Enhancement of Diffusion Due to Irradiation

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It is shown that in α-copper-aluminium alloys interstitials are able to change sites with the copper and aluminium atoms by diffusion. The activation energy for migration of interstitials could be determined to be 0.82 eV. In a well annealed specimen the interstitials and vacancies annihilate nearly exclusively by pair recombination. The production rate of free interstitials is found to be slightly larger than that of free vacancies during an irradiation with fast neutrons. The excess interstitials, which are supposed to originate from depleted zones, form clusters acting as sinks, at which essentially interstitials anneal out. Due to these sinks another steady state equilibrium („fixed vacancy case") among point defects and sinks is achieved by repeated irradiations.

The arrangement of the atoms in an alloy may be changed by the diffusion of point defects. The concentration of point defects is considerably increased over the equilibrium value by irradiation with high energy particles. Therefore, the radiation enhanced diffusion rate can be many orders of magnitude greater than the thermal diffusion rate. The theory of the radiation enhanced diffusion, which was developed by Dienes and Damask [1], distinguishes three cases: radiation induced vacancies and interstitials annihilate either a) by pair recombination, or b) at fixed sinks, or c) both at fixed sinks and by pair recombination ("combined case").

Radiation enhanced diffusion rates have been measured mainly on two alloys, namely on α-brass (Dienes and Damask [1], Arndt and Hines [2]) and on copper-aluminium alloys with 15 at.-% Al (Wechsler et al. [3–7]). The authors show their experimental results to be in good agreement with the prediction of Dienes and Damask [1] provided that 1. only vacancies and no interstitials are able to change sites with the two types of atoms of the alloys and 2. the point defects under the particular experimental conditions annihilate only at fixed sinks [1] or at fixed sinks and by pair recombination [2, 3–7]. In the case of copper-zinc alloys Dienes and Damask [1] assume a fixed sink annihilation mechanism. However, this annihilation mechanism can be shown [8] to be inadequate, since the implied steady state vancancy concentration is found to be 10^7 times larger than that obtainable by irradiation. Furthermore, it has been shown [8] that even the "combined case" as developed by Dienes and Damask [1] cannot explain the experimental results on copper-zinc alloys [2].

Therefore it appears worthwhile to the author, who has participated in some of the experiments on copper-aluminium alloys [7] during a stay at the Solid State Division of the Oak Ridge National Laboratory, to re-consider the results on copper-aluminium. It will be shown that the enhancement of diffusion in copper-aluminium alloys may be satisfactorily explained by an interstitialcy diffusion mechanism. Moreover, the relatively high migration energy of interstitials and the annihilation mechanism of point defects (during irradiation) found in this alloy appears to be a general feature for f. c. c. metals and alloys.

1. Discussion of Quenching and Irradiation Experiments

Using an alloy with 15 at.-% Al, Wechsler and Kernohan [9, 10] found a decrease in the electrical resistivity between 50 and 110 °C during annealing

[1] G. J. Dienes and A. C. Damask, J. Appl. Phys. **29**, 1713 [1959].
[2] R. A. Arndt and R. L. Hines, J. Appl. Phys. **32**, 1913 [1961].
[3] M. S. Wechsler and R. H. Kernohan, J. Phys. Chem. Solids **7**, 307 [1958].
[4] M. S. Wechsler and R. H. Kernohan, Radiation Damage in Solids, Intern. Atomic Energy Agency, Vienna 1962, Vol. II, p. 81.
[5] J. M. Williams, M. S. Wechsler, and J. H. Barrett, Bull. Amer. Phys. Soc. (II) **8**, 197 [1963].
[6] M. S. Wechsler, Radiation Effects on Metals and Neutron Dosimetry, ASTM-STP-341 (Amer. Soc. for Testing and Materials, Philadelphia, 1962) p. 86.
[7] J. M. Williams, M. S. Wechsler, J. H. Barrett, W. Schüle, and B. C. Kelly, Solid State Div. Ann. Progr. Rep., ORNL-3480, May 31, 1963, p. 138, Fig. 15–17.
[8] W. Schüle, Acta Met. 1965 in press.
[9] M. S. Wechsler and R. H. Kernohan, Acta Met. **7**, 599 [1959].
[10] M. S. Wechsler, R. H. Kernohan, J. M. Williams, and J. E. Thomas, Solid State Div. Ann. Progr. Rep. August 31, 1959, USAEC Report ORNL-2829, p. 115 and Fig. 74.

