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Phosphate conversion coatings must be properly removed or the formation of a white layer of iron phosphide can form, leading to embrittlement and poor fatigue performance.

Delta ferrite formation in fasteners

During the manufacture of fasteners, the formation of iron phosphide as delta ferrite can occur during heat treatment. This can have a deleterious effect on fatigue properties of the fastener. In this article, I will review the cause and formation of this microstructural constituent and describe methods for prevention.

INTRODUCTION

A fastener goes through many manufacturing steps to produce the finished product. These are illustrated in Figure 1.

In this process, the manufacture of a fastener starts with a coil of steel wire. Depending on the diameter of the wire, the steel is cold drawn to the desired diameter. The wire is then cut to length and cold headed. Threads are rolled into the body of the fastener and then heat treated to the desired strength. Further processing, such as plating, also occurs.

During the manufacturing process, multiple drawing or forming operations occur. Lubrication is required to prevent excessive heat build-up and to allow proper flow of metal during the drawing, heading, and thread-rolling operation. To aid lubrication during the cold forming processes, fastener manufacturers will buy their wire coil impregnated with a lubricant at the mill. This lubricant is often soaps such as sodium stearate or a zinc (or calcium, manganese, and vanadium) phosphate conversion coating. The phosphate coating can hold many types of forming lubricants due to the morphology of the coating.

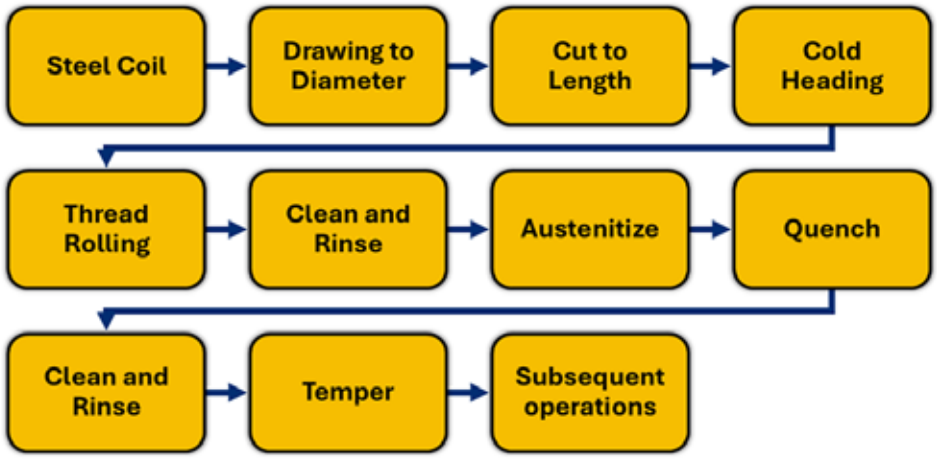

Figure 1: Manufacturing steps required to produce a fastener.

PHOSPHATE CONVERSION COATINGS

These coatings are produced at the mill by immersing the wire in a phosphoric acid solution. The process leaves insoluble crystalline that forms a continuous surface film. The phosphating process usually is done at a temperature of 30-90°C by an electrochemical reaction [1]. In this process, the first surface reaction is:

$$3Zn(H_2PO_4)_2 \leftrightarrow Zn_3(PO_4)_3 + H_3PO_4$$

The phosphoric acid that is formed attacks the steel surface, and releases hydrogen as a by-product:

$$Fe + 2H_3PO_4 \rightarrow H_2 + Fe(H_2PO_4)_2$$

This ferrous phosphate that initially forms is a sub-crystalline layer that serves as nucleation sites for the growth of the crystalline phosphate coating [1]. The release of hydrogen drives the first reaction, and insoluble zinc phosphate is precipitated onto the steel surface [2]:

$$Zn(H_2PO_4)_2 + Fe(H_2PO_4)_2 + 4H_2O \rightarrow Zn_2Fe(PO_4)_2 \cdot 4H_2O + 4H_3PO$$

The coating that forms has a tight bond to the steel surface, with coating weight of 10-11g/m^2 (Figure 2).

