------|---------|----------|
| C70600 | Rem. | 9.0-11.0 | 0.05 | 1.0-1.8 | 1.0 | 1.0 max | |
| C71500 | Rem. | 29.0-33.0 | 0.05 | 0.40-1.0 | 1.0 | 1.0 max | |
| C71640 | Rem. | 29.0-32.0 | 0.05 | 1.7-2.3 | 1.0 | 1.5-2.5 | |
| C72200 | Rem. | 15.0-18.0 | 0.05 | 0.5-1.0 | 1.0 | 1.0 max | 0.3-0.70 |

Erosion-Corrosion Resistance

Erosion-corrosion is a common cause of tube failure in copper alloy heat transfer tubing used in saltwater service for power generation and seawater desalination processes. This form of accelerated corrosion attack is caused by the mechanical disruption of the protective corrosion product films which form naturally in aqueous environments. Such film disruption is commonly caused by excessive fluid flow velocity or localized turbulence that exerts shear forces on the inside tube surface sufficient to damage or remove the protective corrosion product film, thus resulting in accelerated corrosion.

There are three primary mechanisms that cause erosion-corrosion: flow-related erosion-corrosion, blockage-related erosion-corrosion, and erosion-corrosion caused by entrained solids (e.g., sand). The relative ranking of alloy C72200 versus other alloys depends upon the type of erosion-corrosion being considered. All three categories of erosion-corrosion are addressed.

Flow-Related Erosion-Corrosion:

All types of erosion-corrosion are related to flow velocity, but as used in this Technical Letter, the term flow-related erosion-corrosion is meant to imply that other contributing factors such as blockages and/or entrained sand are not present. The most common form of flow-related erosion-corrosion occurs at the inlet or outlet of the heat exchanger tubes due to the high degree of turbulence in these regions. The usual causes of this type of erosion-corrosion are heat exchanger designs with restrictive flow areas that result in excessive turbulence and oversized pumps that result in flow rates in excess of material limitations. Copper alloys are typically characterized by a maximum bulk flow velocity above which erosive attack may be anticipated. This velocity is not only a function of alloy composition but also depends on the nature and composition of the cooling water.

In marine environments, the copper-nickel alloys exhibit superior erosion-corrosion resistance which, in general, increases with nickel content. For velocities up to about 2.4 m/s (8 ft/s) in clean seawater, 90-10 copper-nickel (alloy C70600) resists erosion attack. At higher velocities, alloys that are more resistant to erosion-corrosion (e.g., alloy C71500, alloy C71640, titanium, or alloy C72200) are required.

The unique composition of C72200 leads to its superior resistance to erosion-corrosion as compared to C71500 and C71640, even though the other two alloys have higher nickel content and, thus, higher cost. A review of the accepted maximum design velocities of alloys C70600, C71500, and C72200 will begin to demonstrate this fact (Table 2). Alloy C71500 has a higher maximum design velocity (i.e., resistance to erosion-corrosion) than C70600 due to its higher nickel content. This comparison is useful in illustrating the contribution of nickel content to erosion-corrosion resistance since nickel is the primary alloying element for these two alloys. However, alloy C72200 has superior erosion-corrosion resistance when compared to both C70600 and C71500 despite the fact that C71500 has higher nickel content. The chromium addition to alloy C72200 results in a more tightly adherent protective oxide film and consequent improvement in erosion-corrosion resistance.

The maximum design velocity for each alloy correlates to the shear stress required to strip the protective oxide film from the surface of the tube (Table 3). Again, it is shown that C72200 is superior to both C70600 and C71500.

Table 2. Accepted maximum design velocities for several copper-nickel alloys.

| Alloy | Maximum Design Velocity | | | |
|--------|----------------------------|-------|--|--|
| | m/s | ft/s | | |
| C70600 | 2.4-3.0 | 8-10 | | |
| C71500 | 3.7-4.6 | 12-15 | | |
| C72200 | 6.1 | 20 | | |

Table 3. Critical surface shear stresses for several copper-nickel alloys in seawater.

| Alloy | Critical Shear Stress | | | |
|--------|--------------------------|--------|--|--|
| | Pa | Psi | | |
| C70600 | 43.1 | 0.0063 | | |
| C71500 | 47.9 | 0.007 | | |
| C72200 | 296.9 | 0.043 | | |

Weight loss studies are useful for illustrating the erosion-corrosion resistance of a material. In one such study, alloy C70600, C71640, and C72200 were exposed to flowing seawater at a velocity of 9 m/s (30 ft/s). As shown in Figure 1, a 9 m/s flow rate is clearly above the design limit for C70600, and it can be seen that weight loss continues for the duration of the test. This continued weight loss is due to the fact that the service conditions are too severe for the protective oxide film of alloy C70600 to fully develop. On the other hand, alloys C71640 and C72200 both reach a steady-state condition with

no further weight loss after 20-40 days with alloy C72200 performing slightly better in terms of overall weight loss and time to reach steady-state. It is thus demonstrated that alloy C72200 offers equal or better resistance to flow-related erosion-corrosion as compared to C71640. Although data for titanium is not included in Figure 1, it is a known fact that titanium also exhibits outstanding resistance to erosion-corrosion.

