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Hysteresis in metal–hydrogen systems

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Abstract

Hysteresis in metal–hydrogen systems originates due to the presence of transformation strains during both hydride formation and decomposition. The variation of accommodation energies in the hydride and metallic phases as a function of progress of hydride formation obtained by elastic and elasto-plastic finite element analyses (FEA) have been discussed in relation to pressure hysteresis. The experimental hysteresis curve cannot be obtained by considering pure elastic accommodation. The process of accommodation is reasonably represented by the elasto-plastic analysis which reveals that the plastic energy created in the metallic phase during the course of hydride precipitation (and decomposition) is the major contributor to the accommodation energy. The FEA supports the view that hysteresis losses in metal–hydrogen systems result due to plastic deformation in the metallic matrix during hydride precipitation and decomposition. In physical terms, hysteresis energy loss is the energy expended to create dislocations in the metal phase during both hydride formation and decomposition.

Keywords: Hysteresis; Metal–hydrogen systems; Elastic and elasto-plastic accommodation energies; Finite element method

1. Introduction

Hysteresis in metal–hydrogen systems commonly refers to the phenomenon wherein the hydride formation pressure is higher than the hydride decomposition pressure [1]. This is schematically represented in Fig. 1 which shows the pressure–composition isotherm for a typical hydriding material. Notice that the composition axis has been represented by mole fraction of hydride rather than the conventional H/M ratio. Once the solid solubility of hydrogen is exceeded, hydrides precipitate and grow in the matrix. This should ideally have proceeded at the equilibrium pressure for hydriding p_{eq}. However, this does not occur at this pressure, but rather at a higher pressure p_f, the hydride formation pressure. As the hydrogen pressure can be related to energy, the variation of energy during the process of hydride precipitation is provided in the top portion of Fig. 1. When hydrogen gas is evacuated from the system and the pressure of hydrogen reaches p_{eq}, the hydrides should ideally decompose. However, this does not occur and the pressure has to be lowered to p_d, the hydride decomposition pressure, in order to decompose the hydrides. At the microstructural level, hydride decomposition implies the precipitation and growth of the metallic phase in the hydride.

The origin of pressure hysteresis has been the topic of discussion for several decades and the theories which have been proposed to explain the phenomenon have been

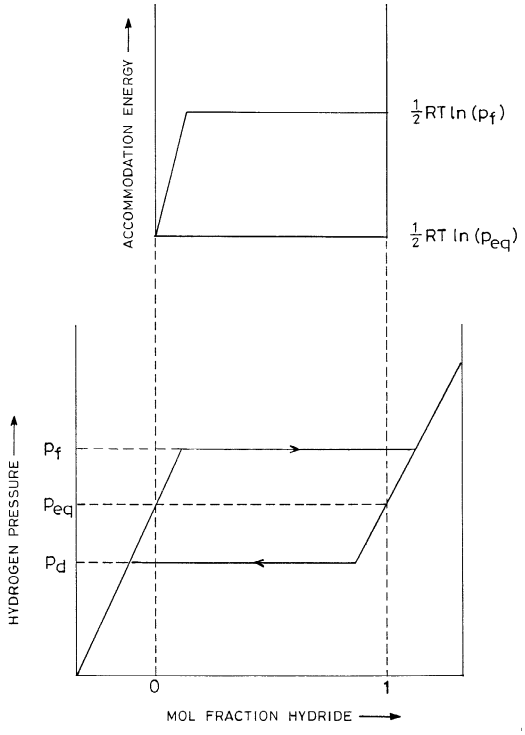

Fig. 1. Schematic pressure–composition isotherm with the inset showing the relationship between accommodation energy and mol fraction of hydride during hydride precipitation.

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critically reviewed in Ref. [2]. The transformation strains during hydride formation and decomposition, which cannot be relaxed as these are solid state transformations, result in hysteresis. The incorporation of the strain energy factor in the phase rule can account for the existence of the two-phase region within the hysteresis loop. From a material viewpoint, the transformation strains that are created during hydride precipitation and decomposition are elasto-plastically accommodated [2], i.e. as plastic energy in the plastic zone surrounding the hydride, and as elastic energy in the hydride, in the plastic zone and outside the plastic zone of the metallic phase. In case the hydride also deforms, a part is also stored as plastic energy in the hydride.

The aim of the present paper is to provide further insights into the origin of hysteresis based on recent results [3–6] of finite element analysis (FEA) of accommodation energies during hydride formation and decomposition in the Nb–H system.

