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A Study of Neutron Damage in Be-doped Copper

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ABSTRACT

The experiments of McIntyre (1967) on the nature of the defects induced by fast neutrons in copper have been repeated, and confirm his result. It is shown that the addition of a small amount of beryllium to the copper does not affect the visible loop density, although beryllium is known to trap interstitials. It is concluded that the interstitial loops cannot be nucleated by the random collisions of free interstitials, but that some other process such as prismatic punching in the thermal spike must be responsible for their creation. Our work provides considerable support for the earlier conclusions of Makin, Whapham and Minter (1962).

§ 1. INTRODUCTION

THE nature of neutron radiation damage in copper has received considerable attention since the first observations of Silcox and Hirsch (1959). Silcox and Hirsch observed black spots after irradiation, and postulated that these were small prismatic dislocation loops formed by the condensation of vacancies. Makin *et al.* (1962) obtained the first loop-size distribution curves for different neutron doses, and noted that homogeneous nucleation could not account for the fact that the density of observed damage was not a saturating function of dose. It was also noted that the damage could be divided into larger and smaller types of defects, and on the basis of considerable indirect evidence, particularly the behaviour of the defects on annealing, Makin and Manthorpe (1963) postulated that clusters smaller than 50 Å in diameter were of vacancy type, whereas defects bigger than this were agglomerations of interstitials.

It appeared possible to verify this hypothesis directly by electron microscopy, but techniques to do this took some time to develop, due to both theoretical and experimental confusion. However, the contrast calculations of Rühle, Wilkens and Essmann (1965) combined with the depth measurement technique of Diepers and Diehl (1966) now make it possible to determine the vacancy or interstitial nature of small defect clusters directly by electron microscopy. The reader interested in the history of this development, together with a summary of the technique, should consult the article by Wilkens (1969): for the purposes of this paper we shall call

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the technique briefly the 'stereo technique' and simply state that under dynamical conditions, a dislocation loop much smaller than an extinction distance in diameter appears to have an image streaked in a direction very nearly parallel to its Burgers vector, and characteristically black on one side and white on the other. Figure 4 shows many examples. If a vector \mathbf{l} is drawn from black to white in the image, then the sense of \mathbf{l} depends both on the depth of the loop in the foil and on its vacancy or interstitial nature. The vector \mathbf{l} changes sign every half extinction distance, and for an interstitial loop has such a sign that $\mathbf{g} \cdot \mathbf{l}$ is positive when the loop lies between the bottom of the foil and $\xi_g/4$ in depth: negative when the loop lies between $\xi_g/4$ and $3\xi_g/4$ in depth, etc. (Here, \mathbf{g} is the operating reflection and ξ_g the corresponding extinction distance.) The object of the stereo technique is to determine the depth of the loop in the foil sufficiently accurately to be able to state whether the loop is vacancy or interstitial in character.

Unfortunately, application of the stereo technique to the problem seems only to have confused the picture. Wilkens and Rühle (1966) obtained the result that the majority of the defects in neutron irradiated copper were of vacancy type, in disagreement with contrast experiments not using the stereo technique by McIntyre and Brown (1966). McIntyre (1967) repeated the determination, using the stereo technique, and confirmed that the loops were interstitial in character: Rühle and Wilkens (1967) revised their technique, but no mistake was found in their work either. Since these measurements, Bourret and Dautreppe (1967) have claimed that the nature of the damage is strongly dependent on the atmosphere surrounding the specimens during irradiation and Rühle, Häussermann, Huber and Wilkens (1968) have found that both types of defect can be present in a given specimen, the larger defects tending to be interstitial in nature.

We have studied the effects of small amounts of impurity upon the nature of the damage, in an attempt to clarify the situation. The reason for doing this was the observation of Kelly and Mayer (1969) that small additions of impurity can greatly affect the number and size of the interstitial loops in neutron irradiated graphite. The impurity selected for our work was Be, because this is known from earlier work to affect the low temperature annealing stages in copper (for a review, see Pugh 1964).