DELTA FERRITE FORMATION DURING HEAT TREATMENT

The formation of thin intermetallic iron phosphide (Fe_3P) occurs when the conversion coating is heated to heat-treating temperatures during austenization [3]. This manifests itself as a white layer

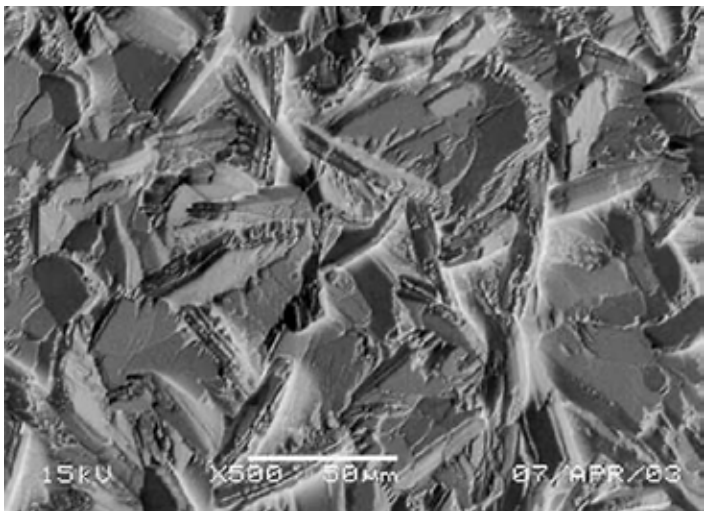

Figure 2: Heavy zinc phosphate crystals that have formed on a steel substrate during phosphate conversion coating [1].

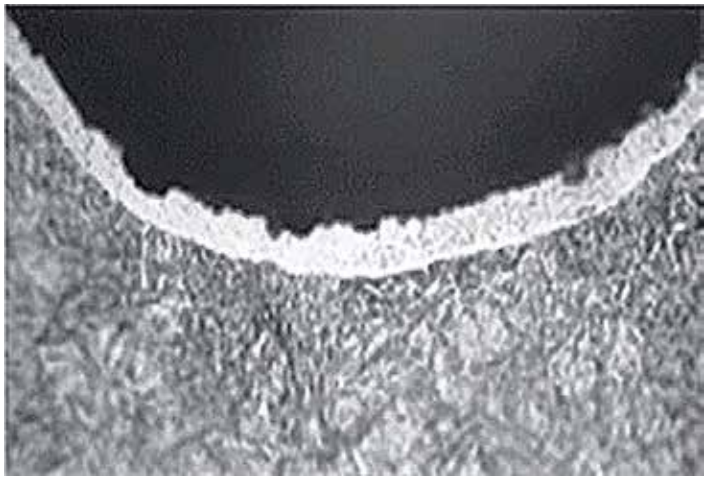

Figure 3: Steel substrate showing the presence of white layer of iron phosphide [4].

of δ-ferrite. The white layer consists of a Fe_2P region on top of a layer of Fe_3P. The growth of the white layer is due to the diffusion of iron toward the surface of the part. An example of white layer formation on a heat-treated steel part is shown in Figure 3.

This white layer of Fe_3P and Fe_2P is brittle and is detrimental to fatigue and embrittlement [4]. Fe_3P has a tetragonal crystal structure while Fe_2P has a hexagonal structure. Typically, this white layer is 10-20µm thick.

The δ-ferrite phase is hard, with a microhardness of 450 HV, with poor toughness. The tetragonal structure of Fe_3P has very few slip systems, so is characteristically brittle. The diffusion of phosphorus into grain boundaries promotes embrittlement of the grain boundaries. Fracture would show an intergranular fracture due to weak cohesion [5].

REMOVAL OF PHOSPHATE COATING PRIOR TO HEAT TREATMENT

Because of the detrimental effects of thermal degradation of the phosphate conversion coating, forming the white layer, it is very important that this conversion coating be removed prior to heat treatment. Historically, phosphate conversion coatings were removed by soaking the phosphate part at elevated temperature in chromic acid. However, due to environmental concerns, this has fallen out of favor due to the presence of hexavalent chromium.

Other methods use hydrochloric and sulfuric acid. However, these are rarely used due to the very corrosive nature of these acids. Parts should be thoroughly rinsed after stripping.

One method recommended by MIL-DTL-16232G [5] is to use a combination of sodium hydroxide and EDTA. The approximate concentration is 125g of NaOH, 125g EDTA to one liter of water. While this procedure is for ambient temperatures, elevated temperatures can reduce the amount of EDTA needed, while maintaining the high concentration of NaOH.

While hot solutions of NaOH are often used, it is imperative that the parts are thoroughly rinsed to remove the presence of the sodium hydroxide on the surface. Failure to remove the NaOH can cause other problems, such as caustic burn on the surface of the fasteners. It can also result in damage to refractory inside the furnace.

CONCLUSIONS

In this column, the purpose and process of phosphate conversion coatings was described. If the conversion coating is not properly removed, the formation of a white layer of iron phosphide can form, leading to embrittlement and poor fatigue performance.

While there are several different methods of removing the coating, an aqueous solution of sodium hydroxide is commonly used. Parts should be thoroughly washed and rinsed to remove any traces of sodium hydroxide on the parts prior to heat treatment.

Should there be any comments on this article, or suggestions for new articles, please contact the editor or the author.

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