Environmentally Assisted Cracking of Magnesium Alloys

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Abstract: Fracture mechanics based techniques can be used to study the phenomena of stress corrosion cracking and hydrogen embrittlement and to model the degradation of metallic materials caused by the uptake of atomic hydrogen. Constant extension rate tensile experiments were performed on both smooth and pre-cracked specimens of Mg alloys at various strain rates in a corrosive environment and, for reference, in laboratory air. The experiments show the embrittlement caused by theuptake of atomic hydrogen which is generated in the corrosion reaction of the magnesium . It is discussed whether these experimental findings can be simulated and to some extent rationalised by applying a mesoscale model which has previously been used to mimic the effect of hydrogen embrittlement in steels.

1. Introduction

Stress corrosion cracking, SCC, is one of the a major causes of failure of engineering components and structures made from metallic materials [1]. A key mechanism causing failure is the embrittlement of the material due to the uptake of atomic hydrogen from the environment [2]. Numerous models exist which describe the material degradation and its effect on the structural integrity caused by hydrogen embrittlement, HE. The proposed mechanisms on which these models are based include hydrogen enhanced decohesion (HEDE), hydrogen enhanced localized plasticity (HELP), adsorption induced dislocation emission (AIDE) and delayed hydride cracking (DHC) [3,4].

Fracture mechanics (FM) methodology has proven to be a useful tool for investigating fracture processes caused by SCC and HE both theoretically and practically and for taking into account environmental effects on the fracture process [5]. In various studies by the authors group experimental data which had been obtained from fracture mechanics tests on smooth and pre-cracked specimens were analysed using a number of modelling approaches for crack initiation and growth caused by hydrogen embrittlement [6-10]. The models proved that they had the potential to simulate the effects of hydrogen embrittlement in the material under investigation.

While earlier work had been focused steels, and in particular on the higher strength structural steel FeE 690, the more recent work focuses on magnesium alloys as potential candidates for lightweight structural constructions. Here, the increasing demand for lighter, more fuel-efficient automobiles has led to renewed

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interest in the use of these alloys for automobile components. A major barrier, however, to the increased use of Mg alloys for automobile components is their high susceptibility to SCC in common service environments [4].

When subjecting magnesium specimens to CERT tests in distilled water, experimental evidence has shown that the SCC consists of a sequence of film rupture events at the specimen surface, leading to the exposure of bare metal to the aqueous environment. The corrosion of the bare magnesium surface thus exposed to the aqueous environment leads to an electrochemical reaction with the water in which magnesium hydroxide and hydrogen are produced according to the following reactions (Eq. 1-3) [11]:

$$2\,Mg \Leftrightarrow 2\,Mg^{+} + 2\,e^{-} \qquad \text{(anodic partial reaction)} \qquad (1)$$

$$2\,H_2O + 2\,e^{-} \Leftrightarrow H_2 + 2\,(OH)^{-} \qquad \text{(cathodic partial reaction)} \qquad (2)$$

with the overall reaction

$$Mg_{(solid)} + 2\,H_2O_{(liquid)} \Leftrightarrow Mg(OH)_{2(solid)} + H_{2(gaseous)} \qquad (3).$$

A part of the atomic hydrogen generated in this reaction recombines and forms, as indicated in Eq. 3, hydrogen gas at the specimen surface which bubbles up in the test solution. Another part of the hydrogen atoms is adsorbed at the specimen surface inside the pit which forms due to the corrosion reaction and enters the bulk of the specimen. Subsequently, the hydrogen atoms diffuse inside the material to the highly stressed regions of the specimen and raise the hydrogen concentration at these sites.

Although there exists a considerable body of research outlining the phenomenology of SCC of Mg alloys, little consensus can be found in the literature regarding the underlying mechanisms [4,12]. Yet, the development of durable Mg alloys for automobile components would require a profound understanding of these mechanisms. One approach towards gaining such understanding is modelling of SCC and in particular of hydrogen induced cracking of magnesium alloys.

