

INTRODUCTION

Cadmium electroplating is widely used on aircraft for the corrosion protection of airframe components and fasteners manufactured from non-corrosion resisting high strength steels. Cadmium plated coatings display a very good barrier corrosion resistance, thus providing long-term protection, especially in the marine atmosphere, which is –among other conditions– frequently experienced by aircraft, and mostly by military aircraft. Their performance can be further improved by the implementation of chromate passivation treatments over their electrodeposited layer. [1]

Cadmium is a sacrificial coating to steel, as its open-circuit potential is more negative than that of steel, suggesting that if the coating is damaged, cadmium will preferentially corrode instead of the exposed steel. In addition, the free corrosion potentials of aluminium alloys 2014 and 7075, widely used in the aircraft industry, are similar to that of cadmium, and hence, there is a low risk of detrimental galvanic interactions occurring between them. [1] (Figure 1) Furthermore, cadmium does not produce voluminous corrosion products, and as a result seizure problems due to their wedging action are less likely with cadmium plated fasteners. [2] Finally, cadmium is self-lubricating and has a low coefficient of friction making it ideal when plating threaded components like fasteners, as only moderate torques are necessary to set the required bolt loading even in the absence of lubricants. [1]

On the other hand, cadmium plating demonstrates an innate problem encountered with many types of electroplating. The electrodeposition of active metallic coatings onto high strength steels increases the risk of the steel substrate failing by hydrogen embrittlement (HE). The electroplating process has generally a current efficiency of less than 100%, and a fraction of that current causes the generation of hydrogen. Part of this hydrogen is incorporated into the electrodeposit, followed by a subsequent diffusion into the steel substrate damaging the tensile properties of high strength steels. However, subsequent de-embrittlement heat treatment is used to overcome this drawback of cadmium plating. For steels exceeding an ultimate tensile strength of 1800 MPa, de-embrittlement consists of baking at a temperature between 190 and 230°C for 24 hours. [2–4]

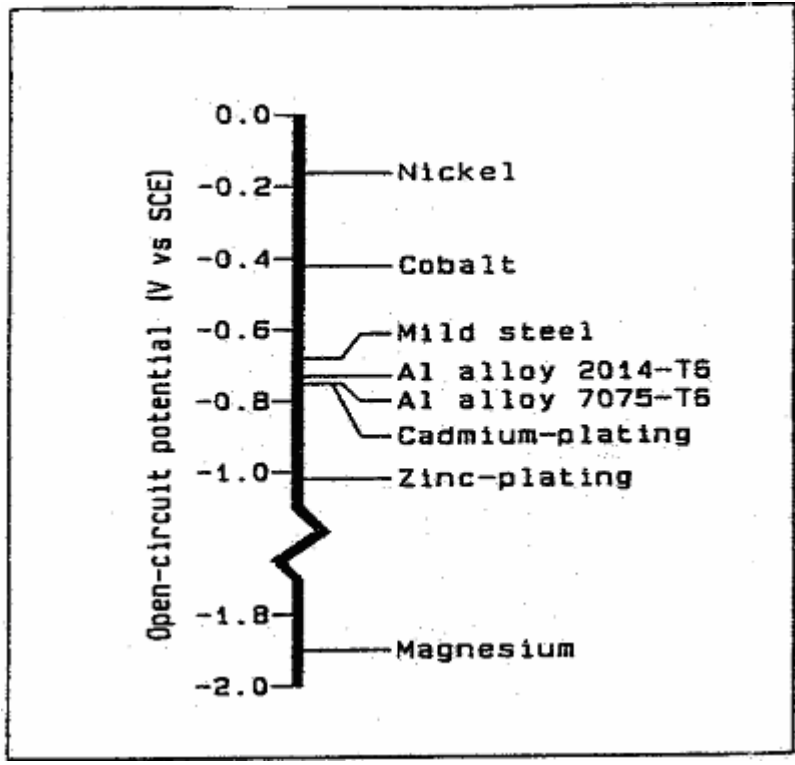


Figure 1. Open circuit potentials of various metals and alloys in quiescent 600 mmol⁻¹ NaCl at 25°C. [1]

Apart from the previously described advantages of cadmium, as well as its disadvantages that can be dealt with by de-embrittlement, there are serious safety and environmental concerns over the high toxicity of cadmium and its compounds. [1, 5, 6] Firstly, cadmium itself is toxic and carcinogenic, and by accumulating in the liver and kidneys makes a long-term exposure to it harmful to humans. [7] Furthermore, the effluent from electroplating operations is subject to rigorous controls, as it contains poisonous cadmium cyanide dissolved in a concentrated sodium hydroxide solution, and only extremely low cadmium levels are allowed to be discharged into the environment. Under European legislation the use of cadmium plating for general engineering purposes is no longer allowed, leading to the search for suitable replacement materials. This need is widely recognised and is in accord with the stringent restrictions on the use of cadmium, existing in various countries including USA and Japan. [1]