after quenching from 450 °C (Fig. 1, curve 1). This decrease has been attributed to an increase of the degree of short range order brought about by migrating vacancies. The decrease in the electrical resistivity due to the annihilation of vacancies is comparatively small and can therefore be neglected in our considerations.

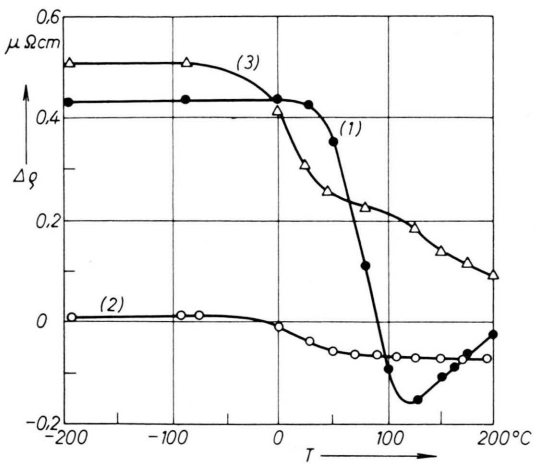

Fig. 1. Change of electrical resistivity $\Delta\varrho$ after different pretreatments (Quenching, irradiation, and quenching and subsequent irradiation) as a function of annealing temperature T of a copper-aluminium alloy with 15% Al. (1) Quenched from 450 °C, (2) irradiated 3 weeks at −120 °C, (3) quenched from 450 °C and irradiated for 3 weeks at −128 °C (see ref. [3, 9–11]).

After a three week neutron irradiation at −128 °C a copper-aluminium (15 at.-% Al) specimen [3] showed almost no decrease in the electrical resistivity during annealing between 50 and 110 °C (Fig. 1, curve 2). The specimen had been cooled slowly from high temperatures to room temperature before irradiation and consequently was partly ordered. There was, however, a decrease of the electrical resistivity between −20 and +50 °C (Fig. 1, curve 2).

In a third experiment a specimen of the same composition was quenched from 450 °C and irradiated during three weeks in a reactor. During subsequent annealing a large decrease in resistivity was found between −20 and +50 °C and a relatively small decrease between 50 and 110 °C (Fig. 1, curve 3) [10, 11]. The difference in annealing behaviour between a quenched and irradiated specimen (curve 3) and a specimen which was cooled slowly to room temperature before irradiation (curve 2) appears to be only quantitative (depending on the initial degree of order).

Wechsler et al. [4, 10, 11] state that the main decrease in electrical resistivity found during annealing between −20 and 50 °C (curves 2 and 3) is also caused by migrating vacancies as in the case of the quenched specimen (curve 1). This assumption can be rejected by the following consideration.

A temperature shift of 70 °C, as derived from the difference of the centers of the annealing stages (curves 1 and 3) can only occur if the concentration of vacancies after annihilation of the interstitials in irradiated specimens is much larger than the concentration of vacancies after quenching, provided that the interstitials are the more mobile defects. From the annealing curves after quenching a value of 1.05 eV for the migration energy of vacancies has been derived [11a], in good agreement with the one determined by Li and Nowick [12] on an alloy with 16.8 at.-% Al (1.08 eV). From the activation energy of self-diffusion (1.80 eV) and the migration energy (1.05 eV), a value of 0.75 eV for the formation energy of vacancies can be derived. Taking this formation energy, the concentration of vacancies obtained by quenching from 450 °C can be estimated to be 10^{-5} (the concentration values are always given in molar fraction). To account for a shift of 70 °C the concentration of vacancies after irradiation would have to be about a factor $3 \cdot 10^3$ larger than the concentration after quenching $[c_v^{(1)}/c_v^{(2)} = \nu_v^{(2)}/\nu_v^{(1)}$, where $T_1 = 280$ °K and $T_2 = 350$ °K; see Eq. (2)]. The vacancy concentration built up during a three week irradiation, even if no annihilation of point defects is assumed, amounts to about $2 \cdot 10^{-4}$, taking for the production rate of vacancies [6] $K = 10^{-10}$ sec^{-1}. This concentration is about a factor 100 smaller than the concentration necessary to account for a shift of 70 °C.

