

CONCLUSIONS

1. Cadmium electroplating caused severe direct hydrogen embrittlement to the quenched and tempered AISI 4340 high strength steel. In contrast, no reduction in times to failure was observed by the application of the SermeTel CR984–LT coating. On the other hand, the electrodeposition of Galvano–Aluminium Alcotec in an organic electrolyte introduced a very small amount of embrittlement, which was proven to be statistically insignificant.
2. A baking treatment at 200°C for 24 hours was found to be fully effective in the de–embrittlement of the steel specimens that had been electroplated with Cadmium, as well as coated with Alcotec.
3. No embrittling effect was observed in the case of unplated steel specimens that were potentiostatically charged and then stressed in air. The range of the applied potentials was more negative than the free corrosion potentials of Alcotec, SermeTel and Cadmium.
4. Re–embrittlement occurred when uncoated AISI 4340 steel specimens were strained and simultaneously potentiostatically charged at a cathodic potential to simulate the corrosion of a sacrificial coating. Higher degree of re–embrittlement was observed at more active potential values showing that the potential of a corroding sacrificial coating is one important factor influencing the extent of re–embrittlement.
5. Hydrogen permeation measurements showed that there is more hydrogen uptake by steel substrates at more negative applied potentials. Moreover, it was found that there is good correlation between the degree of re–embrittlement and the amount of hydrogen absorbed by steel, following a logarithmic relationship for a certain range of applied potentials.
6. Trapping was responsible for the observed longer breakthrough times at more noble potentials in hydrogen permeation measurements, as well as for

differences between hydrogen diffusion coefficients in ideal lattices and in engineering materials.

7. The corrosion of Cadmium, SermeTel and Alcotec caused substantial amount of hydrogen re-embrittlement to AISI 4340 steel when exposed to 3.5% NaCl solution during slow strain rate tests. The severity of re-embrittlement was in the order Cadmium > SermeTel > Alcotec.
8. A second major factor affecting the amount of re-embrittlement is the barrier properties of the coating. Although Alcotec was the most active coating, it caused the least re-embrittlement, because it was the densest coating, and it is thought that it contained fewer pores where the steel substrate was exposed and hydrogen charging could take place. On the other hand, Cadmium was quite porous allowing hydrogen an easier access to the steel substrate, and as a result, its corrosion caused the largest amount of hydrogen re-embrittlement.
9. A small amount of hydrogen re-embrittlement occurred in coated steel tensile specimens that had been exposed to a marine atmosphere for two years prior to the slow strain rate tests, showing that corrosion under applied stress is not a pre-requisite for re-embrittlement to occur, which can take place even if aircraft components are only stressed intermittently. The severity of the marine environment in re-embrittlement was in the order Alcotec > SermeTel > Cadmium. These results are particularly pertinent as marine atmosphere exposure testing is thought to be most representative of service conditions on aircraft.
10. Cadmium and Alcotec both performed well in marine atmosphere exposure, but SermeTel appeared to passivate in these conditions, and after 12 months red rust was visible in scribed regions, as well as the corners and edges of the panels.
11. Substantial re-embrittlement was introduced by the pre-corrosion of coated specimens in a salt spray test underlining the risk of re-embrittlement for corroding aircraft components even when stressed intermittently in service. The extent of the degradation of the steel mechanical properties was in the order

Cadmium > SermeTel > Alcotec. This ranking was in full agreement with the severity of the damage incurred by salt fog conditions to each of the examined coatings. Moreover, salt spray conditions were less detrimental to coatings with better barrier properties, like Alcotec.

12. Open circuit potential measurements of the investigated coatings showed that Alcotec was the most active coating, while SermeTel was fluctuating between more noble values, and Cd was the most noble coating among them.
13. According to linear polarisation resistance results, the self-corrosion rate of the studied coatings in 3.5% NaCl solution was in the order Alcotec < SermeTel < Cadmium. Particularly, the corrosion rate of the isolated Cd coating was by far higher than the rate for the aluminium-based coatings.
14. The galvanic corrosion rate of the examined coatings when coupled to steel after 1000 hours of exposure to 3.5% NaCl solution was in the order Alcotec > Cadmium > SermeTel. In particular, the dissolution rate of Alcotec was by far higher than the galvanic corrosion rate for the other two coatings.