2. Accommodation processes during hydride formation

The elastic and elasto-plastic accommodation energies during hydride formation and decomposition have been recently evaluated in the Nb–H system by the finite element method [3–6]. The advantages of using FEM are free surface effects can be considered and the individual accommodation energies (both elastic and plastic) in the hydride and matrix phases can be obtained. The FEA has been performed for plane stress (2-D) [6] and axisymmetric (3-D) [3–5] cases by considering the transformations (hydride formation and decomposition) to progress from the surface to center and from the center to surface of the specimen.

The FEA revealed several interesting features about these phase transformations. The FEA results for hydride precipitation from the surface to the center of the system for the plane stress case would be discussed. In this case, a ring of precipitate grows into the matrix. The accommodation energies were evaluated for aspect ratios (semimajor axis to semiminor axis) 1, 2, 3 and 4 of the precipitate. The detailed formulations have been presented elsewhere [3,4]. In the presentation of results, the accommodation energy is expressed as *joules per mole of metal in the system*. Although this energy unit cannot be directly related to the energy given by the external hydrogen pressure unlike the unit of *joules per mol metal in the precipitate* [6], it, nevertheless, helps in the understanding of the accommodation processes. The abscissa denotes the volume fraction of hydride in the system at each stage of transformation.

The variation of system elastic accommodation energy during hydride precipitation in the Nb–H system is presented in Fig. 2. The total energy of the system decreases as the aspect ratio of the precipitate increases.

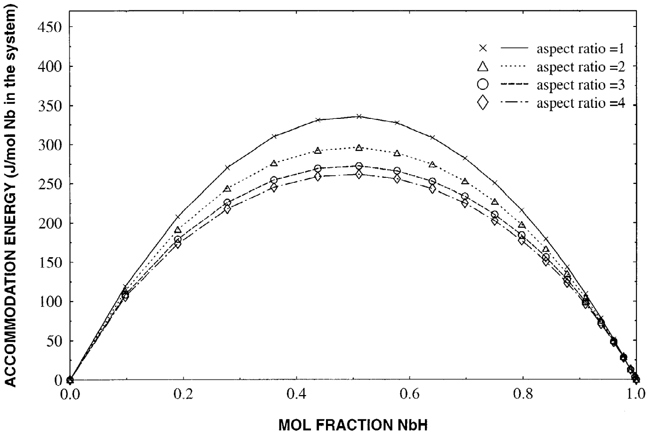

Fig. 2. Variation of system accommodation energy during hydride precipitation through the surface to center path for different aspect ratios of the precipitate using elastic plane stress FEA.

On analysing the individual elastic accommodation energies in the Nb matrix and the NbH precipitate, it was observed that the energy in the matrix increases while the energy in the precipitate decreases with increasing precipitate aspect ratio. Shear stresses develop inside the matrix thereby increasing its elastic deformation and, therefore, the matrix energy increases with aspect ratio. The constraint on the precipitate by matrix decreases with an increase in the aspect ratio. This reduces the strain energy inside the precipitate ring, which is the major contributor to the total energy and hence, the total elastic energy decreases with increase in the aspect ratio of the precipitate. Interestingly, the elastic energy of the outer phase generally dictates the total energy change as most of the energy is accommodated by the outer phase surrounding the inner phase, for all the transformations considered [3,5].

In the case of a purely elastic finite system, the strain energy will be zero at beginning and end of the transformation for all transformation paths, irrespective of the aspect ratio. At any intermediate stage, there will be two phases each constraining the expansion/contraction of other phase which will result in a net strain energy. The parabolic variation of the elastic strain energy as a function of transformation progress has been discussed elsewhere [3]. The parabolic variation of the elastic accommodation energy is difficult to relate to the flat plateau that is obtained for the hydride formation/decomposition during hysteresis and therefore elastic accommodation energies cannot alone account for hysteresis losses.

