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# Elastic fields generated by a semi-spherical hydride particle on a free surface of a metal and their effect on its growth

Y. Greenbaum[a], D. Barlam[b], M.H. Mintz[a,d], R.Z. Shneck[c,*]

[a] Department of Nuclear Engineering, Ben-Gurion University of the Negev, Beer Sheva, P.O. Box 653, Israel
[b] Department of Mechanical Engineering, Ben-Gurion University of the Negev, Beer Sheva, P.O. Box 653, Israel
[c] Department of Materials Engineering, Ben-Gurion University of the Negev, Beer Sheva, P.O. Box 653, Israel
[d] Nuclear Research Center-Negev, P.O. Box 9001, Beer Sheva, Israel

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ABSTRACT

The formation of a metal hydride is associated with a large increase of volume relative to the parent metal and therefore in large strain energies. Effects of elastic energy on the hydriding of metals are revealed in the microstructural evolution and kinetics of hydride growth on free surfaces. In the present work, we study in detail the elastic fields set up by a semi-spherical hydride particle growing at a free surface of metal with cubic symmetry, with and without an oxide layer. These systems combine geometric (structural) and material anisotropies.

Three stages along the microstructural evolution on the surface of some hydride forming metals exposed to hydrogen at constant pressure were described experimentally. For these stages along hydride growth, correlations with the elastic fields are suggested as follows. (a) A hydride particle at the free surface generates regions of tensile and compressive hydrostatic stress in the surrounding matrix. This may induce a preferred nucleation of new hydrides and formation of clusters of hydrides precipitates, which is indeed observed experimentally. (b) Clustering, on the other hand, may contribute to the cease of growth due to competition on hydrogen. In addition, as the particle grows, changes in the stress fields may retard further diffusion from the surface and be another contribution to the cease of growth. (c) A growing hydride increases the stress in the oxide layer and may finely break it. Then the elastic energy per unit volume drops to its minimum value and the growth may accelerate. The formation of such "growth center" is favored for that hydride precipitate that grow alone and not in a cluster.

## 1. Introduction

The formation of a metal hydride is associated with a large increase of volume relative to the parent metal. It is possible to measure this volume change from the difference between the lattice parameters of the metal and the hydride. Recently the bending of thin films of palladium was utilized to directly measure the internal stresses due to this volume change [1]. The elastic energy accompanying the hydride particles growth on metal surfaces may be of the same magnitude as that of the chemical driving force of hydride formation and therefore it may have a significant effect on the reaction characteristics. The influence of the strain energy on hydriding of metals is manifested by several phenomena. The two most common effects are the pulverization of bulk metals during repeated hydriding/dehydriding cycles and hysteresis of the pressure-composition absorption/desorption isotherms. Surface relief, buckling and cracking [2,3] that lead to the pulverization [e.g. [4,5]] are means to relieve the elastic stresses that are set up by the hydrides. The hysteresis is attributed to the suppression of the absorption of hydrogen by the additional strain energy effect. There is a long standing controversy whether it is the plastic energy [6–9] or the elastic energy [2,10,11] that is responsible for the hysteresis and whether the measurements reflect a real thermodynamic equilibrium or a kinetic effect [12,13]. Fundamental, yet less studied aspects of the influence of the strain energy are its effects on the microstructure evolution and on the kinetics and dynamics of the hydriding and dehydriding processes. Theoretically, the elastic energy of a dilating second phase on a free surface is minimal when the shape of the particle is semi-spherical [14]. This prediction is apparently confirmed by experimental observation at the early stages of hydriding [15]. In the case of $ZrH_{1.5}$ definite orientation relations and texture of hydrides were observed that indicate an effect of elastic stresses [16]. A much more complicated aspect is the kinetics and dynamics of the hydriding and dehydriding. These processes are associated with diffusion through three phases: surface oxides, the reacting metal and the hydride, under the effects of significant stress fields. Several kinetic models of the hydriding/dehydriding disregard these stress effects [17–19]. Recently

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* Corresponding author. Tel.: +972 8 6472493; fax: +972 8 6472946.
*E-mail address:* roni@bgu.ac.il (R.Z. Shneck).

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a phase-field model was developed to simulate the morphology evolution of hydride precipitation that considers the elastoplastic behavior of zirconium bulk matrix [20]. The kinetics of hydriding of metal nanoparticles where the stresses are already small was analyzed by Zhdanov [13]. In a recent study [21] a complete wave-like dynamics of adsorbed hydrogen were attributed to stress related phenomena.

Several experimental observations [15,22,23] described the microstructural evolution and kinetics of hydrides growth on surfaces. Initially, many small sub-micron hydride precipitates are nucleated and tend to cluster. These precipitates are formed rapidly but their growth rate strongly decelerates. Following this stage a few of these hydrides are observed to start growing very fast in an irregular manner (referred to as “growth centers”) [23] until they cover the whole surface.