FUTURE WORK

1. SermeTel coating in its present form tends to passivate and its long-term marine atmosphere exposure is not as good as that of Cadmium or Alcotec. This disadvantage could be overcome by the modification of the composition of its metallic particles, in order to achieve sufficient sacrificial corrosion protection and a low risk of hydrogen re-embrittlement to the steel substrate at the same time.
2. Slow strain rate testing on scribed coated tensile specimens in 3.5% NaCl solution gave useful information about the barrier properties and the sacrificial corrosion behaviour of the coatings. Re-embrittlement was exhibited in all tests, but in some cases the specimens failed outside the scribed region, suggesting that hydrogen must have entered the steel where corrosion was occurring at pores in the coating. This effect was quite obvious with SermeTel, but not with Alcotec coated specimens, which failed in the scribe indicating the better barrier properties of this coating. Further investigation is necessary to study these effects more thoroughly.
3. Further work is necessary to investigate suitable baking treatments to remove hydrogen that has been absorbed by a corroding component in service, and which is likely to cause re-embrittlement. Steel specimens coated with Cadmium, SermeTel or Alcotec display different degrees of re-embrittlement after salt spray testing. In a future study, coated specimens could be charged with hydrogen by a salt spray exposure followed by a baking treatment before tensile testing, in order to measure their recovery from re-embrittlement.

APPENDIX

Weibull Statistical Analysis

Modern technology has enabled the design of many complicated systems, the operation and safety of which depend on the reliability of the various components that the systems consist of. For instance, a fuse may burn out, a steel column may buckle, or a heat sensing device may fail. The common aspect of all these cases is that identical components under identical environmental conditions will fail at different and unpredictable times. [113]

More specifically, in this investigation, the absence of a notch in tensile specimens will allow failure to randomly occur at sites of surface imperfections or subsurface defects. Such failures produce non reproducible results due to their random nature. However, when large populations of results are considered, patterns of behaviour are likely to be repeated and a statistical distribution can be obtained for the analysis of these results.

Weibull [112] introduced in 1951 a continuous probability distribution to apply to various random phenomena, like the time to failure of a component, measured from some specified time until it fails. The probability density function $f(t)$ for the Weibull distribution is given as follows :-

$$f(t) = \frac{\beta}{\delta} \left(\frac{t-\gamma}{\delta} \right)^{\beta-1} \exp \left[- \left(\frac{t-\gamma}{\delta} \right)^{\beta} \right] \quad t \geq \gamma$$
$$f(t) = 0 \quad \text{otherwise}$$

Its parameters are γ , $(-\infty < \gamma < +\infty)$ the location parameter, $\delta > 0$ the scale parameter, and $\beta > 0$ the shape parameter. By appropriate selection of these parameters, this density function will closely approximate many observational phenomena. Figure 136 [114] displays some Weibull densities for $\gamma = 0$, $\delta = 1$ and $\beta = 1, 2, 3, 4$. When $\gamma = 0$ and $\beta = 1$ the Weibull distribution reduces to the exponential distribution. For values

of $\beta > 1$, the curves become somewhat bell-shaped and resemble the normal curves, but display some skewness.

