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STABLILITY OF HELIUM-VACANCY CLUSTERS DURING IRRADIATION

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One of the major uncertainties in understanding cavity nucleation and growth is the degree of stability of Helium-Vacancy Clusters (HVCs) in an irradiation field. Such stability is a complex function of irradiation variables (damage rates, helium production rates, and fluence), as well as material parameters (sink density, temperature, and defect parameters). The goal of investigating the stability of HVCs is to understand and consequently to model cavity size distributions. The present research first investigates helium-vacancy binding energies, which are then used in analysing the stability of HVCs under irradiation. The stability studies establish the critical HVC size, i.e. the Helium/Vacancy (He/V) ratio that ensures growth under specified irradiation conditions. Using these models it is possible to understand the cavity size distribution of various simmulation facilities. The fine cavity size distribution seen in many High Flux Isotope Reactor (HFIR) experiments can be explained by the favorable irradiation conditions, which lead to "spontaneous" nucleation of HVCs. In Experimental Breeder Reactor (EBR)-II experiments, on the other hand, the conditions for spontaneous nucleation of HVCs are not met, and nucleation is "delayed", and occurs by stochastic fluctuations.

1. *INTRODUCTION*

Helium introduced by (n,α) reactions is thermodynamically insoluble and thus tends to precipitate into cavities. Whereas helium concentrations in steels typical of fast breeder reactors are in the range 1-10 atppm/year, expected concentrations in fusion reactor environments are about 2 orders of magnitude greater.

Since the displacement rates in these two types of reactors are comparable, the helium to displacement ratio (He/dpa) will be a crucial factor in simulating fusion environments. The He/dpa ratio has a profound influence on the stability of HVCs, as will be discussed later. The stability of a HVC dictates the critical size or He/V ratio which ensures growth. The critical size of HVCs affects the size distribution, which determines the nature of detrimental helium effects on material properties. Two levels of analyses have generally been used to study the degree of stability of HVCs. The first is an atomistic[1] approach in which HVCs are analyzed using appropriate interatomic potentials. Stable configurations and He/V ratios, as well as binding and migration energies are found. Disadvantages of this approach are: (1) the method is not applicable to large size clusters; (2) the effect of kinetic processes due to irradiation cannot be included. On the other hand, purely kinetic descriptions are used to derive simplified analytic expressions for the "critical cavity size" for cavity growth and nucleation[2-3]. This approach may ignore important detailed mechanisms.

The present study is aimed at identifying the mechanisms influencing the binding of the last vacancy and the last helium to a cluster. Binding energy calculations are based upon high-density equations of state for helium. Those equations are quite realistic since they are based on interatomic helium-helium potentials. A nodal-line stability analysis is then

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performed to define the stability boundaries in a two-dimensional vacancy-helium phase-space. Those are determined by solving for the equilibrium conditions corresponding to the emission of the last vacancy, and the last helium atom from a cluster.

2. BINDING ENERGIES

Atomistic calculations by Wilson et al.[1] have provided binding energies for small clusters. However, these calculations can not be extended to investigate larger size HVCs. To obtain reasonable results for large HVCs (He>20; V>2) we must resort to continuum approaches. This leads to the question of a valid equation of state (EOS) for helium that takes into account the high pressures caused by large He/V ratios in HVCs. Such a numerical equation has been formulated by Wolfer et. al.[4] using an interatomic He-He potential.

The work done in compressing residing helium atoms when a vacancy is emitted from the cluster is calculated by:

$$W = -\int_{V_1}^{V_2} P\, dV \qquad (1)$$

Expressing the pressure in terms of virial coefficients:

$$\frac{PV}{kT} = z = 1 + \frac{B}{V} + \frac{C}{V^2} + \cdots \qquad (2)$$

and substituting (2) into (1) we obtain, using up to 3 virial coefficients, the following expression for the work:

$$W \simeq -kT\{\ln\left(\frac{V_2}{V_1}\right) - B\left(\frac{1}{V^2} - \frac{1}{V_1}\right) - \frac{C}{2}\left(\frac{1}{V_2^2} - \frac{1}{V_1^2}\right)\} \qquad (3)$$

The virial constants, B and C, are obtained by fitting equation (2) to Wolfer's EOS over a limited pressure range. Knowing the work done in compressing helium atoms, we now estimate the binding energy (E_v^B) of the last vacancy by adding the energy gained due to the change in surface area (ΔE_S) and the vacancy formation energy (E_v^F):

$$E_v^B = E_v^F + \Delta E_S + W \qquad (4)$$

The results of such calculations for Ni-parameters are shown in Fig.1 .

