THE SPRING RESEARCH AND MANUFACTURERS' ASSOCIATION

# HYDROGEN EMBRITTLEMENT - A LITERATURE REVIEW

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## SUMMARY

Recent technical papers on the subject of hydrogen embrittlement resulting from cadmium and zinc electro-plating have been reviewed.

Conflicting views appear to be held by the various authorities regarding the role of operating current density, type of electro-plating bath and the effect of de-embrittlement treatments on the subsequent mechanical properties of the plated steels.



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It is generally accepted that embrittlement occurring as a result of electroplating is much more severe in hardened and tempered, martensitic iron-carbon structures than in pearlitic structures. No reason for this has yet been established but it is known that hydrogen diffuses much more rapidly in martensitic than in pearlitic structures[1]. Moreover, it has been suggested that certain structures contain "innocuous sites" at which relatively large quantities of absorbed hydrogen can be stored without adversely affecting the mechanical properties[2,3]. It is postulated, therefore, that pearlitic structures contain many more innocuous sites than do martensitic structures, for example at ferrite/pearlite interfaces; thus the volume of hydrogen which can be absorbed safely is much greater for pearlitic structures than martensitic ones. The present SRAMA investigation is concerned primarily with the more serious embrittlement which occurs in high strength martensitic steels; hence only these materials are to be considered in this literature survey. It is well known that chemical cleaning treatments can also result in embrittlement of high strength steels but this investigation will be concerned only with embrittlement due to hydrogen absorbed during the plating process.

Cadmium plating is, traditionally, carried out using an alkaline cyanide electrolyte. This method has the advantage of being very simple to set up and maintain, having good throwing power, and requiring minimal preparation of the sample surface. However, alkaline cyanide baths are toxic and probably result in much greater hydrogen embrittlement than do the alternative acidic electrolytes[4,5,6]. The fluorborate plating baths, which are acidic, require careful replenishment and maintenance and are therefore not widely used.

It has been estimated that less than 1% of the cadmium plating carried out in this country is carried out using acidic electrolytes[7]. This figure may possibly increase, however, as effluent control becomes more stringent. There is some experimental evidence to suggest that even acidic electrolytes can produce hydrogen embrittlement in cadmium plated high strength steel components[8].

The influence of various additions to the conventional alkaline cyanide bath on subsequent embrittlement has been studied by a number of investigators. It is claimed that any addition which slows down the evolution of gaseous hydrogen tends to accelerate the adsorption of hydrogen atoms[6] and hence sodium cyanide solutions are considered detrimental. Sodium nitrate additions have been found to reduce the occurrence of hydrogen embrittlement in hardened and tempered SAE 4340 samples which were cadmium plated from a conventional cyanide bath[9]. If nickel particles are introduced into the electrolyte, then nickel is co-deposited with cadmium. The nickel contained in the electroplate is supposed to absorb atomic hydrogen selectively, thereby reducing embrittlement of the metal substrate[10]. Recent work in Russia[11] has indicated that the addition of organic brighteners to alkaline cadmium plating baths results in an increase in embrittlement. This is also recognised in the Ministry of Defence Standard concerned with the plating of high tensile steels[12] which states that the electrolyte used for cadmium plating should not contain brightening agents.

In zinc plating, both the acid and the cyanide baths are commercially used. The cyanide bath has the advantages of being cheaper to install and requiring less surface preparation of the metal substrate before plating than the acid bath; again, however, alkaline cyanide baths result in a much greater extent of hydrogen embrittlement than acid baths[13]. The choice of solution is mainly determined by the nature of the basis metal: for grey and malleable iron castings, and wrought and forged iron and steel, acid solutions are recommended, but for steel pressings of intricate shape a cyanide solution, which has a better throwing power, is recommended[5].

There are conflicting opinions regarding the role of the operating current density on embrittlement occurring as a result of electroplating. Some specifications suggest that a high current density will reduce embrittlement[4,14], although plating at low current densities is also recommended[15]. Some electroplaters begin plating at a high current density and switch to a lower level once the first cadmium deposit has appeared. The underlying theory is that hydrogen absorption increases with plating time and that, if an electrodeposit can be established rapidly in the initial stages of plating, then it will act as a barrier to further hydrogen absorption.

If the influence of current density is subject to debate, then opinions are even more divided as to the effect of de-embrittlement treatment after plating. Investigators agree that post-plating de-embrittlement baking should be carried out at 190° to 210°C. For high tensile hardened and tempered steels, however, estimates of the time required at this temperature vary considerably. For steels having tensile strengths in excess of 1850 $N/mm^2$, a treatment of not less than twenty four hours is recommended in the specifications[4,14]; in one instance, however, eight hours was found to be adequate[16]. In certain cases the baking treatment has been found to increase embrittlement[11]; this is thought to be attributable to diffusion of hydrogen from the electroplated layer into the metal substrate.

There is conflicting information on the relationship between de-embrittlement time and the subsequent static mechanical properties and very little information could be traced concerning the effect on dynamic properties. The latter has probably been neglected because failure due to hydrogen embrittlement has been regarded as a catastrophic occurrence taking place under the action of applied stress. From the point of view of the spring industry, it would be valuable to discover whether the fatigue properties of a spring which has been electroplated and "successfully" de-embrittled ever return to those of an unplated spring.

The effects of various parameters on hydrogen embrittlement resulting from electroplating, as mentioned above, are necessarily dependant on a method of assessing the level of embrittlement. Apart from direct chemical analysis of the hydrogen content by vacuum degassing, the tests which have been used to measure hydrogen embrittlement can be divided into two categories. Both are mechanical test methods which are usually carried out as soon as possible after plating. Sustained load testing has been used with success by many investigators and a summary of the variations on this technique is given in a recent A.S.T.M. symposium[17]. Tests of this type range from the simple U-bend method[18] to the more sophisticated sustained load notched tensile test[8,9,10,16]. The alternative method of measuring hydrogen embrittlement includes all types of slow strain rate test. Slow bend tests were shown to give consistent and reproducible results in early work on the hydrogen embrittlement of cold rolled strip[19,20] and elsewhere[13] this method has been applied with some success to electroplated wires. Slow strain rate tensile tests have been used more recently to investigate the effect of de-embrittlement time[11]. It is argued that rapid strain rate tests do not give a true indication of the level of embrittlement, since the diffusion of absorbed hydrogen to regions of high stress is time dependant[3], as is the build up of pressure in these regions. This explanation is consistent with the delayed failures which are attributable to hydrogen embrittlement. It is arguable whether slow strain rate tests allow sufficient time for these processes to produce their most deleterious effects.

To summarise, an investigation into the hydrogen embrittlement occurring when high strength, hardened and tempered spring steels are cadmium or zinc plated should cover the following points:

1. the effect of cyanide and acid baths;
2. the effect of current density;
3. the effect of de-embrittlement time;
4. the effect on static and dynamic properties.

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