Phase stability of nanostructured SiC ceramics under irradiation

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Introduction

SIC is a candidate material for use in the fuel matrix, twell shells and other high-temperature structural components in promising nuclear reactors. Radiation stability of has been examined intensely in last years but it still remains not complete [1]. A substantial increase of radiation tolerance can be expected in nanostructured SiC ceramics compared to bulk SiC due to size effect on annihilation of radiation-induced defects at the boundaries and interphases.

We **aim** to study the effect of radiation-induced vacancy saturation on amorphization and phase stability of nanostructured SiC ceramics.

The thermodynamic approach is based on the calculation of the Gibbs free energy for different phase states with vacancy-type defects. Hereby size dependence for the radiation-induced concentrations of point defects is assumed [2].

Methodology 1

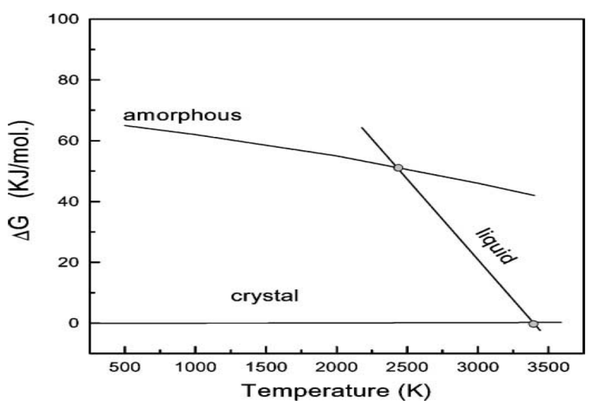

Fig. 1
Bulk free energy diagram for amorphous and liquid SiC [3].

We assume a bulk nanocrystalline (NC) material composed of spherical grains with a grain diameter, d (fig.2).

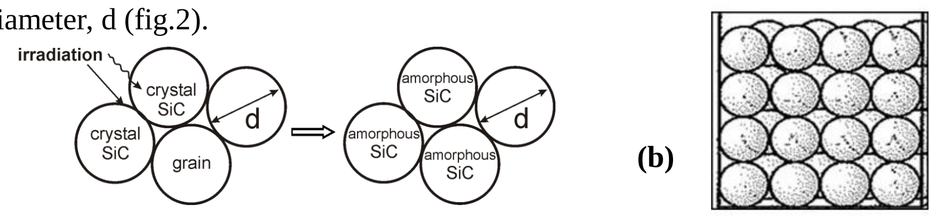

Fig. 2 Nanocrystalline solid SiC grains are modeled as identical spherical balls with the radius R and the diameter d=2R

The change of the Gibbs free energy of NC solid SiC under irradiation, ΔG_1:

$$\Delta G = \Delta G_{pt} + \Delta G_{gb} - \Delta G_{pd}\,, \qquad (1)$$

Here, ΔG_{gb} is the Gibbs free energy of grain boundaries;
ΔG_{pd} is the Gibbs free energy of radiation-induced point defects;
ΔG_{pt} is the necessary excess Gibbs free energy change for the phase transition.

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

ΔH_f is the vacancy formation enthalpy, T is temperature, k_B is the Boltzmann constant, ΔS_f is the entropy change during vacancy formation, N_A – Avogadro number.
the last term is the entropy of ideal mixing.

The vacancy concentration C_v is proportional to square size, R^2:

$$C_v = K_v\,(2R)^2/(56.7D_v) \;\text{ or }\; C_v = C_0\cdot d^2 \qquad (3)$$

$$\Delta G_{øh} = S_{øh}\sigma_{øh}\,,\;\; S_{øh} = V_m/(d^3\pi/6)\;\; (\pi d^2/2) = 3V_m/d \qquad (4)$$

$$\Delta G_{pt} = -2000+6.667(10250 - T) \qquad (5)$$

Here, σ_{gb} is the specific Gibbs free energy of the grain boundary.
In the following we introduce the notation $\Delta g=\Delta G/N_A$, $\Delta g_{pd} =\Delta G_{pd}/N_A$, $\Delta g_{gb} =\Delta G_{gb}/N_A$.

Phase transition criterion. Phase transition in irradiated nanomaterials is thermodynamically possible only when the relationship is fulfilled:

$$\Delta G < 0. \qquad (6)$$

Results

We get three zones at energy change - size diagram for Fe nanoparticle (Fig.3). Another interesting effect is that the Gibbs free energy change phase transformation is the nonmonotonic function of the grain size.

