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Finite element evaluation of hydrogen solubility enhancements due to thermal residual stresses in palladium–alumina composites

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Abstract

Residual tensile stresses in materials result in hydrogen solubility enhancements. The residual thermal stresses and strains developed in Pd–alumina composites on cooling from several different high temperatures have been modeled by the finite element method (FEM). Two cases (alumina forming the inner core in the first case and Pd in the second case) were considered for modeling spherical alumina precipitates distributed in a spherical Pd matrix. The advantage of utilizing the FEM model is highlighted, namely the variation of stress components in different states of stress can be determined as a function of position in the composite. The FEM model provides insights into the locations where hydrogen will segregate. The stresses evaluated have also been related to hydrogen solubility enhancements.

Keywords: Finite element method; Hydrogen solubility; Pd alloys

1. Introduction

Upon exposure of a Pd–M alloy, where M is a dilute base alloying addition, to oxidizing atmospheres at high temperatures, oxygen dissolves in the matrix and results in internal oxidation of the base element. This is called internal oxidation [1]. The final product of internal oxidation is a distribution of ceramic oxide precipitates in a pure Pd matrix, a typical example of a composite material. The size, shape and type of oxide that forms internally is dependent on the internal oxidation experimental conditions. For example, as internal oxidation (IO) proceeds by the movement of an IO front into the material, incomplete oxidation results in an outer zone of ceramic precipitates in a metallic matrix and the inner region of unoxidized alloy. The temperature of internal oxidation is an important experimental variable. The kinetics of IO is generally faster at higher temperatures. From a microstructural viewpoint, the temperature of oxidation affects the nature of the internal oxides because IO occurs by nucleation and growth processes. In the specific case of internally oxidized Pd–Al alloys, it has been shown by transmission electron microscopy, that the shape of the internal alumina precipitates depends on the temperature of internal oxidation [2]. After internal oxidation at lower temperatures, the precipitates can be considered as spherical whereas at higher temperatures, the precipitates are seen to possess prismoid shapes [2].

Thermal stresses develop in the system on cooling down from the IO temperature because the ceramic precipitates and the Pd matrix possess different thermal expansion coefficients. The modeling of these thermal stresses is important as they provide ideas about the state of stress in the material after cooling down the composite from high temperature. While modeling the thermal stresses, the shape of the precipitate and its distribution needs to be also considered. It has been shown that hydrogen can be used as a probe to understand internal stresses because dissolved hydrogen segregates to the internal tensile stress fields in the system [3]. There is an enhancement in the dilute phase hydrogen solubility for Pd systems with internal stresses. Therefore, measuring the dilute phase hydrogen solubilities in Pd alloys is a proven method to understand internal stresses [4]. Typical results for internally oxidized Pd–Al alloys are shown in Fig. 1. With increasing amount of Al, the volume fraction of alumina precipitates also increases, thereby resulting in higher solubility enhancements.

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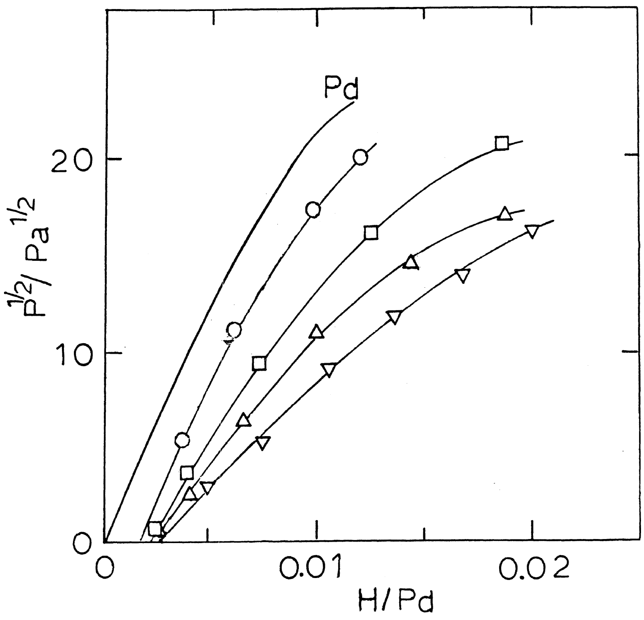

Fig. 1. Dilute phase solubilities (273 K) for internally oxidized (1073 K, 72 h), quenched Pd–Al alloys and Pd. Continuous line, Pd; (○) $Pd_{0.985}Al_{0.015}$; (□) $Pd_{0.97}Al_{0.03}$; (△) $Pd_{0.955}Al_{0.045}$; (▽) $Pd_{0.94}Al_{0.06}$.

