Technical University of Denmark

The efficiency of void formation during annealing of irradiated molybdenum

Evans, J.H.

Publication date:
1973

Document Version
Publisher's PDF, also known as Version of record

Risø-M-1641

A. E. K. Risø

Risø-M-1641

Title and author(s)	Date August 1973
THE EFFICIENCY OF VOID FORMATION DURING ANNEALING OF IRRADIATED MOLYBDENUM BY J. H. Evans	Department or group Metallurgy
	Group's own registration number(s)
pages + tables + illustrations	

Abstract

Results are presented to demonstrate the high efficiency of vacancy retention that occurs when voids are formed by the annealing at 900°C of molybdenum samples neutron irradiated at 60°C. In the particular case examined the efficiency is shown to be some 50 times more than the theoretical maximum expected during the formation of voids under conventional high temperature neutron irradiation. Various aspects of this efficiency are discussed with particular reference to a recent position annihilation study of the processes taking place during annealing. A mechanism for the high vacancy retention is suggested that depends largely on the storage of vacancies in loop form during irradiation below the temperature of vacancy loop shrinkage and the transfer of vacancies to voids on annealing above this temperature. There seems to be only a small possibility that the mechanism could operate unintentionally in reactor situations. On the other hand by ensuring void nucleation the high efficiency of void production by the irradiation-annealing method might be used to advantage in providing inexpensive void samples for experimental purposes. Finally, it is noticed in passing that the behaviour of the vacancy loops could provide a simple explanation of the emperical 0.3 T_m threshold for conventional void formation in metals.

Copies to

Prof.A.R.Mackintosh

Dr. F. Juul

Dr. C. F. Jacobsen

Metallurgy Dept. (40)

Library (100)

Abstract to

Available on request from the Library of the Danish Atomic Energy Commission (Atomenergikommissionens Bibliotek), Risø, Roskilde, Denmark, telephone: 03 35 51 01 ext. 334, telex: 43116.

Fr 25-204

1. INTRODUCTION

In a previous paper (Evans, Mahajan and Eyre, 1972) it was shown using electron microscopy that in certain but not completely specified circumstances voids could be produced in molybdenum by the annealing at 900°C of samples neutron irradiated at 60°C to a dose of 5 x 10^{19}n/cm^2. More recently the processes taking place during the annealing have been followed in considerable detail by Petersen, Thrane and Cotterill (1973) using positron annihilation techniques. The low dose irradiation (1.5 x 10^{18}n/cm^2) used in this latter work prompted the present author to re-examine the results of the microscopy work to obtain some measure of the efficiency with which vacancies were retained in the lattice in the form of voids after the annealing treatment. The purpose of this paper is to present these brief results which show rather unexpectedly that this efficiency is some fifty times more than even the maximum possible in the case when voids are formed by conventional high temperature irradiation. The efficiency value obtained thus helps to confirm the interperatation of the positron annihilation results in terms of void formation. Conversely the positron annihilation results throw considerable light on the processes taking place during annealing and enable a reasonable mechanism for the high vacancy retention to be proposed. Consideration of the role of vacancy loops is of particular interest and leads to the conclusion that the temperature of vacancy loop shrinkage by thermal processes is an important one in the proposed mechanism. Below this temperature (at ~580°C in molybdenum) the agglomeration of vacancies into stable loop form during irradiation effectively prevents appreciable void growth (thus explaining the empirical significance of 0.3 T_m as a lower boundary condition for void growth in metals), while subsequent annealing above this temperature can lead to a large fraction of vacancies being transferred from loops to voids. Although the results presented here show that the voidage produced is significant, the mechanism is probably not relevant in reactor situations. On the other hand it is suggested that the high efficiency of void production by the irradiation/annealing method could have some advantages over the conventional method of high temperature irradiation if bulk void containing samples were required.

2. RESULTS AND DISCUSSION

The paper of Evans et al (1972) paid very little attention to the physical parameters of the observed void structures except to attribute the very obvious difference in void density in two samples (figure 2 of that paper) to differences in heating rate during post-irradiation annealing. The void densities and void numbers in these two particular samples together with a third molybdenum sample have now been measured. All the samples were irradiated at 60°C to a fast neutron dose of 5×10^{19} n/cm^2 and then annealed at 900°C in vacuum for periods up to 1 hour. The parameters measured, together with the calculated swelling values,are shown in the table.

