

Phase stability of nanostructured materials under irradiation

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Introduction

Highly dispersed composite materials (HDCM) are promising materials for new generation nuclear reactors. Under operating conditions, such materials are subject to risks of radiation-induced vacancy saturation (accumulation of vacancy-type defects in them) and swelling (an increase in linear dimensions upon irradiation), damage, amorphization (crystal-to-glass transition) and phase transformation (phase-to-phase transition).

Behaviour of HDCM under irradiation is dramatically size dependent. There is no strong theory to guide studies of HDCM under irradiation. Generalization of experimental data suggests that there exists the competition between the factors influencing on phase stability under irradiation: (i) interfaces being as sinks of irradiation-produced point defects, (ii) defect accumulation (vacancy saturation) as a driving force for a phase transformation, (iii) bulk thermodynamic stimulus and (iv) surface energy contribution for phase transition from one phase to another one. In present work we use this idea for the elaboration a new thermodynamic approach based on the calculation of the Gibbs free energy. A spherical Fe particle in an inert medium is chosen as the model system of NDCM.

We aim to suggest Gibbsian thermodynamics approach taking into account mentioned factors and to study the effects of vacancy saturation and size on phase stability of spherical Fe nanoparticle under irradiation.

Methods

We investigate α -Fe $\rightarrow\gamma$ -Fe phase transformation depending on the particle size and other parameters. In the present work, the "size" is defined as the diameter of a spherical particle (fig.1).

Irradiation



Fig. 1. Schematic representation for irradiation treatment and polymorphic α -Fe $\rightarrow\gamma$ -Fe phase transformation of nanopowder located in an inert medium. Nanoparticles of solid Fe are modeled as identical spherical balls with the radius R and the diameter d=2R.

Nucleation energy criterion. Nucleation is the first order phase transition and yields the appearance of the new interphase surface (fig. 3, with corresponding specific energy $\sigma_{\alpha\gamma}$ and area $S_{\alpha\gamma}$). One can formulate nucleation energy criterion for phase formation:

 $\Delta G^* = 50 k_B T.$

If the value ΔG^* is very high (more than about ΔG^* =50 k_BT), then the phase transition is suppressed. Thus, nucleation and the nucleation barrier need to be taken into account.

To describe nucleation, it is necessary to consider geometrical morphology of transforming system and possible transformation modes. Experiments show the possibility of nucleation through a cap-type two-phase configuration when a new surface-segregated phase grows in a layer-by-layer fashion similar to epitaxial growth towards the inner region. Such epitaxial type of growth has been considered here within a thermodynamic approach.



Fig. 3. Cap type (lentils) nucleation mode for α -Fe $\rightarrow\gamma$ -Fe phase transition in a nanopowder under irradiation with appearance of γ -Fe nucleus at the surface of α -Fe nanoparticle.

We develop corresponding thermodynamic model. When the new γ -Fe phase nucleates, the energy change has to be determined for the two-phase α + γ configurations shown on Fig. 3. Let N_v and N_a=N₀-N_v be the numbers of atoms in the γ -Fe and α -Fe phases, respectively; $\sigma_{\alpha\nu}$ and S_{av} are

the specific interphase energy and area at the boundary of the γ Fe and α -Fe phases, correspondingly.

The change of the Gibbs free energy $\Delta G_{ncl} \equiv \Delta G(N_{\gamma})$ of the nanoparticle related to the formation of a new nucleus is then:

$$\Delta G_{ncl} = N_{\gamma} (g_{\gamma} - g_{\alpha}) + S'_{\gamma} \sigma_{\gamma} + S_{\alpha\gamma} \sigma_{\alpha\gamma} + (S'_{\alpha} - S_{\alpha}) \sigma_{\alpha} - \Delta G_{pd}$$
(6)



Theoretical model.

Let us introduce the change of the Gibbs free energy of a particle under irradiation, ΔG , and the Gibbs free energy for creating point defects in a material, ΔG_{pd} , which changes the initial state and increases the energy of nanoparticle.

