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Comment

Reply to 'Comments on "Behaviour of inert gas bubbles under chemical concentration gradients"'

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Abstract

In reply to the critique of Evans and van Veen, it is pointed out that Evans model of inert gas release suffers from conceptual deficiencies. It is further shown that the experimental evidence is inconclusive on the movement of gas bubbles due to the vacancy gradient caused by the migration of vacancies from surface and grain boundaries towards the bubbles present inside the matrix. Carfully designed experiments on bubble migration under controlled vacancy gradients are needed to resolve various issues arising out of present discussion. © 1998 Elsevier Science B.V.

1. Introduction

In a recent paper [1], Evans proposed that vacancies originating from surface and grain boundaries and migrating to the inert gas bubbles present within the matrix can give rise to a directed up-gradient motion of the bubbles. The present author [2] discussed this proposal in the light of the behaviour of inert gas bubbles in the vacancy flux generated by chemical diffusion. It was concluded that the mere presence of a thermal vacancy gradient is not sufficient to induce bubble migration and the presence of either stress or temperature gradient would seem necessary. The experimental results of Marachov et al. [3] on the behaviour of helium implanted in nickel were also discussed in detail and shown to be consistent with the view point presented in Ref. [2]. In the preceding paper, Evans and van Veen [4] have commented in detail on the various points made in Ref. [2]. In particular, Evans and van Veen conclude that the results of Marachov et al. [3] have been misinterpreted by Tiwari [2]. These authors also present a theoretical calculation of the inert gas profile based on bubble migration which agrees satisfactorily with the experimental data. Further, according to these authors [4] such an agreement provides evidence for the movement of gas bubbles and supports Evans' model [1] on the release of inert gas from UO_2 as well as metals. We shall attempt to show that the criticism of Ref. [2] by Evans and van Veen [4] is not justified.

The plan of this paper is as follows. To begin with, the conceptual problems with Evans model [1] are outlined. This is followed by an alternative explanation for the bubble morphologies and inert gas concentration profiles in the experiments of Marachov et al. [3]. Next the basic assumption made in the calculation of an inert gas concentration profile by Evans and van Veen as well as the results of Pati and Barrand [5] are discussed. Finally, the change of shape and orientation during the migration and the possibility of viewing the bubbles in the diffusion zone are discussed. Important points raised by Evans and van Veen [4] are presented here in the order of their importance as perceived by the author. However, it has not been possible to cover in this article all the issues raised by these authors.

2. Conceptual problems with Evans' model

There are two conceptual difficulties with Evans' model [1]. The first one relates to its basic requirement that the vacancy condensation should take place on bubbles which have acquired equilibrium with respect to size and inert

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gas pressure. It was stated in Ref. [2] that equilibrated bubble will not accept vacancies because they have already achieved equilibrium. Although Evans and van Veen [4] contest this view, no valid arguments have been offered by the authors against this hypothesis. Further, these authors state that "while the total number of vacancies in a bubble in an equilibrium may stay constant, the dynamic nature of vacancy evaporation and adsorption in such a bubble has been known since the classic work of Greenwood et al. [6] and is crucial in the present context". The paper of Greenwood et al. [6] is concerned with the vacancy condensation on the bubbles due to excess vacancies produced through fission induced radiation damage. By inference, it supports the view that, when vacancies are present in thermal equilibrium with the lattice, the vacancy condensation on the bubble surface will not take place. The dynamic vacancy adsorption and evaporation envisaged by Evans and van Veen can only give rise to a random drift of the bubbles. It cannot lead to a directed motion in any particular direction. Another conceptual problem with Evans' model [1] is that the presence of a vacancy gradient by itself is not a sufficient condition for the migration of the inert gas bubble. Thermodynamically what is required is that the chemical potential of vacancies around the bubble must be higher than that in the surrounding matrix which includes the surface as well. This higher chemical potential would then translate itself in a flux of vacancies from the bubble surface to elsewhere in the matrix. According to Geguzin and Krivoglas [7], the velocity of an element of a bubble surface (V_s) as a function of vacancy fluxes is given by

$$V_s = \Omega(J_s - J_\infty), \tag{1}$$

where J_s and J_∞ are respectively the vacancy fluxes at the surface of the bubble and in a region far away from the matrix. If the bubble is in equilibrium and present within the crystal, the chemical potential of the vacancies all over the matrix will be the same and hence there can be no net flow of vacancies between an equilibrated bubble and a free surface. However, as long as the bubble has not acquired equilibrium, it will accept vacancies from the surface and grain boundaries. Dislocations have been found to be ineffective as source of vacancies for the purpose of bubble growth [8].