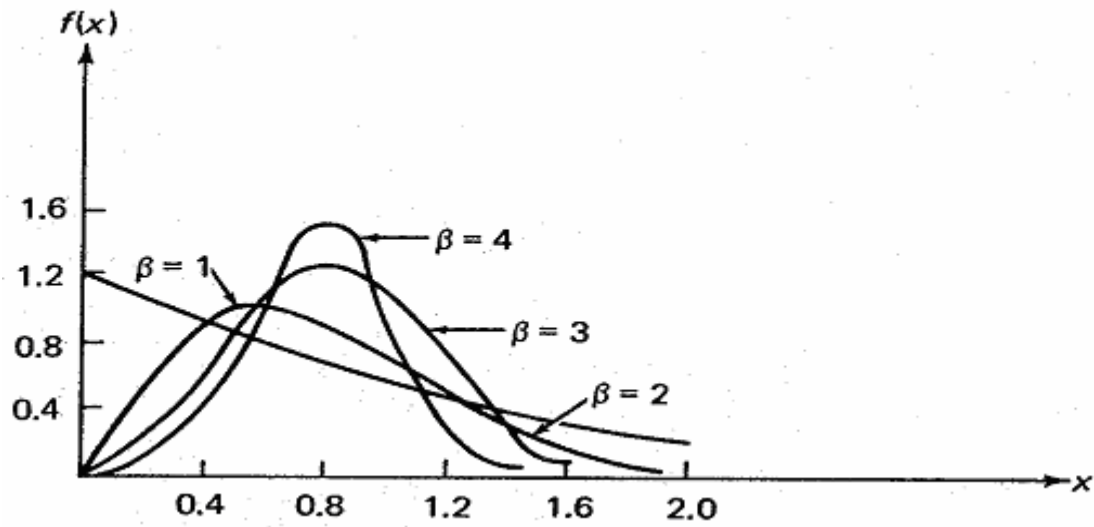


Figure 136. Weibull densities for $\gamma = 0$, $\delta = 1$ and $\beta = 1, 2, 3, 4$. [114]

The distribution function derives from the density function as follows :-

$$F(t) = \int_0^t f(t)dt = 1 - \exp\left[-\left(\frac{t-\gamma}{\delta}\right)^\beta\right] \quad t \geq \gamma$$

The above formula represents the probability of failure of a specimen, and hence, the probability of survival P_s , for at least a specified time under specified experimental conditions, is given by

$$P_s(t) = 1 - F(t) = \exp\left[-\left(\frac{t-\gamma}{\delta}\right)^\beta\right]$$

Weibull analysis [112] was originally developed for the brittle fracture of ceramics and glass and it was Yokobori [115] who adapted the technique to the brittle failure of steel. He mentioned that the probability of a specimen **not** failing within time t (probability of survival) is given by :

$$P_s = e^{-xt}$$

where x is a shape parameter, termed the Weibull slope, which represents the probability per unit time that during time, t , a crack will appear in the specimen of sufficient size to cause failure. Otherwise expressed, the slope x gives the scatter of failure times and is an indication of the range of defect sizes within the specimens. The value of x can be obtained from the negative gradient of a graph of $\ln P_s$ against time t .

Robinson and Sharp [91] found that for specimens being charged and loaded simultaneously there was a minimum incubation time, t_i , corresponding to that time, in the most susceptible specimen tested, for hydrogen to diffuse to the depth where a critical crack length was generated. They accordingly modified the previous equation to the following one:

$$P_s = e^{-x(t-t_i)}$$

Below the minimum crack incubation time, there are no failures, i.e. $P_s = 1$. A schematic Weibull plot of the failure times is given in the graph below. (Figure 137)

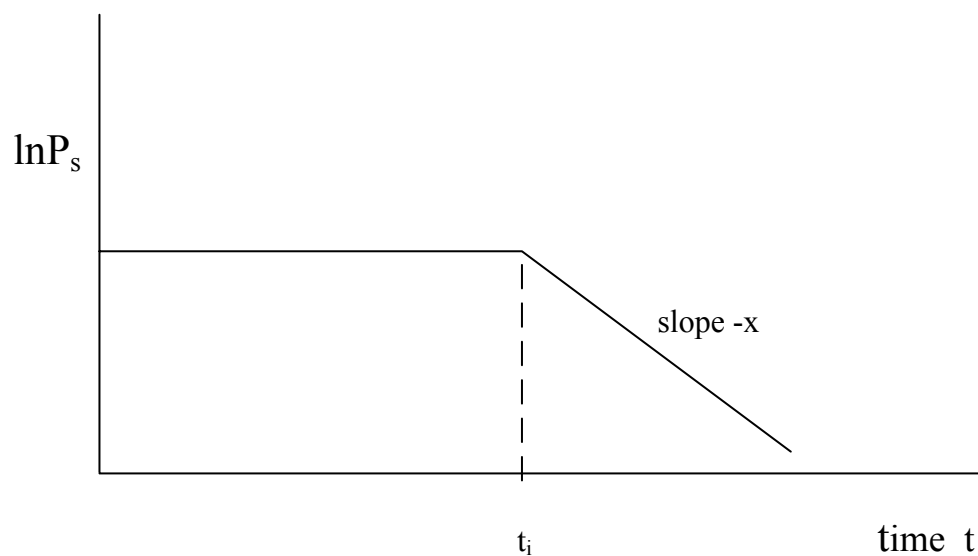


Figure 137. Weibull plot of the failure times.

