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ON THE POINT-DEFECT ANNEALING MECHANISM FOR STAGE III RECOVERY IN IRRADIATED OR QUENCHED TUNGSTEN

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Introduction

In a recent paper Kim and Galligan (1) have presented experimental results on the Stage III recovery behavior of thermal-neutron irradiated tungsten (W) which they claim provides evidence for the long-range migration of a self-interstitial atom (SIA) in this recovery stage. We wish to take this opportunity to discuss, in précis form, our field-ion microscope (FIM) results on electron-irradiated W which we have previously published. (2,3) Our FIM experimental results lead us to the conclusion that Stage III of irradiated W is best explained by the long-range migration of a vacancy and not a second slow SIA. In addition, we feel that there is a considerable body of other, less direct, experimental evidence on irradiated or quenched W, not discussed by Kim and Galligan, which is also consistent with the one-interstitial model: i.e., a highly mobile SIA atom in Stage I and a less mobile vacancy in Stage III; we note that there is no Stage IV in electron-irradiated W. These other, less direct, experiments are also discussed in this letter and a critique of Kim and Galligan’s paper is presented.

The 2.35 MeV Electron Irradiation of Tungsten: Wilson and Seidman

FIM experiments had been performed (2,3) to search for the thermally-converted Stage III SIA (Stage III in W starts at ~500 K), which is required in a two-interstitial model (4), in electron-irradiated W. Within the framework of a two-interstitial model a second slow-moving (Stage III) SIA forms as a result of the thermally-activated conversion of the fast (Stage I) SIA. The Stage I SIA is considered to be metastable with respect to the Stage III SIA and to convert thermally with an enthalpy change of conversion ($\Delta h_{f \rightarrow i}^c$). The mean distance ($\bar{x}$) traversed by the fast SIA before it converts is

$$\bar{x} = \left[ \frac{6D_{14}^0}{\nu} \right]^{1/2} \exp \left[ \frac{\Delta h_{14}^C - \Delta h_{14}^m}{2kT} \right],$$  

(1)

where $\nu'$ is an attempt frequency for the conversion process, $D_{14}^0$ is the pre-exponential factor of the diffusity ($D_{14}$) of the Stage I SIA, $\Delta h_{14}^m$ is the enthalpy change of migration of the Stage I SIA and $kT$ has its usual significance. (3) In addition $\Delta h_{14}^C$ is greater than $\Delta h_{14}^m$, since for W we have previously provided direct evidence for a mobile Stage I SIA. (5,6) A necessary condition for the slow SIA to be physically observable by the FIM technique is that $\bar{x}$ be less than the typical distance to an SIA sink. Equation (1) demonstrates that, for $\Delta h_{14}^C > \Delta h_{14}^m$, the value of...
were subsequently examined in an FIM at \(T_i\) by the pulse field-evaporation technique. A FIM tips at a position that corresponded to a \(T_i\) of \(420\) K during the irradiation. The specific patterns in W-3 at.% Re alloy specimens, which had been irradiated with 30 keV W\(^+\) ion-irradiated platinum (gold) alloys; e.g., see Figs. 8 and 9 in reference (16). In addition, they are different from what one would expect to see for a single SIA, for any of the six possible geometric forms, based on the contrast model suggested by Seidman and Lie. (15) Thus we are led to the conclusion that each complex-contrast pattern must have been caused by a cluster of point defects: the most likely candidate is an impurity atom(s)-SIA(s) cluster. For a high-temperature (430 K) electron irradiation and for the dose rate employed one can rule out the direct formation of di-SIAs produced as a result of the reaction of two Stage I (fast) SIAs with one another. Recently Wei and Seidman (16) have detected qualitatively similar FIM contrast patterns in a series of 30 keV W\(^+\) or Pt\(^+\) ion-irradiated platinum (gold) alloys; e.g., see Figs. 8 and 9 in reference (16). In this case we know that the complex contrast-patterns are caused by SIAs which are trapped at individual gold atoms. Also Nielsen and Seidman (2, 17) have detected complex contrast-patterns in W-3 at.% Re alloy specimens, which had been irradiated with 30 keV W\(^+\) to a dose of \(5.9 \times 10^{12}\) cm\(^{-2}\) at 15 K followed by an isochronal anneal to 393 K; the pulse field-evaporation
experiments were performed at 15 K. These complex contrast-patterns were caused by stable SIA-Re complexes; thus it was concluded that Re atoms trap SIAs in W(Re) alloys with a sufficient binding enthalpy to remain bound up to at least 390 K. However, in the present situation it is difficult for us to say anything about the exact chemical nature of the impurity atom(s)-SIA(s) clusters. In conclusion, we have found no overwhelming evidence for isolated thermally converted SIAs, as required in a two-interstitial model, at a concentration above 5x10^6 at. fr. at T_i = 410 K for an electron irradiation to a dose of 5x10^20cm^-2.