In the present work, we describe and analyze the elastic fields set up by a semi-spherical hydride particle growing on a free surface of a metal with a cubic symmetry and try to interpret their influence on the evolution of the microstructure and on some kinetic characteristics of the growing hydride precipitates. The elastic anisotropy turns to have an important effect on the elastic fields, and the cubic symmetry was chosen for its simplicity and abundance. This system combines geometric (a free surface) and material (cubic symmetry) anisotropies; therefore, we develop our understanding gradually. First, a spherical particle growing in an infinite isotropic matrix is described and compared to a semi-spherical particle on a free surface. Second, a spherical particle growing in an infinite matrix with cubic symmetry is described and compared to a semi-spherical particle growing on a free surface of the same cubic material. Third, the contribution of an oxide layer coating the surface on the stress fields set up by the hydride that grows underneath is studied.

The interaction of the hydride with solute hydrogen atoms in the metal matrix is proportional to the hydrostatic stress set by the hydride on its surroundings [24]. This stress component will affect the supply of hydrogen by diffusion to the hydride and the preference for nucleation of other hydride particles near the initial precipitate [25]. Therefore, in the following analysis emphasis will be given first to find and understand the variation of the hydrostatic stress component around the hydride and second to determine the variation of the total elastic energy with varying of the size of the hydride relative to the thickness of the covering oxide layer.

The outcome of the above analysis is the understanding of the contribution of the mechanical energy to the initial stages of development of hydrides. This includes the very initial nucleation and growth processes where dense hydride “spots” are formed, with decaying growth rates, a clustering tendency [15] and the following development of fast growing hydride “patches” (“growth centers”) that finally coat the surface [23]. It is shown that these development characteristics can be accounted for by the mechanical energy contributions.

## 2. Method of calculation

The calculations were performed by the FEM applying the MSC.NASTRAN [26] code. A 180° spherical segment was modeled. A hydride is assumed to have a semi-spherical shape (see Fig. 1). Both isotropic and cubic symmetries are considered. For anisotropic systems, the crystallographic axes of the matrix and precipitate are assumed parallel to each other. Pure dilatational (misfit) transformation strains are assumed ($\varepsilon_{ij}^{T} = \varepsilon^{0}\delta_{ij}$) and represented as thermal strains in the hydride.

The elastic constants selected for the specific model system of Pd–H are listed in Table 1. For the isotropic cases, the properties of polycrystalline palladium are used for both the metal and its hydride. For the system with cubic symmetry, the elastic constants of single crystal palladium were chosen for the matrix and those of $PdH_{0.6}$ were used for the hydride. The constants of the oxide layer were those measured for PdO. The linear misfit value was calculated from the hydride and metal densities [27] and found to be $\varepsilon_L^0 = 0.034$.

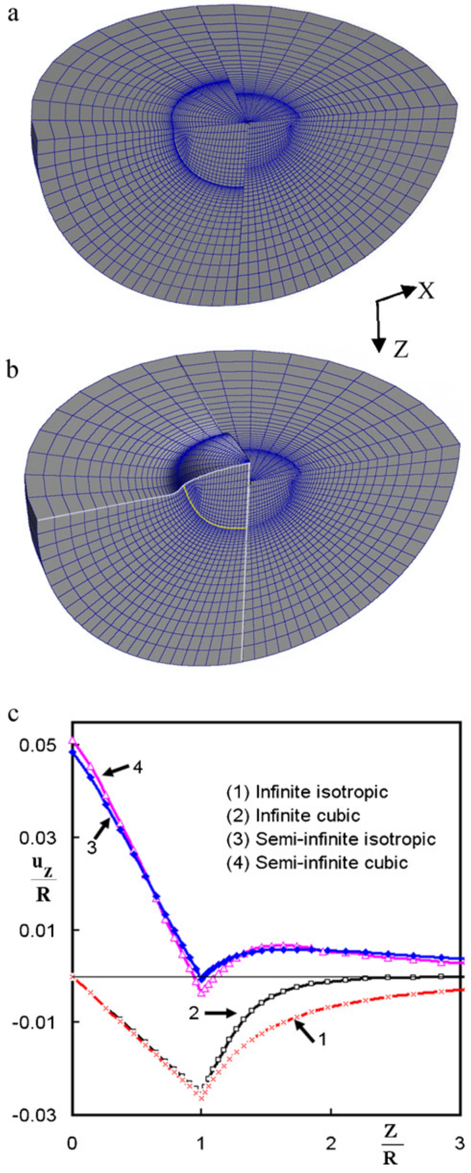

**Fig. 1.** Displacements of isotropic infinite and semi-infinite systems. Comparison of the displacements due to the formation of a semispherical hydride particle: (a) in an infinite matrix (left half), compared to the reference state before the reaction (right half), (b) on a free surface (left half), compared to the reference state before the reaction and (c) displacement profiles $u_z$ along the $z$-axis for infinite and semi-infinite systems, for isotropic and cubic materials. The negative displacement indicates displacement out of the free surface, positive one creates compression relative to the stress free state.

**Table 1**
The elastic constants of the materials used in the models, calculated from the cited references.

| Material | $C_{11}$ (GPa) | $C_{12}$ (GPa) | $C_{44}$ (GPa) | $A$ |
|---|---|---|---|---|
| Pd single cryst. [27] | 224 | 173 | 71.25 | 2.8129 |
| $PdH_{0.6}$ [27] | 211 | 156 | 63.45 | 2.4720 |
| PdO [28] | 339.1 | 216.8 | 61.15 | 1 |
| Pd polycrystal [29] | 241.36 | 154.31 | 43.52 | 1 |