

Electrochemical Protection of Metal Castings During Ceramic Leaching

Andrew Timm

Electrical Engineering and Computer Science Department
Milwaukee School of Engineering
1025 North Broadway
Milwaukee, WI 53202-3109. USA

Rapid Prototyping Center
Milwaukee School of Engineering
1025 North Broadway
Milwaukee, WI 53202-3109. USA

Faculty Advisor: Vito Gervasi

Abstract

This research seeks to arrest mass change in metal castings during the ceramic leaching process by using an impressed current. Previous research shows that metal corrosion can be prevented during the leaching process at the cost of a sacrificial metal. This is a method adapted from the cathodic protection principle for use in metal casting protection. However, cathodic protection inherently electrodeposits the sacrificial metal onto the protected metal casting. This research further evolves the cathodic protection method with an external voltage source to control electrodeposition. Corrosion decreases metal casting mass, deposition increases casting mass; thus, this research seeks the optimum protection voltage to arrest mass change in a sacrificial copper and simulated copper casting system immersed in a sodium hydroxide bath. The results of this research may provide a simple and effective means to allow casting with higher resolution, increased alloy options and reduced surface degradation for the aerospace, automotive, and medical fields.

Keywords: ceramic leaching, impressed current, corrosion, casting protection, sacrificial metal, cathodic protection, electrodeposition

1. Introduction

Investment casting is a unique casting method with a distinct advantage over others: complex internal geometries can be captured. Industry finds particular use of investment casting for creating intricate metal castings; however, the end product's quality is limited by the final step of the investment casting process: ceramic removal. Caustic solutions are used to leach away the ceramic mold from in and around the metal casting's complex form; however, the same caustic solution corrodes away fine details in the casting, which can result in a deficient product. To preserve casting integrity, the metal casting may be protected by another "sacrificial" metal.

1.1. scope

In industry, a typical leaching process includes very highly concentrated caustic solutions, ultrasonic vibration or other fluid circulation, and elevated temperature of the caustic bath. These elements are used to enhance the leaching effect. Leaching in this form may continue for

a number of hours per cycle, and numerous cycles may be performed on the same piece. For this research, two plain copper coils were cleaned and immersed in a high concentration sodium hydroxide (NaOH) solution for approximately 11 hours. One copper coil was considered a sacrificial anode, used to protect the other coil, which was the simulated casting. Elevated temperatures, the presence of ceramic, and circulation were outside the scope of this experiment. All experiments were conducted at ambient room temperature, for consistency. The coils were massed before and after each trial to show net mass gain or loss.

2. Background

2.1. investment casting

Investment casting, also known as the “lost wax” method of casting, was employed by many ancient civilizations all around the world over four thousand years ago, including Egypt, Mesopotamia, China, and Africa. In those times, primarily artwork was created from brass, gold, or other precious metals. For centuries, its applicability was unnoticed, until it was re-introduced to the dental industry in the early 1900s. Modern casting finds more practical use in the aeronautical, automotive, and biomedical industries [1].

A common modern investment casting process is as follows:

1. A wax or plastic pattern is created, usually from injecting a metal mold of the pattern.
2. Numerous such patterns are attached to a sprue to allow mass production of castings.
3. A sprue unit is dipped into a number of ceramic slurries to amalgamate a thick, secure ceramic coating around the wax patterns.
4. After the slurry hardens, the wax or plastic is melted or boiled away and recycled, leaving a void to fill with molten metal.
5. After cooling, the ceramic shell is removed (broken off and/or leached) to leave the casting.
6. The metal castings are cut away from the sprue and checked for defects [2].

2.2. solid freeform fabrication

Wax patterns used in the investment casting process are traditionally created by an injection molding or machined from a wax block. Solid freeform fabrication (SFF), also known as rapid prototyping (RP), is able to create wax-like patterns in an additive fashion (i.e. pattern material is added layer by layer). SFF allows creation of very small, complicated, intricate models that are otherwise impossible to produce with conventional methods. Rapid prototyping machines typically use a laser or other heating device, a material that is hardened by heating, and an adjustable bed. The laser focuses on the bottom layer of the polymer and draws the two-dimensional cross section desired, fusing and hardening the polymer together into a solid. The bed adjusts to expose the next layer, and the process repeats until the top layer is hardened and the model is complete [3].