In the elasto-plastic FEA, NbH was assumed to be elastic and hence the plastic deformation, if any, was confined to only Nb. The system accommodation energy during hydride precipitation is presented in Fig. 3. The most interesting aspect of the results presented in this figure is that when the aspect ratio is greater than 1, the system accommodation energy curve attains a flat nature during the progress of transformation. This nature very

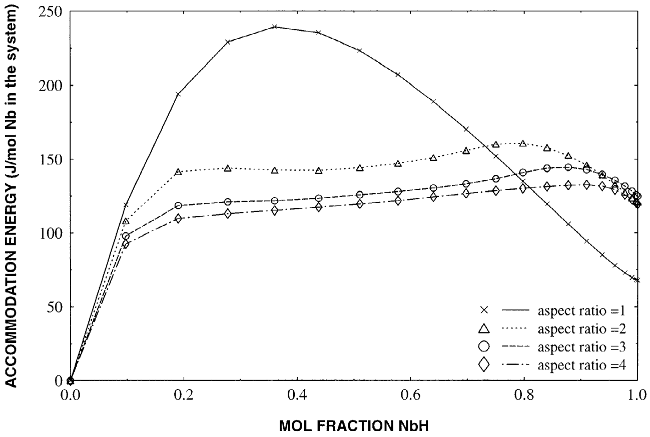

Fig. 3. Variation of system elasto-plastic accommodation energy during hydride precipitation through the surface to center path for different aspect ratios of the precipitate using plane stress FEA.

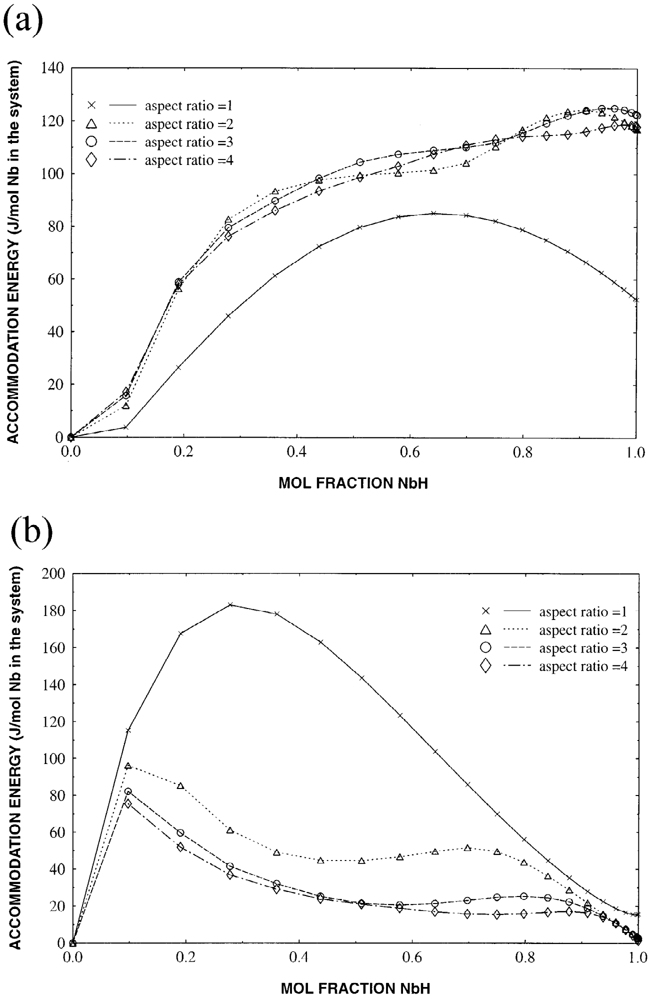

Fig. 4. Variation of elasto-plastic accommodation energy stored in the (a) matrix and (b) precipitate during hydride precipitation through the surface to center path for different aspect ratios of the precipitate using plane stress FEA.