§ 2. EXPERIMENTAL DETAILS

The basic materials were Johnson-Matthey spectroscopically standardized copper 99.998% and beryllium 99.99% purity. A master alloy was made up, analysed chemically, and alloyed in stages to produce alloys of progressively greater dilution. Single crystals 1 cm in diameter were grown under vacuum and annealed afterwards for several hours in an inert atmosphere at 900°C. Chemical analyses of both ends of the crystals were made, the beryllium concentration differing by a factor of less than two at

the two ends. Other impurities were present in a combined total of less than 200 p.p.m.

The irradiations were carried out at the Herald reactor at Aldermaston at a temperature of 40°C under a fast neutron ($E > 1$ mev) flux of the order of 10^{13} n cm⁻² sec⁻¹. During the irradiation the bulk specimens were in direct contact with the reactor water.

After the irradiation, small discs with a $\langle 110 \rangle$ normal were spark machined and then the electron microscope specimens prepared by standard electropolishing techniques. In all cases the 'bottom' surface, i.e. the electron exit surface of each specimen, was marked with small gold islands about 50 Å in diameter. The observations were made in a Siemens Elmiskop I electron microscope, operated at 100 kv. Positive prints were prepared at a total magnification of about 60 000 and the stereo pairs viewed and measured in a Hilger & Watts SB190 mirror stereoscope.

All observations thus refer to single crystal foils of standard foil normal, namely $\langle 110 \rangle$; all neutron doses refer to total fast neutron dose. All concentrations of Be are *atomic* (not weight) per cent.

Since one of the objectives of this work was to improve the accuracy of the stereo technique, some description of our methods is in order. Three factors affect the accuracy of a given depth measurement:

- (1) The magnification of the electron microscope;
- (2) the measurement of the angle of tilt between the two stereo micrographs;
- (3) the precision with which the depth measurements (parallax measurements) can be made in the stereo viewer.

We calibrated the magnification of the microscope using the method developed recently by Murray and Ferrier (1968) and then monitored the objective and intermediate lens currents. Taking into account all uncertainties, the absolute magnification of each micrograph is known to within $\pm 5\%$. The effect of distortions in the image on the final screen was minimized by operating with the projector lens at maximum excitation.

The determination of the tilt angle was always made by using the Kikuchi lines appearing on the diffraction patterns corresponding to the stereo micrographs. First, a Kikuchi map was made around the central $\langle 110 \rangle$ pattern, following the 111, 220 and 200 Kikuchi bands: this method is described in the book by Hirsch, Howie, Nicholson, Pashley and Whelan (1965). A quick comparison between the diffraction patterns and the map enabled us to measure the angle of tilt to within 0.2°. For the usual tilt angles, between 20° and 30°, this means an error in the depth measurement of less than 1%.

The reproducibility and consequently the accuracy of the depth measurements in the stereo viewer can be illustrated by two typical cases. For a defect situated in the first layer (0 to $\xi_g/4$ in depth) a typical set of successive depth determinations is the following: 31, 27, 31, 24, 31, 31, 27, 21, 31, and 27 Å which gives an average value of 28 Å and a most probable

error of 8%. For a defect in the second layer, a set of ten successive determinations gives an average value of 90 Å, determined also within an error of 8%.

In addition to the errors mentioned here, there may be an error associated with the position of the gold islands which mark the surface of the foil, due to an intervening oxide or contaminant layer. Such an effect has been reported by Eades (1969). However, our measurements reported in the next section strongly suggest that in our case the depth of such a layer is less than 15 Å.