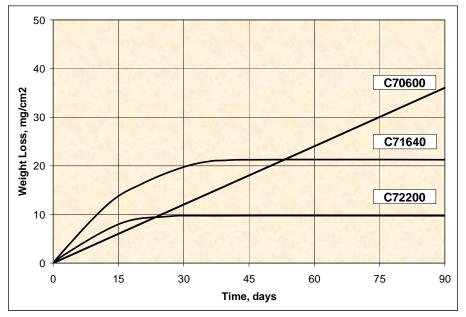


Figure 1. Weight loss versus time curves for C70600, C71640, and C72200 exposed in seawater at a velocity of 9 m/s (30 ft/s).

Blockage-Related Erosion-Corrosion:

Another form of erosion-corrosion is blockage erosion. It occurs when sea shells, rocks, twigs, or other debris in the cooling water are carried into the heat exchanger and partially obstruct a tube. The result is a restricted flow area with high localized water velocity and turbulence. A crevice is also present between the blockage and the tube wall, introducing a factor that is not present in inlet or outlet erosion-corrosion. To evaluate the resistance of various alloys to this type of erosion-corrosion, data was generated by creating artificial blockages in tubing of various alloys. Tubes of each alloy were subjected to flowing seawater at three different velocities for a period of six months. The maximum depth of attack was then recorded for each alloy and flow rate (Table 4 & Fig. 2).

The data show that the blockage erosion resistance of alloy C72200 is superior to that of alloys C70600 & C71500 and is similar to or better than that of alloy C71640.

Table 4. Blockage erosion data for several copper-nickel alloys after six months in seawater at flow rates of 2.2 m/s (7 ft/s), 3.3 m/s (11 ft/s), and 4.3 m/s (14 ft/s).

| Maximum Depth of Attack, mm | | | | | |
|-----------------------------|----------------|------|------|--|--|
| Alloy | Flow Rate, m/s | | | | |
| Alloy | 2.2 | 3.3 | 4.3 | | |
| C70600 | 0.20 | 0.23 | 0.34 | | |
| C71500 | 0.00 | 0.13 | 0.25 | | |
| C71640 | 0.08 | 0.07 | 0.20 | | |
| C72200 | 0.00 | 0.09 | 0.10 | | |

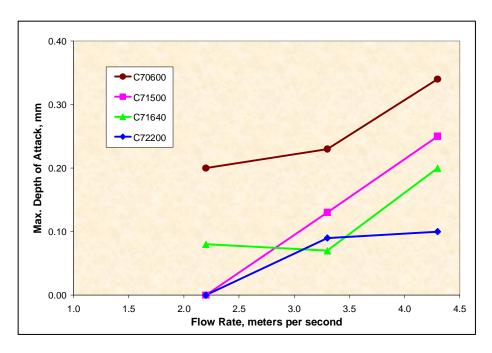


Figure 2. Blockage erosion data showing the maximum depth of attack experienced at three flow rates. The data show the superior performance of alloy C72200 as compared to C70600 and C71500. Alloy C72200 performed similar to or better than C71640.

Sand-Related Erosion-Corrosion:

Sand-related erosion-corrosion is the third category of erosion-corrosion to be discussed. The effects of erosion-corrosion caused by entrained sand in seawater are of great significance in regions where sand is present in the intake water because of geographical considerations such as sea bed topography or wave action. Comparative alloy data is provided in Table 5. The test data is limited, but it indicates that alloy C72200 is much better than alloy C70600, slightly better than alloy C71500, and almost as good as alloy C71640.

Table 5. Weight loss data and extrapolated corrosion rates for several copper-nickel alloys exposed to artificial seawater at 40° C with 1000 ppm sand with a flow rate of 2.1 m/s (~7 ft/s).

| | 12 μm Rc | ound Sand | 5 μm Sharp Sand | | |
|--------|--------------|-----------------|-----------------|-----------------|--|
| Alloy | Weight Loss, | Corrosion Rate, | Weight Loss, | Corrosion Rate, | |
| | mg/cm2 | mm/yr | mg/cm2 | mm/yr | |
| C70600 | 8.79 | 0.256 | | | |
| C71500 | | | 4.53 | 0.132 | |
| C72200 | 2.79 | 0.081 | 3.50 | 0.102 | |
| C71640 | | | 3.03 | 0.088 | |

General Corrosion Resistance

The general corrosion rate of copper-nickel alloys in seawater is very low and decreases over time once an adequate protective oxide film forms. For this reason, premature failure from general corrosion is rarely experienced by the copper-nickel alloys in seawater service. However, some factors that can contribute to higher than expected general corrosion rates for copper-nickel alloys are discussed below.