In the present communication, the internal stresses in internally oxidized Pd–Al alloys would be evaluated utilizing the finite element method (FEM), a very powerful tool for stress analysis in complex systems. Hydrogen solubility enhancements would be estimated based on the FEM analysis. The simple case of spherical precipitates in a finite matrix would be considered. The main advantage of utilizing FEM to obtain stresses is that the variation of stress components (normal, shear, hydrostatic etc.) in different states of stress (spherically symmetric, axisymmetric, plane strain etc.) with the position in the composite and therefore the locations where hydrogen will segregate can also be understood. Hydrogen will only segregate to the tensile stress regions in the Pd matrix and the magnitude of solubility enhancement will depend upon the magnitude of the internal tensile stress [3]. If the tensile hydrostatic stress is much less than the modulus of Pd, then the interaction energy (*IE*) between the stress field and one mole of hydrogen atoms is given by:

$$IE = \sigma_{\mathrm{h}}^{m} V_{\mathrm{H}} \tag{1}$$

where V_{H} is the partial molar volume of hydrogen in Pd ($=1.77\times10^{-6}$ m^3/mol). The absorption of hydrogen in the stress field of the ceramic precipitate is given using the Boltzmann approximation as

$$\frac{n'}{n} = \exp\left(\frac{IE(\sigma_{\mathrm{h}}^{m})}{RT}\right). \tag{2}$$

The solubility enhancement factor, defined in the left hand side of the above equation, is defined as the ratio of hydrogen solubility at a fixed hydrogen chemical potential, i.e. fixed hydrogen equilibrium pressure, in the dilute phase after oxidation treatment (n') to that in pure Pd (n). The main variables considered are the temperature range through which the system cools down and the volume fraction of alumina. The specific case of a spherically symmetric system will be addressed, wherein two cases of alumina distribution would be considered.

2. FEM formulation

Consider a sphere whose internal core of radius a contains a ceramic particle (alumina Al_2O_3) and outer part contains a Pd matrix. Because of the radial symmetry approximation, the two tangential displacement components as well as the three shear components of stress and strain are zero [4]. Further, the normal stress and strain components in φ-direction are equal to the normal stress and strain components in tangential (θ) direction:

$$\sigma_{\varphi\varphi} = \sigma_{\theta\theta},\ \varepsilon_{\varphi\varphi} = \varepsilon_{\theta\theta}. \tag{3}$$

Additionally, the radial symmetry approximation implies that all non-zero displacement, stress and strain components are functions of the radial coordinate r only.

Since, the radial displacement u is a function of radial coordinate r only, the radial and tangential strain components are defined as:

$$\varepsilon_{rr} = \frac{\mathrm{d}u}{\mathrm{d}r}\ \text{(radial strain)}, \tag{4}$$

$$\varepsilon_{\theta\theta} = \frac{u}{r}\ \text{(tangential strain)}. \tag{5}$$

Under the above assumptions, the stress–strain–temperature relations are given by:

$$\varepsilon_{rr} = \frac{1}{E}(\sigma_{rr} - 2\nu\sigma_{\theta\theta}) + \alpha\Delta T, \tag{6}$$

$$\varepsilon_{\theta\theta} = \frac{1}{E}[-\nu\sigma_{rr} + (1-\nu)\sigma_{\theta\theta}] + \alpha\Delta T \tag{7}$$

where E is Young's modulus of the material, ν is Poisson's ratio of the material, α is the coefficient of thermal expansion of the material, and ΔT is the temperature rise above room temperature.

The force balance in r direction in the absence of body forces leads to the following equilibrium equation in terms of the radial (σ_{rr}) and tangential ($\sigma_{\theta\theta}$) stress components:

$$\frac{\mathrm{d}\sigma_{rr}}{\mathrm{d}r} + \frac{2(\sigma_{rr} - \sigma_{\theta\theta})}{r} = 0. \tag{8}$$

The governing Eqs. (4)–(8) are converted into a set of algebraic equations using a standard finite element formulation [5]. These algebraic equations are then solved to obtain the radial displacement u. This is done for various values of ΔT and the material properties provided in Table 1.