Many efforts worldwide have been focused on alternatives to cadmium for the sacrificial corrosion protection of steel components. All the proposals are based on similar concepts and criteria for the selection of a suitable coating. The ideal coating should possess the correct balance between several opposing properties. It needs to be sufficiently sacrificial to protect the steel substrate, but it should not be too electronegative as this would result in an unnecessarily high corrosion rate. At the same time the candidate material should be galvanically compatible with both steel and high strength aluminium aircraft alloys. In this context, the galvanic series both in Figures 1 [1] and 2 [8] can give an indication of possible suitable coatings for cadmium replacement, and the formerly stated requirements are not the only ones to be examined, but just the first to be looked at. Afterwards, hydrogen embrittlement due to the application of coatings, resistance of coatings to aircraft fluids, paint adhesion, torque tension, electrical properties, cost and environmental aspects of the new coating systems should be studied for a complete replacement investigation.

A variety of alternative coatings to cadmium, which have been assessed by the aerospace industry include zinc, zinc alloys, aluminium, aluminium alloys and aluminium pigmented metallic–ceramic coatings. [1, 5] Concerning zinc plating, its corrosion products are voluminous and can cause the wedging of fasteners. In addition, zinc is substantially more electronegative than steel, and consequently, if its coatings are damaged, then rapid galvanic corrosion of zinc will shortly leave the exposed steel substrate unprotected. [1]

As a response to this problem, zinc alloys were investigated with alloying elements being more noble than steel, with the aim of achieving an open–circuit potential slightly more negative than that of steel. Nickel and cobalt are the two additions considered in zinc alloys, and these coatings have seen a large growth in the automotive industry in the past 15 years. In the aerospace industry, Boeing, urged on by legislation, has been examining coatings of Zn–Ni alloy with 10% nickel and Sn–Zn with 20% zinc as possible cadmium substitutes. In the second case, the approach is different with a large proportion of a more noble material than steel, i.e. tin, alloyed with an element more active than steel. [7]