3. Results of Marachov et al. [3]

The experiments of Marachov et al. [3] were carried on 1.5 mm thick samples of pure nickel implanted with helium at 500 keV. The aim of these experiments was to study the rate of bubble growth as a function of depth beneath the original surface. Cross-sectional examination of the specimen was carried out after annealing at 1023 K to develop the bubbles. Two types of results were reported by Marachov et al.: (a) the development of bubble morphologies and (b) gas concentration profiles. These are discussed sequentially below.

3.1. Development of microstructure

The important observation made by these authors [3] was that the source of vacancies for the bubble growth is the free surface on one side of the bubbles and grain boundaries deep in the bulk on the other side. Another important observation is the reduction in the density of the bubbles in going from 2 to 100 h during anneal. Since this reduction in number is accompanied by an increase in their size and Ostwald ripening is not favoured due to very high heat of solution of inert gases in metal matrices, migration and coalescence seem to have an important role in the growth as well as in the development of the bubble morphology. Homogeneous and heterogeneous nucleation (along dislocations and grain boundaries) are possible at this stage. The bubbles involved in this process of migration and coalescence are very small (in the range of 2–4 nm diameter). Such small bubbles can migrate due to the recovery and recrystallisation process in the matrix as a result of irradiation induced defects and strains.

3.2. Inert gas concentration profile

An important fact which has been overlooked by Evans and van Veen [4] as well as Marachov et al. [3] is that the helium atoms introduced into a metallic matrix are initially lodged into the interstitial sites. This has been observed in copper and the same should hold true for the helium–nickel system as well. According to Thompson [9], the presence of helium in the interstitial sites of copper lattice produced by irradiation of copper–boron alloys is demonstrated by the measurement of the lattice parameter of the matrix as a function of time after isothermal annealing at various temperatures, Fig. 1 [10]. Helium passes through three stages after being generated in situ in the copper–boron alloy matrix. Initially, it is present in the interstitial position and this leads to the increase in the lattice parameter. In the next stage, it gets associated with vacancies and submicroscopic bubbles are nucleated. At this stage, a high percentage of lattice vacancies are locked up in their lattice position through their association with helium atoms. The inward relaxation of atoms around the vacancies causes a decrease in the lattice parameter. This condition is reached through migration of helium atoms as well as vacancies. Finally, after sufficiently long time when all the inert gas atoms are precipitated in the form of gas bubbles, the lattice parameter returns to normal. For the nucleation of the bubble, both interstitial diffusion of helium atoms as well as lattice diffusion of vacancies are important. Interstitial mobility is higher than that of vacancies, hence helium atoms are the first to reach out to the vacancies. Such a process will lead to a shift in the concentration profile of helium atoms towards the vacancy sources. In

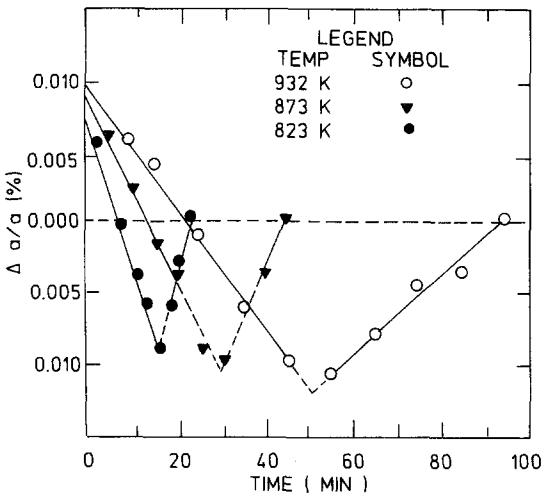

Fig. 1. The effect of annealing on the change in lattice parameter of irradiated copper–boron alloys at various temperatures (after Russell and Hastings [10]).

