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Recent observations and theoretical approaches for ordering of micro-defects and clusters

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Abstract. Formation of ordered arrays of defects has been observed during irradiation for different irradiation conditions and in a wide class of materials. These range from ordering of void cavities, gas bubbles, solid inert gas bubbles, precipitates and formation of periodic walls of defect clusters. This paper gives a brief summary of these experimental observations and outlines the main features of the theoretical approach based on non-equilibrium stability of the irradiation process.

Keywords. Defects; ordered arrays; micro-defects; clusters; irradiation.

1. Introduction

In recent years a number of experimental situations have been found where micro-defects and clusters like voids, gas bubbles and vacancy dislocation loops formed during irradiation develop into ordered periodic structures (Krishan 1982a; Jaeger *et al* 1987). This ordering process is intimately connected with the irradiation processes itself and is brought about due to the nonlinear defect reactions involving the irradiation-produced point defects and the microstructure. In the first part of this paper we review the experimental results and in the second part we identify the main parameters and features of the irradiation process which cause this phenomena.

2. Experimental observations

There are many features which are common to the different ordering phenomena involving microstructural defects formed during irradiation. In all cases initially the defect microstructure forms randomly and no spatial correlations are observed. Only on continued irradiation, at some critical value of the microstructural sink strength, the ordering process commences. This is marked by long range spatial fluctuations and on continued irradiation, a periodic structure emerges with a well-defined characteristic wavelength. Generally the ordering is observed on ion or neutron irradiation where cascade effects are important. These cascades are formed as a result of localized atomic displacements which result in high local vacancy concentrations involving several thousand vacancies. Some of these cascades eventually collapse forming vacancy dislocation loops which subsequently shrink by absorbing interstitials or by thermal emission of vacancies at higher temperatures (Bullough *et al* 1975; Eyre and English 1982). These vacancy loops play an important role in the ordering process. There are relatively few examples of ordering by electrons where vacancy loops are not formed. However, in these cases, the role of impurities which trap some of the vacancies seems to be important (Fischer and Williams 1977). A second aspect of the ordering process is related to the strong crystallographic effects due to the host matrix in which the ordered structure is formed. Generally the periodic defect structure which is produced has the same crystallographic structure and orientation as the host matrix. In a few cases the periodic defect structure forms along the soft crystallographic directions like [001] in fcc matrices (Jaeger *et al* 1987).Though several theoretical models have been advanced to explain this effect it still remains to be one of the relatively less understood aspects of the problem. We give below some of the cases where such ordering effects have been observed.

2.1 *Void lattice*

One of the earliest observations of defect ordering in radiation environments has been the void lattice formation (Evans 1971). Void lattices (see Krishan 1982 for a review and related references) have been observed in a number of bcc metals like Ta, W, Mo, Cb and Nb. In fcc metals like Al and Ni they tend to form at much higher doses and have also been reported in hcp metals like Mg though with lesser perfection. The dose generally required is about 15 to 70 dpa in bcc metals. The dose rate does not appear to be a drive parameter since they form with both neutron and ion irradiation where the dose rate is different by three orders of magnitude. Alloying does not have a significant effect though small concentrations of impurity gases like oxygen seem to promote the ordering process. The observed lattice spacing ranges from approximately 200 Å to 1000 Å with void diameters in the range of 60–100 Å. Recently superlattices have been observed in Al with a lattice spacing as large as 2000 Å (Horswell and Singh 1987).

2.2 *Gas bubble lattices*

Ordered gas bubbles have been observed in a number of metals like Mo, Cu, Ni, Tc and 316 stainless steel (Sass and Eyre 1973; Johnson and Mazey 1980). These are generally formed during room temperature implantation of inert gases like He and Ne at energies in the range of 30–100 keV and dose range of 1 to 5×10^{17} ions/cm^2. In constrast to void lattices they have a lattice spacing of 30–60 Å and a diameter of 20–30 Å which corresponds to very high densities in the range 10^{18}–10^{19} cm^{-3}. Recently interesting observations have been reported where the gas solidifies due to the high pressures and such ordered solid gas bubbles lattices have been reported by Mazey and Evans (1986).

