THE DEVELOPMENT OF AN ULTRA-HIGH STRENGTH CUPRONICKEL ALLOY FOR MARINE APPLICATIONS

C.D.S. Tuck and K.C. Bendall

Langley Alloys Limited, Slough, U.K.

ABSTRACT

In recent years, it has become apparent that nickel, iron and titanium-based alloys are susceptible to hydrogen embrittlement. This has particularly been found when these alloys are operating in a cold worked condition at high stress levels in environments involving cathodically produced hydrogen, such as that resulting from cathodic protection of engineered structures or from the decomposition of hydrogen sulphide.

Results on the ultra-high strength copper-based fastener alloy designated MARINEL[R] under conditions designed to stimulate hydrogen embrittlement using hydrogen sulphides, have shown that embrittlement does not occur and corrosion is limited to general surface roughening over a period of 720 hours. The general behaviour of MARINEL[R] under hydrogen charging conditions is compared to the behaviour of other materials under similar conditions. A relationship is determined between the typical proof stress of these materials and the threshold stress for hydrogen embrittlement such that a guide to hydrogen embrittlement resistance of fastener materials can be devised.

INTRODUCTION

Hydrogen embrittlement of a number of alloy systems has been found to occur through hydrogen entry following a cathodic hydrogen reduction reaction on the metal surface [1]. The most common systems for this to be demonstrated are those of nickel, iron and titanium based alloys. The hydrogen reduction reaction can be the result of a number of processes, which may occur in the course of materials use. For instance, it can be the result of galvanic coupling [2] cathodic protection by impressed current on sacrificial anodes [3], or use of the material in an environment containing hydrogen sulphide [4].

In the latter environment, several investigations have been carried out on copper based alloys [5-9]. The occurrence of hydrogen embrittlement has not been reported, but the formation of a thick porous non-protective layer of copper sulphide has generally been found on cupro-nickel alloys [6]. This allows accelerated attack by chloride ions and it has been found [7] that aeration can increase the corrosion rate and stimulate the hydrogen reduction reaction. Comparison of the corrosion rates of 90/10 and 70/30 cupronickel alloys in a variety of hydrogen sulphide concentrations [8] has determined that corrosion of 90/10 is very high at low hydrogen sulphide concentrations (0.01 p.p.m), whilst 70/30 corrosion is high only after long exposure to higher concentrations of hydrogen sulphide. Fassler [9] reports that corrosion of cupronickel alloys under conditions simulating off-shore sour service (120°C in seawater/20 bar hydrogen sulphide/2 bar carbon dioxide) was of a local nature and rather severe, especially when compared to nickel-based alloys.

The copper-based alloy designated MARINEL®, has been developed as an ultra-high strength cupronickel alloy [10], containing approximately 18% Ni, together with several strengthening additives. It has been shown to be resistant to hydrogen embrittlement through potentiostatically-induced hydrogen charging by a number of workers [11,12], but has not been assessed in terms of its corrosion behaviour and susceptibility to hydrogen embrittlement in hydrogen sulphide environments. This paper describes work designed to determine these properties using the standard hydrogen sulphide testing procedure TM-01-77.

EXPERIMENTAL

MARINEL[R] alloy of composition and properties given in Table 1 was machined to prepare four tensile specimens of 6.35 mm diameter gauge section and 25.4 mm gauge length. These were placed (after degreasing) under static loading conditions at 100%, 90%, 80% and 60% of the 0.2% proof stress respectively in a Pyrex test cell containing an environment of deaerated 5% sodium chloride with 0.5% glacial acetic acid. Once in the test cell, the solution was purged with argon for 20 min to ensure the absence of oxygen and maintained at a temperature of 24°C ± 3°C. The solution was then saturated with hydrogen sulphide at a rate of 100-200 mL/mL for 20 min and then the flow rate was adjusted to 1 mL/mL to allow a gentle bubbling of the gas through the solution. The test duration was 720 hours and, after that time, the specimens were unloaded and examined in terms of corrosion behaviour. During the test, the solution pH became less, the initial pH being 2.68 and final pH ranging between 2.58 and 2.65.

RESULTS

During the early stages of testing, a gradual darkening of the specimen surfaces could be seen, eventually becoming black in colour. No evidence of cracking or gross pitting was discernable during the period of testing and no failures of the samples was experienced. After 120 hours the specimens, once removed from the static loading frame were examined under an optical microscope and no evidence of cracking could be seen. There was seen to be a general pitting of the surface, with pits generally of a size 50-100µm and preferentially lying along the fibrous grain structure parallel to the gauge length.

No differences were seen between the four specimens, thus there was no indication that the corrosion observed was in any way influenced by the loading conditions.