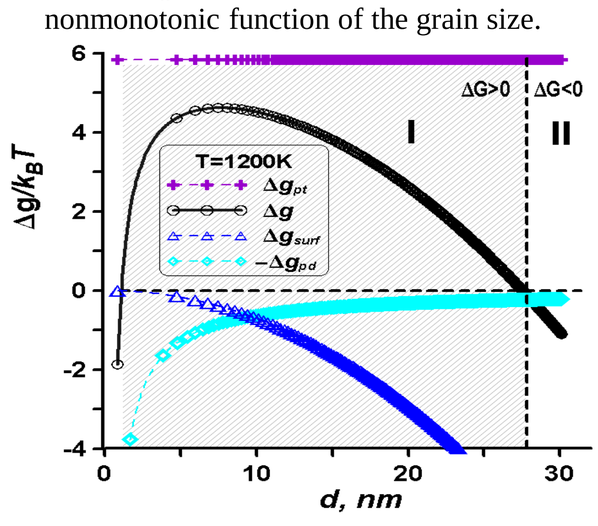

Fig. 3 Size-dependent phase transformation energy of 3C-SiC under irradiation conditions and radiation stability zones.

In stable zone I, $\Delta G>0$ for sizes about $1nm<d<27nm$, amorphization cannot occur regardless of whether the material is irradiated or not.

In unstable zone II, $\Delta G<0$ with large nanoparticles (about $d>27nm$) and amorphization can occur only due to to irradiation.

In zone with very small sizes of SiC nanoparticles (about $d<1nm$), $\Delta G<0$ and amorphization can occur without irradiation due to surface effects. Unfortunately, this case has limitation on thermodynamic approach and therefore, we do not consider the zone with dimensions less than 1 nm

Methodology 2

Amorphization is a first-order phase transition and therefore must pass through the stage of nucleation of a new amorphous phase inside the crystal grain. Due to the competition between the bulk driving force and the surface energy change, the Gibbs free energy change passes through the maximum ΔG^* (nucleation barrier). The probability of phase changes is proportional to the nucleation barrier: $\exp(-\Delta G^*/k_BT)$. Hence, one must account the nucleation barrier and the geometry of the formation of the new phase nucleus (fig.4)

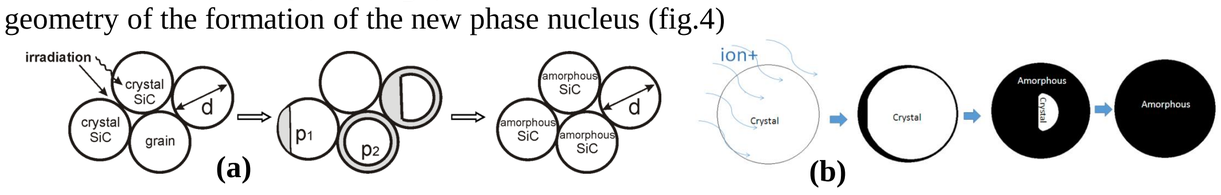

Fig. 4 Possible nucleation mechanisms of crystalline-to-amorphous phase transformation of solid SiC nanopowder located in an inert medium

For NC SiC we chose the simultaneous presence of core-shell type nucleation at the surface of each grain and cap type appearance on the surface with gradual growth inside the grain. This feature is substantiated by experimental results. Mathematically, it may be realized due to arithmetical averaging of two separate mechanisms or weight factors, p_1, p_2 : $p_1+p_2=1$.

$$\Delta G_2 = \Delta G_p - \Delta G_{pd}\,N_0 / N_A\,, \qquad (7)$$

$$\Delta G_p = \Delta G_{bulk} + \Delta G_{surf} = \Delta G_{pt}\,N_0 / N_A + S_{am}\sigma_{am} - S_{cr}\sigma_{cr} + S_{intphase}\sigma_{intphase} \qquad (8)$$

In the following we introduce the notation $\Delta g_p=\Delta G_p / N_0$. $\Delta g=\Delta G_2 / N_0$.

Nucleation energy criterion. Also we use *nucleation energy criterion for phase formation*:

$$\Delta G^*=50kT \qquad (9)$$

Results

Nucleation significantly changes the situation. The phase transition may be prohibited due to a very high value of ΔG^* (fig.5).

