International Journal of Solids and Structures 51 (2014) 1235–1245

Contents lists available at ScienceDirect

International Journal of Solids and Structures

journal homepage: www.elsevier.com/locate/ijsolstr

Formulation of a macroscale corrosion damage internal state variable model

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ARTICLE INFO

Article history:
Received 22 August 2013
Received in revised form 5 November 2013
Available online 12 December 2013

Keywords:
Damage
Corrosion
Internal state variable
Kinematics
Thermodynamics

ABSTRACT

A new consistent formulation coupling kinematics, thermodynamics, and kinetics with damage using an extended multiplicative decomposition of the deformation gradient that accounts for corrosion effects is proposed. The corrosion model, based upon internal state variable (ISV) theory, captures the effects of general corrosion, pit nucleation, pit growth, pit coalescence, and intergranular corrosion. The different geometrically-affected rate equations are given for each mechanism after the ISV formalism and have a thermodynamic force pair that acts as an internal stress. Pit nucleation is defined as the number density that changes as a function of time driven by the local galvanic electrochemical potential between base matrix material and second phase material. Pit growth is defined as pit surface area growth. Pit coalescence is the interaction of the pits as they grow together and is often characterized by transgranular corrosion and is mathematically constructed from Coulomb's Law and the Maxwell stress. General corrosion is signified by thickness loss of the material and is characterized by a modified Faraday's Law. The intergranular corrosion rate is related to the grain boundary effects so that it is characterized by the misorientation between grains. The total damage (void volume or area fraction) is the addition of the general, pitting, and intergranular corrosion. The ability of the model to predict aspects of the corrosion mechanisms and aging history effects of an engineering material are then illustrated by comparison with experimental data of an extruded AZ31 magnesium alloy.

1. Introduction

In many automotive and aerospace structural component applications, ductile polycrystalline materials undergo a combination of mechanical and environmental loading. Magnesium alloys are currently being investigated for use within these industries because of its low density, excellent castability, easy machinability, and high mechanical stiffness (Froes et al., 1998; Jambor and Beyer, 1997). When exposed to saltwater, magnesium has a high corrosion rate, relegating its current use to unexposed locations within the vehicle (Makar and Kruger, 1993; Shaw, 2003; Song and Atrens, 2003). By altering the microstructure with the addition of various elements, including aluminum, zinc, manganese, and rare earth elements, the corrosion rate of magnesium alloys can be reduced (Ambat et al., 2000; Lunder et al., 1985; Song and Atrens, 1999). In addition to the alteration of the microstructure, the method of processing magnesium alloys can also affect the corrosion rate. The presence of an as-cast skin often found on castings, which consists of very small grains formed during alloy cooling, decreases the corrosion resistance of the magnesium alloy (Feliu Jr. et al., 2011; Song and Xu, 2010). While castings are commonly used for parts of a vehicle, such as control arms or engine cradles, extruded metal is also used for bumpers and doors. Therefore, a detailed understanding of magnesium's response to various corrosion conditions from different processing and product environments, through the modeling of general, pitting, and intergranular corrosion is needed.

Over the past few decades, significant research has been published to formulate constitutive model for ductile materials using multiplicative decomposition of the deformation gradient (e.g. Rice, 1971; Murakami, 1988, 1990; Bammann and Aifantis, 1989; Marin and McDowell, 1996; Steinmann and Carol, 1998; Voyiadjis and Park, 1999; Brünig, 2002; Regueiro et al., 2002; Solanki, 2008). The idea of utilizing multiplicative decomposition of the deformation gradient to describe the finite deformation elastic–plastic response was introduced by Bilby et al. (1957) and independently by Kröner (n.d.). For this model, a kinematic approach where the deformation due to internal defects appears naturally and capable of describing the isotropic behavior will be used. Previous researchers (Bammann, 2001; Bammann et al., 1996, 1993; Clayton et al., 2005; Davison, 1995; Francis et al., n.d.; Horstemeyer et al., 2000; Solanki, 2008) have taken the same approach of kinematic decomposition.

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0020-7683/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.ijsolstr.2013.12.007

Coleman and Gurtin (1967) were the first lay out a framework for internal state variable (ISV) theory. Horstemeyer and Bammann (2010) recently presented a history review of ISV theory but did not mention any application to corrosion. In the context of the present article, Horstemeyer et al. (2000) modified the Bammann ISV Plasticity model (Bammann et al., 1993) to capture the stress state dependent damage evolution and to include the heterogeneities of microstructure for damage progression and failure analysis. This model will be used as the basis for our study and requires additional modifications to account for corrosion-based stress state dependent damage evolution. The rate equations are generally written as objective rates with indifference to the continuum frame of reference assuming a Jaumann rate in which the continuum spin equals the elastic spin (Horstemeyer, 2012). The ISV equations are functions of the observable variables: temperature, stress, and strain. In general, the rate equations of generalized displacements, or thermodynamics fluxes, describing the rate of change may be written as independent equations for each ISV or as derivatives of a suitably chosen potential function arising from the hypothesis of generalized normality (Rice, 1971). The selection of the ISVs may, in principle, be somewhat arbitrary, but the kinematic hardening, isotropic hardening, and damage rate equations are physically motivated and strongly influence the history of the material and can be garnered from lower length scale arguments (Horstemeyer, 2012). The ISV model accounts for deviatoric inelastic deformation resulting from the presence of dislocations in crystallographic material, dilatational deformation, and ensuing failure from damage progression (Horstemeyer, 2012). Damage will reduce the material strength, enhance the inelastic flow, and soften the elastic moduli.

