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Cathodic hydrogen charging of zinc

C.N. Panagopoulos [a,*], E.P. Georgiou [b], D. Chaliampalias [a]

[a] *Laboratory of Physical Metallurgy, National Technical University of Athens, Zografos, 15780 Athens, Greece*
[b] *KU Leuven, Dept. Metallurgy and Materials Engineering (MTM), Kasteelpark Arenberg 44, B-3001 Leuven, Belgium*

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ABSTRACT

The effect of cathodic hydrogen charging on the structural and mechanical characteristics of zinc was investigated. Hardening of the surface layers of zinc, due to hydrogen incorporation and possible formation of ZnH_2, was observed. In addition, the residual stresses brought about by the incorporation of hydrogen atoms into the metallic matrix, were calculated by analyzing the obtained X-ray diffraction patterns. Tensile testing of the as-received and hydrogen charged specimens revealed that the ductility of zinc decreased significantly with increasing hydrogen charging time, for a constant value of charging current density, and with increasing charging current density, for a constant value of charging time. However, the ultimate tensile strength of this material was slightly affected by the hydrogen charging procedure. The cathodically charged zinc exhibited brittle transgranular fracture at the surface layers and ductile intergranular fracture at the deeper layers of the material.

1. Introduction

The growing importance of hydrogen among the alternative energy sources has given rise to new studies concerning the effect of hydrogen on the technological properties of metallic alloys [1–4]. However, the interaction of hydrogen with metallic materials has not yet been fully understood. Some of the proposed theories concerning hydrogen incorporation in metals are presented below.

The first theory suggested that molecular hydrogen under the influence of high pressures dissolved into the surface layers of a metallic material through micro-cracks and voids. The increased hydrogen concentration gradient caused increasing stresses in the material, which sometimes led to the formation of blisters [5,6]. Troiano [7] suggested that hydrogen diffuses mainly through easy paths, in the surface layers of the metallic materials. There the hydrogen in interstitial site reduces the atomic cohesive strength, creating localized microdefects and microcracks. Birnbaum and Sorfonis [8] suggested that hydrogen atoms diffuse in the lattice of the metallic material and interact with the existing dislocations. This interaction enhances the dislocation mobility and causes plastic deformation and fracture (HELP theory). However, other investigators found that the concentrated hydrogen in the surface layers of the metallic materials leads to the formation of a severely hardened region [9]. This increase of hardness of the surface layers is attributed to strain-hardening effects caused by the absorption of the hydrogen atoms, which reduce the dislocation mobility [9]. In any case, there is no unequivocal mechanism for hydrogen embrittlement of metallic materials. The above complex phenomena are significantly affected by various factors, such as hydrogen charging conditions [10], heat treatments [11], and forming processes [12].

Hydrogen may be introduced into metallic materials during various processes such as casting, acid pickling, electrodeposition, welding and corrosion. In that perspective, zinc is widely used in a variety of industrial and technological applications, as a bulk material produced by casting processes [13] and/or as a protective coating mainly onto steels deposited by electrodeposition technique [14,15]. In any case hydrogen can be introduced into zinc either during its production and/or during its application e.g. when used as protective coating in contact with acidic solutions [16,17]. In addition, during the last decade there is an increasing interest in the production of hydrogen energy via hydrolysis of zinc [18,19]. However, the interaction between hydrogen and zinc, as well as the effect of hydrogen incorporation into zinc and its influence on the structural and mechanical characteristics of zinc is yet unclear.

Therefore, in this research paper the cathodic hydrogen charging of zinc was studied. In particular, the effect of incorporating hydrogen atoms into the matrix of zinc was investigated with the aid of X-ray diffraction techniques. In addition, the mechanical behaviour of the as-received and hydrogen charged specimens was investigated by micro-hardness and tensile testing measurements, in order to establish a structure–property relationship. It should be also noted that up-to-date, little is known about the effect of hydrogen charging in hexagonal close packed (hcp) metals [20–23], whereas no data have been published on the hydrogen susceptibility of zinc, despite the fact that zinc and its alloys are

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* Corresponding author. Tel.: +30 3210 7722171; fax: +30 3210 7722119.
E-mail address: chpanag@metal.ntua.gr (C.N. Panagopoulos).

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extensively used in contact with acidic media [24] that could possibly result to hydrogen embrittlement phenomena.

2. Experimental procedure

The material used in this study was a commercially supplied zinc sheet. Its wt.% chemical composition was the following: 99.04% Zn and 0.96% Al. The hardness of this material was approximately 45 HVN. From this sheet a number of microhardness and standard tensile specimens were produced. In order to ensure that all the specimens had similar surface topography, all zinc specimens were grinded with SiC papers with increasing finishes and subsequently polished 3 μm diamond paste. The resulting roughness was found to range between 0.4 and 0.45 μm. After mechanical machining, a stress relief procedure was performed, by annealing the zinc specimens at 180 °C for 2 h and slowly cooling them at room temperature, in an automatic furnace with Ar inert atmosphere.

Hydrogen was introduced into the zinc specimens by electrolytic cathodic charging. This procedure was performed in a methanolic solution containing 0.034 M H_2O, 0.6 M H_2SO_4, and 0.008 M NaOH, poisoned with 5×10^{-4} M As_2O_3 as hydrogen recombination inhibitor, at room temperature. The charging current densities employed were in the range of 10–60 mA/cm^2, while the charging time varied from 3 to 60 h respectively. Commercially supplied high density–purity graphite electrodes produced by hot isostatic pressing were used as anodes.