Comparing our results to the atomistic calculations of Wilson and Baskes[1], satisfactory agreement has been found, down to small sizes of HVCs.

In evaluating the helium-binding energy, we use a straight line approximation for evaluating the change in energy content of the HVC; and equation (1) is approximated by:

$$W \simeq -\frac{1}{2}(P_2 + P_1)(V_2 - V_1) \qquad (5)$$

This approach has been chosen because we no longer have a thermodynamic system of constant mass when a helium atom is emitted. By reducing the helium content of the HVC by one atom, we effectively evaluate the energy gained in allowing n-1 Helium atoms expand to a new low pressure.

The helium-binding energy is evaluated by adding the energy of the "Heat of Solution" of helium to the expansion work. Ingelsfield and Pendry[5] concluded that it takes at least 2.07 eV to keep a helium atom dissolved in a Molybdenum matrix. We have used E_H^S= 3.5 eV because no precise value is yet available.

3. NODAL LINE ANALYSIS

Nodal line analysis has been developed for stability studies of kinetic systems. Recently, Russell[6] used the same approach to analyze phase stability under irradiation. We follow here a similar method for the linear stability analysis of helium-vacancy clustering. An important aspect of our work is, that we use vacancy and helium binding energies instead of changes in free energy to describe various HVC

growth and shrinkage processes under irradiation.

We begin by considering HVCs as characterized in a two-dimensional phase space. In such a phase-space, kinetic processes can be represented schematically. An HVC can grow by capturing a vacancy or helium atom ($R^c_{v,h}$), or by emitting a self-interstitial atom(SIA) (R^e_i). Also it may shrink by thermal emission of either vacancy or helium atom ($R^e_{v,h}$), or by capture of SIAs (R^c_i), or by a gas-replacement mechanism (R^{gr}_i) or due to PKA's (R^r_h). The summation of these rates results in corresponding component velocities in phase space, given by:

$$\dot{v} = R^c_v - R^e_v - R^c_i \qquad (6)$$

$$\dot{h} = R^c_h - R^e_h - R^{gr}_i - R^r_h \qquad (7)$$

The rates in equations (6) and (7) are calculated by using quasi steady-state values for C_V, C_i, and C_{He}. In the present analysis we ignore SIA emission.

Ghoniem and Gurol[7] showed approximations for vacancy and SIA concentrations. With knowledge of an effective helium diffusion coefficient[8] as a function of C_V and C_i, we were able to estimate a quasi steady-state helium concentration.

By setting $\dot{v} = 0$ and $\dot{h} = 0$ and plotting the loci of points which satisfy this condition in the helium-vacancy phase-space, we find the helium and vacancy nodal lines. By investigating the trajectories in the vicinity of these nodal lines, regions of growth or shrinkage of HVCs in this phase-space can be determined, as shown in Fig.3 .

We find that:

- In region I, HVCs grow in vacancy but shrink in He-atom content.
- In region II, HVCs shrink in both number of vacancies and He-atoms.
- Region III lets HVCs grow in helium contents but they shrink by a net loss of vacancies.
- Only in region IV do all HVCs experience growth in both number of vacancies and number of He-atoms.

Thus region IV can be termed the "region of stability" which will ensure growth of HVCs. The boundary of this growth region thus separates the stable from unstable HVCs. We can therefore view the HVCs residing on the boundaries of region IV as the "critical HVCs".

4. DISCUSSIONS

Binding Energies

Of particular interest is a comparison between our continuum binding energy calculations to atomistic calculations performed by Wilson et al.[1]. This determines the smallest HVC size to which our continuum approach may still be valid.

A series of 2-D plots comparing our results of binding energies to those of Wilson et al[1] were produced, (see Fig.4). Agreement between atomistic and continuum calculation increases as the size of the HVC increases. From these comparisons, it can be seen that our approach is applicable to HVCs containing as little as 2 or 3 vacancies.

Cavity Nucleation

We have found, using the nodal line analysis/clustering method, that there are two general nucleation modes. In the first one, helium precipitation in bubbles occurs spontaneously (see Fig.2). Very small nucleation barriers exist in this case, and nucleation proceeds homogeneously in the matrix. This occurs under irradiation conditions of high helium generation rates, low temperature, and low sink density. The high helium generation rates tip the competition for vacancies between SIAs and helium atoms in favor of helium atoms. This reduces vacancy anihilation rates and gas-replacement rates by SIAs, and the chance for fundamental

HVCs surviving is enhanced.