2. Experimental Details

Constant extension rate tensile (CERT) tests were conducted on both smooth tensile specimens and pre-cracked compact tension, C(T), specimens at various extension rates. The materials under investigation were the cast alloys AZ31 and AZ91, with the former nominally containing about 3 wt-% aluminium and up to 1 wt-% zinc and the latter nominally containing about 9 wt-% aluminium and up to 1 wt-% zinc, balance magnesium in both cases. The tests were performed in distilled water as a "corrosive environment"; reference tests were conducted in laboratory air. The reason for using distilled water instead of a typical corrosion environment like, e.g., a chloride containing solution was due to severe pitting corrosion occurring in NaCl solutions and which overrides the effect of HE.

For the SCC tests in the distilled water the tailored gauge sections of the tensile specimens and the pre-cracked regions of the C(T) specimens, respectively, were constantly exposed to the liquid while the specimens were stressed at fixed, pre-determined extension rates. Additional SCC tests were carried out on smooth tensile specimens in the form of constant load experiments in which stress levels were applied that corresponded to stress levels at the onset of SCC cracking been determined in preceding CERT tests on similar specimens. Further, the use of an electrical potential drop set-up enabled the identification of the onset of cracking. To this end, a pulsed DC current of alternating polarity was sent through the the specimens and an increase in potential drop signal was considered as an indication of crack initiation [13]. Further details of the test technique used are reported elsewhere together with detailed discussions of the underlying failure mechanisms [14,15].

3. Results

Fig. 1 shows stress vs. apparent strain curves measured at various strain rates on AZ91 tensile specimens in distilled water and in laboratory air. The strain rates were calculated from the corresponding extension rates and are labelled at the curves in Fig. 1. The shapes of the curves reflect the increasing influence of the hydrogen on the specimen failure, i.e., when lowering the strain rate sufficient time existed so that the hydrogen could diffuse into the bulk of the material.

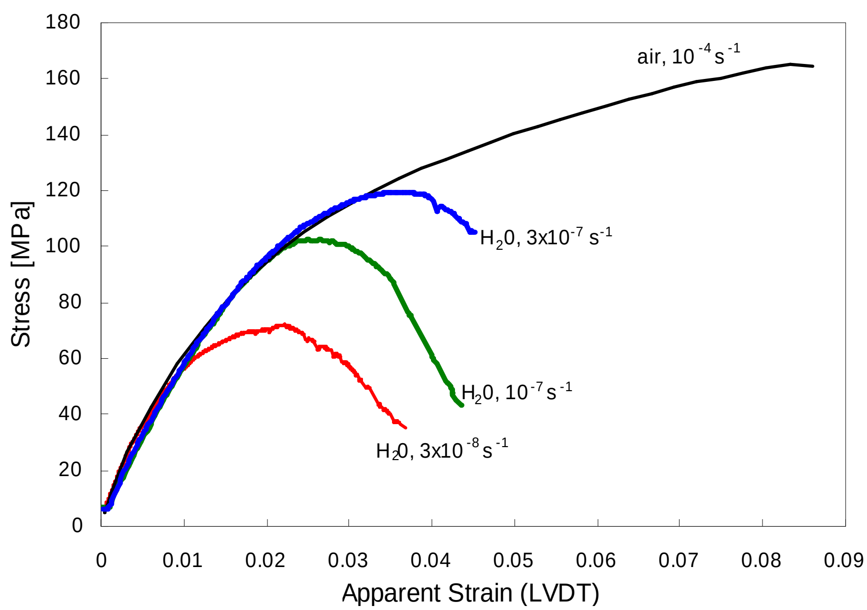

Fig. 1: Stress vs. apparent strain curves measured in CERT tests at various strain rates on tensile specimens of the Mg alloy AZ91 in distilled water and in laboratory air.

Fig. 2 depicts the fracture surface of an AZ91 tensile specimen which was loaded to stress level of 80 MPa in distilled water and was kept under this constant load in the environment until the DC potential drop measurement indicated the onset of cracking. After marking the SCC cracks which had initiated with ink, the specimen was strained to failure in air.