§ 3. EXPERIMENTAL RESULTS

Figure 1 shows a set of results for pure Cu and a dose of 5×10^{17} n cm⁻² obtained after considerable practice with the technique. Each box in fig. 1 refers to a single defect whose measured depth from the electron exit surface is plotted in a 5 Å interval. A box on the left-hand side of the vertical line means that the defect had $\mathbf{g} \cdot \mathbf{l}$ positive: i.e. the defect was white in the direction of positive \mathbf{g} . It will be seen, following the rule quoted earlier, that the great majority of the defects are of interstitial type. Furthermore, the accuracy of the technique is such that the 'dead' areas† between each layer can be clearly seen. Reproduced also in fig. 1 are the results of some calculations of McIntyre and Brown (1966) based on the two-beam dynamical theory. They estimated the size of the 'dead' regions by assuming that a defect is invisible if its image nowhere differs by more than 10% from background. The depth of the denuded layer at the surface was estimated by McIntyre and Brown from a number of indirect experiments. The agreement between the size and position of the observed 'dead' areas and the results of the calculations is extremely good, and gives one considerable confidence in the technique and in the theory‡. The experimentally observed extinction distance from these measurements is 240 ± 15 Å, taking into account the errors mentioned above. The calculated two-beam extinction distance for copper is 242 Å, according to Hirsch *et al.* (1965). The good agreement must be fortuitous, in that many-beam effects should reduce the extinction distance, and the tabulated electron scattering factors for copper are not entirely consistent with one another. The earlier work of McIntyre (1967) gave an erroneous value for the extinction distance, largely because of errors in the measurement of tilt angle, but also because of errors in the magnification of the electron microscope.

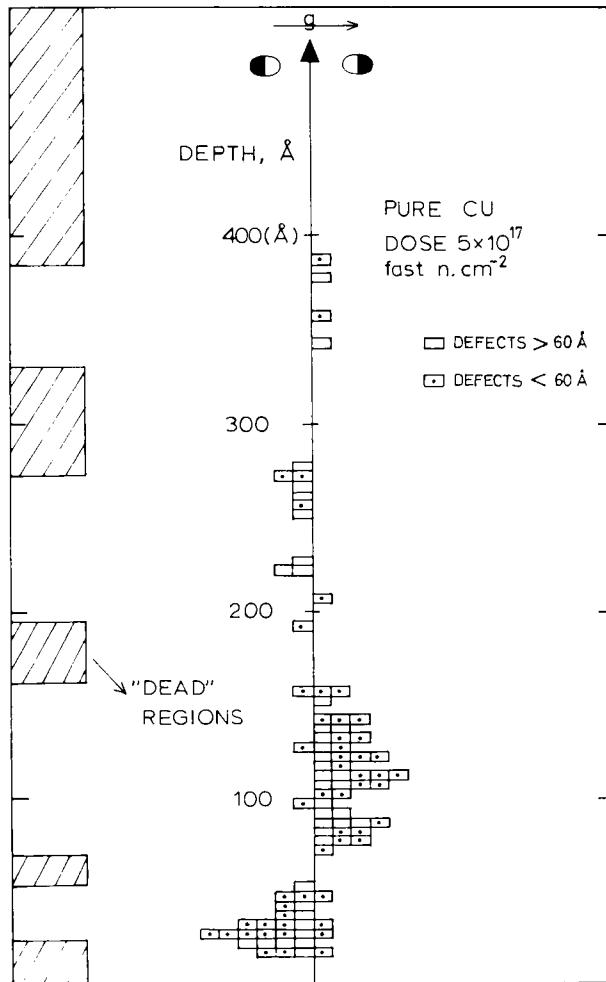
In fig. 1 it will be seen that certain defects run counter to the general trend, in that they appear to have vacancy character. A moment's thought

† i.e. the areas where, because the black-white nature of the contrast is changing, the defect is not visible.

‡ It is worth noting that the ratio of loops with $\mathbf{g} \cdot \mathbf{l} < 0$ to the total number of loops is 0.58 from the data of fig. 1. This corresponds closely to McIntyre and Brown's (1966) value of $f_w = 0.56 \pm 0.02$ for similarly irradiated copper.

shows that this cannot be due to uncertainty in the depth measurement: these defects must truly have vacancy character. They are all less than 60 \AA in diameter, as the data of fig. 1 show, and they form a very small fraction of the total number of observed defects—about 8%. This finding corroborates in a striking way the earlier hypothesis of Makin and his co-workers (referred to in the Introduction) that defects of diameter greater than about 50 \AA are of interstitial character. It appears however still to disagree with the latest results of Rühle *et al.* (1968), for although the work

