Computer Simulation of Hydride Precipitation in Bi-crystalline Zirconium

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ABSTRACT

γ'-hydride precipitation and growth in a zirconium bi-crystal were simulated using a phase field kinetic model. The temporal evolution of the spatially dependent field variables is determined by numerically solving the time-dependent Ginzburg-Landau equations for the structural variables and the Cahn-Hilliard diffusion equation for the concentration variable. The morphology evolution of γ'-hydride with and without external load was simulated. It is demonstrated that nucleation density of the hydride at the grain boundary increases as compared to the bulk and favorable hydride precipitation at the grain boundary become weaker when an external load is applied.

INTRODUCTION

A special case of phase transformations, hydride precipitation in zirconium is chosen for the current study. Zirconium is a primary structural material in nuclear power industry owing to its combination of good mechanical properties, excellent corrosion resistance and low neutron absorption cross-section. However, zirconium gradually pickup hydrogen from environment during service. At a certain level of hydrogen concentration, hydride will form. Since the brittleness of the hydride, the mechanical properties of the material will degrade, and fracture initiation at the hydride may occur[1].

It can be very expensive to study experimentally the morphological evolution of hydride precipitates in irradiated materials because of the cost involved for irradiation protection. Unfortunately, such expensive test is still the only way to study the evolution of hydride morphology in irradiated materials. Computational materials engineering methods have advanced significantly in recent years [2]. Among them, the phase-field kinetic model is an effective model in describing the morphological evolution during phase transformation. It has been successfully applied to study the morphology of the second phase precipitation in many materials [3-7]. It is now possible to apply computer simulation to acquire characteristics of hydride pattern formation, or to have better understanding of the mechanism and to predict the properties and morphology of new phases.

Zirconium has a hexagonal close-packed structure. The γ hydride is formed as a result of either high rates of cooling or long-hold at low temperature, and has a face-centered tetragonal structure. They appear needle-like with axis along three <11\(\bar{2}0\)> directions [8]. The γ-hydride precipitation under an applied load in a zirconium single crystal has been investigated [9] using the phase-field model based on the elasticity theory of Khachaturyan [10]. The morphological evolution process of this system is in well accordance with the experimental observations [8].

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However, most engineering materials are polycrystalline materials and grain boundaries may play significant role in morphology evolution. Therefore, it is necessary to develop computational methods for polycrystalline materials. It should be noted that microstructure evolution during martensitic transformations in polycrystals have been recently studied using a phase-field model [11]. In this report, γ-hydride precipitation in a bi-crystalline zirconium is considered. The effects of boundary and applied stress are discussed.

MODEL DESCRIPTION

In our phase field model, the two-phase multi-domain microstructure in a single crystalline zirconium, is described by the composition field variable $c(r,t)$ and three long range order parameters ($lro$) $\eta_1(r,t)$, $\eta_2(r,t)$, $\eta_3(r,t)$, where $r$ is the spatial coordinate, $t$ is time. While in the case of a bi-crystal, we adopted a total of six $lro$ parameters with three in each grain to describe the different domain of hydrides.

The time evolution of these field variables is described by the time dependent Ginzburg-Landau equations [12,13] for $\eta_p(r,t)$ and the Cahn-Hilliard diffusion equation [14] for $C(r,t)$,

$$\frac{\partial \eta_p(r,t)}{\partial t} = -L_p \frac{\delta F}{\delta \eta_p(r,t)} + \xi_p(r,t) \quad (1)$$

$$\frac{\partial C(r,t)}{\partial t} = M \nabla^2 \frac{\delta F}{\delta C(r,t)} + \xi(r,t) \quad (2)$$

where $L$ and $M$ are kinetic coefficients characterizing structural relaxation and diffusion mobility; $F$ is the free energy of the system; $\xi_p(r,t)$, $\xi(r,t)$ are Langvin random noise terms which are related to fluctuations in the long range order parameter and composition respectively. The noise terms satisfy Gaussian distribution and meet the requirement of the fluctuation–dissipation theorem. Since the above equations are non-linear with respect to field variables, we solve them numerically using a semi-implicit Fourier Spectral method [15].

According to thermodynamics, the equilibrium state of a multiphase system corresponds to minimum free energy. The driving force for the temporal evolution of a multiphase microstructure in single crystals consists of the following four major contributions: the chemical free energy; the interfacial energy between different phases; the strain energy caused by the lattice mismatch between the matrix and precipitates; and the interaction energy between the eigenstrain and external load. The expression of each energy term were given elsewhere (ref[9]).

For bi-crystals, the free energy contribution due to grain boundary should be included. The simulation will include all these five contributions to the total free energy in term of the field variables, $C(r,t)$ and $\eta_p(r,t)$.

