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HELIUM MIGRATION AND PRECIPITATION IN IRRADIATED AND ANNEALED COPPER BORON ALLOY

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ABSTRACT

The paper analyses afresh the data of Russell and Hastings on the changes in lattice parameter during post-irradiation annealing of copper-boron alloy in the temperature range 823-923 K. The changes in lattice parameter are brought about by the generation of helium during irradiation through (n, α) reaction and its subsequent behavior during annealing. The new analytical procedure adopted here follows chemical kinetics route to determine the appropriate activation energies associated with the rate processes controlling the changes in lattice parameter. During the first stage of annealing, the lattice parameter decreases to a value which is below the equilibrium one. The second stage involves the recovery of lattice parameter to the equilibrium value. The diffusion of monovacancy and the jump of helium atom to a vacancy on its nearest neighbor site are identified as the unit processes for the first and second stages of annealing respectively. Finally, it is suggested that a helium–monovacancy complex may act as nucleus for the formation of helium gas bubbles.

Key Words: Helium, Diffusion, Order of Reaction, Precipitation and Bubbles.

INTRODUCTION

The objective of the present paper is to revisit the interesting results obtained by Russell and Hastings [1] on the behavior of helium in a copper matrix produced through (n, α) reaction in irradiated and annealed copper - 0.25 at% boron alloy. The data in the Fig. 1 [1], are unique and provide useful insight into the primordial stages of helium behavior in copper matrix. The figure shows the percentage change in the lattice parameter as a function of isothermal annealing time at temperatures between 823 K and 923 K. Within this temperature range, the change in lattice parameter displays a novel characteristic. At the start of the annealing time, the lattice parameter is higher than the equilibrium value, it being the value for un-irradiated material at room temperature, and thereafter decreases with the progress of annealing. However, the interesting part of this process is that the lattice parameter continues to decrease even below the equilibrium value. After the lattice parameter decreases by about 0.01% below the equilibrium value, recovery starts and ends when the equilibrium value is reached again. Thus the annealing plot at each temperature can be divided in two sections - the first part being associated with the decrease in lattice parameter and the second part with its recovery to the equilibrium value. From phenomenological considerations, it is logical to conclude that two different physical processes are responsible for the decrease and recovery of the lattice parameter as depicted in Fig.1. Using the methodology of chemical kinetics, the present paper attempts to identify the unit processes operating in the two segments. In what follows, we refer to the decrease in the lattice parameter as the forward reaction and the one corresponding to the recovery of lattice parameter as the reverse reaction.

THEORETICAL CONSIDERATIONS

Forward and reverse reactions can be treated as two separate chemical reactions. Any chemical reaction has two facets – thermodynamic and kinetic. The end point of chemical reaction is governed by the free energy of the reactants at the ambient temperature and pressure whereas the kinetics is governed by the law of mass action, which states that rate of a chemical reaction is controlled by the active masses of the reacting substances [2]. As shown below, an analysis of the kinetics of reaction can provide useful information regarding the mechanism of the reaction itself.

A general equation for any chemical reaction can be written as [2],

$$0 = \sum_{B} \nu_B B \ . \tag{1}$$

B is symbol for molecule and ν_B is the corresponding stoichiometric number for the species B. Stoichiometric number is positive for the reactants and negative for the products. The stoichiometric number must satisfy the usual condition for the conservation of atoms and charge for a balanced chemical reaction. The extent of reaction, ξ, is defined by,

$$n_B = n_{B,0} + \nu_B \xi \ . \tag{2}$$

Here n_B is the amount of reactant B at any time *t* during the chemical reaction and $n_{B,0}$ is the amount at the start of the chemical reaction such that ξ is zero when n_B equals $n_{B,0}$. The rate of reaction, K, is defined as:

$$K = \frac{d\xi}{dt} = \frac{1}{\nu_B}\frac{dn_B}{dt} \tag{3}$$

In general, the rate of reaction changes with time since the masses of reactants involved in the reaction undergo a change with time. So long as equation (1) represents a single elementary process, the rate defined in the equation (3) is the same regardless of which species is selected to determine ξ. If the reaction involves more than one elementary process, it is quite possible for one reactant to disappear at a rate quite different from the rate at which other reactants are consumed or the products are formed. However, from the fact that the rate of forward and reverse reactions remains unaltered from the beginning till end, we envisage that only a single elementary process is operating during the forward as well as backward reactions. For a homogeneous reaction occurring in a fixed volume, n_B can be replaced by the concentration *c*, being the amount of the reactant per unit volume. In view of the preceding consideration and the use of equations (1-3), the general differential rate equation for the reaction can be written as,

$$-\frac{dc}{dt} = Kc^n \quad . \tag{4}$$

Equation (4) can be integrated to yield

$$-\int_{c0}^{c} \frac{dc}{c^n} = K\int_{0}^{t} dt \quad , \tag{5}$$

c_0 being the value of *c* at *t*=0 and *n* is the order of reaction. For a zero order reaction, *n*=0. In such a case, equations (4) and (5) give,

$$-\frac{dc}{dt} = K \quad , \tag{6}$$

and

$$c = c_0 - Kt \, . \tag{7}$$

A plot of *c* as a function of time will give a straight line with slope –*K* and intercept c_0. It can be seen from equation (6) that the reaction rate for a zero order reaction is independent of the concentration of the reacting species and time. Equations for higher order reactions can be derived in a similar way from equations (4) and (5). The typical variation of concentration and that of the reaction rate with time for a zero order reaction at any given temperature are shown in Fig. 2.