Actually, however, the discrepance is even greater. Since the main traps for interstitials are vacancies, it is obvious that only very few vacancies will remain after the annihilation of the interstitials. For example, it has not been possible to identify migrating vacancies in noble metals after irradiation and annihilation of the interstitials. Their concentration is suspected to be smaller than 10^{-6}, otherwise they

[11] R. H. Kernohan and M. S. Wechsler, Bull. Amer. Phys. Soc. II, **4**, 136 [1959].

[11a] D. K. Holmes, Chemical Effects of Nuclear Transformations, Intern. Atomic Agency, Vienna 1961, Vol. 1, p. 449.

[12] C. Y. Li and A. S. Nowick, Phys. Rev. **107**, 1493 [1957].

would have been detected by measurements of the electrical resistivity. It is concluded [13] that the interstitials annihilate mainly by pair recombination. On copper-gold alloys, a very small vacancy concentration could be identified during post-irradiation annealing by an increase of the degree of order due to migrating vacancies [14]. By comparison with quenching experiments this vacancy concentration can be estimated to be about 10^{-7}. Since the same annihilation mechanism is also expected to occur in copper-aluminium alloys, we may infer for this alloy about the same vacancy concentration (10^{-7}). This concentration would be about five orders of magnitude smaller than that necessary to account for a shift of 70 °C.

We are thus forced to conclude that the increase of the degree of order in the temperature region between -20 and $+50$ °C is caused by the diffusion of some type of defect which is much more mobile than the vacancies. Di-vacancies, which would be able to change the atomic arrangement quite readily by diffusion, are created in too low a concentration by neutron irradiation to account for the large increase of the degree of order found between -20 and $+50$ °C. Moreover, electron irradiation of copper-aluminium alloys causes a decrease in the electrical resistivity of the same magnitude as after neutron irradiation [4]. Thereby di-vacancy enhanced diffusion is excluded since di-vacancy formation during electron irradiation is negligible with respect to interstitial and vacancy formation.

During neutron irradiation, besides vacancies also interstitials are created and, therefore, we can assume that the increase of the degree of short-range order between -20 and $+50$ °C during annealing after irradiation in the reactor is due to interstitialcy diffusion.

The jump frequencies of interstitials ν_i and vacancies ν_v are given by

$$\nu_i = \nu_0^i \exp\{-M_i/kT\}, \quad (1)$$

$$\nu_v = \nu_0^v \exp\{-M_v/kT\} \quad (2)$$

where M_i = activation energy of migration of interstitials, M_v = activation energy of migration of vacancies, k = BOLTZMANN constant, T = Temperature in °K, ν_0^i = pre-exponential factor for interstitialcy migration, ν_0^v = pre-exponential factor for vacancy migration ($\approx \nu_0^i$).

[13] A. SEEGER, Radiation Damage in Solids, Intern. Atomic Energy Agency, Vienna 1962, Vol. 1, p. 101.

Assuming the concentration of interstitials after quenching and irradiation and that of vacancies after quenching to be about equal, the jump frequencies calculated for the temperature of the centers of the annealing stages ($T_i = 280$ °K and $T_v = 350$ °K; Fig. 1, curve 3 and curve 1) should be about equal. Hence

$$M_i/M_v \approx T_i/T_v. \quad (3)$$

Inserting the temperatures given above we receive for M_i/M_v a value of 0.8. With the migration energy of vacancies $M_v = 1.05$ eV one thus obtains for the activation energy of interstitials $M_i = 0.84$ eV.