Ammonia Effect:

Ammonia in the presence of oxygen can increase the general corrosion rate of copper-nickel alloys. Available corrosion performance data indicates that higher nickel content is beneficial in reducing this type of corrosion. Alloy C70600 is considered to have satisfactory resistance to ammonia attack. Alloys C71500 and C72200 have improved resistance with C71500 performing slightly better. Data for alloy C71640 is not readily available, but it would be expected to perform similar to C71500 based on its nickel content.

Ammonia treatments are often used in power generation plants to adjust pH of the feedwater. In the steam surface condensers of these power generation plants, ammonia and oxygen concentrations in the main body are typically low enough that problems do not arise. While the service conditions in the air removal section are somewhat more severe, both alloys C71500 and C72200 have been used successfully in this application.

Ammonia may also be present in the seawater feed to desalination plants as a result of agricultural run off or industrial plant discharges near the intake. The relative lack of literature on this topic suggests that ammonia attack is not a primary concern for heat transfer tube in desalination plants.

Sulfide Effect:

The presence of sulfides, such as in polluted seawater, can increase the rate of corrosion and cause pitting in copper-nickel alloys. Sulfides cause the formation of a black film of both cuprous oxide and cuprous sulfide that is less protective than the normal cuprous oxide film that forms in clean seawater. This effect is less severe for tubes that are first exposed to clean seawater and have time to fully develop the desired cuprous oxide film. This effect is more severe when the first cooling water introduced to the new tubes contains sulfides. Ferrous sulfate treatment can be used in this situation to aid in the development of the desired protective oxide film.

In general, when there are brief exposures to sulfides during normal operation, problems rarely exist. When long term exposure to seawater containing greater than 10 ppm sulfides is expected, coppernickel alloys should be avoided in favor of titanium.

Chlorination Effect:

All copper-nickel alloys have excellent resistance to crevice-related pitting caused by chlorination at normal levels used to control biofouling. Chlorination levels in excess of 3 ppm can be harmful. However, the natural biofouling resistance of copper-nickel alloys allows them to provide excellent heat transfer with less use of chlorine or other biocides as compared to titanium.

The Effect of pH, Oxygen, and Temperature:

The pH of the cooling water can have a pronounced effect on the general corrosion rate of coppernickel alloys. The protective oxide film becomes increasingly soluble as pH decreases below 7, especially when oxygen is present.

In power utility steam surface condensers, the pH is typically greater than 7 so this is not an issue. In the multi-stage flash (MSF) desalination plants, the tube-side environment for all sections of the plant

is also typically greater than pH 7, but the vapor-side environment can be at a pH of 5 to 6. In the absence of oxygen, this low pH is not detrimental. As a result, copper-nickel alloys perform well in the heat recovery sections of multi-stage flash (MSF) desalination plants despite the low pH levels. However, in the vent condenser where high oxygen levels are present, copper-nickel alloys should be avoided in favor of titanium.

As already discussed, the presence of oxygen affects the general corrosion rate of copper-nickel alloys. In general, the corrosion rate increases with oxygen content. Some oxygen is useful and necessary in forming the protective oxide film. In the water-side of copper-nickel tube, this protective oxide film minimizes the effect of dissolved oxygen within the normally observed oxygen content found in seawater. However, in certain aggressive vapor-side environments, such as the vent condenser in an MSF plant, high oxygen concentrations result in rapid general corrosion.

The temperature of the cooling water can also affect the general corrosion rate of copper-nickel alloys. In general, the corrosion rate increases with higher temperature due to the increased reaction kinetics. However, the corrosion rate may actually be lower at high temperatures due to the decreased solubility of oxygen.

Heat Transfer Comparisons

Thermal conductivity values and gauge correction factors for "new, clean conditions" as listed in the Heat Exchange Institute's "Standards for Steam Surface Condensers" (Ninth Edition) are shown in Table 6 below. Admiralty Brass is included in this table because it is rated at 1.00 for a wall thickness of 0.049" (~1.2 mm) and is considered the standard to be used when making comparisons.