From this, the quantity ΔG for α -Fe $\rightarrow \gamma$ -Fe phase transformation may be written as:

$$G = N_0 (g_\gamma - g_\alpha) + S_\gamma \sigma_\gamma - S_\alpha \sigma_\alpha - \Delta G_{pd}, \qquad (1)$$

Hereby, $\Delta G_{\text{bulk}} = N_0 (g_{\gamma} - g_{\alpha})$ is the bulk free energy change and $\Delta G_{\text{surf}} = S_{\gamma} \sigma_{\gamma} - S_{\alpha} \sigma_{\alpha}$ is the surface energy change term. The change of the Gibbs free energy of a particle without irradiation $\Delta G_p = \Delta G_{bulk} + \Delta G_{surf}$. The energy of point defects, ΔG_{pd} , depends on vacancy concentration (C_v) in the following way:

$$\Delta G_{pd} = N_0 \{ C_v (\Delta H_f - T\Delta S_f) + k_B T (C_v ln C_v + (1 - C_v) (ln (1 - C_v)) \},$$
(2)

where T is temperature, ΔH_f is the enthalpy change for vacancy formation; ΔS_f is the entropy change for vacancy formation.

The concentration C_v in the initial α -Fe particle is proportional to square d size, R²:

$$C_v = K_v (2R)^2 / (56.7D_v) \text{ or } C_v = C_0 \cdot d^2.$$
 (4)

Here, K, is the doze per atom or the defect generation rate (or atomic displacement rate, dpa/s, displacements per atom per second), d=2R is the particle diameter, D_v is the diffusion coefficient for vacancies, $C_0 = K_v / (56.7 D_v)$ is the proportionality factor.

Phase transition criterion. Phase transition in irradiated nanomaterials (α -Fe particle in our case) is thermodynamically possible only when the relationship is fulfilled:

Parameters. The temperature range in our calculations is within the interval 600-1400K (0.3-0.8 of the melting temperature, T_m=1812 K). Model parameters of irradiation are about 4 MeV ions with fluencies from 1×10^{15} to 2×10^{16} ions/cm², the diffusion coefficient for vacancies is estimated as D_v= 3×10^{-24} nm²/s. The temperature is 800K, the proportionality factor C_0 in eq. (10) equals 2×10^{-2} m⁻². For other cases we indicate the values T, C_0 in the main text and figures. The concentration of created vacancies C_v depends on the particle size (4) and varies between 0.1% to 18%.

Results

We get three zones at energy change - size diagram for Fe nanoparticle. Another interesting effect is that the Gibbs free energy change ΔG for α -Fe $\rightarrow \gamma$ -Fe phase transformation is the nonmonotonic function of the nanoparticle size, d (fig.2).



Zone I - particles with sizes up to d_1 =2nm. For particles up to instability point nearly 1.9nm, the transformation can occur without irradiation:

 ΔG_{bulk} >0, ΔG_{surf} <0, ΔG_{p} <0, ΔG_{pd} =0 and ΔG <0.

It can happen due to the surface energy change $\Delta G_{surf} < 0$. Hereby, ΔG_{surf} is the dominant component of the total energy change in eq. (1), when $\sigma_{\alpha} > \sigma_{\gamma}$.

Irradiation (vacancy saturation) causes instability point to shift toward a larger size 2.1nm, when the condition is

The quantities S'_{γ} and $S'_{\alpha}=S_{\alpha}-S'_{\gamma}$, are the external surface areas of corresponding phases of the transforming α + γ -phase particle.

The results of the computations for eq.(5) are shown in Fig. 4 for the different cases. Nucleation account for nanomaterials under irradiation treatment considerably changes the situation (fig.3).



Fig. 4 The energy difference $\Delta {\rm G}_{\rm ncl}$ versus number of atoms N_{ν} at different fixed N_0 : zero point denotes the initial single α -Fe (for last points) shows the total energy Fig.2 according to eq.(1).

Generalization of nucleation energy and phase transformation criteria.

We get two area (or four subarea) for transforming α -Fe nanoparticle under irradiation treatment.



Fig. 5. Representation of size-dependent and temperature-dependent α -Fe phase stability diagrams for α -Fe $\rightarrow\gamma$ -Fe phase transition under irradiation treatment

Conclusions

(5).

