

Aluminum Mold Corrosion and Protection

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Abstract

With the characteristics of high strength/weight ratio, good machinability and thermal conductivity, aluminum alloys are the preferred materials for plastic mold manufacturing. Some of the high strength aluminum alloys used in molds such as Al 7075 don't have good corrosion resistance due to the presence of alloying elements. When exposed to chilled water running through internal water channels and thermal cycles in the molding process, the molds are subject to corrosion. The chilled loops normally have other metals such as carbon steel and copper present as well. Maintaining a proper corrosion control of aluminum molds and other metals present in the chilled loops has been a challenge. Conventionally molybdate, silica, nitrite and nitrate are used as corrosion inhibitors in the water treatment programs for the chilled loops for the aluminum molds. In this study the corrosion of the aluminum and protection of different corrosion inhibitors on aluminum alloys were studied. Newly developed water treatment containing novel corrosion inhibitors showed superior corrosion protection and scale protection of the mold and loops. The protection mechanism and evaluation in the simulation loop is discussed.

INTRODUCTION

Aluminum and its alloys are one of the most used metals in industrial processes because of low cost, easy availability, and many desirable characteristics. In the plastic manufacturing industry, aluminum is currently the preferred choice of material for molds. Compared to steel, aluminum has advantages such as [1] :

- Much better thermal conductivity thus more consistent mold temperature and better mold quality, less need for water lines and more room for additional ejection pins; and faster heat dissipation results in less cycle time and higher productivity
- Easier to machine and polish, resulting in lower cost of mold manufacturing and fast time-to-market product
- No additional treating or stress relieving required

Aluminum alloys 2024, 6013, 6061, 7050 and 7075 are the common alloys used in mold manufacturing. In the selection of the material, more consideration is given to the strength, hardness, machining and polishing characteristics, while less is given to corrosion characteristics. Take Al 7075 for example, it is strong and thermal treatable, with a strength comparable to many steel types. However, it's one of the Al alloys that are most vulnerable to corrosion attack.

Corrosion of Aluminum

In the molding process, the mold is cooled by water running through inside water channels. Aluminum alloys are generally corrosion resistant because of the naturally occurring oxide film, which is dense and able to protect the metal from corrosion to certain extent. When exposed to water, the film is not strong enough to prevent the metal from corroding, especially when Cl^- is present.

There are quite a few studies attempting to understand why alloys such as Aluminum 2024 and 7075 are more vulnerable to corrosion than pure aluminum and some of the other alloys including Al6061 [2-4]. A lot of the findings are pointing to the intermetallics formed by the alloying elements and the potential difference between the Al matrix and intermetallics, resulting in microgalvanic cells. The addition of alloying elements improves the mechanical property of Al, but creates additional phases in the materials that causes corrosion issue.

Galvanic corrosion is also common in the application where Aluminum is used. In Parts made of other metals, e.g. brass fittings, are connected directly to the aluminum molds without electric isolation. As the more active metal, Aluminum corrodes faster at the connection area and the less active metal is protected.

Al protection by corrosion inhibitors

The aluminum molds are the essential to production in plastic modeling. The cost of the molds in some industry is extremely high and the downtime can be costly too, thus maintaining the mold in good working condition and prolong its life is critically important. The chilled water running through internal channels of aluminum molds are treated with corrosion inhibitor to protect it from corroding.

Conventionally chromate, phosphate, molybdate, silica and rare earth metals are used as the corrosion inhibitor for aluminum in different applications including water treatment. Chromate has been almost

phased out due to its toxicity. The others are still being used and their characteristics as related to Al corrosion is briefly discussed as followed

Molybdate

Molybdate is widely used in steel and aluminum corrosion control. It is considered an anodic inhibitor and requires oxygen to protect metal by forming an oxide layer on the substrate. In the presence of oxygen, molybdate forms an insoluble dense ferric molybdate complex that protects the iron from corrosion. In the case of protecting aluminum, the protection mechanism is not well established. Molybdate is believed to be incorporated into the protective film as a hydrated aluminum molybdate [5]. It was also proposed that the corrosion inhibition of aluminum alloys by molybdate is a two-step process and formation of polymolybdate species ($\text{Mo}_7\text{O}_{24}^{6-}$ and $\text{Mo}_8\text{O}_{26}^{4-}$) [6].

It is generally believed that there is a threshold concentration for molybdate to work effectively in water treatment. In closed loops, molybdate is recommended to be dosed over 200ppm MoO_4^{2-} . Due to its toxicity, use of molybdate is regulated in some areas. Certain industries such as food and beverage prefer corrosion control chemistry free of molybdate because of the potential risk of contamination. One advantage of molybdate as corrosion inhibitor in water treatment is that it's not a nutrient for microbes.