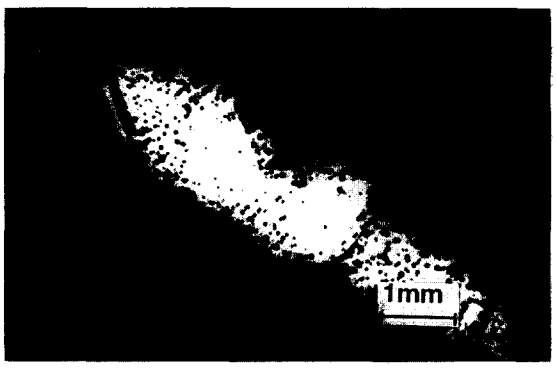

Fig. 3. Microstructure of the irradiated copper-boron alloy heated at 1278 K for 75 h. The picture is taken at low magnification in order to show the entire specimen in a single view. Preferentially higher growth rate at the ends and in the near surface region along the specimen length can be seen. The centre of the specimen is devoid of gas bubbles because the inert gas atoms have migrated to near surface regions of the specimens (after Tiwari and Singh [12]).

the experiments of Marachov et al. [3], the process outlined above will lead to a shift of the concentration profile of helium atoms towards the surface.

These observations are supported by the micrographs shown in Figs. 2 and 3. Barnes irradiated copper crystals with 38 MeV α-particles [11]. This leads to the creation of a helium band at a depth of few μm beneath the free surface. During annealing, the inert gas atoms as well as vacancies migrate and interact to form the gas bubbles. The bubbles' formation and nucleation is taking place preferentially outside the band where helium atoms were originally lodged. This is a proof of the fact that the helium atoms migrate faster than vacancies. Fig. 3 shows the entire cross-section of an irradiated copper–boron alloy wire specimen [12]. Here the helium distribution, which is controlled by the boron distribution, is initially uniform. The bubble growth is absent from the centre of the specimen. It is confined to the ends and the near surface region at the middle sections. There are no bubbles in the central region indicating that the helium atoms have migrated towards the surface. These two examples show that, before the bubbles have grown and acquired equilibrium, there is a considerable movement of helium atoms, which will significantly alter the concentration profile of the helium atoms. Hence, the overall translation of the concentration profile of the helium atoms towards the free surface as well as changes in its character in the experiments of Marachov et al. [3] will be influenced significantly by the diffusion of inert gas atoms and vacancies. It is not necessary to invoke bubble migration for this purpose.

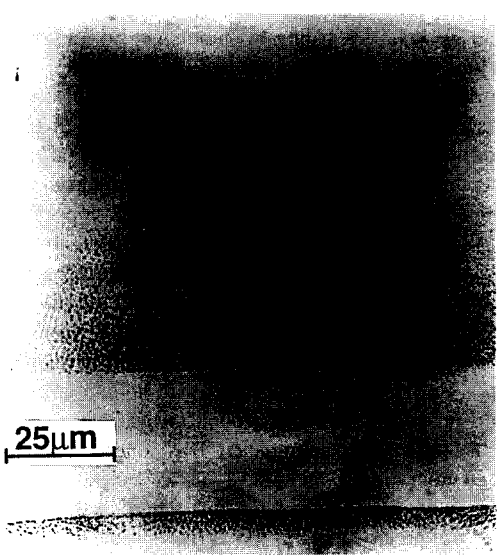

Fig. 2. Photomicrograph of a copper crystal irradiated with α-particles showing the band where helium was initally deposited. The bubble formation and growth are taking place predominantly outside the helium band. Bubble activity is higher on the side which is nearer to the free surface. These features can be explained only through outward migration of helium atoms. Heat treatment is 1 h at 923 K (after Barnes [8]).

4. Modelling of Marachov et al. [3] results

The preceding discussion shows that the development of bubble morphologies as well as the concentration profiles of helium atoms in the experiments of Marachov et al. can be explained by the movement of vacancies and inert gas atoms and their subsequent acquisition by the gas bubbles. Evans and van Veen [4] have theoretically calcu-

lated the concentration profile of inert gas atoms evolved after annealing. As outlined below, these calculations are based on hypotheses which do not seem valid.

(1) The first step in the migration of a bubble mediated by a vacancy is its absorption at its leading edge. The unit step in the bubble migration is completed when this vacancy reaches the trailing end of the bubble through surface or volume diffusion. Since surface diffusion is faster, it will be preferred. If this is so, then the rate of bubble migration will be controlled by surface diffusion and not volume diffusion as assumed in Ref. [4]. The equation for bubble migration used by Evans and van Veen is

$$V_b = -(D_v/2)(dc_v/dx), \quad (2)$$

where V_b is the bubble velocity, D_v is the vacancy diffusion coefficient and dc_v/dx is the vacancy gradient. However, the use of this equation is not justified until it is demonstrated that the rate of bubble migration is independent of its radius.