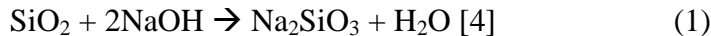
Combining this technology with investment casting yields a technology known as pattern-based hybrid fabrication, a very useful tool for modern applications, where small-scale, intricate, consistent metal castings are required.

2.3. ceramic removal and corrosion

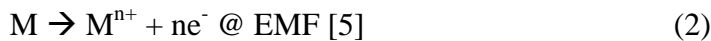
The final step of the investment casting process is to remove the ceramic mold from around the metal casting. A few methods are used:

- Cracking or breaking off the largest pieces by mechanical vibration.
- Air or water blasting with a high-pressure gun.
- Ceramic leaching by a caustic solution, which dissolves away small and hard-to-reach areas still attached to the casting.

Caustic solutions are usually basic and cause the following reaction with silica-based ceramics:



Where SiO_2 is the silica-based ceramic, and NaOH the base supplied by the solution. The undesired result of the presence of this base is metal casting corrosion, which follows the general form:



Where M^{n+} is a metal ion, and $n\text{e}^-$ are the electrons it releases. The number of electrons produced for the specific reaction, abbreviated by n , is specific to the metal used. Each metal reaction occurs at a unique electromotive force (EMF), an arbitrary value which specifies how readily the reaction will react. This reaction shows how solid metal breaks down into metal ions in solution with an equivalent number of electrons. Metal ions entering the solution result in lost metal mass on the casting.

The net effect is that, over prolonged exposure, even this gradual reaction can have significantly damaging effects, as in a seaborne ship's corroding metal hull or deteriorating underground water pipes. In the scope of this experiment, the corroding metal is the metal casting under the influence of the caustic solution, which is intended to attack only the ceramic mold. To minimize production cost and make intricate castings possible, the casting must be protected during the ceramic removal process [6].

2.4. metal protection

Currently there is no industry practice for metal casting protection during the ceramic leaching process. A method adapted from preserving ship hulls, underground water pipelines, and water softener tanks has been proposed as a feasible method for metal casting protection; this method is cathodic protection [6].

2.4.1. cathodic protection

Cathodic protection uses the fact that the electromotive force from equation (2) is particular to the kind of metal used. Exposing two dissimilar metals to the same ionic solution will result in two simultaneous corrosion reactions. However, since different metals exhibit different bond

strengths, one metal will corrode more readily than the other (i.e. corrode with a greater EMF). For instance, copper and zinc exposed to a caustic solution will both corrode according to equation (2). However, zinc will corrode more readily (zinc has weaker bond strength, or larger EMF than copper). By electrically connecting the zinc to the copper, as in Figure 1, the zinc will slow, stop, and reverse the copper's corrosion reaction.

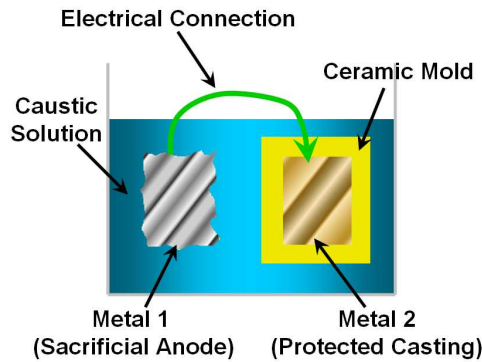


Figure 1 Cathodic protection model

In “reverse”, the copper metal actually gains more metallic mass from free-floating metallic ions in the solution (i.e. zinc ions) [5]. This phenomenon is known as electroplating and has been experimentally confirmed by former undergraduate researcher Timothy Nedimyer. By this method, the copper casting acts as a cathode and is electrochemically protected at the sacrificed zinc anode's expense [6].

2.4.2. impressed current protection

The impressed current method, illustrated in Figure 2, extends the cathodic protection principle to control the applied potential to the copper. Using only a sacrificial anode, a metal casting can be protected only at the set EMF inherent to the metals being used, which can reverse the reaction and result in electroplating. If electroplating is undesired, an external voltage source is added across the sacrificial anode and cathode casting. The voltage supply is calibrated to closely approximate the optimum voltage for casting protection without mass change. This will exactly stop, but not reverse, the casting corrosion equation (2) [5].