Silicate

Silicate is another commonly used corrosion inhibitor for Aluminum. Silicate is generally believed to protect metal by imparting anodic inhibition by forming a hydrated metal-silicate oxide on the surface [7]. The oxide layer may dissolve at low pH thus the silicate treated water system is normally maintained higher than 7. The challenges with silica treatment include: 1) the addition of silica increases the scaling potential. 2). Silica may precipitate over the time and cannot sustain critical concentrations in the long term; 3) maintain an optimal pH window for silica to work in the closed loops can be a lot harder than it appears to be. High pH resulted from treatment overdosing will cause aluminum to corrode and lower pH will render the treatment ineffective.

Silicate is usually used together with other corrosion inhibitors, e.g. molybdate. Silicate also has the advantage of not being a nutrient for microbes.

Nitrate

Unlike nitrite, which is mostly effective as corrosion inhibitor for steel, nitrate is added to water treatment to control the corrosion of aluminum. The two can be used together to make a program that covers both steel and aluminum. Nitrate is an anodic inhibitor and works by contributing to the oxide/hydroxide film formed on the aluminum surface because of its oxidizing capability [2]. Nitrate is also used as pitting inhibitor for aluminum in applications such as in the engine coolants.

Multi-metal protection

In typical closed loop systems, there are components such as heat exchanger, chiller, pumps, pipe, fittings, and process equipment. They can be made with various steel, copper and aluminum alloys. The corrosion control treatment for the closed loops needs to work for all metals. Different metals have different pH ranges of corrosion immunity and furthermore, their corrosion inhibitors may have different optimal operation pH

window. Therefore, developing treatment programs for mixed metallurgy can be a challenge. In the closed loop treatment programs combinations of corrosion inhibitors, e.g., molybdate/silicate and nitrite/nitrate are normally used.

Challenging facing Al mold protection and Al closed loops

With the emerging of using high strength alloys, such as Al 7075 and Al 2024, in the mold manufacturing the challenges of corrosion control have increased. A series of failure analysis found that the corrosion seemed to be a widely existing problem for aluminum molds [8]. Figure 1 shows a typical corrosion on aluminum mold. The areas exposed to cooling water has heavy corrosion, including localized corrosion and exfoliation corrosion. The water channels appear to be covered by iron corrosion product transferred from elsewhere. Areas outside of the water channels also have slight corrosion, likely caused by leaked or spilled water.

The conventional corrosion inhibitors are limited on effectively protecting the aluminum parts, especially when the treatment program is not maintained optimally. Common negligence includes:

No proper shutdown protocol: when the mold is not in use, cooling water needs to be drained and the mold needs to be dried before storage. Otherwise water will remain in the channels and under stagnant conditions, corrosion normally is accelerated. It's good practice to keep the water treated and recirculating even when the mold is not used for product.

Poor loop design: In some loops dead legs exists and water can stay stagnant, while in some loops the water flow may be too high (as high as 60-70ft/sec) causing erosion corrosion, especially when the water contains suspended solids. In addition, sharp turns in water channels is another area where erosion may occur.

Crevice corrosion: Because of constant switching of the molds or improper O-ring sealing (caused by damaged/corroded O-ring groove) water can be trapped between pieces of the molds and crevice corrosion may occur.

pH fluctuation: frequent pH change is seen in the closed loops when new makeup water comes in or additional treatment (e.g. biocides) is fed. pH regulation can be added; however, the pH probes may not be properly calibrated. Dramatic pH change can cause aluminum to corrode fast.

Defects and stress: Part of the internal water channels in aluminum molds are machined and not thermal treated. Mold may be reworked occasionally when needed. Machining creates defects and local stress concentration, and the affected area tends to be the initiation area for localized corrosion.

Failure to maintaining active concentration: Most closed loops have low leak rate or high hold time index and feeding treatment is not frequent. Over the time the actives may degrade or precipitate, leaving less active in the water.

Galvanic corrosion: connecting parts made with dissimilar metals, e.g., connecting copper or stainless steel fittings directly to aluminum or steel parts and expose them to the same water, will cause galvanic corrosion.



Figure 1. Corroded aluminum mold from plastic molding production. The metal is Al7075.

In the closed loops that contain parts made with various metals, protection of all metal is crucial for corrosion protection of the system. The corrosion product can be transferred from one place to another and adhere on a different metal, as shown in Figure 2. Under-deposit corrosion may happen in such case, and if the metal is more active than the corrosion product (for instance, aluminum and iron oxide as in Figure 2), replacement reaction can happen, causing the more active metal to corrode faster.



Figure 2. Aluminum mold from a bottling plant. The mold is made with aluminum alloy 6063.

New environmentally friendly inhibitor

A promising new inhibitor package named TRASAR™ TRAC One[†] from Nalco Water Company (referred to as "the new inhibitor" in this paper) was studied on its corrosion protection of aluminum alloy and compared to conventional corrosion inhibitors. The new corrosion inhibitor is free of molybdate, phosphate and borate and have a near neutral pH. The corrosion protection was studied in the simulated closed loop, and ASTM G31 immersion test. The protection behavior was characterized by using electrochemical techniques.