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P.B. Johnson and D.J. Mazey
Metallurgy Division
AERE Harwell, Oxfordshire
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HYDROGEN GAS-BUBBLE STRUCTURE IN PROTON-IRRADIATED
COPPER AT 300 K

P B Johnson and D J Mazey*

ABSTRACT

Transmission electron microscopy is used to investigate the spatial arrangement of the small gas bubbles produced in copper by 16 keV proton irradiation at 300 K to a high dose. The irradiation parameters have been chosen to match those of earlier studies of helium bubble structure in copper at 300 K. In what is a new result for hydrogen bubbles it is found that the bubble structure can be characterised as an fcc superlattice with principal axes aligned with those of the host matrix. The bubble array exhibits a much wider range of bubble sizes and many more structural defects than are evident in the corresponding helium gas-bubble superlattice. For bubbles with diameter ~ 2 nm a bubble lattice constant, a_b , of ~ 12 nm is found for the hydrogen case compared with $a_b \sim 7$ nm for the helium case. There is evidence to suggest that hydrogen bubbles may move apart as they grow. Even within the same grain there are well-defined separated regions in which the average bubble size is much greater than that in the surrounding matrix. These larger bubbles are faceted and are commonly elongated along particular crystallographic directions.

Department of Physics, Victoria University of Wellington
Private Bag, Wellington, New Zealand.

*Metallurgy Division, UKAEA, AERE Harwell, Oxon, UK

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CONTENTS

	<u>Page Number</u>
1 Introduction	2
2 Experimental	3
3 Results	5
4 Discussion	6
5 Acknowledgements	11
6 References	13

ILLUSTRATIONS

Figure 1 Graph showing calculated atom displacements and atom implanted H Cu ratio as a function of range for 16 keV protons in copper.

Figure 2 Transmission electron micrograph of hydrogen gas bubbles in copper following implantation with $\sim 1.3 \times 10^{23} \text{ H}^+/\text{m}^2$ at 300K.

Figure 3 Transmission electron micrograph of helium gas bubbles in copper following implantation with $\sim 4 \times 10^{21} \text{ He}^+/\text{m}^2$ at 300K.

Figure 4 Transmission electron micrograph of a different area of the grain illustrated in figure 2. The selected area diffraction pattern orientation is also shown.

INTRODUCTION

In future controlled thermonuclear reactors (CTR's) of the tokamak type, the first-wall material will be exposed to high fluxes of helium and hydrogen-isotopes as well as to other particles and to electromagnetic radiation. Physical modification of the first wall by radiation damage may lead to adverse changes in plasma performance by affecting gas recycling from the wall and release of contaminants to the plasma (see, for example, ref 1 and the papers listed in section 4 of the same volume). The processes which occur in metals under hydrogen ion bombardment are also of interest in other applications such as in the development of accelerator targets for use as intense neutron sources (2).

Perhaps the simplest accelerator-based studies are those in which an elemental metal is irradiated with monoenergetic ions of a single species. Studies of this sort (3-7) have shown that helium ion irradiation at low temperature $T \lesssim 0.3 T_m$ can result in the formation within a metal of microscopic gas bubbles spatially arranged on a superlattice. At ion doses near the critical dose for radiation blistering of the metal surface, typical helium bubble diameters and bubble densities are ~ 2 nm and $\sim 10^{25}/m^3$ respectively. It is thought that continued helium irradiation may lead eventually to the development of porosity through bubble interconnection (PBJ to be published). In the present work we report the results of a complementary study of the hydrogen bubble structure in copper following proton bombardment to a dose exceeding the critical dose for blistering. The irradiation conditions were chosen to approximate those used in previous experiments on helium bubble

structure. Although it is not usually regarded as a CTR candidate metal, copper has advantages for basic investigations of this sort because it has been the subject of a wide range of both experimental (eg. ref. 2, 5-10) and theoretical studies (eg. ref. 11, 12). Hydrogen is largely insoluble in copper (13) and in this sense it is similar to helium. Thus the use of copper in the study allows the effects resulting from the differences between the two ion species, such as in mobility and in the damage per implanted atom, to be investigated without the complicating factor of a high hydrogen solubility in the host metal.