Actually the resistivity decrease observed during annealing after quenching is about twice as large as that obtained by quenching and subsequent irradiation. Therefore one may assume that the vacancy concentration after quenching is somewhat larger than the interstitial concentration after irradiation. The estimated value for the migration energy of interstitials represents therefore an uppper limit, and may in reality be slightly smaller than 0.84 eV.

2.1 Results of in-pile Measurements
(Single Irradiations)

Copper-aluminium (15 at.-% Al) specimens partly ordered by annealing at 210 °C were irradiated at various temperatures [4, 7]. The increase of the degree of order during irradiation was followed by measurements of the electrical resistivity. Plotting the logarithm of the half completion time $\tau_{1/2}$ (i. e. the time necessary to achieve half of the total increase of the degree of order) versus the reciprocal temperature, a straight line is found (Fig. 2, curve 1). The half completion time is inversely proportional to the radiation enhanced diffusion rate. Accordingly, the slope of curve 1, Fig. 2, gives the activation energy for the decrease of the degree of order during irradiation, namely 0.41 eV. In Fig. 3 the logarithm of the production rate K is plotted against the logarithm of the half completion time, and a slope of $-1/2$ is observed showing that $\tau_{1/2} \sim \sqrt{K}$. WECHSLER et al. [4, 7] state that the "combined case" as derived by DIENES and DAMASK [1] fits the observed dependences of the half completion time $\tau_{1/2}$. From the formulas of the "combined case" a migration energy of vacancies of 0.82 eV may be derived. This value

[14] J. A. BRINKMANN, C. E. DIXON, and C. J. MEECHAN, Acta Met. **2**, 38 [1954].

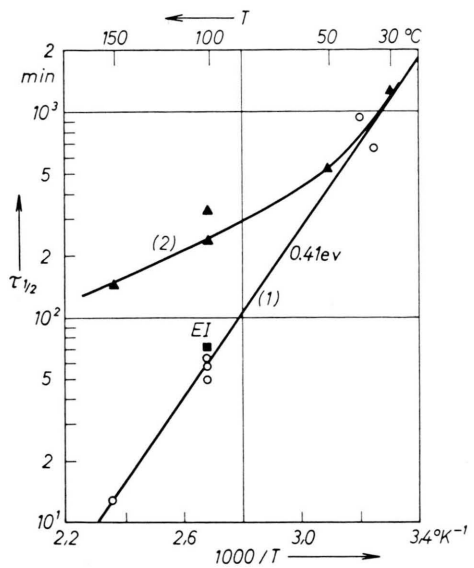

Fig. 2. Temperature dependence of the half-completion time $\tau_{1/2}$ of irradiated copper-aluminium alloys with 15% Al: Curve 1, first irradiation of fresh samples, $E=0.41$ ev; Curve 2, repeated irradiation after annealing at 210 °C; EI: electron irradiated, $1.8\cdot10^{12}$ electrons/cm² sec (see ref. [4, 5, 7]).

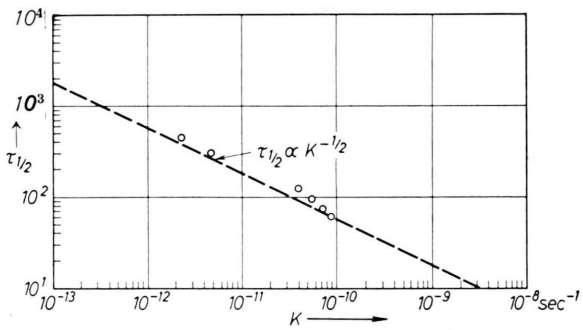

Fig. 3. Time for half-completion $\tau_{1/2}$ of the decrease of resistivity upon neutron irradiation of copper 15 at.% aluminium at 100 °C versus displacement production rate per atomic site, K (see ref. [4–7]).

for M_v does not agree with the experimental results ($M_v=1.05$ eV).