The second mode of nucleation is that of delayed nucleation (see Fig.3). Here, cavity formation proceeds with substantial nucleation barriers (such as regions I, II or III in Fig.3), which must be overcome by subcritical HVC embryos, in order to reach stable configurations. This case is best achieved at high temperatures, high dislocation sink density and low helium generation rates. The combination of high temperature and high sink density renders short defect mean-life times. These coupled with low helium generation rates increases SIA's chances in competing against helium for vacancies. These effects (nucleation barriers) suppress the production of stable HVC embryos. Therefore stable HVCs must be produced by some mechanism, such as a stochastic one, able to overcome the nucleation barriers.

Spontaneous and Delayed Nucleation Regimes

To simulate fusion irradiation environments with existing facilities, extensive use has been made of the HFIR, the EBR-II, and accelerators. These facilities differ mainly in their He/dpa ratios. In HFIR the He/dpa ratio is 57 while in EBR-II it is 0.1 at 10^{-6} dpa/sec of damage production.

The basic experimental findings[9] concerning cavities in the temperature range of 300 to 650°C are as follows: (1) In HFIR cavities appear to be bubbles rather than voids, (2) they are about 10 times smaller, and (3) they are 20 to 50 times more numerous in HFIR than voids are in EBR-II irradiated steels.

Scanning a temperature range between 300 and 650°C with other irradiation conditions (He/dpa ratio, dislocation sink density, and dpa) fixed, we were able to trace the loci of points which separate regions of spontaneous from delayed nucleation as a function of temperature and He/dpa ratios (see Figures 5 and 6).

We find (Fig.5) for EBR-II irradiation that all cavity nucleations proceed as "delayed". Nodal line analysis for EBR-II conditions show strong nucleation barriers, such as shown by region II in Fig.3 . Nucleation of critical HVCs is delayed because any size HVC outside of region IV disossociates to subcritical clusters. When the He/dpa ratio is increased, the nucleation barrier, region II, (see Fig.3) is reduced until it vanishes completely. These conditions are met in HFIR experiments where small cavities with a high number density are found.

Deacreasing the dislocation line density shifts the spontaneous nucleation region to higher temperatures and lower He/dpa ratios (see Figures 5 and 6).

Investigating accelerator conditions ($\sim 10^{-3}$ dpa/sec) similar spontaneous and delayed nucleation regimes can be identified (see Fig.6). The basic difference as compared to reactor conditions (10^{-6} dpa/sec) can be seen in the low temperature region. Here we see the reappearance of a nucleation barrier after a minimum between 400 and 500°C. The growth of the nucleation barrier shifts the nucleation mode back into the delayed one. This can be explained by the high re-solution taking place in accelerator environments. As the temperature is increased from 300 to 400°C, the re-solution becomes less significant, because helium capture rates increase with increasing temperature. By further increasing the temperature beyond 500°C, the helium emission rates take over and the nucleation barriers become stronger.

This high temperature behavior of HVC number densities in accelerator environments has been established experimentally[10] as a function of temperature and He/dpa ratios.

The effect of HVC re-solution at lower temperatures (<400°C) can be investigated in the following manner: The dashed line in Figures 5 and 6 represents the same calculations but with the re-solution parameter set equal to zero. In a parametric study we can vary the re-solution parameter. Experiments at low temperatures

could be performed and the best fit of our parametric study would then allow us to deduce a value for the re-solution parameter.

5. SUMMARY CONCLUSIONS:

1. A continuum approach has been used to solve for vacancy and helium binding energies for large clusters which match well with atomistic calculations for very small HVC.

2. Utilizing these binding energies in a nodal-line formulation, critical HVC sizes have been determined as function of He/dpa ratios at various temperatures.

3. Regimes of spontaneous and delayed nucleation have been identified as functions of temperature and He/dpa ratios for both reactor and accelerator conditions.

4. Consistent with experimental results, we always find delayed cavity nucleation for EBR-II irradiation conditions. In HFIR, a transition from spontaneous to delayed nucleation modes occurs at higher temperatures. This is also consistent with experimental findings.

5. In accelerator conditions, we find an upward shift in the demarkation line between spontaneous and delayed nucleation modes by about 50 to 100°C This shift is due to increased dynamic cavity formation processes compared to thermal dissociation mechanisms.

6. The exact temperature separating spontaneous and delayed nucleation regions is sensitive to the re-solution parameter. This fact can be used in experiments designed to measure this parameter.