EXPERIMENTAL

As in the helium studies (5, 6) the target was in the form of foil 200 μm thick cut from Johnson Matthey "Specpure" copper sheet. (The levels of the main impurities do not generally exceed a few ppm). The foil was vacuum annealed for 2 hours at 1000 K, mechanically polished and then electropolished to produce a high surface finish. Irradiation to a fluence of $\sim 1.3 \times 10^{23} \text{ H}^+/\text{m}^2$ was at 300 K in vacuum with 16 eV protons (from the break-up of 48 keV H_3^+) at normal incidence. The damage and implanted atom profiles shown in fig 1 were calculated using the Harwell version (14) of the computer code E-DEP-1 of Manning and Mueller with the electronic and nuclear stopping data of Anderson and Ziegler (15). The calculated values for the mean projected range, the rms spread in projected range and the mean depth of maximum damage in copper are respectively: 118 nm, 35 nm, and 80 nm for 16 keV H^+ ; and 148 nm, 56 nm and 110 nm for 30 keV $^4\text{He}^+$. The rms spread in the

distribution of damage with depth is close to the rms spread in the range distribution in each case, however, these calculations are subject to appreciable uncertainties. For example the experimentally measured mean projected ranges of Terreault et.al. (9) for He in Cu when extrapolated to 30 keV helium energy indicate a value for the mean projected range which is $\sim 12\%$ less than that calculated here. For this reason it was thought not worthwhile seeking a closer match between the corresponding parameters for the two ion-species. The implantation rate used ($\sim 8 \times 10^{18} \text{ H}^+ \text{ m}^{-2} \text{ sec}^{-1}$) was chosen so that the damage rate calculated for the depth of maximum damage ($\sim 5 \times 10^{-3} \text{ dpa sec}^{-1}$) fell in the range covered in the helium experiments.

A disc specimen, 3mm in diameter, was cut from the irradiated foil and a thin section was prepared for TEM examination using a method which has been described elsewhere (6). The aim was to encompass within the specimen thickness both the peak in the damage and the maximum of the hydrogen concentration profile. A Philips EM 301 transmission electron microscope with a high-resolution double-tilt goniometer stage was used at 100 keV for specimen examination under bright-field imaging conditions. To confirm that the features seen had not been influenced by thin-foil effects resulting from the introduction of a back-thinned surface close to the implanted layer, the results obtained were checked by examining the thicker parts of the foil (to an estimated thickness of 300 nm) using the Harwell AE1 HVEM operated at 1 MeV.

RESULTS

The hydrogen bubbles are shown in a near-focus condition in the micrograph of fig 2. Electron diffraction from the selected area showed the electron beam to be incident along (110) in the matrix; the plane of the bubble layer (and of the specimen surface) is therefore (110) for this grain. Considerable bubble alignment is found with bubble rows conforming to crystallographic features in the copper. For example, in fig 2 dense-packed bubble rows can be seen to run in the directions (as deduced from electron diffraction from the matrix) of the matrix (111) planes in the (110) surface plane. Elsewhere, rows are found to run parallel to matrix slip traces and to assume appropriate new directions on crossing grain boundaries. In this respect the bubble structure is similar to that found for helium bubbles produced by 30 keV He^+ irradiation of copper at 300 K to a level of $\sim 4 \times 10^{21} \text{ He/m}^2$ (see fig 3). There are some striking differences, however.

In the helium case the uniformity of bubble size is a feature: the mean helium bubble diameter is 2.0 nm with an rms spread in bubble size of only 0.3 nm (7). For grains in (110) orientation (the most common orientation) there is little variation in helium bubble size either between different areas of the same specimen or between different specimens. For the hydrogen case there is a wide variation in the bubble sizes even within small regions of the same grain. See for example the patch of larger bubbles evident in the micrograph of fig 4. This patch is typical of others found both on the same grain and on other grains in different orientation. These larger

bubbles are faceted and are commonly elongated, with the long axis in the direction of one or other of the traces of the (111) planes in the (110) surface plane for grains in (110) orientation.

DISCUSSION

The bubble rows in the hydrogen case are similar in general features to those seen in the helium experiments (5-7). In the latter case it was possible to confirm by electron diffraction from the bubble array the inference already drawn from the evidence of direct transmission electron micrographs, namely, that the helium bubbles lay on an fcc superlattice with principal axes aligned with those of the host matrix (5). In the hydrogen case, the greater bubble spacings, the higher level of imperfections in the spatial arrangement of bubbles and the wider spread in bubble sizes have combined to prevent conclusive electron diffraction patterns being obtained. While the results of stereo-microscopy are also somewhat inconclusive there are strong indications that the spatial arrangement is three-dimensional in nature, at least in some areas. It should be emphasised however that there are many imperfections, such as unoccupied bubble sites, evident in the array and that the lattice may be less-well developed in the direction normal to the specimen surface.

