matters arising

Mechanisms for radiation-induced shrinkage of voids

EVANS¹ has recently reported on the radiation-induced shrinkage of voids in molybdenum and its alloy TZM (Mo, 0.5% Ti, 0.1% Zr). Electron microscope measurements made on 3-mm disks irradiated in a fast reactor at $450 \pm 25^\circ\text{C}$ reveal that initially produced swelling of 0.57 and 0.34% at a total neutron dose of $3.5 \times 10^{26} \text{ m}^{-2}$ equivalent to 17.5 displacements per atom (d.p.a.) reduced on re-irradiation to 0.20 and 0.01% at a neutron dose of $8 \times 10^{26} \text{ m}^{-2}$ or 40 d.p.a. in molybdenum and TZM respectively. A related though opposite behaviour is found in the vacancy type loop structure, typically 5 nm in diameter, whose concentration increased to $6 \times 10^{22} \text{ m}^{-3}$ and $1.3 \times 10^{23} \text{ m}^{-3}$ at the highest dose level in molybdenum and TZM respectively.

Three mechanisms can give rise to negative swelling rates. First, solute atom segregation at the void surface considered by Marwick² which makes the voids biased against vacancies, a possibility discussed by Evans. Second, shrinkage due to thermal emission from voids having a radius less than a critical value^{3,6}, a mechanism which requires high temperatures and is unlikely to be important in the present context. The third mechanism^{5,6}, which is applicable at relatively low temperatures of 450°C and in conditions where vacancy loops are produced, seems to be pertinent for the observations reported for molybdenum and TZM. The trapping of a fraction ϵ of the radiation-produced vacancies as vacancy loops or as impurities would require that a certain minimum dislocation density ρ_{crit} should develop so that the bias Z_i would allow a sufficient number of vacancies to go to neutral sinks like voids. An expression for ρ_{crit} involving the recombination parameter α , dose rate K and vacancy and interstitial diffusion constants D_v and D_i respectively can be obtained within the framework of the BEK model⁷. The voids will therefore shrink if the total dislocation density due to network and loop dislocation is less than^{5,6}

$$\rho_{\text{crit}} = (\alpha K / D_v D_i)^{1/2} \epsilon / (Z_i - 1)$$

The high vacancy migration energy of about 2.0 eV for molybdenum will make

D_v small and ρ_{crit} large at low temperatures. Though accurate values of the parameters are not known an estimate using $\alpha / D_i = 10^{20} \text{ m}^{-2}$, $K = 10^{-6} \text{ d.p.a. s}^{-1}$ and $\epsilon \sim (Z_i - 1) \approx 0.05$ would give ρ_{crit} in the range $10^{15} - 10^{16} \text{ m}^{-2}$. This compares very favourably with the observed vacancy loop densities of $9 \times 10^{14} \text{ m}^{-2}$ and $2 \times 10^{15} \text{ m}^{-2}$ for molybdenum and TZM respectively calculated from the loop size and concentration values reported. The mechanism therefore seems to be relevant for explaining the radiation-induced shrinkage of voids observed by Evans. The reason that the voids should initially grow at these temperatures and dislocation density values needs careful examination and explanation.

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1. Evans, J. H. *Nature* **278**, 728-729 (1979).
2. Marwick, A. D. *J. Phys.* **F8**, 1849-1861 (1978).
3. Krishan, K. *Rep. RRC-12* (Reactor Research Centre, Kalpakkam, 1976).
4. Hayns, M. R. *AERE Rep. R-8806* (1977).
5. Krishan, K. & Nandedkar, R. V. *Proc. Indo-German Seminar on Radiation Damage*, 156-199 (Reactor Research Centre, Kalpakkam, 1977).
6. Krishan, K. & Nandedkar, R. V. *Pramana* (in the press).
7. Bullough, R., Eyre, B. L. & Krishan, K. *Proc. R. Soc. A* **346**, 81-102 (1975).
8. Brimhall, J. L., Simonen, E. P. & Kissinger, H. E. *J. nuclear Mater.* **48**, 339-350 (1973).

EVANS REPLIES—Krishan and Nandedkar correctly point out that negative swelling rates can arise in a situation where a fraction of the radiation-produced vacancies are effectively removed from the system in the form of vacancy loops. Their expression showing the importance of dislocation density is for the mutual recombination dominant regime. For situations where recombination can be ignored but where thermal emission of vacancies from the loops is still negligible it is easy to show that the condition for void shrinkage is given by $\epsilon > (Z_i - 1) / (Z_i + y)^{-1}$, where Z_i is the bias and y is the ratio of void sink strength to dislocation sink strength. This expression may be more appropriate to the molybdenum case if a vacancy migration energy of 1.3 eV (ref. 1) is accepted.

To apply the mechanism suggested by Krishan and Nandedkar to my void shrinkage results² one must, as they point out, explain the growth of voids in the earlier stages of irradiation. In theory this is not too difficult: if one considers the

expression above, an initial high dislocation density (and low y) could allow growth of voids. If the dislocation density remains constant the associated increase in y actually leads to a novel saturation condition for swelling but a subsequent drop in dislocation density would lead to the required void shrinkage. However, this picture is too inconsistent with experimental observations to be seriously considered for the molybdenum situation. One example from the void shrinkage results is the simultaneous large increase in dislocation density contrary to the requirements above, but more generally there is the problem of void growth in molybdenum at temperatures down to 330°C (ref. 3) ($\sim 0.21 T_m$) even when the void sink strength is dominant ($y \sim 10$), and where the Krishan and Nandedkar assumption $\epsilon(Z_i - 1)^{-1} \sim 1$ would imply negative swelling rates. The only easy way out of this dilemma is to accept that in molybdenum $\epsilon(Z_i - 1)^{-1} \ll 0.1$ and in contrast to materials such as 316 stainless steel^{4,5}, assume that the vacancy loops play a negligible part in swelling processes below the $0.3 T_m$ threshold. The differences between cascade collapse behaviour in molybdenum and f.c.c. metals during ion bombardment⁶ apparently support this viewpoint.

The suggestions of Krishan and Nandedkar may have applications elsewhere, for example, in a thermal cycling situation ((A. J. E. Foreman, personal communication) but cannot easily explain the molybdenum and TZM results. I still feel that the explanation already provided^{3,7}—where the segregation of a transmutation impurity (probably technetium) to void surfaces imposes an effective bias on the voids simply by having a low exchange probability for a vacancy—fits the experimental facts reasonably well. Note that this explanation does not depend on the reverse Kirkendall flux that Marwick⁸ has suggested for concentrated alloys. However, it does closely fit the surface energy barrier model recently suggested by Fikus and Johnson⁹.

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1. Balluffi, R. W. *J. nuclear Mater.* **69**, 240-263 (1978).
2. Evans, J. H. *Nature* **278**, 728-729 (1979).
3. Bentley, J. thesis, Univ. Birmingham (1974).
4. Bullough, R., Eyre, B. L. & Krishan, K. *Proc. R. Soc. A* **346**, 81-102 (1975).