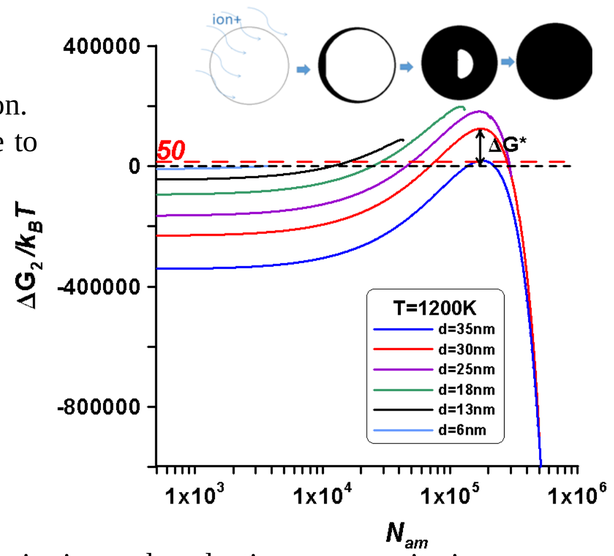

Fig. 5. The dependence ΔG_2 on number of atoms in an amorphous phase, N_{am}, for different sizes

The results of application of phase transition criterion and nucleation energy criterion are presented in Figs. 6-7:

In (white) zone I of small sizes of SiC nanoparticles, $\Delta g<0$, amorphization can occur without irradiation due to surface effects.

In (gray) zone II of medium sizes, $\Delta g>0$, amorphization cannot occur regardless of whether the material is irradiated or not.

In zone III of large nanoparticles, $\Delta g<0$, amorphization can occur only due to irradiation: the light gray zone (A) corresponds to high nucleation energy and result in the expansion of zone II up to 35 nm, the white zone B corresponds to the small nucleation barrier and high probability of amorphization.

Comparing the results of two methodologies one can resume: taking into account the energy barrier expands the stability zone II (fig.3) of SiC from the 6-25nm interval to the 6-35nm interval. Our calculations yield as well that the ability of NC SiC to accommodate defects increases (by 5%) compared to the single-crystalline material (from 14% to 19%) for the 35nm size. In this case, the width of the stability zone is the same as without taking into account the barrier, whereas K (defect generation rate) is twice smaller.

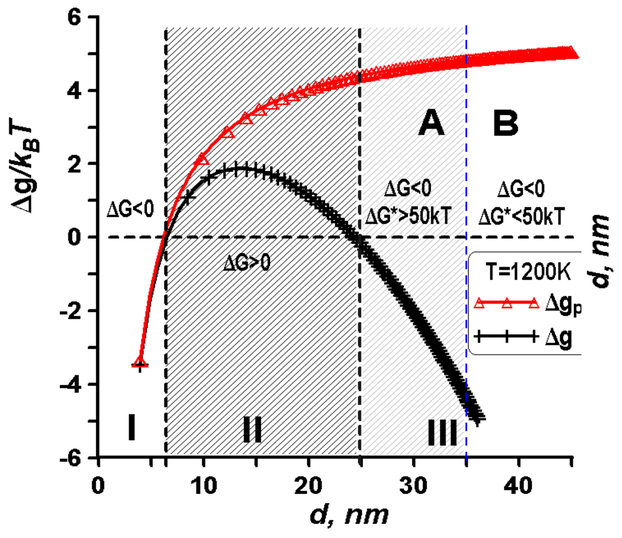

Fig. 6. The size-dependent amorphization energy of SiC particle without irradiation and under irradiation conditions

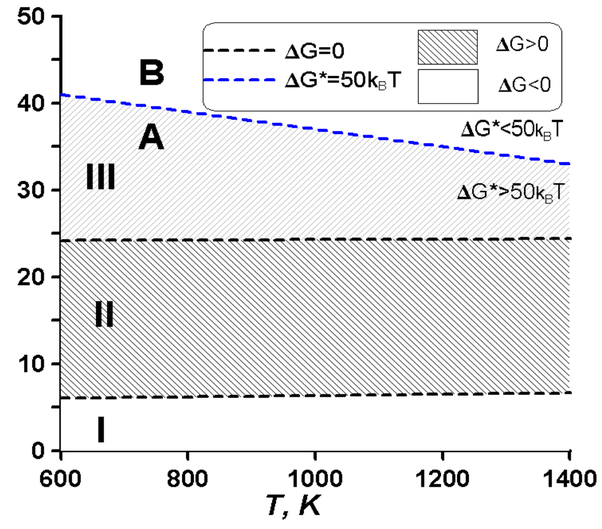

Fig. 7. Phase stability diagrams for SiC amorphization under irradiation treatment.

Conclusions

The radiation stability of 3C-SIC can be understood in terms of competing effects: (I) on the one hand, the smaller grain size reduces the accumulation of vacancies inside the grain and free energy, (II) on the other hand, the lower grain size increases free energy due to growth particles of area between the grains (interphase surface).

It is obtained that at a speed of defect generation $4x10^{-6}$ dpa/s (parameters of irradiation 2 MeV ions with fluence 10^{15} – $2x10^{16}$ ions/cm^2) for a temperature interval of 600-1500K, zone of radiation stability (absence of amorphization) of 3C-SiC corresponds to grain sizes less than 25-35 nm.

References

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