The bubbles within a particular region are commonly of similar size whereas the average bubble size may vary greatly from one region to another, even within the same grain. (In view of these regional differences it is felt that it would be misleading to quote an average bubble size). It is assumed that bubbles in different regions represent different stages of

bubble development. In particular, the bubble structure, within those regions which contain large bubbles, is thought to have developed from an earlier stage in which the structure was similar to that seen here in the regions where the bubbles are smaller.

In the earliest stage that can be identified, the bubbles are typically ~ 2 nm diameter and are in rows whose measured spacing corresponds to a bubble lattice constant, a_l , of ~ 12 nm. (The method used for calculating a_l is described in ref 6). This value is to be compared with the value of ~ 7 nm found for helium bubbles of similar size (5). When unoccupied bubble sites are taken into account, the nucleation density of hydrogen bubbles arranged on a superlattice of this spacing is estimated to be a factor ~ 10 lower than in the helium case. It is interesting that whereas the calculated damage rates (in dpa/sec) are similar in the two cases, the calculated damage per implanted atom is a factor of 10 lower for the hydrogen irradiation.

There are places in the specimen where the average bubble size is ~ 4 nm and the measured row spacing corresponds to a value of $a_l \sim 26$ nm. This could indicate that bubbles move apart as they grow. (An alternative explanation based solely on bubble coalescence is thought to be less likely). A similar increase in bubble separation has been observed to accompany helium bubble growth under 1 MeV electron irradiation(7).

On the basis of measurements made on copper loaded with hydrogen by quenching from higher temperatures it has been shown (10, 13) that hydrogen becomes mobile around 140 K and may be trapped by certain impurities. Above 170 K hydrogen dissociates from

impurity atoms and may precipitate into bubbles at room temperature. Trapping of hydrogen by vacancies is indicated above 150 K, with no significant detrapping having been observed below 450 K (10). The concentrations of hydrogen and of vacancies produced by quenching are low compared with those which are likely to be built up during H^+ irradiation. For example, in the absence of a large-scale migration of hydrogen from the implanted layer, the hydrogen concentrations would rise to the high values shown in fig 1. The concentration of vacancies produced in displacement collisions could also reach high values. Other differences that may need to be considered in this case include the high stresses and large concentration gradients which can accompany ion irradiations and the possibility of a radiation stimulated movement of hydrogen and of defects.

For the helium case, it has been suggested that the most likely bubble growth mechanism is one in which overpressurised bubbles punch out interstitial dislocation loops (16). Wampler et.al. (13) have observed such loops punched out from hydrogen bubbles in copper at 300 K. In that case the bubbles were roughly spherical and fairly uniform in size with typical diameters of ~ 0.2 to $0.4 \mu m$ and so were somewhat larger than is typical here. It is not clear whether or not the bubbles in the present case will be overpressured since this will depend on the relative numbers of hydrogen atoms and vacancies that have reached the bubbles. However, considering the high mobility and low solubility of hydrogen in copper, it seems a reasonable assumption that the density (in atoms/ m^3) of hydrogen held interstitially in the matrix (in contrast to that held in vacancies) will be no greater

than the density of hydrogen in the bubbles. Under this assumption an estimate of an upper limit on the loading of hydrogen held interstitially in the matrix can be made as follows.

An equation discussed by Evans (16) gives the gas pressure required in a bubble for punching a dislocation loop in terms of the shear modulus of the host metal, the radius of the bubble and the Burgers vector of the resulting loop. The pressure required is greatest in bubbles of the smallest size. For bubbles of radius ~ 1 nm, the smallest size seen in the present case, the gas pressure required for punching a loop in virgin copper has been estimated (17) to correspond to a hydrogen density of 8×10^{28} H atoms/m³ in bubble cavities. (Because of the considerable uncertainties associated with deducing atomic density from pressure at high pressures, this figure should be regarded as providing an upper bound, only). If the interstitial hydrogen in the matrix were at a similar density the H/Cu atomic ratio there would be ~ 1 . For Cu, the interstitial sites for H are the octahedral interstices (18, 19) and it could be expected that at most half these sites would be occupied (see, for example, ref 19). A site occupancy of one-half corresponds to an H/Cu ratio of unity, the same value as that estimated here as an upper bound on the basis of dislocation punching from the smallest visible bubbles. This agreement may be no more than a coincidence, however. Certainly selected-area electron diffraction patterns taken through regions of the specimen containing only small bubbles have shown no obvious evidence of hydride formation.