Table 6. Comparative heat transfer data for commonly specified alloys of copper-nickel and titanium. Admiralty brass data is included for reference purposes.

| Alloy | Thermal HEI Gauge Correcti | |
|-----------------|----------------------------|-------------------------|
| Alloy | Conductivity* | Factor @ Wall Thickness |
| Admiralty Brass | 64 | 1.00 @ 0.049" (1.2 mm) |
| C70600 | 26 | 0.96 @ 0.035" (.9 mm) |
| C71500 | 17 | 0.92 @ 0.035" (.9 mm) |
| C71640 | 17 | |
| C72200 | 19.9 | |
| Ti-50A (Gr. 2) | 9.5 | 0.95 @ 0.020" (.5 mm) |

^{*} BTU-ft/ft²-hr-°F (@ 68°F)

Gauge correction factors are not available for alloys C71640 and C72200; however, based on the thermal conductivity values, it is reasonable to assume them to be bounded by those of alloys C70600 and C71500 for the same wall thickness. While titanium possesses lower thermal conductivity, its higher strength and excellent corrosion resistance allow it to be used at a lighter wall thickness. The result is that copper-nickel alloys and titanium offer about the same heat transfer ability at the wall thicknesses that are commonly specified in power generation and desalination plant applications.

The Effect of Biological Fouling:

The attachment of marine organisms such as algae, mussels, and barnacles to heat exchanger tube surfaces has a significant adverse effect upon heat transfer capability. Copper alloys are well known to have an inherent resistance to this type of fouling whereas titanium does not. Chlorination and sponge ball cleaning are effective countermeasures for titanium provided that these countermeasures are routinely utilized and maintained.

Cost Comparisons

Cost indices for the heat transfer tube materials commonly used in seawater service are presented in Fig. 3. These indices are based on actual prices quoted in March of 2005 for two representative items: ¾ inch O.D. x 12.67 feet Long and 44 mm O.D. x 24 meters Long. For these two items, the aluminum brass and copper-nickel alloys were quoted at 0.028" wall and 1.0 mm, respectively; titanium was quoted at 0.020" and 0.7 mm, respectively. For ease of comparison, a cost index of 1.00 was assigned to alloy C72200.

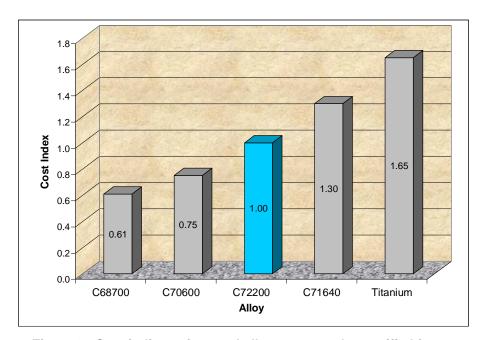


Figure 3. Cost indices of several alloys commonly specified for seawater applications based on actual prices quoted in March 2005. Alloy C72200 was assigned a cost index of 1.0 for ease of comparison.

As can be seen, alloy C72200 truly represents a cost-effective alternative to C71640 and titanium when erosion-corrosion resistance is a primary requirement for the heat transfer tube material.

Recommended Applications

In steam surface condensers of power generation plants, alloy C72200 offers excellent performance due to its high resistance to erosion-corrosion and ammonia attack. It is suitable for installation in both the air removal section and the main body of the condenser.

In desalination applications, alloy C72200 is well suited for environments where ammonia and/or low pH are not present in combination with high levels of oxygen. For example, alloy C72200 is recommended for the heat recovery section of an MSF plant but not the vent condenser.

Where erosion-corrosion resistance is a primary requirement, alloy C72200 has been shown to be superior to alloy C71640 in terms of resistance to flow-related and blockage-related erosion-corrosion. The resistance of alloy C72200 to sand-related erosion-corrosion is almost as good as that of C71640.

In summary, alloy C72200 offers similar or better performance than C71640 at lower cost. It is also a cost-effective alternative to titanium where its level of performance is not required.

Metallurgical Considerations & Precautions

The superior erosion-corrosion resistance of alloy C72200 is due to the 0.3 - 0.7 % chromium addition. The mere presence of chromium, however, does not guarantee good performance. In metallurgical terms, some chromium will be "solutionized" and some will be "precipitated". At least 0.25% solutionized chromium must be present for superior erosion resistance and *end-users should specify "0.25% min solutionized chrome measured by the resistivity method*".

Solutionized chrome can come out of solution, i.e. precipitate, as a result of heat treatment operations such as welding, brazing, or annealing. To maintain 0.25% min chromium in solution, water quenching immediately after welding, brazing, or annealing is an absolute necessity.

Finally, with regard to brazing, the phosphorus in phosphorus-containing brazing alloys will combine with the nickel in the alloy C722 to form brittle nickel phosphides and this will likely result in failure of the brazed joint. Only brazing alloys which do not contain phosphorus should be used.