(2) In a detailed discussion on the stability of inert gas bubbles [13], it has been shown that the equation $p = 2\gamma/r$ (p is pressure, γ is surface tension and r is radius of the bubble) is completely inadequate to characterise the thermodynamic stability of an inert gas bubble trapped within a solid. When the volume of the matrix is constant, the right hand side of this equation contains an additional term to account for the energy changes associated with the volume of the matrix as a result of bubble formation and growth. When the growth of a bubble occurs in unconstrained state of the matrix, the stability criterion is

$$nRT \ln(V_0/V_f) + \gamma \Delta A = 0, \quad (3)$$

where n is the number of moles in the bubble, V_0 and V_f represent the initial and final volume of the matrix and ΔA represents the increase in surface area due to bubble growth. In the experiments of Marachov et al., the nickel matrix containing helium is annealed in vacuum and is therefore unconstrained during the bubble growth. Hence Eq. (3) and not $p = 2\gamma/r$ is the appropriate equation to describe the conditions for the equilibrium of inert gas bubbles. It is, therefore, believed that in view of the invalid assumption made in calculations for the inert gas profile, their significance for Evans' model [1] is doubtful.

5. Change of shape during bubble migration

In general [7], a micropore or gas bubble migrates under the influence of any external constraints only if its different sections are affected by it in varying degrees. Alternatively, the chemical potential of the atom in the peripheral section will not be the same. Another necessary criterion is that the atomic mobility through the surface and/or volume diffusion should be adequate to modulate the migration under the action of the applied constraints.

Fig. 4. Photomicrograph of lenticular and elongated voids in oxide fuel migrating under the influence of temperature gradient roughly normal to the major pore dimension (after Sens [14]).

Both of these conditions preclude the existence of equilibrium shape prevailing in the absence of external constraint. Fig. 4 shows migrating inert gas bubbles in UO_2 [14] which have acquired a lenticular shape during migration.

The motion of gas bubbles in alkali halides was investigated by Geguzin and Simeonov [15]. This system thermodynamically simulates helium in the copper and nickel systems because in either case the bubble is trapped within a crystalline matrix which is chemically inert with respect to the gas present within the bubble. It was noticed that whenever the bubble was in motion, its shape was altered from spherical to elongated geometry. Further, the movement was observed only when a temperature gradient was applied. Whenever the temperature gradient was removed, the bubble became stationary and its original geometrical shape was restored. Therefore contrary to the suggestion of Evans and van Veen [4], a migrating bubble cannot retain sphericity and will undergo change in shape or realignment of its axes. In the experiments of Marachov et al. [3], the bubbles have remained spherical at all stages and hence it is believed that these might have experienced practically negligible extent of migration.

6. Results of Pati and Barrand [5]

Pati and Barrand [5] studied the helium bubble growth in irradiated copper–boron alloys and showed that the rate of the bubble growth varies inversely with the distance

from the external surface, the rate of growth being faster for those located nearer to the surface and vice versa. To explain this observation, the following equation (based on the assumption that the surface is the most important source of vacancies) was derived [2]:

$$dS/dt = D_v \Omega C_{sv}/x, \quad (4)$$

where S represents the swelling at a distance x from the external surface, t is time, D_v is the vacancy diffusion coefficient, Ω is the atomic volume and C_{sv} is the equilibrium concentration of vacancies on the surface. The term on the left hand side of this equation represents the instantaneous rate of swelling at any point in the matrix which varies inversely with its distance from the external surface.

The importance of the results of Pati and Barrand [5] for the present discussion is that they represent a clear cut case of vacancy growth effected by a thermal vacancy gradient. If the migration can indeed occur because of thermal vacancy gradient, it must be reflected in the overall bubble morphology. One of the consequences of the bubble migration towards the free surface will be the decrease in the density of bubbles in near surface areas. However, experimentally, what is observed is that the cross-sectional area occupied by the bubble is maximum near the surface and steadily decreases as the value of x increases, see fig. 6 in Ref. [2]. As before [2], it is again stressed here that the results of Pati and Barrand [5] do not support Evans' concept of thermal vacancy induced bubble migration.

Evans and van Veen [4,16] hypothesize that the incoming vacancies from the external surface are initially absorbed on the surface of the first row of the bubbles. Once the first row of the bubbles is equilibrated, the fresh incoming vacancies are absorbed on the leading side of the bubble, migrate along its surface to the trailing side and finally leave it to be absorbed by the next row bubbles. In this way, these authors [4] postulate the existence of interface between the equilibrated and non-equilibrated bubbles and the parameter x in Eq. (4) is interpreted as the distance between this interface and the free surface. This is an unrealistic assumption and has no experimental or theoretical basis. In Eq. (4), dS/dt represents instantaneous swelling at a distance x from the free surface. In that case x must pass through the centre of the bubble. The difference between these two interpretations of x is shown in Fig. 5. The interpretation of Eq. (4) given by Evans and van Veen [4] is erroneous.