Volts vs Saturated Calomel Reference Electrode

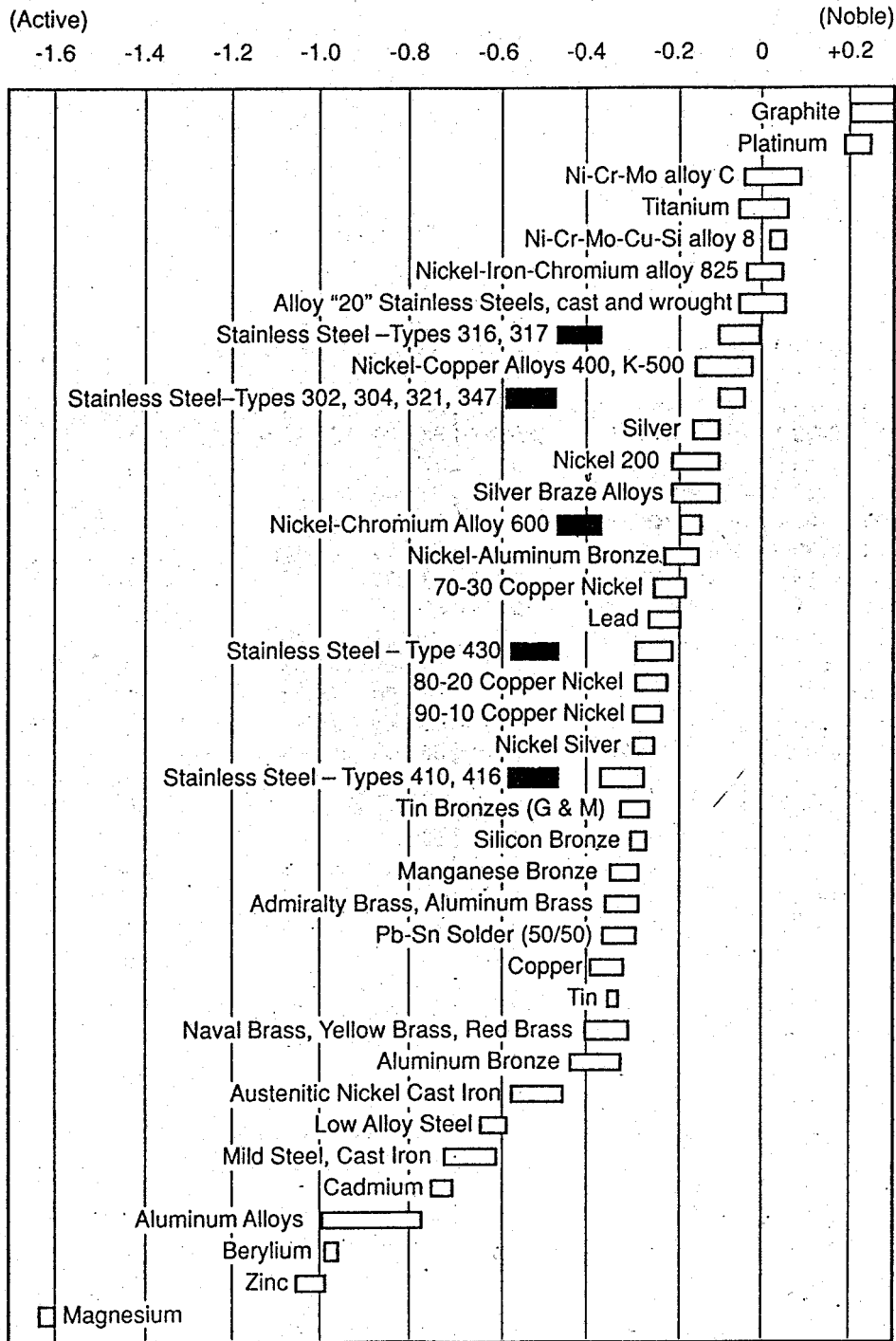


Figure 2. Galvanic series of various metals and alloys in flowing seawater at 2.4 to 4.0 m/s for 5 to 15 days at 5 to 30°C. [8]

Both Zn–Ni and Zn–Co coatings have been examined for aerospace applications in recent research studies at Cranfield. [9–12] Zn–Ni alloys appear to display suitable properties, with the optimum corrosion resistance in neutral salt spray tests occurring at a composition of 14–wt% nickel. These coatings exhibit a better corrosion resistance than pure zinc and they do not form the voluminous corrosion products that can develop on zinc exposed to marine atmosphere. In addition, the rest potential of zinc–nickel alloys is, like cadmium, compatible with that of aluminium alloys used to manufacture aircraft. [10] Moreover, from a HE point of view, Zn–Ni plating on an AISI 4340 high strength steel caused less embrittlement than cadmium plating, and a subsequent baking treatment at 200°C for 24 hours contributed to the complete recovery of the ductile properties of the steel. [9, 13] However, it is believed that Zn–Ni alloys could react with aircraft fuel, which is stored in the wings, and for this reason they would be unsuitable for use on fasteners.

As far as Zn–Co coatings are concerned, a very recent study at Cranfield showed that Zn–Co electroplating caused serious HE on an AISI 4340 high strength steel, and the mechanical properties of the zinc–cobalt plated steel were not fully recovered by either a standard 24 hour baking treatment at 200°C or even a 48 hour baking process at the same temperature. This behaviour was improved by the deposition of either a cobalt or nickel layer before the application of a standard Zn–Co plating. [11, 12]

Aluminium alloys are another interesting field when considering substitutes for cadmium. In Figure 2 it can be viewed that aluminium alloys demonstrate a broad range of potentials. This enables the design of a suitable aluminium based replacement coating by manipulating its composition, in order that the candidate material display a free corrosion potential slightly more active than steel. In that way, the potential aluminium coating could be both sacrificial to steel, as well as possess the smallest possible corrosion rate. Moreover, such coatings are the most likely to be galvanically compatible with the aircraft aluminium alloys, minimising the risk of bimetallic corrosion between steel components and the structural aluminium alloys with which they might come into contact. From the above it is concluded that aluminium coatings fulfil the basic criteria for a viable sacrificial corrosion protection of steel components in aerospace applications.

Concerning other issues, such as hydrogen uptake as a result of the electroplating process, it should be emphasised that aqueous electrolytes are strictly avoided. Aluminium-based coatings cannot be plated from an aqueous electrolyte, as the potential would be more active than that for hydrogen ion reduction, which would occur in preference. For this reason the employed techniques for the application of aluminium-based coatings onto high strength steels comprise electrodeposition from organic electrolytes, paint spraying as in the case of aluminium pigmented metallic-ceramic coatings, physical vapour deposition and unbalanced magnetron sputtering. In all these techniques, aluminium coatings are usually chromated to provide supplementary corrosion protection and to promote paint adhesion. [1]

Aluminium-based coatings electrodeposited from non-aqueous electrolytes are commercially available since the 1970s. [1] Electroplated aluminium possesses the advantage that its coatings are very dense and exhibit good adhesion to the substrate. A representative of these coatings is the Alcotec Galvano-Aluminium marketed by Alcotec GmbH. This coating consists of pure aluminium electroplated from an organic electrolyte based on toluene with additions of Al alkyl complexes. Its producers consider its application process as non-embrittling. [14, 15] As this coating is one of the investigated cadmium substitutes in this research programme, the previously cited contention for this material will be one of the issues to examine.