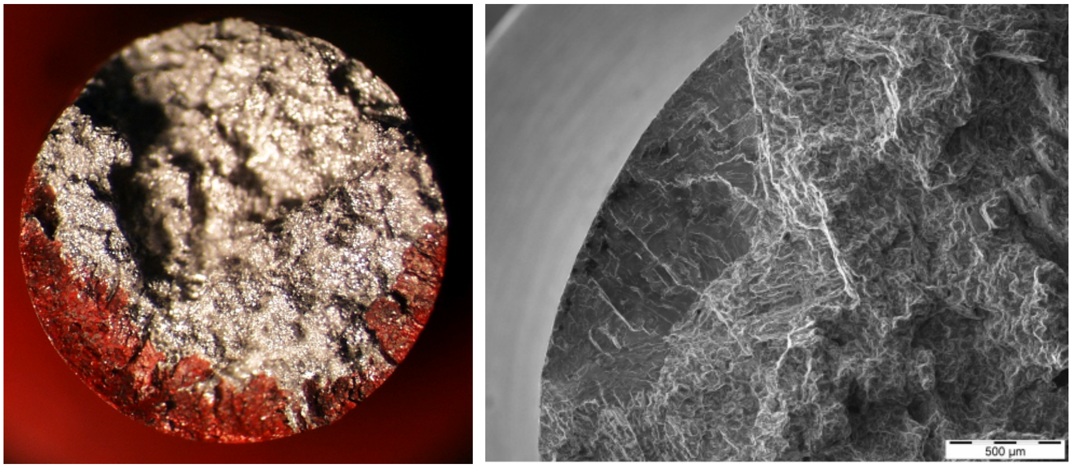

Fig. 2: Fracture surfaces of an AZ91 tensile specimens tested under constant load in distilled water, showing areas of hydrogen induced cracking; left: optical microscope, right: scanning microscope.

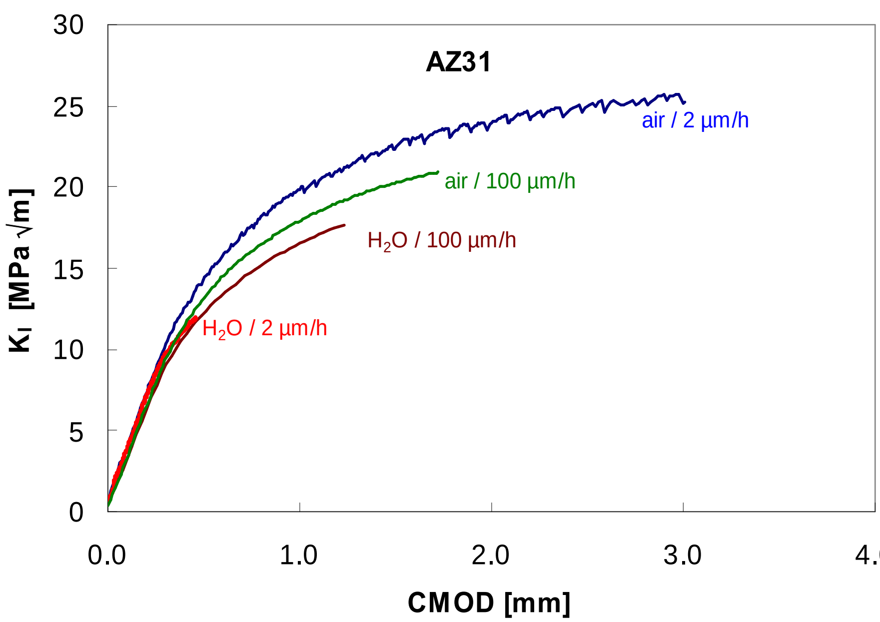

Fig. 3: Curves of the stress intensity factor, K_I, vs. crack mouth opening displacement, CMOD, measured in tests on pre-cracked C(T) specimens of the Mg alloy AZ31 at two extension rates in distilled water and in laboratory air and plotted up to the onset of cracking observed in each test.

In Fig. 3 the results of the fracture mechanics based SCC tests on pre-cracked C(T) specimens are displayed in the form of values of the stress intensity factor, KI, plotted as a function of the crack mouth opening displacement, CMOD. The tests shown here were conducted at constant extension rates, measured in crack mouth opening position, of 2 µm/h and 100 µm/h, respectively. The curves are plotted up to the point at which crack initiation was indicated by an increase in the DCPD signal. Although the overall slopes of the curves appear to some extent similar, it can be seen that cracking in distilled water, i.e. under the condition of hydrogen embrittlement, occurred at lower values of the CMOD than in the reference tests in air. This was most pronounced for the tests at the lower of the two extension rates, 2 µm/h, where crack initiation was observed after less than 0.5 mm increase in CMOD, corresponding to a test duration of about 300 hours, whereas cracking in the specimen tested at the same extension rate in air occurred only after more than 2100 hours.

