RECEIVED BY TIC JUN 28 1972

COO-3158-7

A CRITIQUE OF L. M. BROWN'S
"A SIMPLE EXPLANATION OF VOIDS IN MATERIALS UNDER IRRADIATION"

by

David N. Seidman and R. W. Balluffi

9 June 1972

Cornell University
Ithaca, New York 14850

MASTER

Report #1810

Issued by

The Materials Science Center

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

124

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

A CRITIQUE OF L. M. BROWN'S "A SIMPLE EXPLANATION
OF VOIDS IN MATERIALS UNDER IRRADIATION"

David N. Seidman[†] and R. W. Balluffi
Cornell University
Department of Materials Science and Engineering
Ithaca, New York 14850

In a recent note Brown (1) has presented a calculation from which he concludes that "an equilibrium array of voids may well be a very general consequence of irradiation to a large enough dose to produce a steady-state". It is the purpose of the present note to refute this conclusion, since this conclusion is based on an erroneous application of equilibrium thermodynamics to a highly non-equilibrium situation.

We begin with a brief description of the formation of voids in a metal which is being irradiated at an elevated temperature (T) where both vacancies and interstitials are mobile. The energetic particles (e.g., fast neutrons) entering a typical specimen produce Frenkel pairs throughout the bulk and tend to establish a "sea" of excess mobile vacancies and interstitials. These defects may be continuously annihilated by mutual recombination, dislocation climb, or precipitation in the form of dislocation loops or voids. It can be shown in a very general manner [e.g., see Balluffi and Seidman (2)] that for a quasi-steady state situation in a system with different types of sinks, the total loss of vacancies to sinks must equal the total loss of interstitials to sinks. Thus, if only one type of sink is present no void growth can occur, while if two or more types of sinks develop (e.g., voids and dislocations), and if there is a divergence in the vacancy and interstitial currents into a particular type of sink, then, and only then, is void growth possible. There is experimental evidence that a small fraction of the excess interstitials precipitates out in the form of dislocation loops during irradiation, and that a small fraction of vacancies precipitates out in the form of voids. This is explained by the fact that there is a preferential drift of interstitials to the dislocations leaving behind excess vacancies which are available to precipitate as voids [see, for example, Norris (3)]. In general, the entire defect system may be regarded as being in a quasi steady-state, since the loop and void sizes tend to increase gradually, and the point defect

[†] John Simon Guggenheim Memorial Foundation Fellow 1972-73.

concentrations tend to decrease gradually due to the increasing sink densities (see, for example, Fig. 3 in Ref. 2). It seems possible that such a kinetic system could eventually achieve a steady-state in which every vacancy would effectively recombine with an interstitial and where no further net dislocation climb or void growth would occur (see final paragraph for speculation on this point).

Brown attempts to find the void configuration corresponding to an assumed steady-state in a system of this type by use of a thermodynamic argument. The starting assumption of his analysis is that a steady-state condition has been achieved in which the defect structure of the specimen consists of a regular array of identical voids of diameter ℓ and a "sea" of vacancies and interstitials. Any effects due to dislocations are neglected. Each void is surrounded by a Wigner-Seitz type cell where the distance between adjacent cell centers is L . Next, an approximate expression for the distribution of point defects is found in each cell as a function of ℓ and L , by solving an approximate steady-state diffusion equation. The total Gibbs free energy (G_{total}) per cm^3 (relative to the crystal in thermal equilibrium) of this system[†] is then given by

$$G_{\text{total}} = \rho_{\text{void}}(L) \int_V \mu_i c_i(r) dV + \rho_{\text{void}}(L) \int_V \mu_v c_v(r) dV + \rho_{\text{void}}(L) \pi \ell^2 \gamma, \quad (1)$$

where μ_i and μ_v are the chemical potentials per interstitial and vacancy, respectively; $\rho_{\text{void}}(L)$ is the density of voids; the $c_i(r)$ and $c_v(r)$ are the radially dependent concentration (cm^{-3}) profiles of the interstitials and vacancies in each cell; V the volume of the cell; and γ is the isotropic surface free energy associated with the void-metal interface. The values of μ_i and μ_v are determined by

$$\mu_i = kT \ln (c_i/c_i^0) \quad (2a)$$

$$\mu_v = kT \ln (c_v/c_v^0), \quad (2b)$$

where k = Boltzmann's constant, and c_i^0 and c_v^0 are the equilibrium concentrations of interstitials and vacancies, so that when the crystal is in equilibrium $\mu_i = \mu_v = 0$. Finally, Brown assumes that in the steady-state the voids adjust their size and spacing so that G_{total} is minimized. He then goes on to find the steady-state void configuration on this assumption.