In addition SCHÜLE [8] has shown that the steady-state solution of the "combined case" normally cannot be applied to f. c. c. metals due to the fact that according to the theory of the "combined case" the concentration of vacancies in steady-state is much larger than the concentration of sinks. Nevertheless the removal of vacancies by di-vacancy formation was neglected by DIENES and DAMASK [1]. On the other hand the experimentally observed dependences of the half completion time $\tau_{1/2}$ (Fig. 2, curve 1; Fig. 3) are satisfactorily described by the formulas for the "pair recombination" case, i. e. annihilation of interstitials with vacancies only. In case of "pair recombination" we must distinguish between vacancy and interstitialcy enhancement of diffusion. For interstitialcy enhancement the activation energy of 0.41 eV found for the increase of the degree of order during irradiation (Fig. 2, curve 1) is half of the migration energy of interstitials; i. e., we obtain $M_i=0.82$ eV. Nearly the same value (0.84 eV) for the migration energy of interstitials in a copper-aluminium alloy of the same composition (15 at.-% Al) was determined from irradiation and quenching experiments. If the enhancement of diffusion were attributed to vacancy migration, the activation energy of 0.41 eV would be equal to $M_v-M_i/2$. With $M_v=1.05$ eV, M_i would become larger than M_v, whereas the reverse is accepted.

2.2 In-pile Measurements
(Multiple Irradiations)

If a copper-aluminium (15 at.-% Al) specimen previously irradiated at 100 °C is annealed at 210 °C in order to restore the initial degree of order and then irradiated again at 100 °C the half-completion time becomes about a factor five larger than the value obtained in the first irradiation. Since on repeating of the same treatment no further increase of the half-completion time is observed (Fig. 2), we conclude that during repeated cycling a steady state equilibrium holds. A longer half completion time is observed also for other irradiation temperatures and the temperature dependence of the second run is considerably smaller than that of the first run (Fig. 2, curve 2). This phenomenon was first observed by WILLIAMS et al [5]. Since the production rate of point defects has been equal during all irradiations, the larger half completion time observed in the second run must be due to alterations in the material caused by irradiation. We suggest that sinks were formed during the irradiation before the second run so that the concentration of interstitials during the second run is decreased with respect to the first run.

There is still a further experimental result which is able to help clarify the second run phenomenon. It was stated in section 1. that quenched and irradiated specimens (Fig. 1, curve 3) during annealing showed almost no increase of the degree of order during annealing between 50 and 110 °C. By con-

trast, a significant increase was found in this temperature region for a specimen which has only been quenched (Fig. 1, curve 1). In the quenched specimen the thermodynamic equilibrium state of order corresponding to 110 °C would seem to be fully achieved by migrating vacancies during annealing. But in the quenched and irradiated specimen the equilibrium state of order is apparently not obtained during annealing, and therefore we must conclude that the quenched-in vacancies were annihilated during irradiation and/or during annealing. This may be understood if we postulate that more free interstitials than free vacancies are produced during the irradiation in the reactor and the interstitials recombine with the vacancies produced by quenching and irradiation.

The following model would account for the excess of interstitials. During an irradiation with fast neutrons so-called depleted zones [13] are formed. Such zones can be seen in the electron microscope in copper [15–18]. They are stable up to high temperatures. It is concluded that the atoms originating from the depleted zones must have either converted into stable interstitials far from their origin or annihilated along their path with vacancies or at sinks. In neither case they would be able to return to their place of origin.

Besides these zones other types of clusters are visible in the electron microscope [15–18]. These clusters are formed by free interstitials and not by vacancies since they are built up in a temperature region where vacancies are not mobile, as has been shown by MAKIN and MANTHORPE [17]. The number of interstitial clusters seems to be constant during repeated cycling after the second run according to the fact that no further increase of the half completion time occurs (Fig. 2). Therefore we have to conclude that the interstitials produced during the irradiations after the second run annihilate at the clusters, so that only their size is suspected to increase. The size of the clusters, however, appears to be less important for the steady state concentration of defects during further irradiations. The influence of the depleted zones acting as sinks for point defects can only be small, as their concentration is increasing during further cycling while the half-completion time remains constant.