ANALYSIS OF THE DATA

The data in the Fig.1 have been analyzed in the following way. It is assumed that at any given temperature, the starting point of forward reaction is the point where the lattice parameter is at its maximum, this being the point where the line representing the forward reaction intersects the y-axis. The end point of the forward reaction is at the minimum in the lattice parameter. This is also the starting point of the reverse reaction. The end point of reverse reaction is the point where equilibrium value of lattice parameter is restored. To ascertain the kinetics of forward and reverse reactions, we have to separately determine the rate of reaction at each temperature for both the cases.

The percentage change in the lattice parameter at different time intervals for a given temperature is taken as a measure of the extent of reaction (ξ). It is then plotted against the respective time period. The data fall neatly into a straight line for all the temperatures. Typical plots of ξ for forward reaction as a function of time at the lowest (823K) and highest (923K) temperatures respectively are shown in Figs. 3 and 4. The two noteworthy features of the data in these figures are: firstly the rate of reaction does not change with time and secondly, the slope of the plot is positive. The important implication of these two features is that the rate of reaction does not depend on the amount of reactants. This is typical of a zero order reaction. The slopes of the least square fitted straight lines give the rate constant, K_f, for the forward reaction at the respective temperatures. The magnitudes of K_f at 823K, 848K, 873K, 898K and 923K are found to be $3.501 \times 10^{-4}\ \text{sec}^{-1}$, $4.268 \times 10^{-4}\ \text{sec}^{-1}$, $5.692 \times 10^{-4}\ \text{sec}^{-1}$, $8.276 \times 10^{-4}\ \text{sec}^{-1}$ and $10.7 \times 10^{-4}\ \text{sec}^{-1}$ respectively.

The same exercise is repeated for the reverse reaction by plotting the fractional change in the lattice parameter, considered as a measure of the extent of reaction, at different time intervals for a given temperature against the respective time period. Nature of all these plots is identical with that for the forward reaction. Typical plots of ξ as a function of time at the lowest (823K) and highest (923K) temperatures are shown in Figs. 5 and 6 respectively. The rate constants for the reverse reaction, K_r, at 823K, 848K, 873K, 898K and 923K are found to be 3.4237×10^{-4} sec^{-1}, 5.7154×10^{-4} sec^{-1}, 10.6×10^{-4} sec^{-1}, 16.9×10^{-4} sec^{-1} and 19.3×10^{-4} sec^{-1} respectively.

The above noted reaction rates for both the forward as well as reverse reactions are plotted as a function of inverse temperature to find the activation energy for these reactions. The Arrhenius plots of K_f and K_r are shown in Figs. 7 and 8 respectively and the activation energies for forward and reverse reactions are 0.76 ± 0.05 eV/atom and 1.2 ± 0.1 eV/atom respectively.

The activation energies associated with the two segments of the Fig. 1 can also be determined in an alternative manner. The slopes of the straight lines at each temperature give the rate of reaction for the forward and the reverse reaction. An Arrhenius type of equation for forward as well as backward reaction can be written as follows:

$$K_f = K_{f0} \exp(-Q_f/RT) \tag{10}$$

$$K_r = K_{r0} \exp(-Q_r/RT) \tag{11}$$

K_{f0} and K_{r0} are respectively the frequency factors for the forward and reverse reaction. Russel and Hastings [1] used this procedure. These authors obtained activation energy values of 0.76 eV/atom and 0.96 eV/atom respectively for the forward and reverse reactions. The agreement is satisfactory between the two sets of values.

DISCUSSION

1. Role of Order of Reaction

Wert and Zener [3] were the first to suggest that the process of diffusion is akin to a chemical reaction. Following this, the forward and backward reactions have been treated like a chemical reaction in the previous section. It is indeed gratifying to note that activation energies evaluated by Russell and Hastings [1] through the direct application of Arrhenius formalism match satisfactorily with those obtained by treating the forward and reverse processes as pure chemical reactions. The fair agreement between the two different procedures for evaluating the activation energies justifies the procedure adopted here and supports the hypothesis of Wert and Zener [3]. The procedure adopted here consists of two parts. At first, the order of reaction is determined and then it is followed by the evaluation of activation energy. The advantage of establishing the order of reaction is that one can identify the number of species taking part in the reaction. In the case of reactions involving atomic migrations, this procedure can be useful in determining whether the process of interest is mediated by the movement of single specie or the coordinated movement of two or more species. The significance of this observation will be apparent later during the identification of unit processes associated with the forward and reverse reactions.

2. Role of Surface in the Forward and Reverse Reaction

Irrespective of the temperature of annealing, the end of forward reaction occurs when the lattice parameter contracts by about 0.01% below the equilibrium value. If this contraction were to take place uniformly over the entire specimen, it would require the application of pressure in the range of the bulk modulus for copper. However, the contraction occurs at ambient pressure. Hence, it seems very likely that the contraction followed by relaxation, associated with forward and reverse reactions respectively, is confined to a thin surface layer of the specimen.