To capture the corrosion behavior in a macroscale continuum model, the kinematics, thermodynamics, and kinetics of the ISVs must be coupled together to have a consistent theory that captures the entire process. The proposed model will capture the degradation effects as a scalar variable. A scalar damage variable which represents a strength decrease was first introduced by Kachanov (1958). Kachanov postulated that the loss of stiffness and integrity attributed to microcracks can be measured by a deterministic, macroscopic damage parameter and its change may be defined by the evolution of an ISV that depends on the expected value of the micro-defect density (Bammann and Solanki, 2010; Kachanov, 1958). Essentially, the damage state can be thought of as the void volume fraction (or void area fraction).

Although the complex interactions of pit nucleation, pit growth, and pit coalescence as related to surface effects are recognized, no hydrogen bulk effects are addressed. For example, in a deleterious corrosive environment, hydrogen ions can diffuse into the magnesium lattice and induce what is often called hydrogen embrittlement (HE) (Kappes et al., 2013; Toh and Baldwin, 1956). By reviewing prior work (Song et al., 1997), the overall reaction for the corrosion of pure magnesium is shown as

$$\mathrm{Mg} + 2\mathrm{H_2O} \rightarrow \mathrm{Mg(OH)_2} + \mathrm{H_2} \tag{1}$$

This shows the production of hydrogen gas from the system which, in its ionic state, in-turn can absorb, and desorb, into the matrix of the magnesium (Kappes et al., 2013). General corrosion under stress is quite different from stress-free conditions (Walton et al., 2013). The combined action of corrosion and stress can cause premature failure compared to the failure rate of the two loading cases separately. The conceptual interrelationship of corrosion, stress effects, and HE play a huge role in the understanding all of the key mechanisms. The most serious practical situation is when all three phenomena interact. The prominent damage mechanism explaining the interaction of Mg alloys under simultaneous corrosion and stress environments is called stress corrosion cracking (SCC) (Toh and Baldwin, 1956). SCC is broken down into two main forms: intergranular stress corrosion cracking (IGSCC) and transgranular stress corrosion cracking (TGSCC) (Atrens et al., 2011; Winzer et al., 2008). IGSCC is typically caused by a continuous second phase along grain boundaries where TGSCC is caused by an interaction of hydrogen with the microstructure (Atrens et al., 2011). The transformation in physical–mechanical properties and microstructure of a solid under the influence of chemical reactions which proceed on specimen surfaces causing additional dislocation flux is called the chemomechanical effect (Unigovski et al., 2007). Hence, the influence of active and aggressive environment on mechanically induced stress manifests itself through the influence on the dislocation evolution observed in the form of chemomechanical effect (Unigovski et al., 2007). The kinetics behind this phenomenon will not be addressed in this study.

The research presented here is the first of its kind in creating a physically-based macroscale ISV inelasticity model for corrosion. The corrosion ISVs are essentially added to the thermomechanical plasticity-damage model of Bammann (2001), Bammann et al. (1996, 1993), Horstemeyer (2012) and Horstemeyer et al. (2000) but includes electrochemical environments using conservation laws and empirical relationships. The kinematics, thermodynamics, and kinetics of the surface corrosion progression are introduced in a self-consistent manner. In Horstemeyer and Bammann (2010) a history of the development of internal state variable models are described and the key is the interconnectivity between the thermodynamics, kinematics, and kinetics. Although many researchers focus on the kinetics without considering the kinematics and thermodynamics, they miss the constraints that the kinematics and energy provide on the constitutive equations. As such, they might appear to be physical but in reality they might violate conservation laws. Hence, this paper starts with the kinematics and thermodynamics. Quantification work on mass loss, pit nucleation, pit growth, pit nearest neighbor distance (NND), and intergranular corrosion effects similar to prior work (e.g. Alvarez et al., 2010; Martin et al., 2010a,b, 2011, 2012; Walton et al., 2012) are available to validate such a model. The ability of the model to predict aspects of the corrosion process (general, pitting, and intergranular corrosion) as a history effect are then illustrated by comparison with experimental data of an extruded AZ31 magnesium alloy (Walton et al., 2012).

1.1. Notation

Standard notation will be followed in this formulation. In this text, tensors are denoted by **boldface** font while scalar value will have the standard weight. All tensor components are written with respect to a fixed Cartesian coordinate system. Special care is given to specify configurations throughout the derivation by using accent marks where the tilde ($\widetilde{B}$), circumflex ($\hat{B}$), and macron ($\overline{B}$) represent different intermediate configurations. The following definitions are used in the text: $\boldsymbol{AB} \Rightarrow (\boldsymbol{A} \cdot \boldsymbol{B})_{ij} = A_{ik}B_{kj}$, $\boldsymbol{a} \otimes \boldsymbol{b} \Rightarrow (\boldsymbol{a} \otimes \boldsymbol{b})_{ij}$, $\boldsymbol{A} : \boldsymbol{B} = A_{ij}B_{ij}$, $tr(\boldsymbol{A}) = A_{ii}$, $(\boldsymbol{A}^T)_{ij} = A_{ji}$, and $\|\boldsymbol{A}\| = (A_{ij}A_{ij})^{1/2}$. The over-dot denotes the material time derivative.

2. Kinematics for a elastically damage material with corrosion

From standard continuum mechanics, all equations are written in the current configuration. Any motion, $\boldsymbol{x}$, maps a particle from its initial position, $\boldsymbol{X}$, in the reference configuration to its position in the current configuration can be represented by the deformation gradient, $\boldsymbol{F}$.

$$\boldsymbol{F} = \frac{\partial \boldsymbol{x}}{\partial \boldsymbol{X}} \tag{2}$$