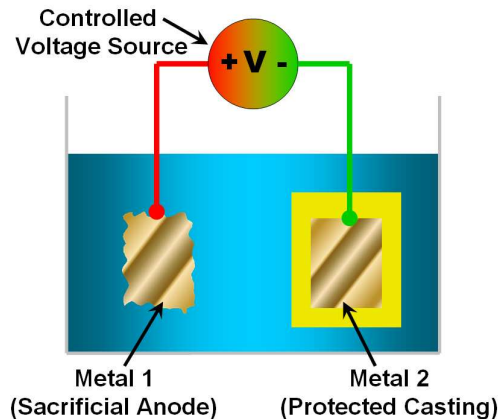


Figure 2 Impressed current model

Controlling the potential difference between these two metals means controlling the amount of electroplating that occurs and the direction in which it occurs. This has one unique advantage over cathodic protection: theoretically, any metal can protect any other metal. Thus, there is no longer a restriction to sacrifice a metal with a higher EMF for a metal casting with a lower EMF. Two of the same metals can even be driven, one to protect the other (this is the case Figure 2 depicts). Driving copper to protect copper was the focus of this study, as this has practical use in industry. An excess piece of the same metal used to create a casting (e.g. sprue) could thus be used to protect the casting.

3. Approach

Setup equipment included six independent power supplies, six plastic Tupperware™ tubs, twelve 1 meter 20 AWG copper coils, a multimeter, and 1M sodium hydroxide (NaOH) solution. Each power supply afforded a set voltage to each of the six tubs filled with the NaOH solution. Hence, each trial ran six different tests simultaneously. Below is Table 1, which lists of all the variables in this experiment and how they were held constant.

Table 1 variables present and how each was held constant.

Variable	How It Was Held Constant
Metal Coils	Ordered from the same company, McMaster-Carr, Inc. All coils had similar surface areas and masses (about 4.5 grams), as they were cut to 1 meter lengths from 20 AWG wire.
Cleaning Metal Coils	Wiped with steel wool and washed in tap water before testing. Afterward, all coils were cleaned with tap water (to remove deposited NaOH), and air-dried before massing again.
Distance of Separation	Coils were grasped approximately in the middle to the power source by alligator clips, which were taped to the sides of a Tupperware™ dish, 12 cm. apart.
Solution	Controlled at 1M NaOH for each solution. The researcher personally massed sodium hydroxide pellets (ordered from Sigma-Aldrich, Inc.) and combined with distilled water (supplied by MSOE) to control the concentration.
Temperature and Pressure	All experiments were conducted in the same area of the laboratory, underneath a ventilation hood. Temperature and pressure were not recorded, since this variance was small enough to be considered negligible.
Time	All samples were exposed for roughly the same amount of time, between 10 and 12 hours. Percent changes were divided by the exact time to account for this time difference.
Voltage	Supplied by XP-660 Elenco Precision, Inc. power supplies, which were calibrated by a K-5318B Knight Electronics, Inc. multimeter before and a few minutes after pouring the NaOH solution. After the test, voltage was recorded again, and an average was used to generate a graph representing mass change as a function of the applied voltage.

4. Results and Discussion

4.1. range of optimum voltage protection

After a number of trials, a trend was found which indicated the general range within which the desired voltage may be found. As expected, the copper cathode (imitating the metal casting) gained more mass and the sacrificial copper anode lost mass with increasing voltage.

More data points were taken between the 0V and 70mV range to generate a higher resolution trend, shown in Figure 3, below:

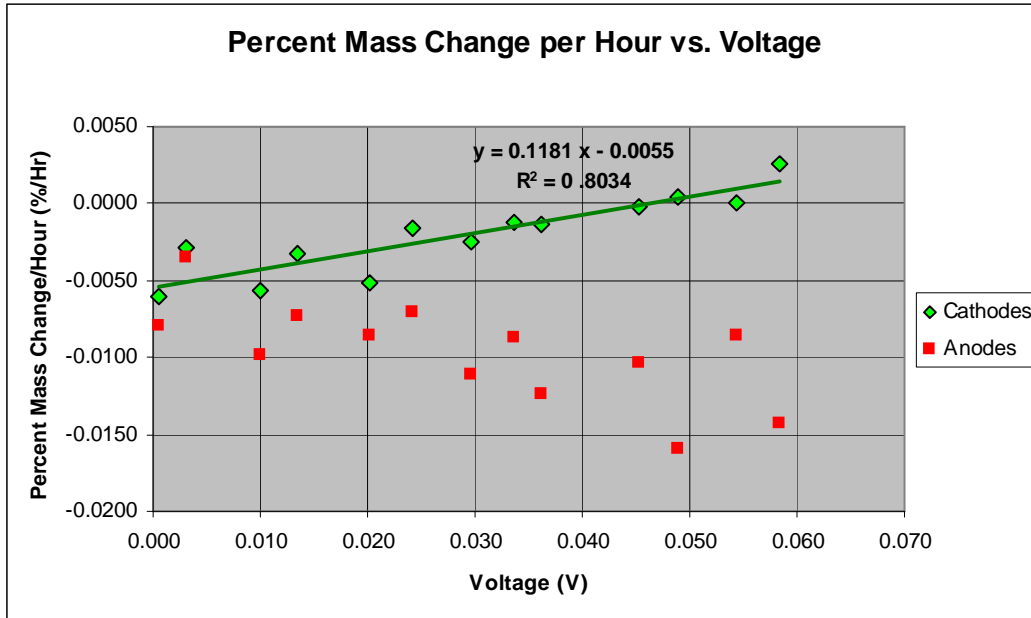


Figure 3 Optimum voltage range found

In Figure 3, a mass change of both the cathode and anode are plotted with respect to the voltage applied. At very low voltages (less than 50mV), there is mass lost to both the anode and cathode, because there is not a sufficient potential difference to drive the copper anode to protect the copper cathode. At higher voltages, however, the cathode gains mass, because there is a large enough potential difference that the anode corrodes to leave metal ions in the solution, which then plate on to the cathode. As can be seen, there is a certain area where the cathode mass change trend line crosses the x-axis. This indicates a mass change of approximately zero and is the approximate optimum voltage to protect a copper casting.

4.2. a capacitive system

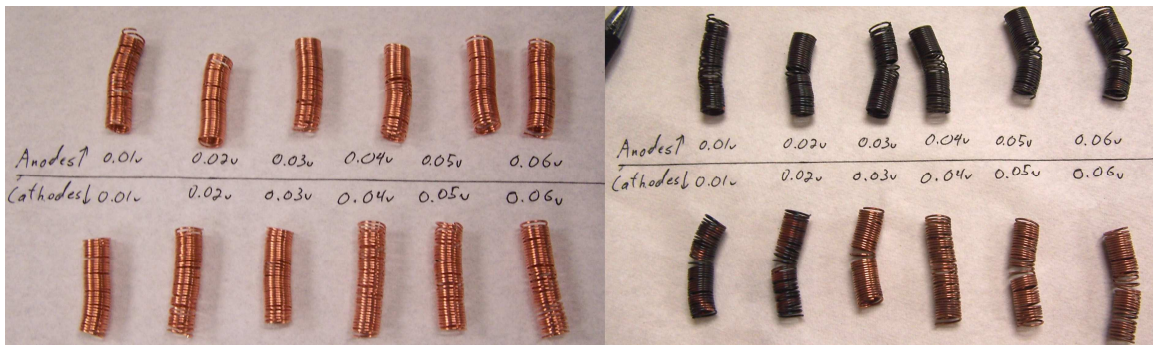
Initially, an arrested mass potential of approximately 0.34v was expected, since that is the half-cell electrode potential specific for copper at standard temperature and pressure. However, tests indicate that is clearly not the case—there is a sufficient amount of mass gain at approximately 0.34v to rule out that possibility. At one point, the suggestion was raised to find the point where no current passed through the system at all. Testing the current in the system as a function of voltage resulted in finding that this system never has a current, regardless of the applied voltage. The solution acts as an electrolyte—not a conductor. Thus, no electrons pass from one terminal to another. Rather, an electrostatic field is supplied by the power source on either copper sample, wherein a charge is stored that reacts with the solution according to equation (2). Since there is no current flow in this system, this system acts as a capacitor.