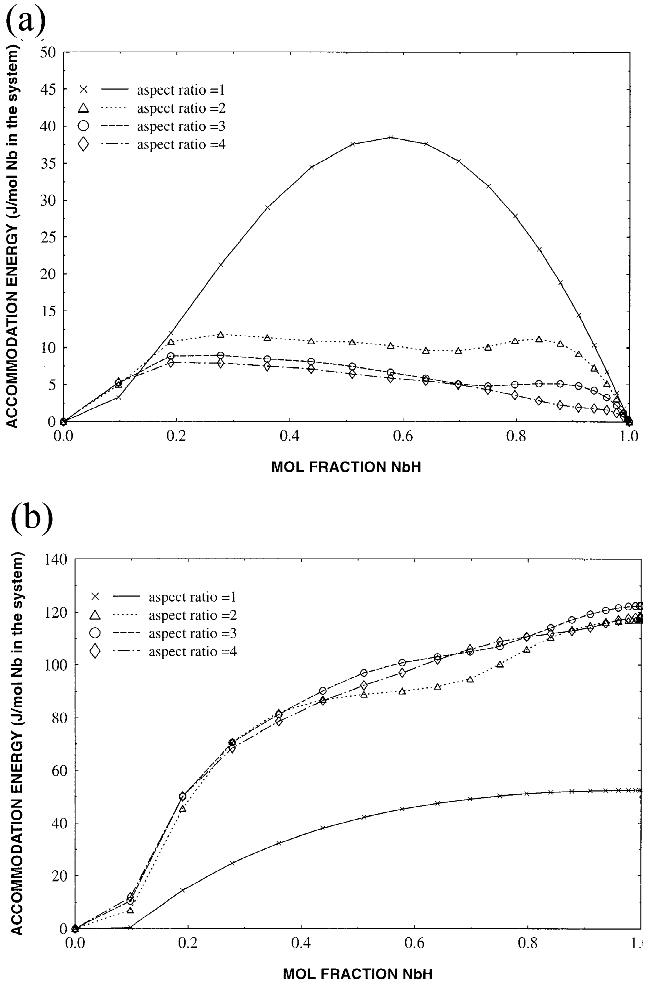

Fig. 5. Variation of (a) elastic and (b) plastic part of accommodation energy stored in the matrix during hydride precipitation through the surface to center path for different aspect ratios of precipitate using plane stress FEA.

closely resembles the nature of the variation of energy in the region where hydride precipitation occurs (refer to Fig. 1). Moreover, although the total accommodation energies decrease with increasing aspect ratio during the course of transformation, the residual energies at the end of the transformation are nearly the same for all aspect ratios greater than 1. The individual energies stored in the matrix (Nb) and the precipitate (NbH) have been shown in Fig. 4. Most of the energy is accommodated in the Nb matrix phase. On analyzing the plastic and elastic components of the matrix accommodation energy (Fig. 5), it is noticed that most of the accommodation is plastic in nature, especially for aspect ratios greater than 1.

3. Origin of hysteresis loss

Although the FEA clearly revealed the importance of both the elastic and plastic accommodation processes during hydride formation, it is the purpose of this section to examine the major factor contributing to the loss in energy. The elastic energies are generally accommodated within the hydride and the metallic matrix and the plastic energy in the metallic matrix only, as it was implicitly assumed in the FEA that the hydride does not deform. It could readily be appreciated from Fig. 5 that the accommodation energy at the end of the transformation is the plastic energy generated in the metallic matrix. This plastic accommodation energy is strictly lost to the surroundings and, in physical terms, implies the creation and movement of dislocations, in the matrix. Therefore, the major contributor to hysteresis loss is the plastic deformation process. The elastic energy is strictly not lost to the surroundings and this can, under ideal circumstances, be retrieved. Finite element modeling of hydride formation and decomposition clearly reveals that although the barrier to nucleation (due to the elastic component of the accommodation energy) is present at the beginning of the transformation (Fig. 4(b)), the origin of the hysteresis energy loss during each cycle of hydriding and de-hydriding is due to irreversible plastic deformation in the metallic phase. A part of the energy is lost as heat to the surroundings and the rest is used for creating and moving dislocations in the system. The FEA confirms the proposal of Flanagan and co-workers [1,7] who have attributed the origin of hysteresis loss to the energy required to create dislocations in the metallic matrix. The observation that the dislocation density observed after the entire cycle of hydriding and dehydriding is twice that of the density after just hydriding lends further support to the above proposal [7]. Therefore, although the strain energies during hydride precipitation and decomposition are accommodated in an elasto-plastic manner, the energy loss that is observed in the experimental PC isotherm reflects that part of the total energy lost as irreversible plastic deformation.

4. Conclusions

The parabolic variation of the elastic accommodation energy is difficult to relate to the horizontal plateau that is obtained for hydride formation/decomposition during hysteresis and therefore elastic accommodation energies are not the major cause for hysteresis losses. The process of elastic accommodation cannot result in the observed variation of accommodation energy as a function of transformation progress. Elasto-plastic FEA of accommodation energies during hydride precipitation reveal that plastic energy in the metallic matrix is the major contributor to the system energy. This strongly suggests that although the process of hydride precipitation and decomposition is elasto-plastic in nature, the origin of hysteresis loss is the plastic deformation energy, which physically implies dislocation creation/movement in the metallic matrix.

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