Fig. 1

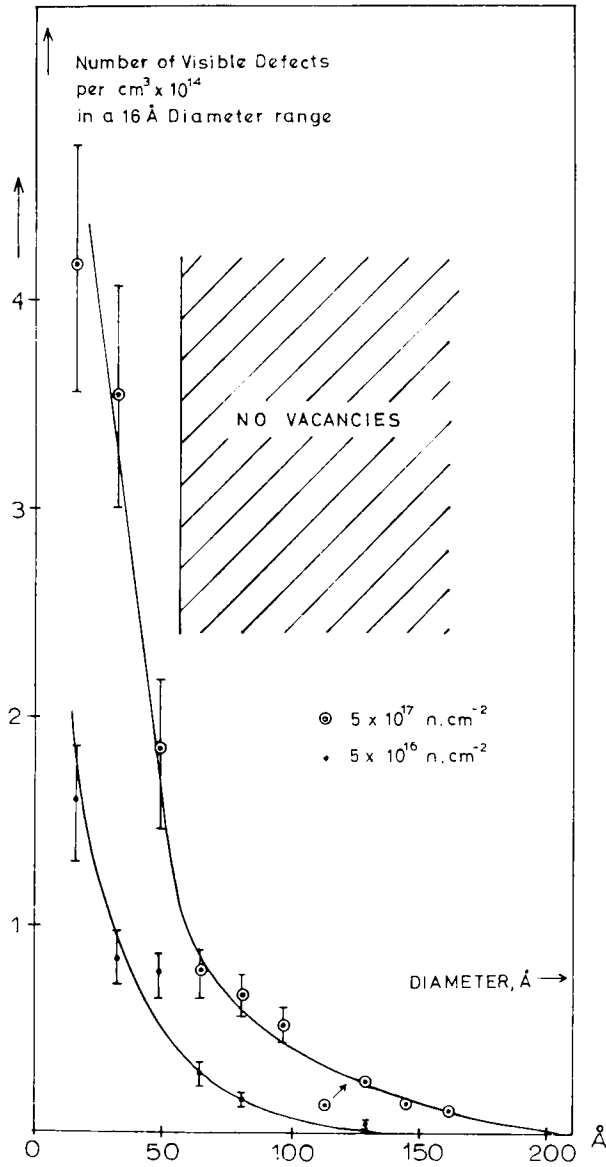


The variation of $1. g$ with depth for defects observed in pure copper. Defects with an image white in the direction of positive g are represented by a box on the left-hand side. The images are from defects near the electron-exit surface of a foil viewed in bright field conditions.

of the Stuttgart school shows a tendency for the larger loops to be interstitial in character, they observe a far greater fraction of vacancy defects than we do.

We have looked for the 'atmosphere effect' described by Bourret and Dautreppe (1967). We irradiated copper specimens 1 cm in diameter and

Fig. 2



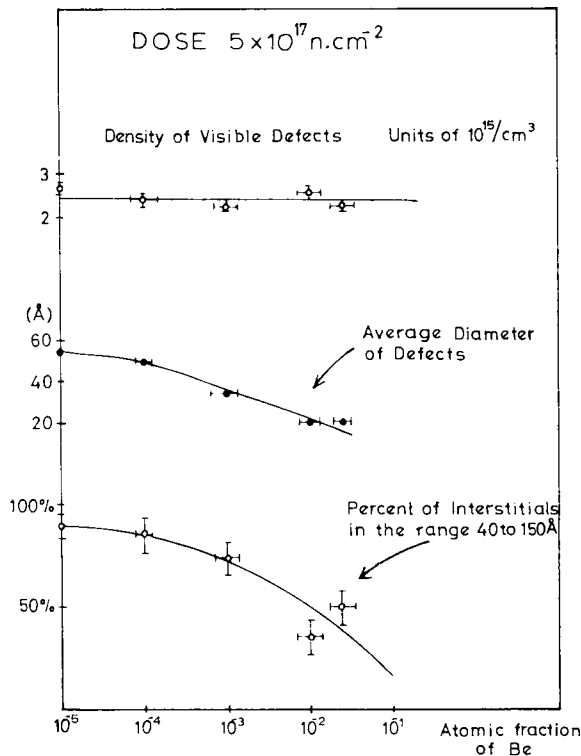
The loop-size distribution observed for two different doses.

about 1 cm thick in helium atmosphere and in air; also specimens whose surface had been tinned or covered with evaporated aluminium. The same results as for the standard irradiation were always obtained.