Figures

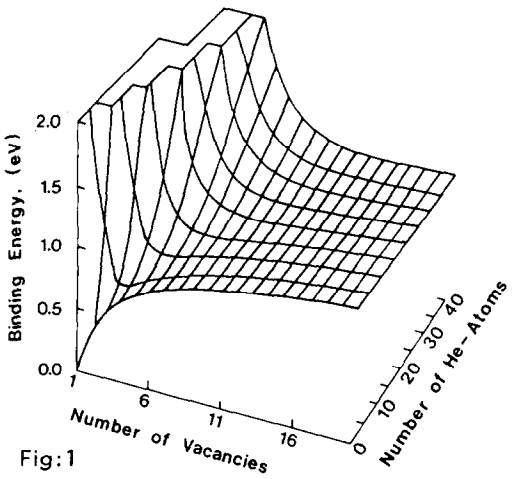

Fig:1

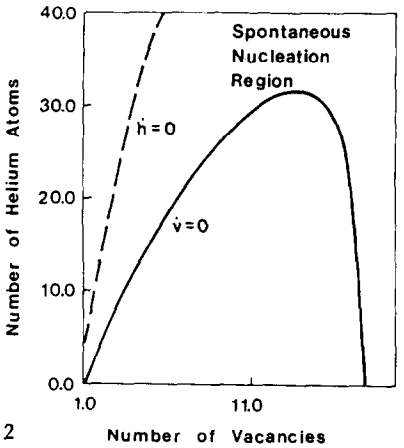

Fig:2

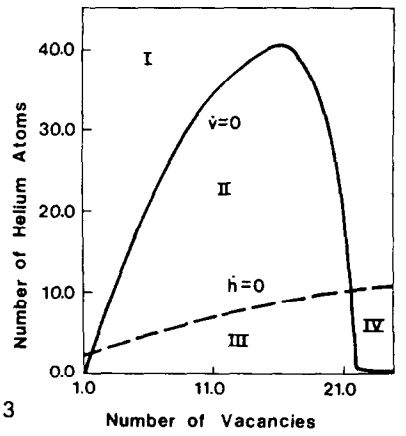

Fig:3

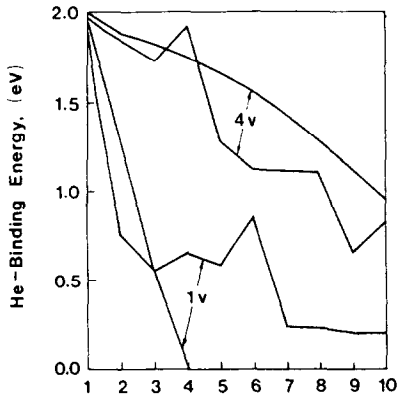

Fig:4

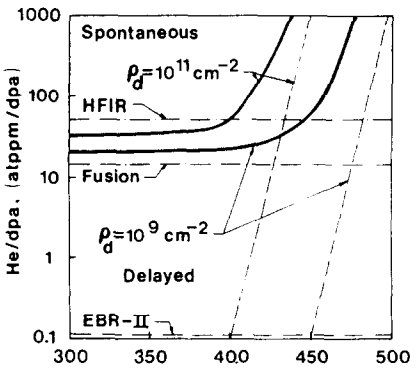

Fig:5

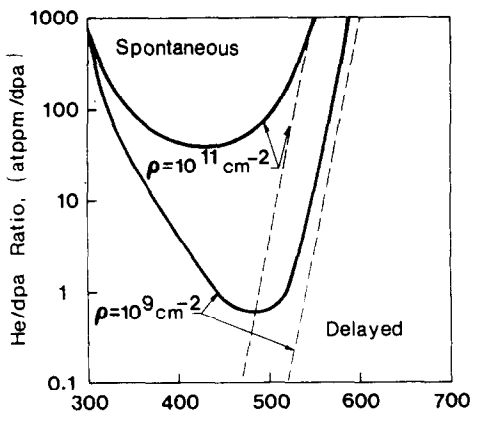

Fig:6

FIGURE CAPTIONS :

Fig.1: Vacancy binding energy to a HVC.

Fig.2: Stability analysis for HVC showing spontaneous nucleation (T = 500°C, = 10^{10} cm^{-2}).

Fig.3: Stability analysis for HVC showing delayed nucleation (T = 500°C, = 10^{11} cm^{-2}).

Fig.4: Comparison of atomistic[1] to continuum helium binding energies to a single-,and to a four-vacancy-cluster. (Continuum-smooth curve)

Fig.5: Nucleation Regime Analysis for Reactor Conditions showing spontaneous and delayed regions (dotted line: re-solution parameter = 0).

Fig.6: Nucleation Regime Analysis for Accelerator Conditions showing spontaneous and delayed regions (dotted line: re-solution parameter = 0).

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