2.3 *Ordering in alkali earth halides*

In compounds like CaF_2 and SrF_2 irradiation by electrons with 100 keV energy in an electron microscope can produce displacements of flourine atoms by non-radiative energy transfer processes. The flourine atoms form into gas bubbles while the Ca(Sr) anions form ordered precipitates with a simple cubic structure (Chadderton *et al* 1976). Interestingly Ca forms a coherent precipitate and a perfect lattice while Sr forms an imperfect lattice due to slight difference in the Sr and SrF_2 lattices. Ba in BaF_2 has an incoherent precipitate and no ordered structure has been seen in this case. The observed lattice spacing is in the range of 192–283 Å with a precipitate diameter of 20 Å.

2.4 *Periodic defect walls*

One of the very interesting observations made recently is the formation of periodic defect walls in Cu and Ni irradiated by 3 MeV protons at room temperature (Jaeger *et al* 1987). This temperature is well below the void swelling temperature and therefore a large concentration of stacking fault tetrahedra and dislocation loops is observed. These micro-defects which are about 30 Å in size initially form randomly but subsequently order one-dimensionally along [001] habit planes resulting in periodic defect walls with a periodicity of 600 Å. The defect concentration within the walls is very high while the regions midway between are defect-free.

3. Theoretical approach

The ordering of extended defects in radiation environment can be understood as a non-equilibrium phase transition. An initially random or homogeneous state bifurcates at a critical value of the microstructural sink densities to produce a periodic structure. The irradiation process can be viewed as a dissipative system where point defects are continuously produced and dissipated via the various defect reactions. In this paper we will not give a detailed mathematical description of this process which can be found elsewhere (Krishan 1980; 1982a, b) but rather develop the subject qualitatively which will provide an insight into the physical processes involved.

3.1 *Basic rate processes*

Let v and i be the non-equilibrium vacancy and interstitial concentrations. The *net* vacancy fraction (per unit volume) trapped as voids or stacking faults will be represented by Q_1. Similarly by Q_2 we represent the vacancy fraction in vacancy loops and by $-Q_3$ the *net* interstitial fraction arriving at network dislocations which results in their climb during irradiation. Since all the defects produced must either recombine in pairs or must result in fluxes to the extended defect structures, the rates will be subjected to the constraint

$$\dot{i}-\dot{v}=\sum_{q=1,3}\dot{Q}_q. \tag{1}$$

This equation is often further simplified since the point defects which are mobile quickly acquire quasi-steady state equilibrium with the microstructure, so that $\dot{i}=\dot{v}\simeq 0$, and hence

$$\sum_{q=1,3}\dot{Q}_q=0. \tag{2}$$

This equation is strictly valid only for homogeneous microstructural defect distribution. If spatial variations are involved additional point defect fluxes are produced. We will latter discuss some of the consequences of these fluxes which can sustain spatially-dependent periodic states.

The rate $\dot{Q}_q$ of arrival of vacancies and interstitials at the various microstructural components q are proportional to ρ_q the sink density of the microstructural defect and the net difference of the point defect arrival rates. This sink density is a parameter which depends on the average number and size of the microstructural defects and slowly evolves with time and can be algebraically related to Q_q. In the case of vacancy loops, interstitial loops and network dislocations, q can be identified as the dislocation density. Due to this high strain field of interstitials as compared to the vacancies; interstitials have a small preferential bias ΔZ (about 1–10%) to flow to dislocations. Since the total flow rates are constrained by (2) one of the microstructural defects, namely voids, is a neutral sink so that excess vacancies flow to it. Another important parameter which determines the kinetics is ε which is the fractional difference in the production rate of interstitials and vacancies and is usually in the range of 1–4%. Though the vacancies and interstitials are produced in pairs, a small fraction ε of vacancies directly form vacancy loops due to the collapse of cascades, so that these vacancies are no longer available for the diffusion process. It may be observed that ΔZ and ε have somewhat opposite roles, a large bias leads to enhanced growth rates of vacancy type defects while a large ε reduces the growth rate.

