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Chemomechanical effects on the separation of interfaces occurring during fracture with emphasis on the hydrogen-iron and hydrogen-nickel system

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ABSTRACT

During fracture new surfaces are formed by a propagating crack. Depending on the chemical potential of the constituents of a material and their mobility the composition of the newly formed surfaces changes. Thus the surface energy as part of the work to fracture will be affected. This will be treated by combining the work to fracture representing the mechanical aspect and the Gibbs Adsorption Isotherm covering the chemical aspect. Compared to previous studies the present one provides a more generalized but also a simpler insight into chemomechanical effects. In extreme cases separation of lattice planes or separation of two crystals with a common interface occurs without applied external forces. Closed solutions for the work of fracture are derived for brittle fracture and surface segregation of solutes in the limit of a mean field approach. Chemomechanical effects including plastic deformation by dislocation or vacancy generation are discussed qualitatively.

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1. Introduction

Solute impurities introduced during preparation and/or service of materials often have deleterious effects on the mechanical behavior of materials. Among these impurities hydrogen is particularly insidious as it is ubiquitous in the form of water and enters materials via corrosive, chemical or electrochemical reactions. In addition, hydrogen atoms are often very mobile at room temperature and, therefore, are able to reach regions of weak cohesion like grain boundaries in a polycrystalline material or interfaces in multi-phase materials.

Since the pioneering work of Gibbs [1] it is known that impurities segregating to interfaces including surfaces, grain and phase boundaries are reducing the interfacial energy γ according to the following equation [2–5]

$$\left.\frac{\partial \gamma}{\partial \mu_i}\right|_{V,T,A,n_m} = -\left.\frac{\partial n_i}{\partial A}\right|_{V,T,\mu_i,n_m}, \tag{1}$$

where γ is the interfacial energy, μ_i is the chemical potential of the impurity, n_i is the number of impurity atoms and n_m the number of matrix atoms comprising the material, A is the interfacial area and V and T are volume and temperature, respectively. Eq. (1) is especially suitable for partly open systems with respect to the impurity (μ_i = const.) but closed regarding the matrix atoms (n_m = const.). Often a simplified version of Eq. (1) is used in the following form

$$d\gamma = -\Gamma_i d\mu_i, \tag{2}$$

with the excess Γ_i of impurity atoms segregating at the interface. The excess is defined as the right hand side of Eq. (1) without the negative sign, i.e. it corresponds to the number of impurity atoms dn_i which have to be added from a reservoir of impurities with constant chemical potential μ_i after an incremental increase of the interfacial area dA by keeping V, T and n_m constant. This way the definition of excess does not require knowing the position of the dividing interface [6]. Eq. (2) is often used for liquids where molecules called surfactants are added which segregate to surfaces and thus reduce the surface energy. In the present context solids are discussed. The term impurities is used despite the fact that any chemical element being present either as an impurity or an intentional

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constituent is reducing γ, if the element is present as positive excess at the interface.

For a general discussion of plastic deformation of materials preceding brittle failure it is also important to know that Eq. (2) is valid for other crystalline defects besides interfaces [3–5]. These point defects, line defects and interfaces comprise vacancies, dislocations, stacking faults, etc. Their formation under external stress may determine the elastoplastic response of a material. Chemistry comes into play via Eq. (2) as it describes the changing formation energy γ of the defects as a function of the chemical potential of component i. In this context a chemical element which leads to an excess near the defect is called defactant [5] as it reduces the formation energy of the defect in the same way as surfactants do at interfaces. If defect formation is the rate controlling process for mechanical deformation, a decrease of the defect formation energy leads to an enhanced deformation. Thus Eq. (2) becomes the governing equation for chemomechanical behavior of materials undergoing deformation. Before this scenario is discussed further, Eq. (2) is integrated assuming a regular solution of solute i at the interface. This has been done for an ideal dilute solution within the pioneering work of Hirth and Rice [7] and Rice and Wang [8] discussing the separation of grain boundaries. Besides the extension to a regular solution model the present work elucidates conditions under which an interface separates without applying external stress. In addition, the effect of solutes (namely hydrogen) on the plastic work during crack formation is discussed extensively.

2. Regular solution for adsorbates and Gibbs Adsorption Isotherm

In Statistical Thermodynamics the chemical potential of surfactant molecules either on a surface or an interface is approximated via a Langmuir Isotherm. Interaction among the adsorbed species could be taken into account via a mean field term like in lattice gas models [9] equivalent to the Frumkin isotherm [10]

$$\mu_{i,f} \cong \mu_{i,f}^o + 2W\frac{\Gamma_i}{\Gamma_{sat}} + RT\ln\frac{\Gamma_i}{\Gamma_{sat} - \Gamma_i}, \qquad (3)$$

where the subscript i,f corresponds to surfactants of type i at the interface f, $\mu_{i,f}^o$ is the standard value of the chemical potential (cf. Appendix A), W is an interaction energy parameter, $R = 8.314$ J/K/mol is the gas constant and Γ_i is the excess solute at the interface with Γ_{sat} being its saturation value corresponding to a fractional coverage of Γ_i/Γ_{sat}. The interaction term is proportional to the occupied fraction of the surface (coverage). A similar linear term is also appearing in mean field theories of condensed matter or a corresponding regular solution model [9,11,12]. The Langmuir isotherm is included in Eq. (3) as a limiting case with $W = 0$. Inserting Eq. (3) into Eq. (2) yields the following expression

$$d\gamma = -\Gamma_i\frac{d\mu_{i,f}}{d\Gamma_i}d\Gamma_i = -\left[2W\frac{\Gamma_i}{\Gamma_{sat}} + RT\frac{\Gamma_{sat}}{(\Gamma_{sat} - \Gamma_i)}\right]d\Gamma_i. \qquad (4)$$