Figs. 9 and 10 provide microstructural evidence in support of the observation that the forward as well as the reverse reactions are confined only to the near surface region of the specimen. Fig. 9 shows the microstructure of copper annealed after injection of helium through ion bombardment with alpha particles [4]. The entire bubble activity is confined near the surface region. Fig. 10 shows the microstructure of an irradiated 2mm diameter copper-boron alloy specimen. Here, helium is generated by (n,α) nuclear reaction. This viewgraph has been taken at low magnification so that the whole specimen can be covered. Again, the bubble activity is confined to regions bordering the external surface. Uninterrupted supply of vacancies is essential for the formation and growth of the gas bubbles [5, 6]. Only a free external surface can be a perennial source of vacancies. To a limited extent , the grain boundaries also can serve as a source of vacancies but the line defects such as dislocations and twin boundaries are ineffective in this regard [7]. Therefore, the sections of specimen having easy access to the outer surface experience significantly enhanced bubble activity.

3. Identification of Forward and Backward Reactions

In what follows, an attempt is made to delineate the mechanistic aspects of the forward and reverse reactions in order to identify the physical processes responsible for these reactions. Kinetically, the forward as well as the reverse reactions are zero order reactions; the implication being that both these reactions are mediated by a single reactant. Zero order reactions take place when the reactants, in this case helium atom and vacancy, are present in extreme dilution. This condition holds good for helium atoms whose concentration is approximately 0.012 atom% in the copper matrix [1]. Similarly, the vacancy concentration in copper in the temperature range 823K-923K lies between 1.4×10^{-8} and 1.0×10^{-7} [8]. Thus the criterion of extreme dilution is fulfilled for both the reactants.

In the present case, the irradiations were carried out at 373 K. Interstitials as well as vacancies are mobile at this temperature in copper. Therefore, the helium atoms had sufficient mobility to diffuse within the lattice and occupy octahedral sites which are the energetically most favorable sites for interstitial atoms in an FCC lattice [9]. The lattice dilation of the irradiated matrix can be attributed to this feature. The atomic sizes of copper and helium atoms are nearly the same. Hence, helium atoms could also form substitutional solid solutions. As pointed out by Russell and Hastings [1], the lattice dilation shows that helium atoms have occupied interstitial sites. The heats of solution for the formation of an interstitial and substitutional solid solution of helium in copper are 2.5eV/atom and 5.5eV/atom respectively [10]. Hence, octahedral interstitial site is the preferred site for the lodging of helium atoms.

The unit processes associated with forward reaction can be identified from its activation energy. The magnitude of activation energy for forward reaction, as obtained by our analysis as well as that obtained by Russell and Hastings [1], is 0.76 eV/atom. The activation energy for monovacancy migration in copper is given as 0.70 eV/atom [8]. As stated by Thompson [6], the unit process for the forward reaction can therefore be identified as that of monovacancy migration. The driving force for this process is the strain energy of the lattice caused by interstitially located helium atoms. The presence of a vacancy at the nearest–neighbor site of an interstitial helium atom will reduce the lattice strain energy and lead to the formation of a stable helium-vacancy complex. The multiplication of helium-vacancy complexes within the lattice will cause an inward relaxation of copper atoms giving rise to a (instead of the) reduction in the lattice parameter. In a crystalline matrix, the vacancy constitutes an equilibrium defect. Accordingly, the vacancies are always maintained in a fixed concentration which is governed by the ambient temperature and activation energy for the vacancy formation. Therefore, if the vacancies are consumed in any process taking place within the matrix, they are regenerated and the concentration is restored to its equilibrium value. This allows the vacancy mediated reaction to continue in an uninterrupted manner till the availability of the driving force.

Fig.1 shows that the progressive decrease in the lattice parameter continues unabated even after the lattice parameter has reached its room temperature equilibrium value. Further, the rate of decrease in the lattice parameter remains unchanged throughout the forward reaction. This behavior may be attributed to the continued availability of driving force for the forward reaction even after the lattice parameter has acquired its equilibrium value. With the continued inward relaxation of copper atoms, accompanied by a decrease in the lattice parameter, the lattice strain energy goes on getting diminished. The process continues till all the interstitial helium atoms get attached to the vacancies and the lattice strain is minimized. This stage marks the completion of forward reaction.

At this stage, it is important to rationalize as to why the forward reaction continues even after the lattice parameter has acquired the equilibrium value of the un-irradiated copper boron alloy. The total amount of inward relaxation is approximately 0.02 %. Of this, nearly 50% of the relaxation occurs before the lattice parameter has reached the equilibrium value of un-irradiated matrix and the rest of it happens after this stage. Thus, the accretion of vacancies around the interstitial atoms should account for the net inward relaxation of nearly 0.02%. The atomic size of copper and helium atoms are roughly the same[1]. According to Lomer [10,11], the self-interstitial in copper causes an elastic strain equal to twice the atomic volume of copper. Hence, at least two vacancies per helium atom are needed to release the total elastic strain associated with the interstitially located helium atom. All the sites around the interstitially located helium atoms are equally preferred energetically and the forward reaction will continue with vacancy migration in a random manner till all the elastic strains are released. Attainment of equilibrium value of the lattice parameter also coincides with the restoration of fifty percent of net relaxation which is recovered at the completion of forward reaction. Since two vacancies per helium atom are needed for total inward relaxation, each interstitial atom, on an average, has been joined by a lone vacancy when the lattice parameter has acquired its equilibrium value. The forward reaction via migration of monovacancies continues till each helium atom is joined by two vacancies on its nearest neighboring lattice sites. Such a combination of two vacancies is called divacancy. It thus appears that the reason for the continuance of forward reaction after the lattice parameter has acquired its equilibrium value is the random accretion of vacancies to the interstitial helium atom.