Table 1
Material properties of Pd and alumina

Property	Palladium	Al_2O_3 ceramic
Poisson's ratio (ν)	0.375	0.25
Young's modulus (E)	123×10^9 Pa (N/m^2)	380×10^9 Pa (N/m^2)
Coefficient of thermal expansion (α)	11.5×10^{-6}/K	8.0×10^{-6}/K

Once the radial displacement u is determined, the radial and tangential stresses are calculated using Eqs. (4)–(7). Then, the hydrostatic stress (σ_h) is given by:

$$\sigma_h = \frac{1}{3}(\sigma_{rr} + \sigma_{\theta\theta} + \sigma_{\varphi\varphi}) = \frac{1}{3}(\sigma_{rr} + 2\sigma_{\theta\theta}). \tag{9}$$

Finally, the hydrogen solubility enhancement in the Pd matrix is evaluated using Eq. (2).

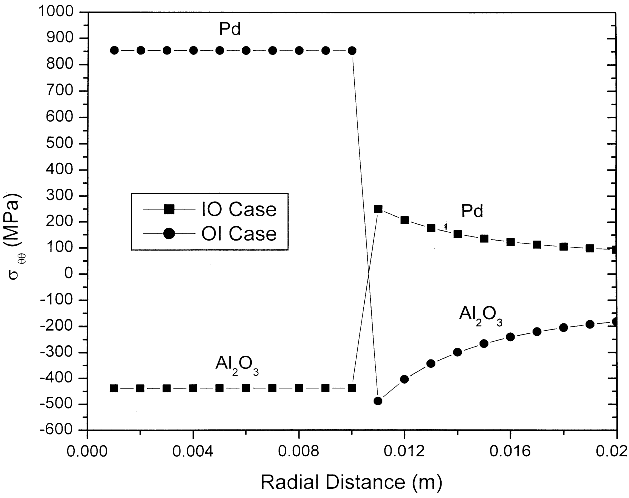

Fig. 3. Variation of tangential stresses as a function of distance for the case of $\Delta T = -1000$ and the interface is located at the middle of the system.

3. Results and discussion

Two specific situations are considered in the analysis: the precipitate forms inside the matrix and grows outward (this will be referred to as the IO case) and it forms on the external surface and grows inward (to be referred to as the OI case).

The radial (σ_{rr}) and tangential ($\sigma_{\theta\theta}$) stresses developed in the system for the case when the interface is about half of the system radius are provided in Figs. 2 and 3, respectively. The IO and OI cases are indicated in the figures. As the densities of alumina and Pd are different, the volume fraction of alumina is 0.875 for the OI case whereas it is 0.125 for the IO case. The tangential and radial stresses are constant in the inner phase. The radial stresses are compressive in both the matrix and the precipitate for the IO case, while it is tensile for the OI case. The tangential stresses are always tensile for Pd in both the IO and OI cases. This is due to the thermal expansion coefficient of Pd being higher than that of alumina. The tensile hydrostatic stresses estimated are shown in Fig. 4. It is seen that the hydrostatic stress is tensile in the Pd matrix for both cases, as expected with regard to the physical picture. The above results are compatible with the results of the model of Kim et al. [4] where the tensile hydrostatic stress developed in the matrix has been shown to be independent of distance from the precipitate–matrix interface. They considered an infinite matrix in contrast to the present case where free surfaces were considered in the analysis.

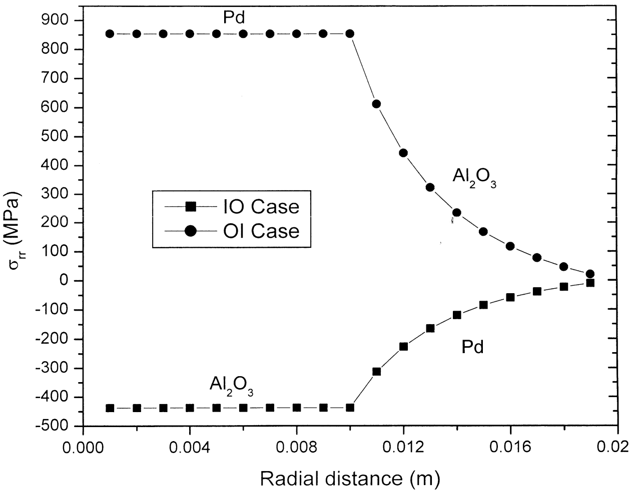

Fig. 2. Variation of radial stresses as a function of distance for the case of $\Delta T = -1000$ and the interface is located at the middle of the system.

