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Techniques for Chemical and Electrochemical Passivation of Chromium Steels

1. Introduction

Chromium alloys, stainless steels, are regularly selected for application in corrosive environments. These steels are selected for such application because they are able to resist chemical attack without the expense of additional coatings.

Resistance to attack is derived from the unique structure of the alloy's surface.

The alloy's surface is described as having a *passive* film. In simple terms the *passive* film is made up of the alloy element Chromium in conjunction with Oxygen and Water.

Although this film forms rapidly it is sensitive to contaminates such as metal residues from the fabrication process. Such residues may initiate aggressive attack on the article in question, and render it unserviceable in a short period of time (days or even hours).

While much is written about the corrosion resistances of the Chromium alloys there is little comprehensive literature about the *passive* film and its manipulation. The purpose of this text is to assist the reader to comprehend the nature of passivation and the range of ways in which it can be achieved.

2. The Passive Film

In thickness the *passive* film is only a few angstroms. The *passive* film may be best described as the outer skin of the parent metal.

At its simplest, the *passive* film consists solely of Chromium, Oxygen and Water. The film may be described in chemical terms as a Chromium oxy hydrate.

The *passive* film over lays the base metal, which may contain various ratios of Iron, Nickel, Chromium, etc.

Where the Chromium alloy incorporates Molybdenum and /or Tungsten, then these two elements are also present in the *passive* film structure. Suffice to say they enhance corrosion resistance through the process of steric hindrance.

Because the *passive* film is a metallic oxy hydrate it requires exposure to oxygen and water through either direct interaction with atmosphere or as dissolved in the media contained by the article. The *passive* film is dynamic, that is, it interacts with oxygen and water to develop an equilibrium.

The *passive* film is cathodic in nature. The base metal is anodic.

Maximum corrosion resistance only occurs when the *passive* film develops as a continuous, unbroken film across the entire structure. Any breaks in the *passive*, *cathodic*, film means that the *anodic* base metal is in contact with the corrosive environment. As such an electrochemical pathway opens which will result in corrosion of the base metal.

While many terms are used to describe corrosion of Chromium steels, the basic mechanism of electrochemical (galvanic) corrosion is common to all.

The corrosion is also assisted by the relative ratio of *cathodic* area to *anodic* point.

3. Constructing a Passive Film

Passivation is the term used to describe the removal of impurities from the surface of Chromium steel after the steel has been worked or formed to produce an item of the required form.

Passivation may be achieved by Electropolishing, Chemical Passivation, or a hybrid technique known as Selective Abstraction.

Each of the listed passivation techniques may be done in a variety of ways and it is not the intention to cover the details of these at this time. Rather, a general description of each process follows.

3.1. Electropolishing

This process utilizes a reducing acid environment in conjunction with substantial DC power. The article to be polished is suspended in the medium via means of a conductive support, which is connected, to the +ve terminal, *anode*, of the power supply.

A similarly supported *cathode* is placed in the bath at a suitable location with respect to the article to be polished.

The article is polished by the progressive removal of metal from the article's surface.

The electropolishing process removes Iron and Nickel from the metal surface to a depth of some 20-30 angstroms (depending on exposure time). The result is a dense film of Chromium oxyhydroxide across the metal surface, and so the surface may be defined as *passive*.

At completion of polishing the article is removed from the bath and rinsed.

Electropolishing provides the most dense and durable passive film that it is possible to achieve. Electropolishing should be the consumer's choice of preference for maximizing a stainless product’s durability.

3.2. Chemical Passivation

Chemical *passivation* is used to remove residues from the alloy surface. There are a number of approaches that may be taken. In each case the objective is to remove surface residues that may affect the passive film structure by chemical treatment.

3.2.1. Pickling

Pickling is a chemically aggressive process where the article is immersed in a solution of Hydrofluoric Acid (HF) and Nitric Acid (HNO3) for a period of time. This process is very difficult to control and, as a side effect, "brightens" the article through having micro-etched the item's surface. Some texts also describe the circulation of such solutions within closed systems. It is the author's opinion that such practices are exceedingly dangerous, care needs to be taken to ensure all components of such a circulation path will withstand exposure to the combined acids.

It is the lack of process control with pickling combined with the O H & S risks that make it a poor choice for *passivation.*

3.2.2. Chelant Passivation

Chelant (sometimes referred to as citric acid) *passivation* may be used for article immersion or for reticulation within a circuit. This process can be readily controlled through monitoring the chemical processes occurring.

Chelant passivation utilizes the well-known effects of chelants, in the completing of metal residues in conjunction with a reducing acid environment. The process chemistry can be manipulated to target a particular contaminate or widened to target all likely residues.

The process is used in conjunction with surface tension modifiers and flocking agents. The process consists of a series of steps and may use two or three solutions in conjunction with rinsings.

Chelant passivation is a chemically formulated way to remove contaminant residues.

3.2.3. Selective Abstraction

This technique is an extremely effective process. It utilizes specifically formulated abstraction chemistry in conjunction with electrolysis. To some degree it replicates electropolishing, however, it is a process that removes only the readily soluble passive film contaminants such as Iron, Nickel, Aluminium (grinding residue),etc.

This process may take place in a bath, or the process may be used to spot treat selective structures.

The treated surface is identical in profile to the original surface except for any pitting that may have developed under surface contaminants.

The process is rapid and may be done either cold or hot, 60°C.

Where the solution is being reticulated through a cell to treat a remote portion of a structure the solution doubles as a coolant.

4. Conclusion

All Chromium Steels need to be *passivated* prior to going into service. The choice of *passivation* process is very much determined by application. While the consumer has a number of choices the table below categorizes the comparative durability of a surface derived from each process.

Process	**Durability of Surface**[1]
Electropolished	10
Selective Abstraction	7
Pickling	5
Chelant Passivation	4

[1] This is in an indicative value only, score out of 10.