The inward lattice relaxation caused by one atom percent of single vacancy is approximately 0.6 percent [12]. At the rate of two vacancies per helium atom, the concentration of vacancies in the matrix at the end of forward reaction is nearly 0.024%, the concentration of helium in the lattice being 0.012 atom% [1]. Hence, total decrease in lattice parameter due to inward relaxation around vacancies at this level of vacancy concentration is estimated to be 0.0144%. The agreement between the experimentally observed lattice relaxation and the estimated value is considered satisfactory for the following reasons:

(a) The end point of forward reaction is centered at the decrease of 0.01% in the lattice parameter. At the lowest annealing temperature of 823 K, this parameter is about 10% higher than the mean value of 0.01. At the highest annealing temperature of 923 K, this value is nearly 20% lower.
(b) The theoretical estimates of inward relaxation of atoms around vacancies may be accurate within a limit of only 10 %.

On the basis of the preceding discussion, we may conclude that the end product of the forward reaction is a helium interstitial bound with a divacancy located at its nearest neighboring site, as shown in Fig. 11(a). This observation is the starting point for identification of the unit process responsible for the reverse reaction.

In the present context, the two species which could be instrumental in mediating the reverse reaction are a vacancy and the helium atom. Because of the qualification of zero order reaction associated with the reverse reaction, we have to select only one of these two entities. If the reverse reaction is attributed to the addition of vacancies to helium-vacancy complex formed during forward reaction, it would lead to further inward relaxation of neighboring lattice and continued decrease in the lattice parameter while the reverse reaction is associated with an increase in the lattice parameter. Hence, this suggestion must be discounted. Our own analysis yields 1.2 ± 0.1 eV/atom as the activation energy for reverse reaction . Russell and Hastings give a value of 0.96 eV/atom. These values are 71% and 37% higher than the activation energy for monovacancy migration in copper [8]. On this ground also, we can discount vacancy as the agency responsible for recovery of lattice parameter during the reverse reaction. Therefore, we conclude that the reverse reaction is mediated by the migration of helium atom. To complete the identification of the unit process for reverse reaction, the nature of this migratory step needs to be elucidated.

At the beginning of the reverse reaction, all the helium atoms are located in the interstitial sites. Then, the helium atoms taking part in the reverse reaction can go either to an interstitial site or to a lattice site adjoining the helium-vacancy complex. One of the ways a helium atom can go to a lattice site is via interstitialcy mechanism. Interstitialcy mechanism involves knocking off a lattice atom by the migrating interstitial atom. The interstitial atom involved in the process then occupies the lattice site held earlier by the knocked out lattice atom and leads to the creation of a self-interstitial. The creation of a self-interstitial in copper requires an activation energy of nearly 4.5 eV/atom [13,14]. Hence, the creation of a self-interstitial in copper is not feasible in equilibrium conditions. In addition, helium atom itself will not have sufficient energy to knock off a copper atom from its lattice site. In metals like copper, self-interstitial can be created only by irradiation with energetic beams. The possibility of helium atom occupying a lattice site via interstitialcy mechanism is therefore, practically, negligible. As the helium and copper atoms have nearly the same size [1], the activation energy for diffusion of helium atom via interstitial mechanism would be the same as that for copper self-interstitial. This parameter has a value equal to 1.5 eV/atom [13,14]. Hence, the helium atom migrating to the neighboring interstitial site will require activation energy equal to 1.5 eV/atom. Besides the fact that the reverse reaction is associated with the activation energy of 1.2 eV/atom, contraction of lattice would not be nullified if the helium atom were to shift from one interstitial site to another.

The possibility exists that the helium atom can occupy one of the lattice sites occupied by its two neighboring vacancies. The energy required for this migratory step would be smaller than that for helium diffusion via interstitial mechanism because the absence of two atoms from the nearest neighboring sites will lower the repulsive energy at the saddle point. In the absence of any evidence to the contrary, it may be presumed that 1.2 eV/atom is the energy required for jump of an interstitial helium atom to one of its neighboring vacant lattice site. Figure 11(a) shows schematically the migration of helium atom from its interstitial position to one of the nearest neighbor lattice vacancy, which is a constituent of the divacancy. After the migratory jump, helium atom occupies a substitutional site and has one vacancy as its nearest neighbor, as shown in Figure 11(b).