This estimated upper limit of unity for the atomic loading for interstitial hydrogen should be compared with the atomic ratio ~ 16 that would result if all the hydrogen atoms were to remain at their initial place of implantation in the matrix. Although a large-scale movement of matrix hydrogen from the implanted layer would not be unexpected at 300 K, some hydrogen, particularly that trapped at vacancies and in cavities would be expected to remain. It is known for example, from deuterium depth profiling measurements (2) that appreciable amounts of deuterium are retained in copper at 300 K following 200 keV D^+ irradiation. In summary while it is almost certainly the case that the cavities seen in this work are bubbles rather than voids, it has yet to be demonstrated conclusively that the bubbles are overpressured in the sense that the gas pressures in bubbles are greater than equilibrium values.

There have been many observations of the spatial ordering of voids and the theoretical description of cavity lattices has concentrated almost exclusively on the void case. The basic processes involved in lattice formation are still the subject of debate (20). The analogy between bubble and void lattice formation has yet to be firmly established, but it would be surprising if radically different mechanisms were found to be involved. Although neither individual cavity faceting nor cavity motion have been observed for the void superlattice (20) it would be premature yet to claim that the bubble faceting and the apparent movement of bubbles reported here are indicative of significant differences between the two cases. The following sequence for void superlattice formation has been suggested (21):

- (a) the initial formation of many small, randomly distributed voids;
- (b) the growth of voids, possibly with coarsening from the growth of large voids at the expense of small ones;
- (c) the appearance of local ordered regions where the void distribution happens fortuitously to be favourable; followed by
- (d) the spread of order to adjacent regions.

Various degrees of void ordering have been observed with a two-dimensional array representing an intermediate stage of order (2). The hydrogen bubble lattice seems to fall somewhere between a two dimensional lattice and the fully developed three dimensional array seen in the helium case.

It is interesting that hydrogen bubbles reach a stage of development similar to that of the helium bubbles, only after an H^+ dose which is ~ 10 to 20 times the helium dose. The damage doses are comparable in the two cases. This suggests that it is the rate at which atomic displacements are induced by the primary ion beam rather than the rate of deposition of gas which governs the rate of growth of bubbles. That 1 MeV electron bombardment causes helium bubbles to grow⁽⁷⁾ is further evidence that atomic displacements play an important role in bubble growth. (Some possible mechanisms are listed in ref. 7.). The evidence is still too fragmentary however, to allow the precise mechanisms involved to be identified more clearly.

CONCLUSION

The spatial arrangement of the small gas bubbles produced in copper by 16 keV proton irradiation to high dose at 300 K, is best characterised as an fcc superlattice with principal axes aligned with those of the host metal. The bubble array exhibits a much wider range of bubble sizes and many more structural

defects than are evident in the corresponding helium gas-bubble superlattice. At comparable bubble sizes the density of superlattice-sites available for bubbles in the hydrogen case is a factor ~ 5 less than for helium under similar irradiation conditions; also fewer of the potential sites are occupied by bubbles in the hydrogen case.

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AERE - R 9685 Fig. 1

The dashed curve (left hand scale) gives the damage in atom displacements per atom (adpa) versus depth for 16 keV protons in copper. The solid curve (right hand scale) gives the implanted hydrogen concentration ratio to host atoms with depth assuming that H atoms do not move from their initial place of implantation in the matrix. (The method of calculation is described in the text). The scales are for a fluence of $1 \times 10^{23} \text{ H}^+/\text{m}^2$.

AERE - R 9685 Fig. 2

A direct transmission electron micrograph in near-focus of hydrogen gas bubbles in copper following proton irradiation to a fluence of $1.3 \times 10^{23} \text{ H}^+/\text{m}^2$ (approx) at 300 K. The electron beam is along (110) in the matrix and is normal to the plane of the bubble layer. The direction of the trace of a $(\bar{1}\bar{1}1)$ matrix plane in the (110) plane is indicated by the arrow. The (110) matrix electron diffraction pattern in the correct relative orientation (approx) is appended to fig. 4.

AERE - R 9685 Fig. 3

A direct transmission electron micrograph of helium gas bubbles in copper following helium ion irradiation to a fluence of $4 \times 10^{21} \text{ 30 keV He ions}/\text{m}^2$ (approx) at 300 K. The grain orientation is the same as in fig. 2; the focus condition is similar to that in fig. 2 to aid comparison.

AERE - R 9685 Fig. 4

A direct transmission electron micrograph of a patch of larger hydrogen bubbles in a different part of the same grain as fig. 2. (The specimen orientation and focus conditions are the same as in fig. 2). The arrow gives the direction of the trace of a $(\bar{1}\bar{1}1)$ matrix plane in the (110) plane of the bubble layer as deduced from the selected-area electron diffraction pattern appended beneath. The (110) matrix pattern is from an area, in the same grain, which contains only small bubbles and is shown in the correct orientation (approx) relative to the direct micrograph above.