Our observations of defects smaller than 50 Å in diameter suggest that these are dislocation loops and *not* three-dimensional clusters; they show \mathbf{l} vectors always nearly parallel to the trace of $\langle 111 \rangle$ direction, or (very occasionally) parallel to the trace of a $\langle 110 \rangle$ direction.

In fig. 2 we show the loop-size distribution for two neutron doses. The size of the loop is taken to be its 'diameter'; that is, the width of the image perpendicular to the direction of the \mathbf{l} vector. To find the absolute values of the loop density, the foil thickness was measured by the stereo technique. Figure 2 shows that for both doses, differing by a factor of ten, no loop whose diameter is greater than 60 Å has vacancy character. The data for the higher dose can be compared with those of Makin *et al.* (1962) and agree extremely well if it is remembered that only one loop in four will be visible using a $\langle 111 \rangle$ reflection with a $\langle 110 \rangle$ foil normal. In agreement with Scheidler, Makin, Minter and Schilling (1966) the number of loops with diameter d can be represented by $k \exp(-d/b)$, with the constant b given

Fig. 3



The variation of visible loop density, loop diameter, and percent of interstitial loops, with concentration of beryllium.

by 33 \AA for both neutron doses. The constant k is given by 5×10^{23} visible loops cm^{-4} for the higher dose, and 1.5×10^{23} visible loops cm^{-4} for the lower dose. Our value for the constant b is slightly higher than that which describes the data of Makin *et al.* (1962), namely $b = 26 \text{ \AA}$, indicating that our loop-size distribution contains a somewhat smaller fraction of larger loops than theirs. However, the discrepancy is barely outside the experimental error.

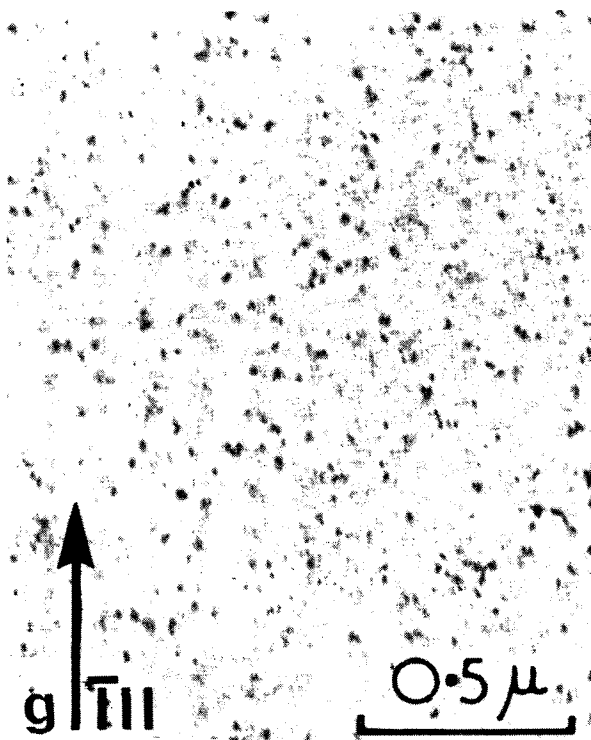
We turn now to the effect of the beryllium additions. The major results are summarized in fig. 3. The total neutron dose was held constant at $5 \times 10^{17} \text{ n cm}^{-2}$, but the concentration of beryllium was varied as described in the Introduction. With the addition of Be,