Aluminium containing metallic-ceramic coatings are another category of sacrificial coatings proposed for the replacement of cadmium. In this case, aluminium is used by its incorporation in a powder or flake form in an inorganic slurry based on phosphates or chromates. SermeTel type coatings are classified in this sort of materials and have found use on landing gear components as a substitute for cadmium. [1] For aerospace applications dense packing of the aluminium pigment particles is applied, and two coatings of this type are produced by Sermatech International Inc., SermeTel CR962 and SermeTel CR984-LT. Both coatings are sprayed as a slurry, and thickness can be precisely controlled, so that geometrically complex parts can be coated. SermeTel CR962 can be cured between 191 and 343°C. However, SermeTel CR984-LT was selected as a representative coating of this category for cadmium replacement investigation, as its cure temperature between 163 and 191°C does not affect the tempering treatment of the AISI 4340 steel, a high strength steel selected in the

current project as the testing material. Finally, the application of SermeTel coatings is considered not to cause HE, as also supported in the case of Alcotec Galvano-Aluminium. This argument is checked for SermeTel CR984-LT as well in this programme. [5]

Aluminium coatings applied by Physical Vapour Deposition (PVD), including Ion Vapour Deposition (IVD) show good substrate adhesion. However, they tend to be highly porous, and consequently, glass beading is necessary to compact the structure, as well as improve the corrosion resistance and protection performance of the IVD coatings. The IVD process is commercially known for many years with the McDonnell Douglas aircraft company developing the IVADIZE process to coat landing gear parts, engine mountings and fasteners with aluminium. [1, 16]

Drawbacks of the IVD technique can be avoided by applying another vacuum technique, termed as Unbalanced Magnetron Sputtering (UMS). Steel parts are cleaned, placed in a vacuum chamber, and afterwards sputter-cleaned under an argon atmosphere prior to coating with aluminium. A major advantage of this technique is that the aluminium coatings are very dense. [1] Aluminium-magnesium alloys have been recently proved to be able to be deposited by the UMS technique, and they have also displayed an improved corrosion resistance at an approximately 20-wt% Mg. [17]

Aluminium-based coatings, Alcotec Galvano-Aluminium and SermeTel CR984-LT are being considered as possible corrosion coating replacements for cadmium on high strength steels (UTS exceeding 1800 MPa) commonly used in the aerospace industry. These coatings are supposed to provide steel substrates with sacrificial corrosion protection, whilst their application is believed not to affect the ductile properties of high strength steels.

However, there is a concern that hydrogen might be absorbed by the steel substrate when a sacrificial coating corrodes in service, thus causing re-embrittlement of high strength steels. This phenomenon is not related to the embrittlement observed as a result of plating processes, but occurs in service, after de-embrittlement has taken place. Hence, it could be termed as the hydrogen re-embrittlement of the steel

substrate emphasising not the different source of the embrittling action, which is hydrogen, but the different hydrogen generating conditions that take place after embrittlement and de-embrittlement.

The risk of the steel substrate becoming hydrogen re-embrittled because of the corrosion of a sacrificial coating has not been widely considered. However, Pollock [18, 19] has studied the degree of hydrogen embrittlement on cadmium plated and baked 4340 steel specimens produced by plating processes, paint strippers and aircraft maintenance chemicals by using the slow strain rate testing method. The premature failure of these steel specimens in some service and maintenance environments indicates that hydrogen re-embrittlement could be a real concern for steel components, coated with sacrificial protective coatings corroding in service.

Moreover, Hinton et al. [16] investigated ion vapour deposited (IVD) aluminium coatings for the corrosion protection of steel. Apart from examining their corrosion behaviour, they brought forward some practical considerations for the use of IVD coatings, including some hints about re-embrittlement. As previously mentioned, IVD coatings can be highly porous, and they are further protected by painting, without guaranteeing the exclusion of any moisture penetration. As a result, rapid perforation of a porous coating exposed to moisture, and corrosion of the steel substrate could lead to premature stress corrosion cracking (SCC). Moreover, hydrogen can be admitted to the steel substrate, firstly as an active pit grows and secondly as the steel is galvanically protected by the aluminium. From the above, it is clear that some aluminium coated steel specimens can suffer from re-embrittlement as a result of the corrosion of the aluminium-based coating. A general description of the hydrogen re-embrittlement phenomenon is outlined below.