4. Modelling Approach

In order to rationalise these and other experimental findings, a delayed hydride cracking (DHC) model for transgranular stress corrosion cracking (TGSCC) of Mg alloys was presented in one of our earlier publications [8], Another modelling approach which is followed is based on a mesoscale model in which the material under test is represented by a bundle of parallel bars or fibres. Details of this model can be found in the literature [6,10,16-19].

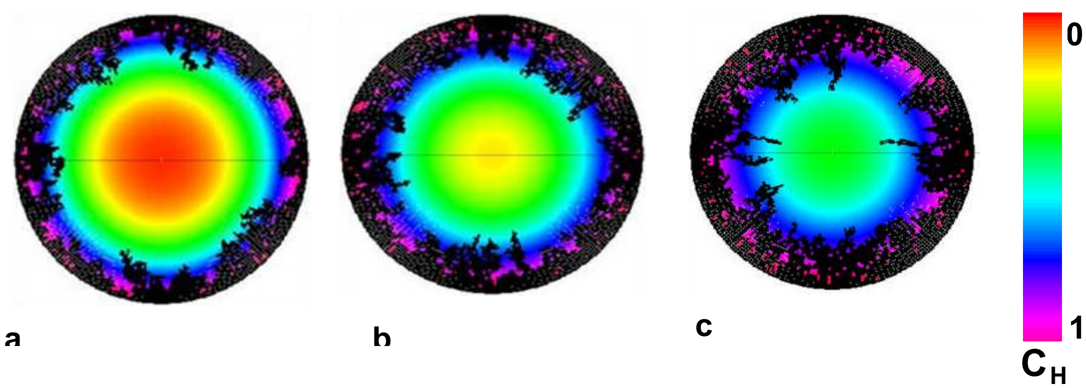

Fig. 4: Simulation of the hydrogen induced failure of a tensile specimen; the pictures show cross sections of the specimen at various stages of the failure process, the black areas indicate pits/broken fibres, the area in the centre represent uncracked ligament, and the seams around the black areas indicate different concentrations of hydrogen in the diffusion front according to the bar at the extreme right.

A bundle-of-parallel model had earlier been employed to mimic SCC/HE in steel, where the heterogeneity of the material was taken into account by assuming a site-dependent critical strain [6]. In this model, failure was assumed to be caused by stress transfer to neighbouring sites from a site which failed and a failure probability was introduced. By relating failure probability and failure strain to the local concentration of the atomic hydrogen diffusing into the material from the crack tip, it was shown that the model could simulate crack propagation and the appearance of crack fronts resulting from hydrogen induced failure.

Since for magnesium room temperature hydrogen diffusion data which would be required for this kind of modelling are not yet available, a somewhat similar approach, the fibre bundle model, was employed to simulate the results of CERT tests on smooth tensile specimens as shown in Fig. 1 [10]. Another outcome of the mesoscale modelling is shown in Fig. 4, in which the development of hydrogen induced failure of a tensile specimen under constant load with time was simulated. The various pictures show cross sections of this specimen at different stages of the failure process. Here the hydrogen is assumed to be generated in pitting corrosion processes taking place at the circumferential area of the specimen. In this figure , the dark areas indicate pits, represented by broken fibres, and the centre area of the specimen represents the uncracked ligament. The seams around the black areas represent the distribution of the hydrogen concentration in the diffusion front according to the bar indicated at the extreme right of the figure.

5. Discussion

The hydrogen embrittlement of magnesium alloys can experimentally be revealed in CERT tests at low extension rates on smooth and pre-cracked samples performed in an environment, i.e., destilled water, which promotes HE. The example related to Figs. 2 and 4 further shows that the modelling approach provided by the mesoscale fibre bundle model can, to some extent, reproduce the experimental findings for this combination of material and environment. Previous experience with the a similar model had also proven the capibility of this approach in rationalising the results of fracture mechanics SCC tests on steel samples. Combining thes experieneces should, in a next step, allow to mimic curves like those shown in Fig. 3 and to thus contribute to a better understanding of the SCC/HE processes leading to the environmentally assisted failure of magnesium.

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