The bubble growth in the experiments of Pati and Barrand [5] is believed to take place as follows. Initially all the bubbles are in a nonequilibrium state and ready to accept vacancies. The matrix surrounding the bubbles maintains a defnite concentration of vacancies which is in thermal equilibrium with its constituent atoms. The vacancies from the matrix condense on the bubbles leading to a fall in the concentration of vacancies below the equilibrium. This decrease in vacancy concentration is made up

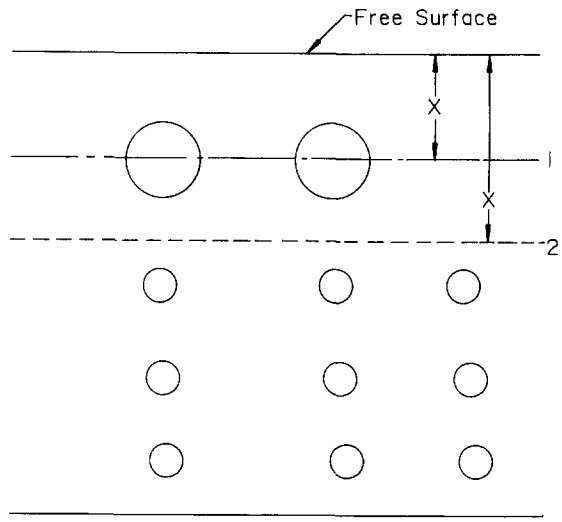

Fig. 5. Two different interpretations of the parameter x in Eq. (4): 1: this paper; 2: Evans and van Veen [4]. The larger bubbles in the figure have achieved equilibrium while the smaller ones are not equilibrated.

by their migration from the free surface to the matrix in the vicinity of the bubbles. The process repeats itself till all the bubbles reach equilibrium. Bubbles in the second row and onwards are growing relatively slowly as vacancies take longer time to reach them because of extra distance involved. Thus bubbles in successive rows grow together albeit at different rates.

7. Migration of bubbles in a concentration gradient

If the vacancy supersaturation exists in a region containing bubbles, they can migrate via surface/volume diffusion. This process has been modelled by Geguzin and Krivoglas [7]. This situation is qualitatively different from Evans' model where the bubbles are located at the lower concentration level of the vacancies compared to the free surface. During chemical diffusion, a bubble present in the diffusion zone will experience vacancy supersaturation due to the differing atomic mobilities of the diffusants such as in a diffusion couple prepared between nickel and irradiated copper–boron alloys [2]. The use of Eq. (2) is valid in these conditions and it can be used to establish the vacancy gradient needed for bubble to migrate by at least 1 μm which is taken as a limit of resolution in fig. 2 of Ref. [2]. The total time of diffusion is 137 h, hence the required bubble velocity is

$$V_b = 10^{-6}/137 \times 3600 \text{ m/s}.$$

Therefore, the magnitude of dc_v/dx needed to move bubble over the desired distances is

$$dc_v/dx = 10^{-6}/2 \times 137 \times 3600 D_v \approx 10^3, \quad (5)$$

where $D_v = 9.55 \times 10^{-16}$ m^2/s is the chemical diffusion

coefficient taken at 60% at.% of Cu. The ease with which the pores have formed in the diffusion zone shows that this degree of supersaturation must have been reached. From the micrographic examination of the diffusion zone, however, it is difficult to discern any evidence for bubble migration. Therefore though the condition for migration up to 1 μm exists in this case, experimental evidence is inconclusive because experiments with inert maker at varying time periods are needed to arrive at a definite answer to this matter.

8. Conclusions

An attempt is made to reply to the most of the basic issues raised by Evans and van Veen in the preceding paper. In addition to the conceptual difficulties with Evans' model [1], it is felt that the results of Marachov et al. [3] as well as those of Pati and Barrand [5] do not provide support for thermal vacancy gradient induced migration of the inert gas bubble. It appears, therefore, that experimental as well as theoretical evidences are inconclusive in favour of bubble migration due to the movement of vacancies from surface and grain boundaries towards unequilibrated growing bubbles.

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