Competition between the energy of accumulated vacancies in the particle, the bulk energy of phase transformation and the surface energy of the particle is shown to be responsible for the specific behaviour of irradiated nanocrystalline Fe.

small.

phase-transformation.

phase particle, intermediate points explain cap-type two-phase α + γ configurations, last points of all curves correspond to the single γ -Fe phase particle (Fig. 3). The dashed line change ΔG (corresponding $\Delta g = \Delta G / N_0$) on

Area I – stable α -Fe phase particle. The phase

transformation cannot occur whether the

material is irradiated or not. Even if γ -Fe phase

In subarea A, $\Delta G^* < 50k_BT$ and the probability of

such phase change fluctuations is high but the

final stage will be metastable. In subarea B,

 $\Delta G^* > 50k_BT$ and the probability of nucleation

through a cap-type two-phase configurations is

Area II – unstable α -Fe phase particle. The

phase transformation can occur in different

In subarea C, $\Delta G^* > 50k_BT$ so that such transition

may be prohibited because of the small

nucleation probability. In subarea D, $\Delta G^* < 50 k_B T$

and it is the most easy way for α -Fe $\rightarrow\gamma$ -Fe

is formed, it will be metastable: $\Delta G>0$.

Fig. 2. The free energy changes $\Delta g = \Delta G/No$ and $\Delta g_p = \Delta G_p / \text{No for } \alpha - \text{Fe} \rightarrow \gamma - \text{Fe phase}$ transformation (in a spherical α -Fe nanoparticle under irradiation and without radiation, correspondingly) as functions of a particle size (d). In zone I the transformation can occur without irradiation, in zone II the phase transformation cannot occur whether the material is irradiated or not, in zone III the phase transformation can occur only with irradiation.

satisfied:

 $\Delta G_{\text{bulk}} > 0, \Delta G_{\text{surf}} < 0, \Delta G_{\text{p}} < 0, \Delta G_{\text{pd}} > 0, \Delta G = 0.$ The difference between the sizes 2.1nm and 1.9nm is very small, 0.1nm, so that it may be difficult to see it experimentally.

Zone II - particles with sizes from d_1 =2nm to d_2 =6 nm. The phase transformation cannot occur whether the material is irradiated or not. The positive bulk energy change is the dominant component of the total energy:

 ΔG_{bulk} >0, ΔG_{surf} <0, ΔG_{p} >0, ΔG_{pd} >0 and ΔG >0.

Zone III - particles with sizes larger than $d_2=6$ nm. The phase transformation can occur only due to irradiation. Hereby, the energy change, ΔG_{p} , is positive and less than the Gibbs free energy for creating point defects ΔG_{pd} : ΔG_{bulk} >0, ΔG_{surf} <0, ΔG_{p} >0, ΔG_{pd} >0 and ΔG <0.

Vacancy saturation causes increase of the energy of initial state of the α -Fe nanoparticle so that the phase transition becomes preferable: $\Delta G < 0$. In other words, for nanoparticles larger than $d_2=6$ nm irradiation yields to the phase transition: the energy of vacancy defects dominates in eq. (1).

For α -Fe nanoparticle we get three zones at energy change - size diagram. In zone I with nanoparticle sizes up to 2nm α -Fe $\rightarrow\gamma$ -Fe phase transition can occur without irradiation due to surface effects, in zone II with sizes from 2nm to 6 nm the phase transformation cannot occur whether the material is irradiated or not, in zone III with nanoparticle sizes larger than 6 nm α -Fe $\rightarrow\gamma$ -Fe phase transformation can occur only due to irradiation.

Nucleation account considerably changes the situation. In the framework of the corresponding generalization, at the temperature-size phase stability diagram we get two areas and four subareas: (i) area I of stable α -Fe phase nanoparticle when the phase transformation cannot occur and (ii) area II of unstable α -Fe phase particle, when due to high nucleation barrier such transition may be prohibited or, contrariwise, when due to small nucleation barrier it is the most easy way for α -Fe $\rightarrow\gamma$ -Fe phasetransformation.

Reference

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