Metallographic study of the surface of both the cathodically hydrogen charged and the fractured specimens was performed with the aid of a Jeol 6100 scanning electron microscope, which was connected with a Noran TS 5500 Electron Dispersive X-ray Analyzer (EDAX). A Siemens D 5000 X-ray diffractometer, with Cu Kα radiation, Cu filter and a graphite monochromator, was also used for the structural study and residual stress analysis of the as-received and cathodically charged zinc specimens. Mechanical testing was carried out immediately after charging, in order to minimize the loss of hydrogen. All the tensile tests were performed at a strain rate of 11×10^{-4} s^{-1}, at room temperature. Microhardness testing was performed using a Shimadju Vickers indenter, imposing 0.15 N for 15 s. The given values of the experimental parameters presented are the mean value of five independent experiments.

3. Results and discussion

Structural characterization by means of X-ray diffraction of the hydrogen charged zinc specimens revealed that they were consisted of a zinc solid solution and zinc hydride (ZnH_2), Fig. 1(a). The presence of zinc hydride in the surface layers of hydrogen charged zinc was a result of increased hydrogen concentration, which excided the solubility limit of hydrogen in zinc [25]. However, Fischer et al. [26] reported that it is extremely complicated to derive the permeability of hydrogen in metals, as it is strongly influenced by the local hydrogen concentration and by the density and depth of traps. Therefore, hydrogen diffusion cannot be described by a constant diffusivity, as hydrogen content can vary over several orders of magnitude depending on the density and depth of traps. In addition, a significant increase in the peak intensity of the zinc hydride was observed for the specimens having higher hydrogen charging time and/or charging current density, thus indicating an increase of hydrogen fugacity in the surface layers of zinc, Fig. 1(b).

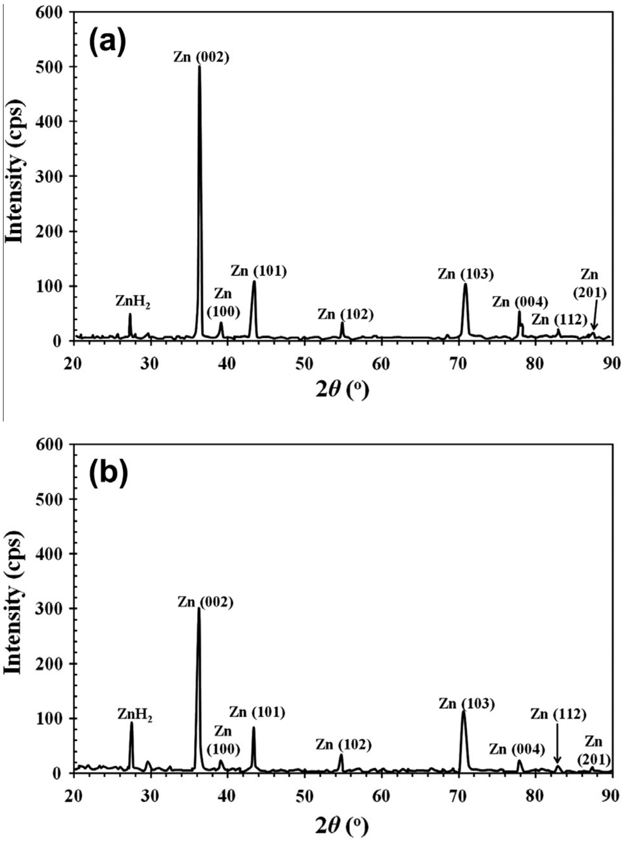

Fig. 1. (a) XRD spectrogram of hydrogen charged zinc specimen at 10 mA/cm^2 current density and for 20 h. (b) XRD spectrogram of hydrogen charged zinc specimen at 60 mA/cm^2 current density and for 20 h.

The macro-strain residual stresses in the surface layers (10–15 μm) of the as-received and hydrogen charged zinc specimens were determined by carefully measuring the lattice parameters and applying Panagopoulos et al. relationship [27]. According to these investigators the macro-strain residual stresses of metallic materials can be approximately calculated from the “shift” of the experimental X-ray diffraction peaks (θ_{exp}) in comparison to the Bragg’s theoretical peaks (θ_{th}) which are given for the same material. In addition, if $\theta_{exp} > \theta_{th}$ the residual stresses are tensile, whereas if $\theta_{exp} < \theta_{th}$ compressive stresses are observed. Quantitative analysis of these stresses can then be made by applying the following equation:

$$\boldsymbol{\sigma} = \frac{E}{2\nu} \sin\theta_{th} \left(\frac{1}{\sin\theta_{th}} - \frac{1}{\sin\theta_{exp}} \right) \qquad (1)$$

where $\boldsymbol{\sigma}$, residual stresses in surface layers (MPa); E, Young’s modulus of zinc (MPa); ν, Poisson’s ratio for zinc; θ_{th}, Bragg’s theoretical angle for zinc (°); θ_{exp}, Bragg’s experimental angle for zinc (°).

In Fig. 2. the macro-strain residual stresses as a function of (a) hydrogen charging time, for a constant value of charging current density, and (b) charging current density, for a constant value of charging time are presented. In all cases, the residual stresses were observed to be tensile, as the X-ray diffraction peaks shifted to higher Bragg angles. It has been proposed [28] that hydrogen dissolution into metallic matrixes and/or the formation of hydrides leads to an expansion of the materials lattice. However, subsequent release of the diffused hydrogen and/or decomposition of the metastable hydrides, cause the occurrence of tensile stress as they bring about a shrinkage of the lattice. In addition, higher tensile stresses were observed with increasing hydrogen charging time and charging current density, as the more intense charging conditions resulted in a higher hydrogen incorporation in the surface layers of the material. Under certain charging conditions (charging