The electron-irradiation (2,3) experiments demonstrated that at the end of Stage II we have isolated monovacancies and SIAs trapped at unidentified impurity atoms. Therefore, the two-interstitial model would require the detrapping of SIAs from the impurity atom-SIA complexes and hence one would expect the activation energy for Stage III recovery to be a function of the initial or irradiation-induced impurity-level of the W specimens; that is, the recovery kinetics would be a function of the dissociation enthalpy (Δh^d) of an SIA bound to an impurity atom and in general one would expect Δh^d to be different for each type of impurity atom (16). We shall present, in the following sections, results which indicate that there is no evidence for the detrapping of SIAs from impurity atoms and that Stage III is governed by the migration of monovacancies to impurity atom-SIA complexes.

Other Stage III Experiments: Electron Irradiation

The electron irradiation studies of Neeley et al. (18), Kunz et al. (7), Kunz (8) and Cornelis et al. (19) demonstrated that at the end of Stage III essentially all the irradiation-induced resistivity had recovered; i.e., there is no Stage IV in electron-irradiated W. Kunz (8) also showed that for pre-quenched and electron-irradiated specimens that: (1) the recovery of the Stage III defect could not be separated from the annealing of the quenched-in defects; and (2) pre-quenching the electron-irradiated specimens shifted Stage III recovery to a lower temperature. Furthermore, the Stage I pre-quenching experiments of Kunz et al. (7) and Kunz (8) in conjunction with the FIM experiments of Park et al. (9), Park (10) and Huang (11), on quenched W, provide very convincing direct evidence that a portion of the quenched-in resistivity increment must be monovacancy in character.

Since it is now generally agreed that quenching experiments freeze-in some monovacancy population, we are led to the conclusion that Kunz et al.'s (7,8) experiments are simply interpreted in terms of the migration of monovacancies to SIAs in impurity atom-SIA complexes.

Other Stage III Experiments: Quenching

The superfluid-helium quenching technique had been employed by Kunz and Schultz (20), Gripshover et al. (21) and Rasch et al. (22) to study the isochronal annealing behavior of vacancies in quenched W for quenching temperatures (T) between 2735 to 3400 K. All these workers found a single major isochronal recovery stage centered at temperatures between 800 and 1200 K; see Fig. 9(a) in reference (23). The maximum in the recovery stage tends to decrease towards a lower temperature with increasing quench temperature. The reason why the main isochronal stage (800 to 1200 K) of quenched W lies somewhat above Stage III (500 to 1000 K) of electron or neutron-irradiated W is simply that the quenched-in monovacancy increment was always less than the monovacancy concentration remaining at the beginning of Stage III of irradiated W (23); i.e., the average number of jumps made by a vacancy, in Stage III, before it is annihilated in quenched W is greater than in the case of irradiated W. Thus, we believe that denoting the isochronal annealing stage in quenched W as "Stage IV" is incorrect. (25)

* The transmission electron microscope (TEM) observation of voids in quenched W, by Rasch et al. (22), is additional strong evidence that the dominant defect in thermal equilibrium at elevated temperatures is the vacancy. Furthermore, the positron annihilation studies of Maier et al. (24) on W, under thermal equilibrium conditions, is also evidence in favor of the vacancy as the dominant defect in equilibrium at elevated temperatures.
Activation Energies

One of Kim and Galligan's (1) major conclusions is that the activation enthalpy of migration of 1.71 ± 0.05 eV, that they measured for Stage III recovery, is not consistent with the activation enthalpy of migration of a monovacancy (Δh_m^v) as deduced from quenching and tracer self-diffusion experiments. This conclusion is inconsistent with the published results concerning this point.