Since a steady state equilibrium among the point defects and sinks is also obtained during the second run the "fixed vacancy case" [8] might be applied to describe the experiments. If interstitials are able to change with both types of atoms by diffusion, a temperature independent enhancement of diffusion during irradiation would be required in this case [8]. But the experiments (Fig. 2, curve 2) show that such an independence is not achieved.

The steady state concentration of point defects decreases with increasing irradiation temperature. Therefore the probability for interstitials to form clusters is also decreasing with higher irradiation temperatures even though the production rate of the excess free interstitials is independent of temperature. This means that the concentration of sinks is also decreasing with increasing irradiation temperature and a higher steady state concentration of interstitials than according to the "fixed vancancy case" will be obtained. The consequence is a slight temperature dependency of the half completion time.

According to these considerations no further increase of the sink concentration after the second run will occur by irradiations at the same temperature. Therefore the formulas of the "fixed vacancy case" should closer fit the experimental data. In fact, if the specimens are not exposed to a higher neutron flux during the cycling than they had been during the first one a linear dependency of the half completion time $\tau_{1/2}$ on the production rate K is found [7], as required by the formulas.

3. Conclusions

BRINKMANN et al. [14] found that in copper-gold alloys (Cu_3Au) only vacancies and not interstitials are able to enhance diffusion by their migration. This was explained by the large difference between the formation energies of copper and gold interstitials resulting from the difference in size of the two types of atoms (12%). Since interstitials are able to enhance diffusion in copper-aluminium alloys, we have to conclude that the difference of formation energy of the two types of interstitials in these alloys is smaller than in copper-gold alloys. This is in agreement with the fact in the α-copper-aluminium alloys the aluminium atoms appear to be compressed

[15] J. SILCOX and P. B. HIRSCH, Phil. Mag. **4**, 1356 [1959].
[16] M. J. MAKIN, A. O. WAPHAM, and F. J. MINTER, Phil. Mag. **6**, 465 [1961].
[17] M. J. MAKIN and S. A. MANTHORPE, Phil. Mag. **8**, 1725 [1963].
[18] U. ESSMANN and M. WILKENS, phys. stat. sol. **4**, K 53 [1964].

in size and to be only 6% larger than the copper atoms, as it can be estimated from the deviation from VEGARD's law. In order that interstitials can exchange sites with both types of atoms the difference of their formation energies does not have to be zero, but only smaller than the reduction of free energy obtained by an increase of the degree of order.

The ability of interstitials to enhance diffusion was also found in copper-zinc [8], copper-nickel [19], and aluminium-zinc alloys [20]. For these three alloys the difference in atomic sizes of the two components is also smaller than in copper-gold alloys (7%, 3% and 1%, respectively).

For the migration energy of interstitials in these copper-base alloys values between $0.7 - 0.8$ eV are found, which are only slightly higher than those in copper and the other noble metals [21, 22].

By in-pile measurements on copper-aluminium alloys and copper-zinc alloys [8] the same annihilation mechanisms for the point defects are observed. If the sink concentration is small compared to the concentration of interstitials and vacancies, the defects in the copper-base alloys annihilate almost exclusively by pair recombination. It is deduced from the second order kinetics for the annihilation of the point defects after a low temperature irradiation in the noble metals that in these metals the point defects annihilate mainly by pair recombination, too.

[19] W. SCHÜLE and H.-P. KEHRER, Z. Metallkde. **52**, 168 [1961].
[20] W. SCHÜLE, Phil. Mag. **10**, 913 [1964].
[21] W. SCHÜLE, A. SEEGER, F. RAMSTEINER, O. SCHUMACHER, and K. KING, Z. Naturforschg. **16 a**, 323 [1961].
[22] F. RAMSTEINER, W. SCHÜLE, and A. SEEGER, phys. stat. sol. **7**, 937 [1964].