(a) the total density of visible defects did *not* change, but remained constant at $2.4 \pm 0.3 \times 10^{15} \text{ cm}^{-3}$ (corresponding to a total defect concentration of about 10^{16} cm^{-3} when allowance is made for invisibility due to diffraction contrast effects);

(b) the average diameter of the defects *decreased*;

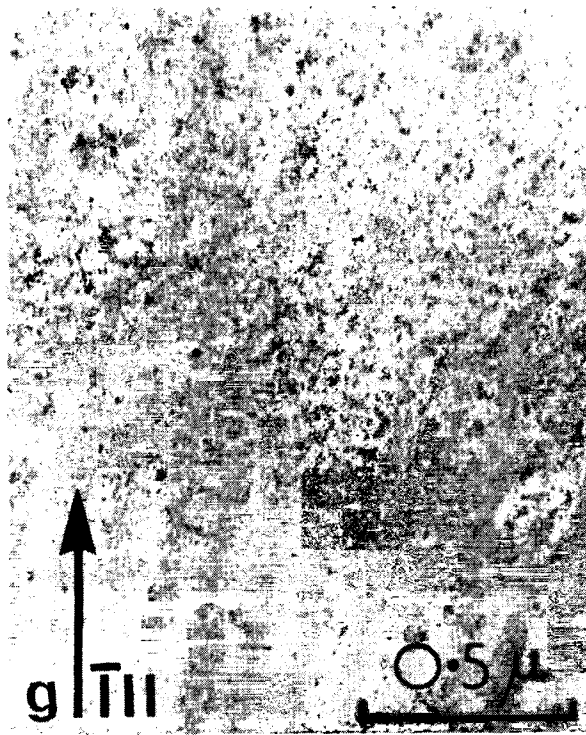
(c) the proportion of defects of interstitial character decreased, but never to below 40% of the total observed.

Fig. 4



(a)

Fig. 4 (continued)



(b)

(a) shows the appearance of the damage in pure copper, and (b) its appearance in an alloy containing 2.4 at. % Be. The thickness of the two foils is similar, and both pictures are taken under dynamical conditions ($s=0$) with $g=111$, foil normal $[110]$. Both foils have been decorated with gold for stereomicroscopy.

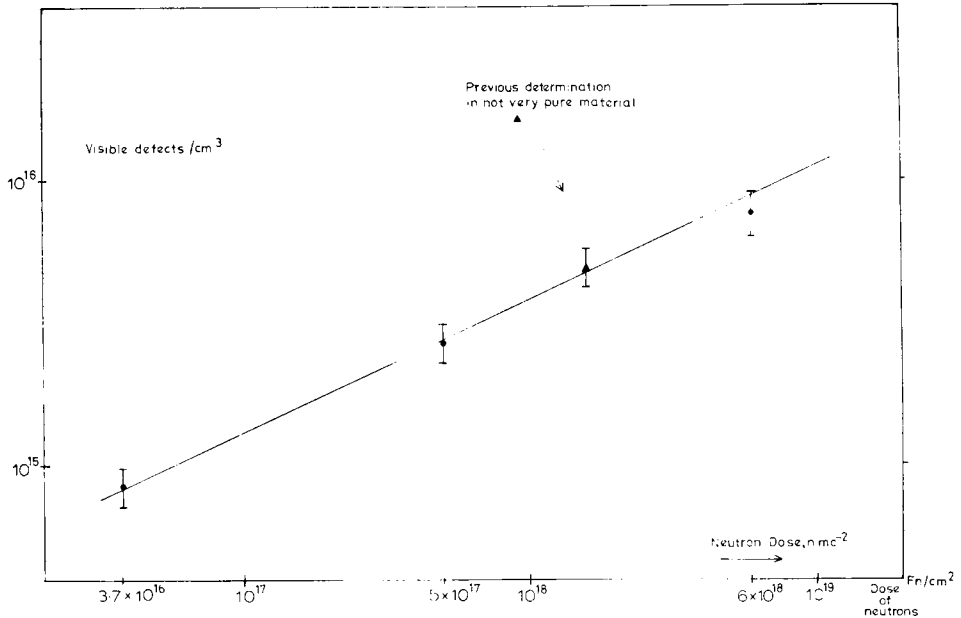
In fig. 3, the 'pure' copper is shown as being purer than the alloy containing $10^{-2}\%$ Be, although the residual impurities in it may well cause it to be effectively of the same purity as that alloy. Only in the alloys of higher Be concentration does the amount of Be dominate other impurities.