First we note that the recent careful isothermal annealing experiments of Rasch et al. (22), on quenched W, yielded Δh_m^v equal to 1.78 ± 0.1 eV. In earlier, and less precise work, by Gripshover et al. (29) they determined a Δh_m^v of 1.5 ± 0.2 eV, employing the change-of-slope method, for the isothermal recovery of tungsten quenched from above 3200 K. Hence, the recent available recovery data on quenched W all point to an Δh_m^v of less than 1.9 eV; whereas Kim and Galligan (1) assert that Δh_m^v is between 2.65 and 2.8 eV. Also all the determinations of the activation enthalpy of formation of a mono-vacancy (Δh_f^v) point towards a best value of 3.6 ± 0.2 eV. This value of Δh_f^v is consistent with the resistivity measurements of Gripshover et al. (29), Rasch et al. (22), Park et al. (9-11) and the positron annihilation studies of Maier et al. (24); for a more detailed discussion of Δh_f^v for W see Balluffi (23) and Siegel (30). Thus a conservative upper limit to the experimentally determined sum

\[ Δh_m^v + Δh_f^v \]

is 5.7 eV; this sum is the activation energy required for self-diffusion by a monovacancy mechanism (DSD).

A very recent comprehensive and accurate study of the tracer self-diffusion coefficient (DSD) in W has been performed by Mundy et al. (31). They measured DSD in W single-crystals over the temperature range 1700 to 3400 K; also see Mundy et al. (31) for a critical discussion of the earlier determinations of DSD in W. The standard Arrhenius plot of log DSD versus 1/T is curved (the data span nine orders of magnitude in DSD) and Mundy et al. fitted the data points to the expression;

\[ DSD = (0.04\exp(-5.45 \text{ eV/kT}) + 46\exp(-6.9 \text{ eV/kT}) \text{ cm}^2 \text{ sec}^{-1}, \]

where the first exponential term (the low-temperature term) corresponds to diffusion by a monovacancy mechanism and the second term may represent diffusion by a divacancy mechanism. The activation energy of 5.45 eV in the first term of Equation (2) is consistent with the sum Δh_m^v + Δh_f^v, determined by both a combination of quenching and recovery experiments and positron annihilation studies. Thus we conclude that the value of 1.71 ± 0.05 eV, measured by Kim and Galligan, is consistent with both the quenching and tracer self-diffusion experiments.

A further point with respect to activation energies is that the activation enthalpy of migration of the point defect that migrates in Stage III of neutron (thermal or fast) irradiated W has been consistently determined to be 1.7 - 1.8 eV; over a wide range of initial impurity conditions and dose; see the papers by Kinchin and Thompson (32), Thompson (33), Keys and Moteff (34), and Cornelis et al. (19). Also recently both Cornelis et al. (19) and Kuglar et al. (35) have studied the Stage III recovery behavior of electron-irradiated W and measured an activation enthalpy of migration of 1.70 ± 0.03 eV and 1.79 ± 0.04 eV, respectively. Thus Stage III in quenched or irradiated W is governed by essentially the same activation enthalpy, which must be the case if the same point defect is responsible for the recovery behavior. We emphasize, once again, that the temperature range of Stage III in quenched W is often different from that of irradiated W because of the larger number of jumps made by a vacancy before it is annihilated in quenched W; (23,27,36-39) also see Fig. 12 in reference (22) and Fig. 3 in reference (34).

In discussing activation energies we have excluded all values that were determined under the assumption of a particular annealing kinetics as this approach often leads to incorrect values. (26,27,28) Thus, for example, Gripshover et al. (29) also assumed second-order annealing kinetics and calculated a value of 2.5 eV for the isochronal recovery of quenched W; we note that Gripshover et al. also rejected this higher value for similar reasons.