It is for this reason the researcher believes the point at which the voltage crosses zero is dependent upon the capacitance of the system rather than just the metals used. Thus, the applied voltage, the distance of separation of the metals, the exposed area of the metals, and the temperature and pressure are new variables that affect the system. A general experiment was

performed that confirmed the capacitance of this system is at approximately 5 picofarads. Time constraints did not allow further examination of this phenomenon.

4.3. equilibrium reaction

There is a possibility that mass is lost and gained in equilibrium at this optimum voltage. Plated copper appears duller and red, while corroded copper appears dull and brown. If there is an equilibrium reaction occurring to any significant extent, there should be a visual change in appearance of the samples near the optimum protection voltage. Figure 4 is a photo taken after a trial run with voltages varying 10mV around the expected optimum voltage. Though the copper samples retain their shiny luster around the optimum protection voltage, there is some browning due to the trial run.



5. Conclusion

There is an optimum voltage where the metal can be protected from mass loss due to corrosion while avoiding mass gain due to electroplating. This research approximates that point to be about 50 mV under the given test conditions. If this voltage is tuned, this technology may be critical for saving high resolution, feature-rich metal castings as they are exposed to the caustic leaching solution.

The system created by this method is capacitive in nature, and thus is affected by a number of other variables. Since Figure 4 depicts an apparent discoloration at the surface of the tested metal, altering these other variables may help preserve the shiny metallic finish on the surface of such metals as copper.

6. Future Recommendations

As yet, impressed current protection of metal castings is rather undeveloped—there are a large number of possibilities yet to explore and relations to define. In order to define a more commercially viable system, the following elements should be included in future studies:

1. Increased caustic solution concentration
2. The presence of ultrasonic vibration or circulation
3. Leaching at elevated temperatures
4. The presence of ceramic in the solution
5. Casting geometry and orientation

Of course, higher resolution of the mass change vs. voltage relationship (as in Figure 3) is necessary in future research in optimizing protection performance. Higher resolution was not possible within the scope of this research.

7. Acknowledgments

The author thanks the National Science Foundation (NSF) for funding that makes undergraduate research projects possible. The author also thanks Milwaukee School of Engineering (MSOE) and its Rapid Prototyping Center (RPC) for hosting the summer REU program. Special thanks are also given to Vito Gervasi (project advisor) for outstanding help, encouragement, criticism, and support throughout the project, as well as Ann Bloor and Betty Albrecht for their continual support. Finally, Allison Block, a former REU student, is especially recognized for her great help and encouragement in pursuing this REU program.

This material is based upon work supported by the National Science Foundation under Grant No. EEC-0139142. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation.

8. References

- [1] Hitchiner Manufacturing Co., Inc. 1998. The Legacy of Investment Casting. [Internet, WWW]. Available: Hitchiner company website; ADDRESS: <http://www.hitchiner.com/himco/History.html>. [Accessed: 6 June, 2006].
- [2] Hitchiner Manufacturing Co., Inc. 1998. The Basics of the Investment Casting Process. [Internet, WWW]. Available: Hitchiner company website; ADDRESS: <http://www.hitchiner.com/himco/Basics.html>. [Accessed: 6 June, 2006].
- [3] Milwaukee School of Engineering. 2004. What is Solid Freeform Fabrication? [Internet, WWW]. Available: Milwaukee School of Engineering; ADDRESS: <http://www.msOE.edu/reu/ssf.shtml>. [Accessed: 6 June, 2006].
- [4] Hank Litchfield. PM Engineer. 25 August 2000. Zinc. [Internet, WWW]. Available: PM Engineer website; ADDRESS: http://www.pmengineer.com/CDA/ArticleInformation/features/BNP__Features__Item/0,2732,9010,00.html.
- [5] Mars G. Fontana. 1986. Corrosion Engineering. Rao, Sanjeev. New York: McGraw-Hill, Inc. pp. 4, 294-296. http://www.pmengineer.com/CDA/ArticleInformation/features/BNP__Features__Item/0,2732,9010,00.html. [Accessed: 6 June 2006].
- [6] Timothy Nedimyer. August 2004. "Galvanic Protection of Metal Castings During Ceramic Leaching."
- [7] Nipendra P. Singh and Jane M. Neubauer. April 2003. "What Every Commercial, Aerospace, IGT Investment Caster Needs to Know about Ceramic Cores." Incast, pp. 18-21.