We may conclude from the preceding discussion that the end product of the reverse reaction is a complex consisting of a helium atom present as substitutional impurity and a vacancy on one of its nearest neighboring lattice sites. In a discussion of nucleation of inert gas bubbles in uranium and its alloys inside a nuclear reactor, Greenwood et al. [15] suggested that this nucleus is likely to be formed by two inert gas atoms and a vacancy. In their case, there is a continuous supply of inert gas atoms and creation of defects due to <u>the</u> ongoing fission of uranium atoms. The nature of bubble nucleation during post-irradiation annealing could, therefore, be different from that occurring inside a nuclear reactor. The net helium content in the matrix is 0.012% [1]. Hence, at the end of the reverse reaction we also have the same number of vacancies in copper matrix. At 0.6% of lattice relaxation per atom percent of vacancy, 0.012% of vacancies would cause shrinkage of approximately 0.0072%. This figure is about half the total shrinkage observed at the end of forward reaction and 3.6 times higher than the estimated accuracy of (remove 'the') measurement of the lattice parameter [1]. However, this shrinkage could be mitigated to some extent on account of the following consideration.

The electronic configuration of outer electronic shell in copper is $3d^{10}s^{1}$. The lone s-electron goes to the conduction band and <u>the</u> lattice atoms have completely filled d-shell as the outermost orbit. Similarly, as an inert gas, helium atoms also have completely filled outer shell with extremely high ionization energy in the range of 10-25 eV. Hence, the outermost $1s^{2}$ orbit of helium atom and completely filled d-shell of copper atom would repel each other. Helium atom will not interact with neighboring copper atoms to form hybridized orbitals unlike any substitutional metallic impurity. This could reduce to some extent the inward relaxation of the copper atoms surrounding the vacancy. The point is that the inward relaxation brought about by a lone vacancy may be reduced by the presence of an inert gas atom on one of its neighboring sites.

We have noted above that the end result of forward reaction is the formation of a complex consisting of an interstitial helium atom associated with a divacancy. Russel and Hastings [1] as well as Thompson [6] have stated that the migration of this complex is the unit process responsible for the reverse reaction. This proposal can be discounted on the basis of following reasons:

(a) Our analysis of the data shows that the reverse reaction, similar to the forward reaction, is mediated by a lone agency and not a complex consisting of more than one entity.
(b) The migration of a complex consisting of a helium atom and a divacncy would require the migration of helium atom and one of the vacancies. Energetically, these twin jumps cannot be accomplished with the activation energy of 1.2 eV/atom, the value experimentally found to be associated with the reverse reaction.

Russel and Hastings [1] have commented that the rate of forward and backward reaction decreases with time. This is factually incorrect since the rate of change of lattice parameter during forward as well as backward reaction remains unaltered till the end. Russel and Hastings [1] further stated that the recovery of lattice parameter during reverse reaction is due to the diffusion of residual helium atom to the helium-divacancy complex and formation of gas bubbles through coalescence of these complexes. As discussed above, there are no free helium atoms available at the end of forward reaction and the migration of helium-divacancy complex is not favored on energetic considerations. Moreover, the vacancy must be consumed during reverse reaction, as lattice contraction is reversed and lattice parameter is restored to its equilibrium value. These criteria are met by the unit process for the reverse reaction identified as the migration of interstitial helium atom to one of its nearest neighbor vacancy.

Finally, the present authors believe that the nucleus of a helium gas bubble in an irradiated and annealed copper-boron alloy comprises of a helium atom-monovacancy complex. This nucleus is stable against thermal fluctuations, as its break-up will lead to the formation a substitutional helium atom which requires a net activation energy of 4.48 eV/atom; 2.5 eV is required for the creation of a random substitutional helium atom and 1.98 eV which is the activation energy for self-diffusion in copper [8]. The later value is selected because copper and helium atoms have the same size. On account of such a high heat of solution, the nucleus will remain stable even up to the melting point of copper. This nucleus may grow by the acquisition of vacancies from the surface. Gradually, this nucleus will convert itself into a bubble, i.e. void containing inert gas atom. The transformation of a helium-vacancy complex into a bubble requires investigation. Finally, by combining Russell and Hastings [1] types of lattice parameter measurement after isothermal annealing of irradiated material, with high resolution electron microscopy and concomitant monitoring of electrical resistivity, useful and interesting information can be gleaned on the mechanism of formation and precipitation of inert gas bubble in crystalline matrices.

SUMMARY

The data of Russell and Hastings on the changes in lattice parameter during post-irradiation annealing of copper-boron alloy in the temperature range of 823-923K are one of a kind and deserve greater attention than they have received till date. The sequence of changes in the lattice parameter in two annealing stages reported by these authors offer an insight into the early stages of behavior of helium which ultimately leads to the formation of gas bubble. The two stages of lattice parameter changes are treated as chemical rate processes and correct values of activation energies associated with either stages of annealing are derived. In addition to the yield of proper activation energy values, chemical kinetics route provides information regarding the number of reacting/diffusing species taking part in either stages of annealing. It is shown that the first stage of annealing associated with the decrease of lattice parameter to a level below the equilibrium value for un-irradiated copper-boron alloy is mediated by the migration of a monovacancy. On the other hand, the jump of an interstitial helium atom to a vacancy on its nearest neighbor lattice site is the unit process responsible for the recovery of lattice parameter to its equilibrium value during the second stage of annealing. The end of annealing cycle results in the formation a helium-monovacancy complex which may act as a nucleus for growth of helium gas bubbles in irradiated copper-boron alloy. Thus, the measurement of lattice parameter can provide very useful and interesting information regarding the behavior of inert gas atoms in a crystalline matrix.