† We exclude the work of Neely et al. (18) from this compilation as they assumed second-order reaction kinetics in their analysis of the recovery data.
In addition, it is noted that we have also obtained direct FIM evidence for the trapping of SIAs at Re atoms at temperatures at least as high as 390 K in 30 keV W⁺ ion-irradiated W-3 at.% Re alloys. This strongly suggests, as we pointed out earlier, that in the neutron-irradiation experiments with a significant thermal neutron dose, such as those of Galligan and co-workers (1,25,42), that the SIAs are trapped at the Re atoms produced as a result of transmutation processes; e.g., a thermal neutron dose of \( 10^{20} \text{ cm}^{-2} \) produces a Re concentration of \( 10^{-3} \) at. % (34). In the Kim and Galligan experiments the temperature range of Stage III was independent of the initial impurity level because they irradiated all their specimens to the same thermal-neutron dose and hence produced the same concentration of Re atoms in all their specimens. The Re atoms masked out any effects due to the initial impurity atoms, so that the migrating monovacancies always saw essentially the same sink structure. Alternatively in the Kugler et al. (35) work they employed specimens with \( R=80,000 \) and 1700 and irradiated with 3 MeV electrons to both high and low doses. They found that for low-dose irradiations that Stage III resistivity recovery took place between 750 and 900 K: this lies within the temperature range for the resistivity recovery of quenched W; see Fig. 3 of reference (35). In addition for electron-irradiated W the temperature range for Stage III recovery depended on the initial impurity level. The reason for this is that the impurity atoms trapped SIAs and thus the sink structure, for the monovacancies that migrated in Stage III, was determined by the initial concentration of impurity atoms.

A final point with respect to activation energies concerns the possibility of the Stage III (or slow SIA), in the two-interstitial model, having the same activation enthalpy as a monovacancy. We argue against this possibility on the basis of our FIM results (2,3), on electron-irradiated W, which detected only SIAs trapped at impurity atoms and not isolated thermally-converted SIAs and the recovery experiments. The detrapping of SIAs from impurity atoms involves the dissociation enthalpy which is the sum of \( \Delta H_{\text{diss}} + \Delta H^0 \): where \( \Delta H^0 \) is the binding enthalpy of an SIA to an impurity atom. (16) Thus, the kinetics of Stage III recovery governed by SIAs detrapping from impurity atoms followed by annihilation at monovacancies would be controlled by \( \Delta H_{\text{diss}} + \Delta H^0 \): in this case \( \Delta H_{\text{diss}} + \Delta H^0 \neq \Delta H^0_{\text{v}} \), if \( \Delta H^0_{\text{diss}} \neq \Delta H^0_{\text{v}} \), and different activation energies should have been observed for the recovery of electron or fast-neutron irradiated W versus quenched W.

**Kim and Galligan's Experiment**

In this section we present a critique of Kim and Galligan's results and discussion; we also refer the reader to our earlier comments (2,42) concerning references (25) and (41). The main points are as follows:

1. The conclusion that a contrast effect in an FIM image is produced by a single SIA requires the pulse dissection of a crystallographic plane one or two atoms at a time: this often involves examining and analyzing two to three-hundred frames of 35 mm cine film of a single contrast pattern; for examples, see Fig. 3 (259 frames of film) in reference (3) and Fig. 8 (327 frames of film) in reference (16). Thus the three-frame sequence presented by Kim and Galligan in Fig. 10(b) of their paper could certainly be that of an SIA trapped at a Re atom. This is an important point because the two-interstitial model requires the observation of single thermally-converted SIAs.

2. Kim and Galligan accept the fact that SIAs are trapped at Re atoms, but then assume that "the migration of interstitials tungsten or rhenium" can be treated on "an equivalent basis." We are unaware of any evidence which indicates that Re moves by an interstitialcy mechanism in W. The fact that "rhenium diffuses in tungsten with the same activation energy as does tungsten"(44) would indicate that Re diffuses in W by a vacancy mechanism and not an interstitialcy mechanism. Thus, Kim and Galligan's discussion doesn't directly confront the problem of the detrapping of the SIAs from the Re atoms, as would be required if the SIAs had migrated to the monovacancies and not vice-verse.