Integrating Eq. (4) gives

$$\gamma = \gamma_o - \Gamma_{sat}\left[W\left(\frac{\Gamma_i}{\Gamma_{sat}}\right)^2 + RT\ln\frac{\Gamma_{sat}}{(\Gamma_{sat} - \Gamma_i)}\right]. \qquad (5)$$

The last equation together with Eq. (3) provides the relation between γ and μ_i using Γ_i as a parameter. Corresponding diagrams are shown in Fig. 1 for $\gamma_o = 1$ J/m^2, $\mu_{i,f}^o = 0$, $\Gamma_{sat} = 2.10^{-5}$ mol/m^2 (about a monolayer for most solid surfaces) and various values of W. Eq. (5) also reveals that γ decreases linearly with increasing $\mu_{i,f}$ for $\Gamma_i \to \Gamma_{sat}$.
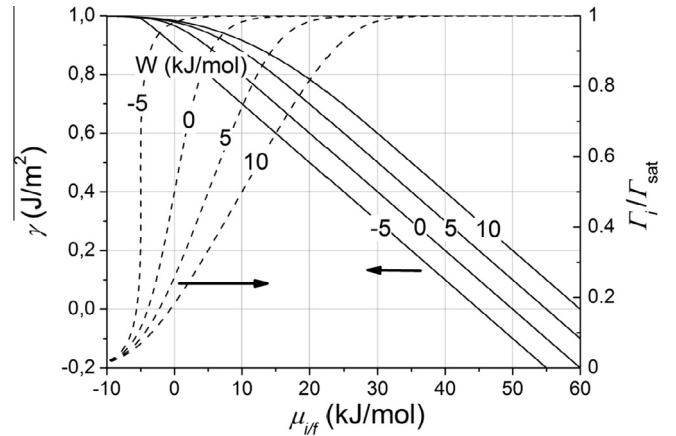

Fig. 1. Interface formation energy γ as a function of the chemical potential $\mu_{i,f}$ of segregating impurities. Data were calculated from Eqs. (3) and (5) by using Γ_i/Γ_{sat} as a varying parameter and for three different values of the interaction parameter W. Additional parameters are $\gamma_o = 1$ J/m^2, $\mu_{i,f}^o = 0$, $\Gamma_{sat} = 2 \cdot 10^{-5}$ mol/m^2 (solid lines). Corresponding adsorption (segregation) isotherms presenting the fractional excess Γ_i/Γ_{sat} are calculated from Eq. (3) and shown as dashed lines.

Negative values of W correspond to attractive interaction among the species segregating to the interface, while positive values of W represent repulsive interaction. For all values chosen for W the dependence of the interfacial energy γ on the chemical potential $\mu_{i,f}$ is in agreement with the general behavior proposed in Fig. 2, i.e. $\gamma \to \gamma_o$ for $\mu_{i,f} \ll \mu_{i,f}^o$ and $d\gamma/d\mu_{i,f} \to -\Gamma_{sat}$ for $\mu_{i,f} \gg \mu_{i,f}^o$. This behavior is more pronounced as the interaction transitions from repulsive to attractive. Decreasing W below -5 kJ/mol the $\mu_{i,f}$ versus Γ_i/Γ_{sat} curve exhibits a relative minimum and maximum corresponding to a phase separation into dilute and nearly saturated regions of the interfacial area or surface, respectively. This is well known for phase separation in solids described by the regular solution model or the gas/liquid equilibrium as described by the Van der Waals Equation.

Zero interfacial energy is reached at a critical chemical potential μ_{cr} with the corresponding critical excess $\Gamma_{cr} \cong \Gamma_{sat}$ leading to the following condition given by Eq. (5)

$$\Gamma_{sat}\left[W\left(\frac{\Gamma_{cr}}{\Gamma_{sat}}\right)^2 + RT\ln\frac{\Gamma_{sat}}{(\Gamma_{sat} - \Gamma_{cr})}\right] = \gamma_o. \qquad (6)$$

The important conclusions for the $\Gamma(\mu_l)$ isotherms and the resulting $\gamma(\mu_l)$ relation for limiting cases do not depend on the special choice of the regular solution model or the Frumkin-Isotherm,
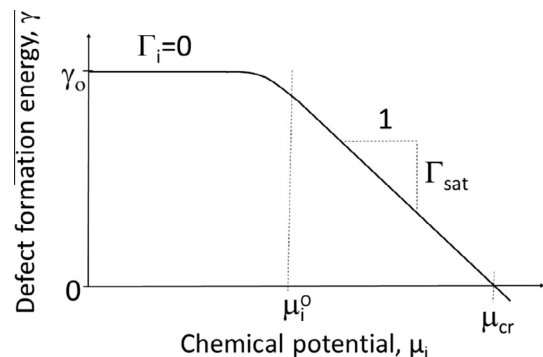

Fig. 2. Schematic presentation of the dependence of the defect formation energy on the chemical potential according to Eq. (2). Saturation of the defect during segregation with an excess Γ_{sat} is assumed. The two limiting cases of (i) $\mu_i \ll \mu_i^o$ with $\Gamma_i = 0$ and (ii) $\mu_i \gg \mu_i^o$ with $\Gamma_i = \Gamma_{sat}$ are shown.