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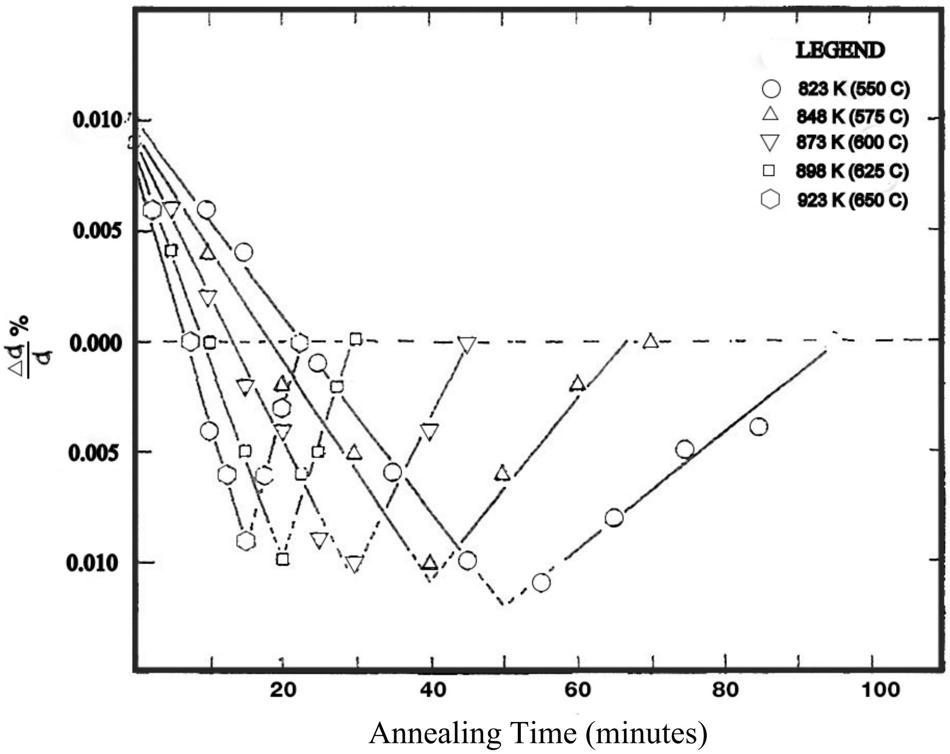


Fig.1 The effect of annealing time upon percentage change in lattice parameter (Δ*a/a %*) over a range of isothermal annealing temperatures for thermal neutron irradiated copper containing 0.25 atom% natural boron [1]. The estimated helium content after irradiation is 0.012 atom%.

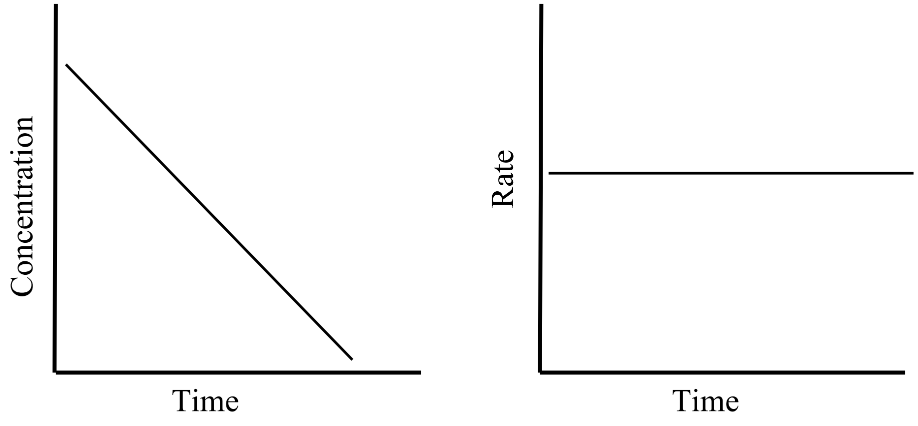


Fig.2 Typical variation of concentration and reaction rate with time for a zero order reaction.

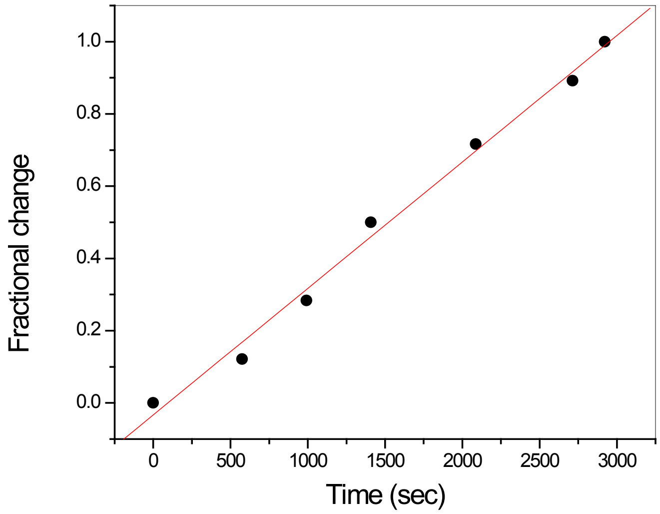


Fig.3 Fractional change for forward reaction as a function of annealing time at 823K yielding a value of 3.501×10^{-4} $\sec^{-1}$ for the rate of reaction.