We wish to point out that the mathematical minimum which Brown calculates does not correspond to the minimum Gibbs free energy of the total system, since his procedure yields a lattice containing concentration gradients. The presence of defect concentration gradients corresponds, of course, to the presence of chemical potential gradients, and the basic definition of thermodynamic equili-

[†] We have reformulated the problem in terms of a Gibbs free energy function and chemical potentials, as opposed to the internal energy function employed by Brown. These refinements do not affect any of the arguments or conclusions of the present note.

brium demands that for the whole system to be in equilibrium the chemical potential of each species must be the same throughout. The procedure that Brown employs yields a local mathematical minimum in G_{total} , since he builds in the presence of concentration gradients and voids throughout the system and finds the values of ℓ and L which minimize G_{total} subject to the condition that the total system is maintained in a non-equilibrium steady-state. The application of an equilibrium thermodynamic condition to such a non-equilibrium situation is incorrect. The "equilibrium" values of ℓ and L which he calculates for the total system are therefore without physical significance.

This same conclusion may be reached by a simple kinetic argument. Suppose that the steady state system visualized by Brown (which is without dislocation sinks or the concurrent nucleation of new point defect precipitates) is suddenly subjected to a step function change in the irradiation rate which is subsequently held constant. The concentrations of point defects would change to new steady state values, and according to Brown, the void structure would also adjust to a new "equilibrium" geometry in order again to minimize G_{total} . However, we see that there is no way in which the void system is able to respond in this manner, since there is no detailed balance between the point defect system and the void system (such as is required in any equilibrium or local equilibrium situation). In the present case equal numbers of vacancies and interstitials are created, equal numbers of vacancies and interstitials are annihilated by mutual recombination, and therefore equal numbers of these defects must join the voids. The voids therefore remain unchanged, and there is no immediate equilibrium relationship between the void geometry and the point defect "sea".

We conclude with a few remarks about how we believe a steady state situation could eventually evolve in practice. First of all, we emphasize that a steady-state can only arise as a result of a combination of kinetic factors which are entirely unrelated to any equilibrium thermodynamic considerations of the type assumed by Brown. As mentioned above, the basic requirement is to achieve a situation in which each vacancy effectively recombines with an interstitial. This could conceivably occur when the void system is sufficiently dense so that the point defect concentrations are low enough so that dislocation loop and void nucleation no longer occur, and every dislocation present intersects a void. Under these circumstances any point defects reaching the dislocations could be quickly transported to the voids by fast dislocation pipe diffusion. Alternatively, any dislocation climb (caused by point defects) which would tend to bow out dislocation segments between the voids could be nullified by point defect currents along the dislocations (induced by line tension) which would tend to straighten out the dislocation segments. The end result in either case would be the effective recombination of every vacancy and interstitial and a complete absence of any net dislocation climb and void growth. It is also conceivable that any dislocation

structure is unstable in the presence of a very dense distribution of voids. Under these conditions a negligible density of dislocations would be present, and the vacancy and interstitial currents entering the voids would be equal. Other kinetic situations leading to this same result undoubtedly exist. The main point is that the steady-state is kinetically determined and not thermodynamically determined as assumed by Brown.

ACKNOWLEDGEMENTS

This work was supported by the U. S. Atomic Energy Commission. Additional support was received from the Advanced Research Projects Agency through the use of the technical facilities of the Materials Science Center at Cornell University.

REFERENCES

1. L. M. Brown, Scripta Met. 6, 387 (1972).
2. R. W. Balluffi and D. N. Seidman, in Radiation-Induced Voids in Metals, edited by J. A. Corbett and L. C. Ianniello, pp. 563-604. U. S. Atomic Energy Commission (1972).
3. D.I.R. Norris, Phil. Mag. 23, 135 (1971).