The appearance of the damage as a result of the beryllium additions is shown in two micrographs in fig. 4. The direction of streaking of the images does not change; most of the defects have \mathbf{l} vectors parallel to the trace of $\langle 111 \rangle$ directions as before.

Finally, we have studied the dose dependence of the visible defect concentration over a range of doses from 4×10^{16} to $6 \times 10^{18} \text{ n cm}^{-2}$. The data presented in fig. 5 refer to pure copper, but checks on the alloy containing 1% Be showed the same concentration of defects as is observed in the pure copper. The visible defect concentration varies approximately as the one-half power of the dose. This result appears to conflict slightly

with the results obtained by Makin *et al.* (1962) but our data agree quite well (within the experimental error) with the data presented in their fig. 3; however, our range of dose variation is 20 times greater than theirs, and it is clear from our data that the number of visible defects varies much less rapidly than linearly with dose.

Fig. 5



The variation of the number of visible loops as a function of neutron dose.

§ 4. DISCUSSION

The first point to make is that the dependence of the neutron-induced damage on the beryllium concentration in copper is very different from the case of the neutron damage in boron-doped graphite. In the latter case the observations of Kelly and Mayer (1969) and the theory of Brown, Kelly and Mayer (1969) show that the density of visible defects is proportional to the square-root of the impurity concentration. In our beryllium-doped copper, this would mean a variation in the observed density of damage by a factor of at least ten. As fig. 3 shows, such a dependence is not observed.

Brown *et al.* (1969) suggest that a strong impurity dependence of loop density will occur whenever the motion of the defect which nucleates the loops is 'impurity controlled'—that is, when the defect spends an appreciable fraction of its time bound to an impurity. At first sight, then, our data suggest that copper interstitial ions are not strongly bound to beryllium impurities, at least for beryllium concentrations of up to 2%. This interpretation of the data cannot be true. First, as mentioned in the Introduction, the addition of beryllium shifts stage I of the low temperature

annealing stages to higher temperatures; 1 at. % of Be shifts stage I to 200°K. We thus expect interstitials to be strongly influenced in their motion at room temperature by additions of this amount of beryllium. Second, the addition of beryllium affects the *size* of the loops observed, so that the addition of between 0.1% and 1% of the impurity suppresses the formation of the large interstitial loops (fig. 3): clearly the beryllium does have some effect. Third, and most important, in the case of electron irradiation of these alloys, where one imagines that the theory of Brown, Kelly and Mayer will have some validity (Brown 1969), the visible density of interstitial loops depends strongly upon the beryllium concentration in the range 0.1% to 1% at room temperature (M. Ipohorski and M. S. Spring, to be published). It seems that the mechanism of formation of the interstitial loops in the case of neutron irradiated copper is qualitatively different from the mechanism in either neutron irradiated graphite or electron irradiated copper. The interstitial loops must be nucleated directly in the spike itself: neither homogeneous nucleation, nor heterogeneous nucleation (in the sense of nucleation on impurities) can play a significant role. Thus our data strongly support the contention of Makin *et al.* (1962) that the damage event itself produces the loops; the stereo technique enables us to say with more confidence than could be said on the basis of the earlier work that *both* vacancy and interstitial loops result directly from the kinetic energy of the damaging ion.