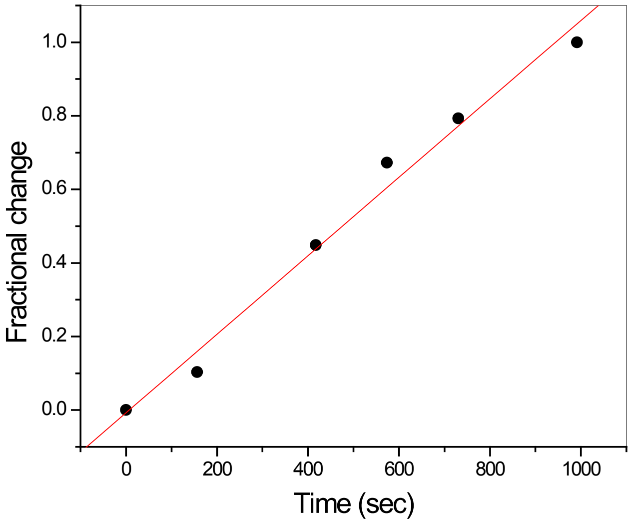


Fig.4 Fractional change for forward reaction as a function of annealing time at 923K yielding a value of $10.7 \times 10^{-4} \sec^{-1}$ for the rate of reaction.

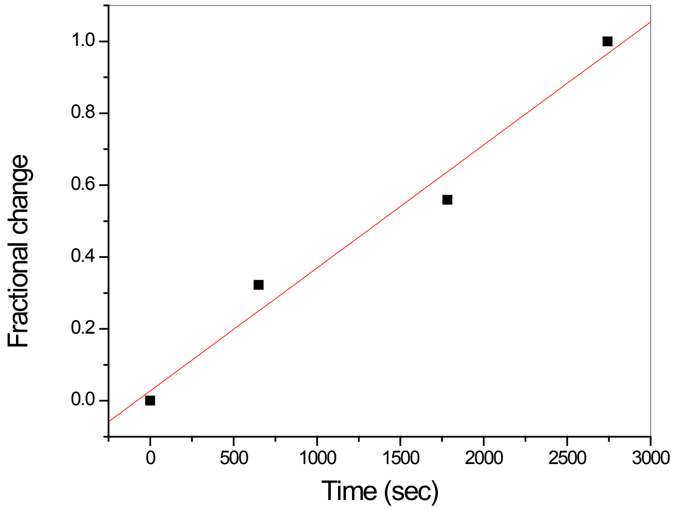


Fig.5 Fractional change for reverse reaction as a function of annealing time at 823K yielding a value of 3.4237×10^{-4} sec^{-1} for the rate of reaction.

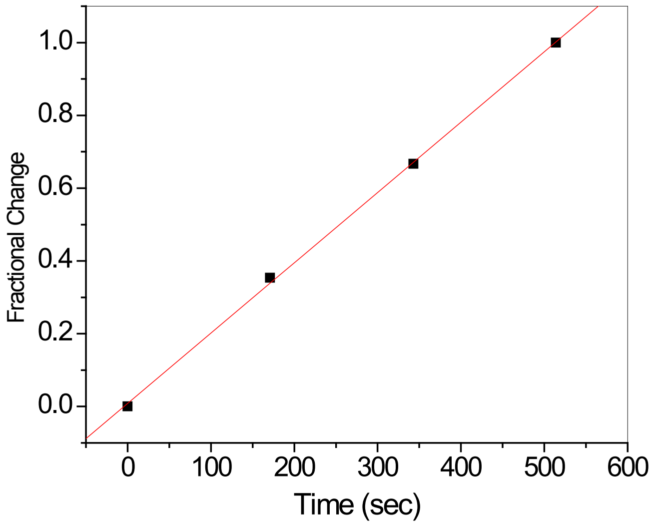


Fig.6 Fractional change for reverse reaction as a function of annealing time at 923K yielding a value of 19.3×10^{-4} sec^{-1} for the rate of reaction.

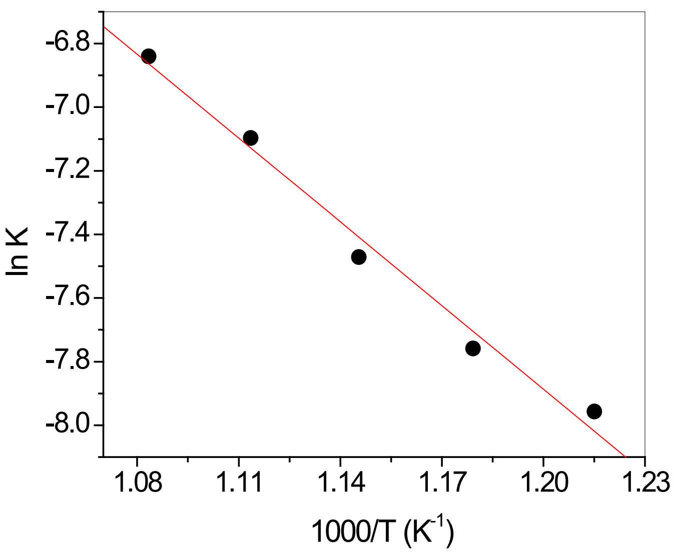


Fig.7 Arrhenius plot for forward Reaction yields an activation of 0.76 ± 0.05 eV/atom.