For a bi-crystal, we assume that the grain boundary energy has the form as suggested by Wagner and Chalmers [16]: in the small angle regime ($\theta < 15^\circ$) the grain boundary energy increases with the orientation difference $\theta$ between the two grains:

$$E_b = E_0 \theta (A - \ln \theta) \quad (3)$$

where $E_0$ and $A$ are constants, depending on the material. In the large angle regime ($\theta \geq 15^\circ$), the grain boundary energy is assumed to be constant. In addition, it was observed in TEM experiments that grain boundaries were often the nucleation site for the hydride [10]. We assume that, (i) there is a stronger driving force at the grain boundary region for hydride formation as compared to the bulk and this driving force is proportional to $\eta_p^2$; and (ii) once
hydrides are formed at the grain boundary, the grain boundary energy $E_b$ is minimized due to the replacement of part of the original grain boundary by hydride particles. To reflect these two assumptions, we added a free energy term only in the grain boundary region, i.e.,

$$E = E_b \left[ 1 - \sum \eta_p(r,t) \right]$$

(at grain boundary)\hspace{1cm}(4)

This is similar to a concept used to simulate the effect of random defects on phase transition temperature[17]. In our simulation, this grain boundary region was specified as a thin layer having a few grid element widths.

SIMULATION RESULT AND DISCUSSION

Our simulation was conducted in a 256×256 two-dimensional uniform grid with the c-axis of Zr crystal normal to the grid. In the chemical free energy term, we assume that all the parameters are the same as in our earlier work [9]. The elastic constants of zirconium are given in ref. [18]. A hexagonal to tetragonal transformation of $\gamma$-hydride precipitate from a single crystalline zirconium generates three possible equivalent orientation variants. The stress-free transformation strains for the first orientation domain are: 0.551%, 5.64%, 5.70% [19]. The strains for the other two orientations are obtained by rotating the first orientation domain by 120° and 240° about c-axis respectively. In this simulation, the grain boundary is a vertical line through the center of the grid. In the left hand grain, one [1120] direction is along the horizontal axis, while in the right hand crystal one [1120] direction has an angle $\theta$ with respect to the horizontal axis. The kinetic coefficients $L_p$ and $M$ in equations (1) and (2) are assumed to be 0.4. $A$ in equation (3) is assumed to be 2.5 and $E_0$ in equation (3) and (4) to be $4\times10^7$ J/m$^3$. Reduced time $t^* = t/t_0$ was used to represent the aging time, where $t_0$ was given in ref. [9]. For each iteration, the time step was $\Delta t^* = 0.0008$.

The initial value of $C_0(r,t)$ is 0.1, all $\eta_p(r,t)$ were zero and two noise terms in equations (1) and (2) were turned on during the first 1000 time steps to mimic the local thermal fluctuations of $C(r,t)$ and $\eta_p(r,t)$.

Figure 1. Simulation of $\gamma$-hydride precipitation in zirconium bi-crystal at the different time. (\hspace{1cm} grain boundary ) $\theta = 20^\circ$; (a) $t^* = 1500$, (b) $t^* = 4000$.  

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Fig.1 shows the nucleation and growth process of γ-hydride precipitate in a bi-crystal zirconium matrix. The orientation of the right hand crystal is rotated by 20 degrees with respect to the left hand crystal. It can be seen from Fig.1(a) that, after nucleation process, the density of the hydride nuclei near the grain boundary is larger than that at other places. In Fig.1(b), one can see that in growth stage, these nuclei grow along habit planes with an angle about 120° from each other. It is also shown that hydride precipitated in one grain will likely stop growing across the grain boundary.

Figure 2. Simulation of γ-hydride precipitation in bi-crystal at different orientation angles. 

\[ t^* = 4000; \quad (a) \theta = 0^\circ; \quad (b) \theta = 5^\circ; \quad (c) \theta = 30^\circ. \]

Fig.2 presents hydride morphology after 4000 time steps for different orientation differences between two crystals. Fig.2(a),(b),(c) together with Fig.1(b) show that the density of hydride precipitated at the grain boundary increased with the orientation difference between the crystals at the range of small angles, while kept constant for the large angles. We can also see that habit planes of the hydride at the right hand crystal changes with the orientation of the crystal.

Figure 3. Simulation of γ-hydride precipitation under a tensile strain applied vertically. Strain was applied both in nucleation and growth process. (↓ grain boundary, ➩ applied load)

\[ \text{Tensile strain} = 0.32\%, \quad t^* = 4000; \quad (a) \theta = 20^\circ; \quad (b) \theta = 30^\circ. \]

In fig.3, the tensile load is applied along the vertical direction. The [11\(\bar{2}0\)] direction of left-hand half crystal is along the horizontal axis and that of the right-hand half crystal is in an angle \(\theta\) with x-axis. We can see the patterns of hydrides in the right hand side changes with the angle. Hydrides prefer to grow in the habit planes that are mostly near the perpendicular direction of

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applied load. Comparing all the figures, one can also notice that when there is an applied load, the favorable grain boundary precipitation become weaker. When the load level is high, the nucleation promoted by applied load will be dominant.

CONCLUSIONS

• By adopting a total of six lro with three lro in each grain, the hydride precipitation process in a bi-crystal system has been simulated.
• The simulation result shows that nucleation density of the hydride at the grain boundary increases as compared to the bulk under the assumption in equation (4).
• Hydrides will grow in the habit planes, but most likely in those planes that are most near the perpendicular direction of the applied tensile load.
• The effect of external load can be stronger than that of grain boundaries.

ACKNOWLEDGEMENTS

This work was supported by grants from the Research Grants Council of Hong Kong (B-Q411) for Shi and Woo, from Hong Kong Polytechnic University (G-V851) for Ma, and from the U.S. National Science Foundation (DMR 96-33719) for Chen.

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