DISCUSSION

The overall result of testing MARINEL[R] under conditions stimulating possible hydrogen-induced cracking, is that embrittlement does not occur and there is no evidence that any stress-induced corrosion effects are produced. The general pattern of the attack agrees with the work of other investigators, who have stated that an overall filming of the surface with copper sulphide occurs fairly rapidly [6] and that corrosion is of the form of surface pitting.

In a general discussion on the behaviour of hydrogen-sensitive materials, it has been reported [1] that their susceptibility to hydrogen-induced cracking is related to some extent on their hydrogen solubility. The solubility of hydrogen in copper is 0.003 mL/mL, which is several orders of magnitude less than that of hydrogen solubility in stainless steels (typically 7.5 mL/mL). Figure 1 shows a comparison of several materials used in fastener applications plotted as a schematic diagram relating general copper content of the alloys with a normalised stress level. The latter is taken as the proof stress of the material divided by the threshold stress for hydrogen embrittlement and a curve drawn on the figure denotes a boundary such that the reduction in area of a tensile test after hydrogen charging is at least 95% of that before charging. Thus, alloys to the left of this boundary could be stated to be hydrogen-embrittlement free. Another way of comparing some of these alloys is by means of Figure 2, which shows the typical mechanical properties of comparable fastener alloys relative to the minimum proof stress used in high strength bolting applications (taken as 700 MPa). Iron and nickel-based alloys exhibit typical proof stresses which are acceptable for the application, but are above or near the threshold stress for hydrogen embrittlement. MARINEL[R], due to its lack of hydrogen sensitivity, does not exhibit a threshold stress for hydrogen embrittlement susceptibility. Figure 2 can be used to provide an indication of possible hydrogen-induced fracture susceptibility for these materials by evoking the relationship

$$\frac{700\ \text{MPa}}{\%\ \text{Copper}} < 10\ \text{MPa}$$

In this expression, the value of 700 MPa represents the maximum proof stress for high strength bolting, and the equation seems to be true for those high-strength alloys exhibiting immunity to hydrogen embrittlement which have been investigated to date. Further work to determine the general applicability of this equation is currently being undertaken.

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TABLE 1

Composition (%) and Mechanical Properties of MARINEL[R] Alloy Specimens

Ni	Al	Mn	Cr	Fe	Nb	Cu	0.2% Proof Stress(MPa)	UTS (MPa)	Elongation(%) [$4\sqrt{S_0}$]
18.0	1.9	5.0	0.4	1.0	0.7	Bal	741	993	20.5

Figure 1 - Graph showing the relationship between normalised values of stress and copper content for a number of alloys. The curve shown is such that the reduction in area of a tensile test after hydrogen charging is at least 95% of that before hydrogen charging.

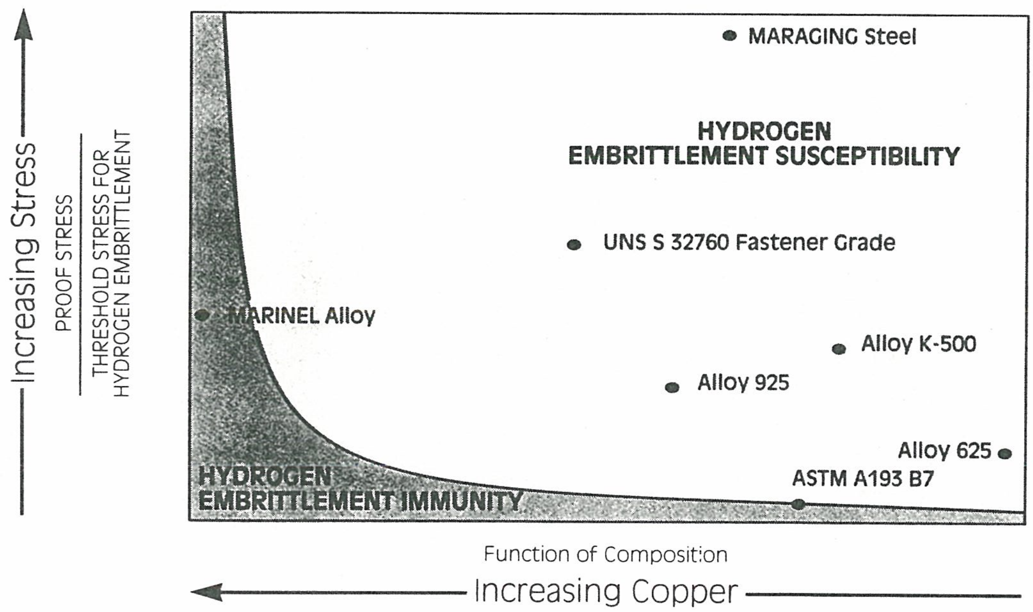

Figure 2 - Bar chart showing the general relationship between stress level under normal service conditions and threshold stress for hydrogen-induced fracture for four types of fastener alloys.