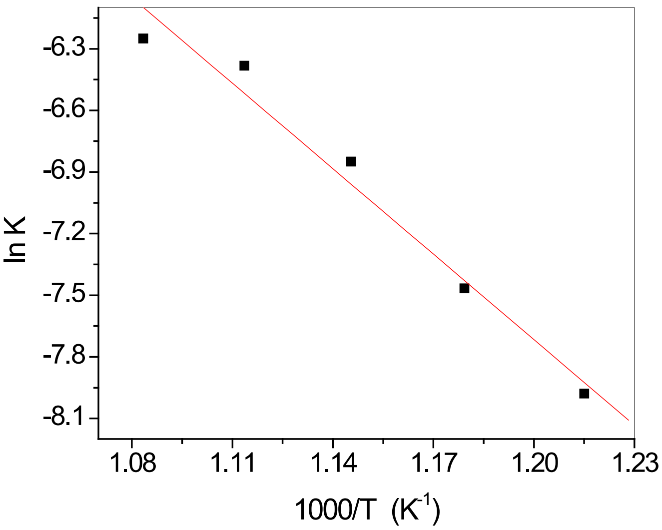


Fig.8 Arrhenius plot for reverse reaction yields activation energy of 1.2 ± 0.1 eV/atom

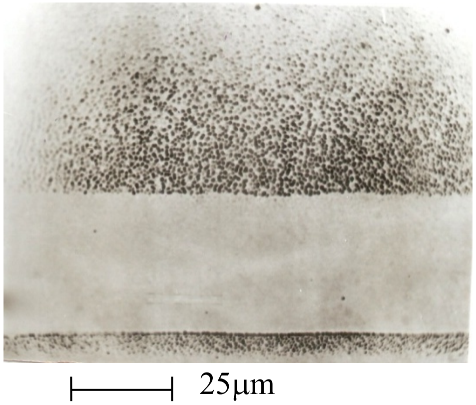


Fig.9 Photomicrograph of a copper crystal irradiated with α-particles showing the band where the helium was initially deposited. The bubble formation and growth are taking place predominantly outside the helium band. The bubble activity is confined mainly to near surface regions.

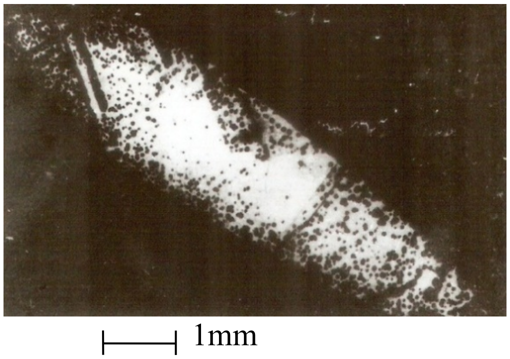
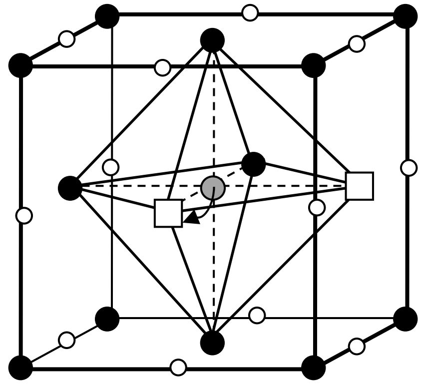
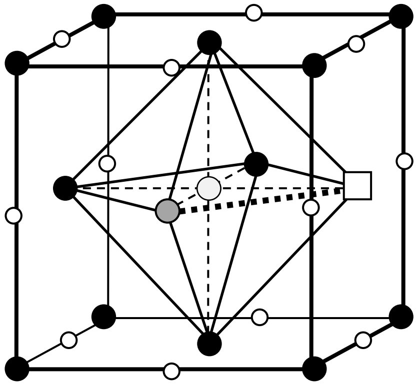


Fig.10 Cross section of a thermal neutron irradiated (total fluence 1.6×10^{20}) copper-0.3 at% boron alloy after annealing at 1278 K for 75 h. The low magnification was selected so that the entire specimen can be viewed in one frame. It is obvious that proximity to free surface has an overriding influence on growth of the gas bubble.



(a)



(b)

● Cu Atoms
○ Interstitial sites
□ Vacancy
◉ He Atom
◯ Vacant Octahedral interstitial site after migration of He atom to a vacant lattice site

Fig. 11(a) He-divacancy complex in Cu lattice, formed at the end of the forward reaction. The arrow in this figure indicates the jump of He atom from interstitial position to nearest vacant lattice site during reverse reaction.

Fig. 11(b) Position of He atom after the jump and formation of a He-monovacany complex (shown by dotted line joining the helium and the monovacancy) at the end of the reverse reaction.