3. Their statement that the results presented in Table 4 and Fig. 11 of their paper prove that the "vacancy concentration decreases more slowly, with temperature, than does the concentration of interstitials" is not convincing because the SIA concentration was assumed to be...
equal to the vacancy concentration and then both point-defect concentrations were normalized to unity at room temperature. For this type of experiment to be significant both the absolute SIA and vacancy concentrations must be separately reported; in addition, it would be extremely interesting to see the detailed data, i.e., the absolute number of vacancies, SIAs and atoms counted for both point-defect populations.

4. The data exhibited in Fig. 11 does not prove that there are vacancies remaining at the end of Stage III in the purest specimens (Group B). The FIM specimens were only annealed isocratically up to 400°C, while their resistivity data (see data for specimen E-3 in Figs. 3 and 4) demonstrates that Stage III recovery is not complete until ~475°C.

Summary

1. In previously published FIM studies (2,3) we have found no overwhelming evidence for isolated thermally-converted SIAs, as required in a two-interstitial model, at a concentration above 5x10^{-6} at.fr. at T_{1} 2 430 K for an electron irradiation to a dose of 8x10^{20} cm^{-2}. The FIM microstructure of the electron-irradiated tungsten (both R = 15 and R = 5x10^{4}) consisted of immobile isolated monovacancies and a second defect which possesses a complex contrast-pattern that extends over five to fifteen successive atomic layers. The complex contrast-patterns were interpreted in terms of a SIA(s) trapped at impurity atom(s) to form a cluster. Thus, we are led to the conclusion that Stage III recovery of electron-irradiated W must involve the migration of monovacancies to SIAs trapped at impurity atoms.

2. The published electron-irradiation recovery studies, on W, indicate the complete absence of a Stage IV; and that the recovery of the Stage III point defect could not be separated from the annealing of the quenched-in vacancies. This constitutes very strong indirect evidence that the vacancy migrates in Stage III of electron-irradiated W.

3. The behavior of vacancies in quenched W is such that all the vacancies recover in a single major isochronal recovery stage centered at temperatures between 800 to 1200 K. It is incorrect to call this recovery behavior Stage IV even though it lies somewhat above the Stage III (~500 to 1000 K) of electron or neutron-irradiated W. The reason why Stage III recovery of quenched W often lies above Stage III of irradiated W is simply that the average number of jumps made by a vacancy, in Stage III of quenched W, before it is annihilated is greater than in the case of irradiated W. This is, the temperature range of Stage III is a sensitive function of the sink structure of the specimen.

4. The best value of the activation enthalpy of migration of a monovacancy (\Delta h_{m}^V) is 1.78 ± 0.1 eV, as determined from isothermal-annealing experiments on quenched W.

5. The best value of the activation enthalpy of formation of a monovacancy (\Delta h_{f}^V) is 3.6 ± 0.2 eV, as determined from resistivity measurements and positron annihilation studies.

6. The sum of \Delta h_{f}^V + \Delta h_{m}^V is 5.4 ± 0.1 eV and this value is in agreement with the activation energy for self-diffusion by a monovacancy mechanism (\Delta S_{D}) as determined by tracer self-diffusion experiments on tungsten single-crystals; this best value of \Delta S_{D} is 5.4 eV.

7. The activation enthalpy for recovery of neutron (thermal or fast) or electron-irradiated W has been consistently found to be 1.7 - 1.8 eV; this value is essentially a constant independent of the irradiation flux or dose, and the initial impurity content of the W. We associate this activation enthalpy with \Delta h_{m}^V: i.e., Stage III recovery of irradiated W is governed by the migration of the monovacancies to SIAs trapped at impurity atoms.

8. FIM experiments have provided evidence for the trapping of SIAs at Re atoms, in W-3 at.% Re alloys, up to at least as high as 790 K. This suggests that in neutron irradiations with a thermal-neutron component to the dose that the SIAs are trapped at the Re atoms which are produced as a result of transmutation reactions.

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References


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