The picture of the nucleation which most economically leads to this result is the picture of the 'plastic spike' first suggested by Seitz and Koehler (1956). We imagine that the primary knock-on (the copper atom which receives kinetic energy from the neutron itself) generates a number of free vacancies and interstitials, as well as a number of vacancy loops and interstitial loops. The latter are generated in such a way that each vacancy loop is formed with an interstitial loop of equal size, by a process of prismatic punching†. There will be a distribution of loop sizes, the largest loops arising from the largest energy transfers to the lattice. We may tentatively identify the largest vacancy loop observed (about 60 Å in diameter) with the largest of these loops. The free interstitials, and perhaps small interstitial clusters, can migrate; the effect of their migration is to make the interstitial loops *grow* and the vacancy loops *shrink* and disappear. The free vacancies are relatively immobile. Thus, after a long irradiation, the defects are found in the form of large interstitial loops, and, below 60 Å in diameter, in the form of mixed vacancy and interstitial loops. The addition of impurity binds the free interstitials, and prevents the separation of the two loop populations by suppressing the growth of the interstitial loops and the shrinkage of the vacancy loops. In conditions where the free interstitials cannot migrate at all, a population of equal numbers of vacancy and interstitial loops, of maximum size about 60 Å, should be observed.

† The picture we are presenting here differs slightly from the original version by Seitz and Koehler (1956) in that they did not appear to envisage prismatic punching.

Various quantitative statements can be made in support of this model. First, from fig. 2, the number of free interstitials which have migrated to interstitial loops is equal to the number contained in the loop size distribution curve to the right of the critical 60 Å size. For a dose of 5×10^{17} n cm⁻², this is about 10^{19} interstitials per unit volume; this number is a factor of ten less than the number needed to saturate the beryllium impurity (at the rate of one interstitial per beryllium atom) in the 0.1% alloy. This shows that we need not worry about the saturation of the traps.

Second, if the same number of interstitials found their way to vacancy loops as to interstitial loops, this would be enough to remove *all* the vacancy loops, assuming that their average diameter is about 40 Å. Thus we expect to see very few vacancy loops, only those created just before the specimen was removed from the reactor. Of course, large numbers of single vacancies remain.

Third, Seitz and Koehler (1956), in their original treatment, suggested that the diameter of the dislocation loop produced by a 300 eV spike would be about 30 Å. Their calculation is sufficiently approximate that our tentative figure of 60 Å for the largest spike diameter produced in our bombardment cannot be considered to be in major disagreement with theirs.

Although the interpretation we have been giving is extremely attractive, in that a very simple theoretical picture can explain the qualitative features of our results, additional assumptions are necessary to explain the observed dose-dependence of the defect density. A preliminary attempt at a quantitative theory predicts a much greater loop density than is observed, unless small loops are sufficiently mobile at room temperature that a number of them are lost by amalgamation and mutual annihilation. This is not inconceivable, as a number of authors have observed an enhanced concentration of quite large loops in the neighbourhood of dislocations, presumably as a result of loop mobility (see, for example, Scheidler *et al.* 1966).

An interesting consequence of the model of the plastic spike is that one might expect to find a correlation in position between pairs of vacancy and interstitial loops. A preliminary search for such a correlation has been unsuccessful.

We have said nothing about the probable existence of sub-microscopic defect clusters. It is possible to argue that the interstitial loops are homogeneously nucleated, but that the addition of beryllium increases their number and decreases their size in just such a way that the total number visible remains constant. It does not seem possible to dismiss this explanation entirely, but certainly in the case of electron irradiation, the visible density is observed to increase. It therefore seems unlikely that this explanation can be correct.

It now appears that the major discrepancy between the results of different observers of defects in neutron irradiated copper concerns the number of vacancy loops, especially in the very small size range. An up-to-date

account of the work in this field may be found in the paper by Rühle, Häussermann and Rapp (1970). If our model of the damage process is correct, large numbers of isolated vacancies will be present in the irradiated copper. The visibility of these vacancies will depend sensitively on the treatment of the copper during and after irradiation—a few minutes at 100°C should allow many of the vacancies to cluster. Furthermore, the visibility of these vacancies will depend upon the resolution of the microscope. It seems as a result of our work most improbable that the presence of small amounts of impurity can greatly affect the number of large interstitial loops; and on the number and size of these all observers are in substantial agreement.

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