Student's t-test

Given two populations of values, each following a normal distribution, it can be determined, under some conditions, if the second population could belong to the first or not. Variances of the two groups may be compared statistically to see how close their population parameters lie. If the parameters lie within acceptable limits then the two populations may be considered, with some justification, to belong to the same population, as stating that any two groups of numbers belong, with certainty, to the same population is impossible. It is possible, however, by examining the variance of the two groups to determine a statistical confidence that they cannot be assumed to belong to separate populations. [9, 113]

Let two groups of numbers be referred to by subscripts 1 and 2.

σ Standard deviation of the population

σ^2 Variance of the population

μ Mean value of the population

Taking a random sample from each of two populations, of sizes n_1 and n_2 , the sample variance of these smaller, representative groups can be determined.

s Standard deviation of the small group

s^2 Variance of the small group

s_p Pooled standard deviation of both groups combined

$\bar{x}$ Mean value of the small group

$v = n_1 + n_2 - 2$ Degree of freedom for a pair of samples

α Significance level

$(1-\alpha)100\%$ Percentage of confidence

t Test statistic

$$t = \frac{(\bar{x}_1 - \bar{x}_2) - (\mu_1 - \mu_2)}{s_p \sqrt{\frac{1}{n_1} + \frac{1}{n_2}}}$$

$$s_p = \sqrt{\frac{(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2}{n_1 + n_2 - 2}}$$

For any given values of α and v , a limiting value for the t-statistic can be determined from tables of t distribution. If the calculated value of t from experimentally determined values is more than the tabular value, then we are $100(1-\alpha)\%$ confident to assume that the two samples belong to different populations. In this work the significance level is taken to be 0.05.

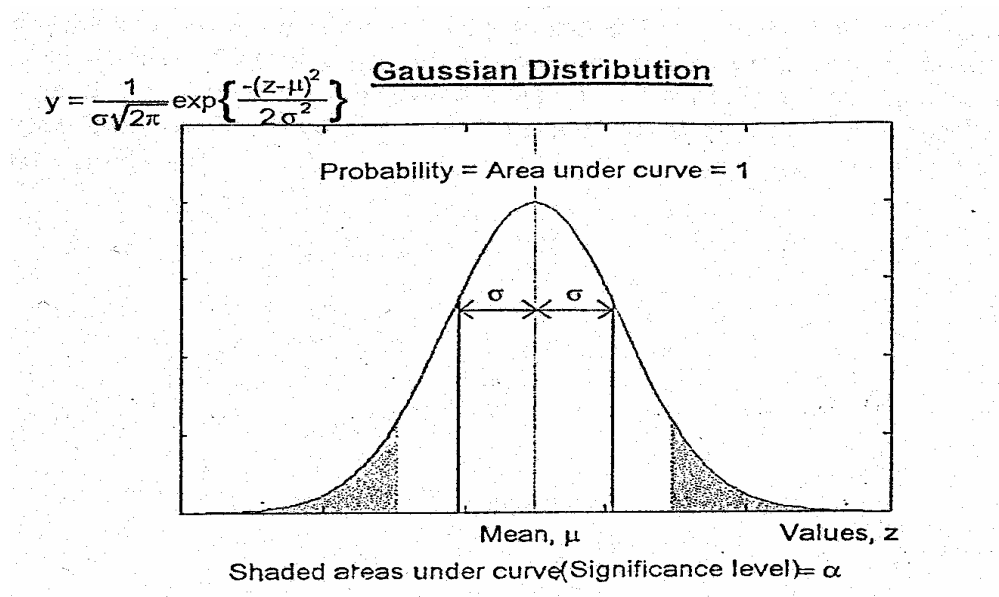


Figure 138. Normal distribution and the Student's t-test.

If the populations, where the two randomly selected samples belong to, are not proved to follow a normal distribution, the t-statistic is modified and calculated by the computational formula below. [143]

$$t = \frac{(x_1 - x_2) - (\mu_1 - \mu_2)}{\sqrt{\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}}}$$

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