Aluminium-based coatings are assumed to be more active than cadmium, and hence more attention is paid to hydrogen re-embrittlement caused by them, as more hydrogen could be absorbed from the cathodic reaction of water reduction. This reaction occurs in parallel with the other cathodic reaction of oxygen reduction, as well as the anodic dissolution of aluminium. A summary of the phenomena taking place in the vicinity of a coating defect, where the steel substrate is exposed to the aqueous corrosive solution, is pictorially displayed in Figure 3. The hydrogen

evolution reaction from the water reduction is the source that could re-embrittle the steel substrate.

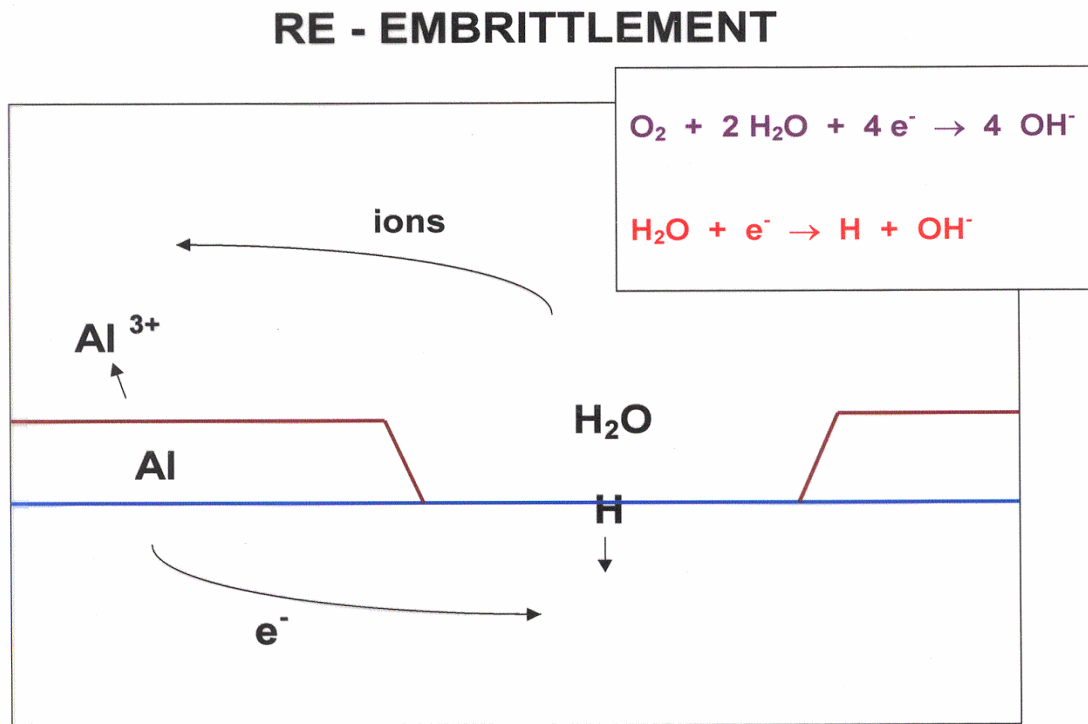


Figure 3. Schematic representation of the conditions and reactions leading to the hydrogen re-embrittlement of steel substrates protected by aluminium-based coatings.

Bearing in mind past experience concerning the efforts to replace cadmium, as well as the promising properties and behaviour of aluminium-based coatings, the aim of the current study was the evaluation of such coatings for cadmium replacement. More specifically, this goal was divided in the following objectives; -

- 1) To assess the risk of direct hydrogen embrittlement of coated high strength steel as a result of the application of Cadmium, SermeTel CR984-LT and Alcotec Galvano-Aluminium coatings, and moreover, to evaluate the risk of hydrogen re-embrittlement of coated high strength steel as a result of the corrosion of the aforementioned coatings in a variety of environments.

2) To study the corrosion behaviour of SermeTel CR984–LT and Alcotec Galvano–Aluminium coatings as potential cadmium replacements. The ideal coatings should be sufficiently active to offer sacrificial corrosion protection to steel, but not so active, as they would cause re–embrittlement to the steel substrate when they corrode in service. Finally, the ideal coatings should be galvanically compatible with aircraft Al alloys, resistant to repassivation, and possess good barrier properties.