Much higher hydrostatic stresses are developed for the case of OI due to the radial stresses being tensile for Pd in the OI case. The variation of the solubility enhancements

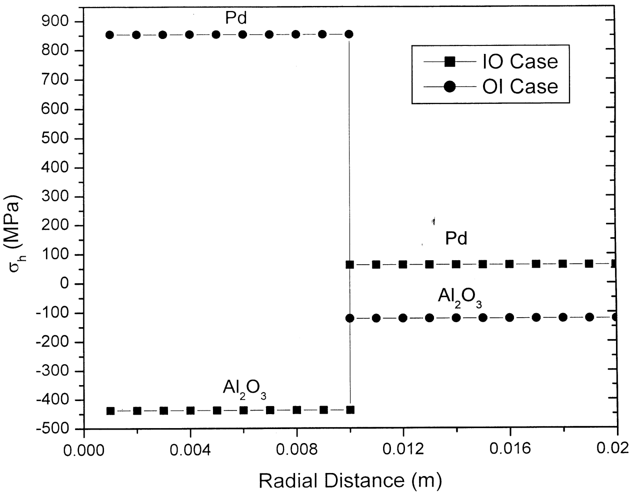

Fig. 4. Variation of hydrostatic stresses as a function of distance for the case of $\Delta T = -1000$ and the interface is located at the middle of the system.

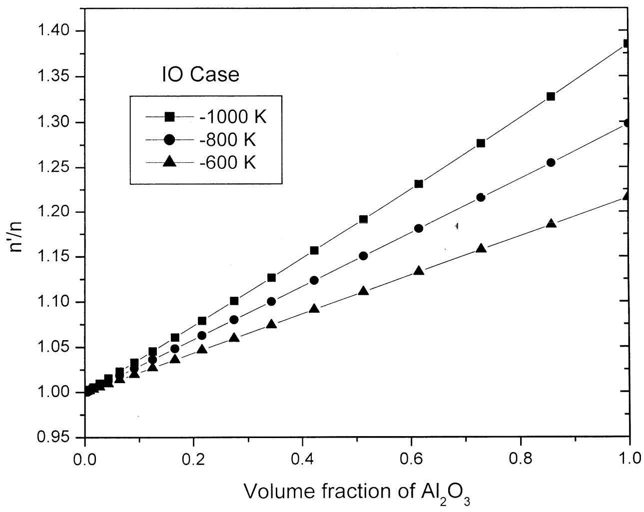

Fig. 5. Variation of solubility enhancement ratio as a function of alumina fraction for IO case.

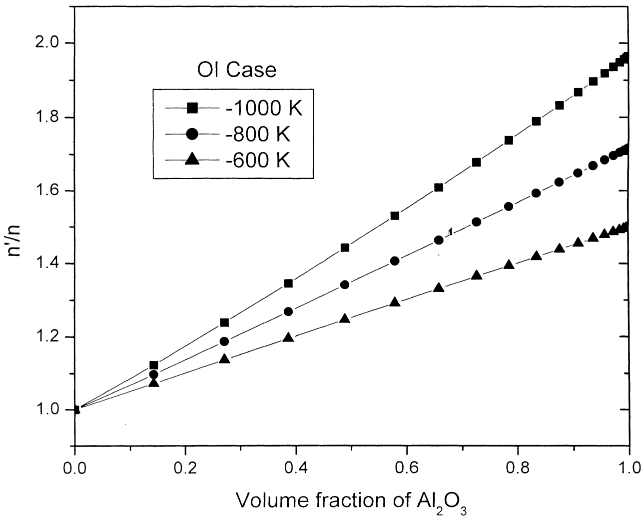

Fig. 6. Variation of solubility enhancement ratio as a function of alumina fraction for OI case.

in the Pd matrix for both the IO and OI cases is provided in Figs. 5 and 6. In both these figures, at any fixed volume fraction of alumina, the solubility enhancements are higher the larger the temperature range through which the composite was cooled down. There is an increase in the solubility enhancement with increasing volume fraction of alumina.

4. Conclusions

Hydrogen solubility enhancements due to thermal residual tensile stresses in internally oxidized Pd–Al alloys have been estimated by the finite element method. Residual thermal stresses have been estimated by FEM in Pd–alumina composites after cooling from several different high temperatures. The model considered spherical alumina precipitates in a spherical Pd matrix and two cases were considered: alumina forming the inner core in the first case and the Pd in the second case. The variation of stress components has been determined as a function of position in the composite. The evaluated stresses have been related to hydrogen solubility enhancements. The solubility enhancements are higher when the temperature range through which the composite was cooled down is larger, at any fixed volume fraction of alumina. The solubility enhancement increases with increasing volume fraction of alumina.

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