	Specimen A	Specimen B	Specimen C
Number density	1.5×10^{16} cm^{-3}	1.0×10^{17} cm^{-3}	7×10^{16} cm^{-3}
Average void radius	37Å	19Å	26Å
Void swelling	0.32%	0.25%	0.51%
Average swelling	0.36%		

There are two important points arising from these simple results. Firstly with regard to the positron annihilation experiment (Petersen et al 1973) where the fast neutron dose was 1.5×10^{18} n/cm^2, a linear extrapolation of the present results could in their case give a void swelling in the region of 0.01% after their anneal to 900°C. This is by no means a negligable amount of voidage and therefore adds useful quantitative evidence to corroborate the analysis of the positron annihilation data in terms of voids.

The second point concerns the efficiency of vacancy retention. According to the "Half-Nelson" model (Nelson et. al 1971) a dose of 5.10^{19} fast neutrons/cm^2 gives0.026 displacements per atom (d.p.a.) in molybdenum; combining this with the average measured fractional voidage of ~.0036 gives a vacancy retention in the samples of around 14%. It is interesting to compare this comparatively large value with the maximum vacancy retention possible under conventional irradiation conditions. Several workers (Foreman 1971, Evans 1973, Brailsford and Bullough 1972) have shown that if void formation results from the preference of dislocations for interstitials then the maximum swelling rate of voids is 1/4 x preference (%) per d.p.a. In other words the efficiency of vacancy retention cannot be more than 1/4% if the suggested value (e.g. Bullough and Perrin 1971) of 1% preference is used. The production of voids by low temperature irradiation and subsequent high temperature annealing is thus in the present case fifty times or so more efficient than the maximum possible under high temperature irradiation. The reasons that might lead to this large difference are not difficult to see: while the high temperature irradiation case depends on a slight preference of dislocations for interstitials to create the vacancy - interstitial inbalance, in the annealing case a massive inbalance is obtained simply because (1) the vacancy and interstitial defects surviving the irradiation are spatially separated into frozen displacement spikes and interstitial clusters respectively and (2) the interstitial clusters form loops which are very stable. Thus the interstitials are effectively removed from the system leaving the vacancies and divacancies in the spikes favourably situated when they become mobile to collapse into loops or voids. On further annealing the interstitial and vacancy components of damage develop almost independently: the annealing of the interstitial component is via a glide and climb mechanism while the development of the vacancy component occurs primarily through bulk diffusion (Eyre and Maher 1971). The two main annealing stages of the vacancy component that leads to the final void population at 900°C have been demonstrated in the positron annihilation results of Petersen et. al. (1973). At 580°C the vacancy loops present begin to shrink and clearly an appreciable fraction of the released vacancies will be trapped at voids. Later at ~750°C the voids will coarsen as the smaller voids shrink by thermal emission. It is not difficult to show by using the appropriate loop and void shrinkage equations (e.g. Eyre and Maher 1971, Smallman and Westmacott 1971) that these temperatures are theoretically in the correct range.

On the other hand it seems difficult at this stage to make sound theoretical estimates of the efficiency with which the vacancies created by the neutron irradiation are retained in the form of voids. Naively one could say that 50% of the created vacancies are annihilated in the displacement spike while further vacancies will be lost in other spikes as the remaining 50% of interstitials hunt around the lattice for sinks. A total loss of 75% during irradiation would leave 25% of the created vacancies free to form voids or loops. On annealing it is not inconceivable that half of the vacancies released from the loops finally end at voids thus giving an overall vacancy retention of 12½%. While no stretch of the imagination could call this a sound theoretical estimate, it does indicate that the measured 14% efficiency is not totally unreasonable.

Besides the possibility that the annealing model can lead to relatively high vacancy retentions other points arise. One of the main ones concerns the important role, brought to light by the positron annihilation results, of the part played by the vacancy loops in storing vacancies until they can be transferred to voids. The necessity for a large fraction of spikes to be nucleated as voids does not now seem so important though clearly some nucleation is essential. The positron annihilation evidence indicates that voids form during the collapse of spikes when the divacancies and vacancies become mobile but it is not impossible that further nucleation takes place when the vacancies are released by the vacancy loops. In either case it is convenient to attribute the nucleation to some gaseous impurity in the metal but it is worth reiterating the experimental fact that in molybdenum the nucleation of the voids appears to be the exception rather than the rule (Evans et.al. 1972). With regard to the positron annihilation study (Petersen et.al. 1973) it is felt that their pre-irradiation anneal in argon at 1100°C (Cotterill, private communication) might have been particularly conducive for the transfer of oxygen impurities from the argon into the molybdenum.