3.2 *Spatial instability*

Having introduced the basic parameters we are now in a position to discuss the stability of the homogenous state. Let $\rho_q(x)$ be a small inhomogeneity in the microstructural sink density at a spatial point x. We are interested in examining whether this inhomogeneity will further grow or shrink in the radiation environment. Firstly we observe that the growth rates are directly proportional to ρ_q. This implies that an increase in ρ_q would lead to an increase in the growth rate of the inhomogeneity (and vice versa). On the other hand a large local sink density would lead to increased defect trapping and therefore lowering of the local point defect concentrations. These two factors together impose the condition, that if

$$\frac{\Delta Z}{\varepsilon}\,\frac{\rho_2+\rho_3-\rho_1}{\rho_1+\rho_2+\rho_3} \geqslant 1, \tag{3}$$

then the inhomogeneity will grow. This is in the nature of a 'buoyancy' effect where the microstructural growth rates are inherently unstable to spatial variations for critical relative values of the sink density parameters. Opposing this 'buoyancy' effect is the point defect diffusion flux which we have not taken into account so far and which we now discuss.

The local changes in the vacancy and interstitial concentrations due to point defect diffusion fluxes arising from the spatial inhomogeneity will be given by

$$(\dot{v})_{\mathrm{Diff}} = D_v \nabla^2 v \quad \text{and} \quad (\dot{i})_{\mathrm{Diff}} = D_i \nabla^2 i. \tag{4}$$

We observe that with these additional diffusion terms equation (1) is no longer valid even in a local sense. If δv and δi are the local variations in v and i over a typical length scale of λ then the additional fluxes which would be produced will be of the order of

$$(\delta\dot{v})_{\mathrm{Diff}} \sim -D_v \frac{\delta v}{\lambda^2} \quad \text{and} \quad (\delta\dot{i})_{\mathrm{Diff}} \sim -D_i \frac{\delta i}{\lambda^2}. \tag{5}$$

We have already seen that any inhomogeneity will be amplified under irradiation if condition (3) is satisfied. These diffusion fluxes will on the other hand try to oppose this inhomogeneity. This however depends on the length scale λ. If λ is too small the inhomogeneity will completely decay while for some intermediate value it will attain the highest growth rate. A more detailed analysis shows that a balance is set up when

$$\lambda \sim (\Delta Z/\varepsilon)^{1/2}(\rho_2+\rho_3)^{-1/2}$$

and a periodic structure with this typical wavelength λ can be expected to form. For typical sink densities encountered for example in the formation of void lattices one finds that $\lambda \simeq$ 600–1000 Å in good agreement with experiments.

The difference in the vacancy and interstitial production rates and bias play an important role in destabilizing the homogeneous state. If the cascade efficiency is small ($\varepsilon \to 0$) we observe that λ becomes large and under these conditions no periodic structure is expected to emerge. However since the state still remains to be unstable, an initial microstructural inhomogeneity will be enhanced. This explains why in electron irradiation where cascade effects are absent it is difficult to obtain void ordering. The parameters ΔZ and ε which play an important role in the ordering mechanism can manifest in various ways in different irradiation conditions. For example in the case of small pressurized gas bubbles the bubble strain field will produce a bias for the vacancy and interstitial absorption. At the same time the growth of the bubble forced due to the high gas pressure will result in additional interstitial production mechanism producing again an asymmetry in the defect production rates which is analogous to ε. It is therefore not surprising that a highly pressurized gas bubbles also result in the formation of ordered arrays.

3.3 *Pattern selection*

It was seen that the final defect structure is closely related to the crystallographic structure of the host matrix. Many of the earlier theoretical models were based on this observation to explain the ordering process. However the problem of dynamic pattern formation in the framework of a nonlinear theory has been recently discussed by Schober *et al* (1986) for a model one-dimensional system. In the present case several mechanisms have been proposed. These range from interactions mediated by the elastic anisotropic forces (Willis and Bullough 1969), to models which depend on one-(Woo and Frank 1985) and two-(Evans 1983) dimensional diffusion of interstitials. Though it is evident that such anisotropic effects come into play, the theoretical understanding of this aspect of the problem within the framework of nonlinear defect dynamics is currently being examined.

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