Further consideration of the role of vacancy loops in the annealing mechanism brings the important suggestion that the irradiation temperature need not be below the vacancy migration temperature. Instead it seems that the upper limit is given simply by the temperature at which the vacancy loops thermally evaporate, i.e. $\sim$580°C in molybdenum (Petersen et.al. 1973). Below this temperature the collapse of spikes into loops and voids takes place during the irradiation rather than during annealing but the final transfer of vacancies to voids at higher temperatures will take place exactly as before. Evidence that the collapse of displacement spikes into vacancy loops does take place at high neutron irradiation temperatures in molybdenum has been given in the recent paper by Eyre and Bartlett (1973). They were able to deduce this from the presence of vacancy loops at the end of their irradiation at 650°C. It is significant that their irradiation temperature was near the centre of the vacancy loop annealing stage, 580-750°C in the positron annihilation results.

Whether the extension of the irradiation temperature over which the high vacancy retention mechanism might operate could make the mechanism significant for components in reactors is uncertain. The difficulty mentioned earlier in getting the correct void nucleating conditions together with the correct temperature sequences leads one to suggest that it probably does not. Even if all the conditions were met there must be a limit to the number of vacancies that could be stored in the system as vacancy loops before being later transferred to voids. This would naturally limit the amount of voidage possible by the present mechanism and although the efficiency of the mechanism was high in the present results it could well drop off sharply at higher doses. It would obviously be of particular interest to know how the efficiency would vary with displacement dose and at what point possible saturation mechanisms (such as loop interactions) would begin to operate.

It is interesting to note that the temperature below which the vacancy loops in molybdenum are thermally stable is $0.3\ T_m$, an oft-quoted figure for the lower temperature limit for void formation in metals during conventional high temperature irradiations. This appears to be no coincidence and leads one to the conclusion that the apparent $0.3\ T_m$ threshold could be very easily explained in terms of vacancy loop stability. Below $0.3\ T_m$ the vacancies are trapped as loops and therefore have only a small probability of reaching voids during irradiation, while above $0.3\ T_m$ although the loops still form (Eyre and Bartlett 1973), they quickly release the vacancies back into the system (to voids or dislocations). This explains the suggestion of Eyre and Bartlett that the temperature dependence of void growth will be a function of the temperature dependence of vacancy emission from loops as well as that of vacancy migration. Furthermore the vacancy loop idea fits in well with the model of Kulcinski and Kissinger (1970) who first suggested that the 0.3 T_m threshold was related to the trapping of vacancies.

Finally, returning to the production of voids by irradiation at low temperatures (e.g. below 0.3 T_m) and post-irradiation annealing, if voids are required in bulk materials for basic experimental studies (e.g. mechanical property experiments, etc.) then it would seem potentially attractive to utilize the high efficiency of void production by this method. Instead of forming voids and high activity specimens using high doses of high cost neutrons at high temperatures in fast reactors one could save on time, money and specimen activity by using low doses of low cost neutrons at ambient temperatures in thermal reactors. Choosing the optimum post-irradiation anneal conditions should provide little difficulty but further work would be necessary on each material to ensure that voids were nucleated.

REFERENCES

BRAILSFORD, A.D., and BULLOUGH, R., 1972, J. Nucl.Mat. 44, 121.

BULLOUGH, R., and PERRIN, R.C., 1971 BNES Void Conference Report, Reading. p. 79.

EVANS, J.H., MAHAJAN, S., and EYRE, B.L., 1972, Phil.Mag. 26, 813.

EVANS, J.H., 1973, Radiat. Effects, 17, 69.

EYRE, B.L., and BARTLETT, A.F., 1973, J. Nucl. Mater., 47. 143.

EYRE, B.L., and MAHER, D.M., 1971, Phil.Mag. 24, 767.

FOREMAN, A.J.E., 1971, BNES Void Conference Report, Reading. p. 121.

NELSON, R.S., ETHERINGTON, E.W., and SMITH, M.F., 1971, UKAEA Report TRG 2152 (D) available from H.M.S.O.

PETERSEN, K., THRANE, N., and COTTERILL, R.M.J., 1973, Phil.Mag. to be published.

SMALLMAN, R.E., and WESTMACOTT, K.H., 1971 BNES Void Conference Report. Reading. p. 159.

ACKNOWLEDGEMENTS

The measurements reported in this paper were prompted by the positron annihilation work frequently referred to above. The author would therefore like to thank the authors of this paper together with O. Mogensen, M. Eldrup and B. Singh for discussions on their results. In addition the author appreciates the facilities and hospitality extended to him by Dr. N. Hansen and colleagues during his stay at Risø.