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Journal of Nuclear Materials 275 (1999) 206–210

journal of nuclear materials

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Letter to the Editors

Effects of thermal cycles on ^{222}Rn permeability in Au

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Received 15 April 1999; accepted 19 July 1999

Abstract

The effect of the thermal cycles of negative magnitude (TCNM) on the ^{222}Rn permeability in Au, pre-annealed at different temperatures was studied at 150°C, after prolong equilibration at the same temperature. It was found that TCNM enhance the permeability and reduce the activation energy of permeation. The results have been explained in terms of capture of vacancies by diffusing large ^{222}Rn atoms and/or opening up of small 'channels' of atomic dimension. These defects tend to annihilate during prolonged isothermal holding at ambient temperature. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Permeation of inert gases at low partial pressure is of particular interest in nuclear technology. Pabi and Hahn [1] developed a highly sensitive α-spectroscopic method for measuring ^{222}Rn permeation flux on atomic scale ($\sim 10^4$ atoms m^{-2} s^{-1}) at low partial pressure ($\sim 10^{-7}$) over an extended period of time (e.g., months). Recently a more advanced version of this α-spectroscopic method [1] has been developed by Bhattacharyya et al., which seems to have a good potential in materials characterization using ^{222}Rn as a probe [2–6]. This equipment was used to study the ^{222}Rn permeability in Pb at high homologous temperatures T_H ($\geqslant 0.68$) [2] and in Au at low T_H ($\leqslant 0.32$) [3]. It was reported that during isothermal treatment, permeation occurs with exceptionally low activation energy Q_P in Pb (~8.2 kJ/mol) [2] and Au (~35 kJ/mol) [3,5,6], and pre-annealing temperature has pronounced influence on ^{222}Rn permeability in Au [5,6]. It has also been reported that thermal cycles of negative magnitude (TCNM) can remarkably enhance the ^{222}Rn permeability in Pb at high T_H ($= 0.72$) and reduce Q_P to a trivial level of 1.2 kJ/mol possibly by opening up of small 'channels' of atomic dimension [4]. These results gave the first indication that the small thermal fluctuations in a reactor atmosphere may have a profound influence on the gas permeability through the reactors structural components. In the present investigation it is aimed to study the effect of TCNM on the ^{222}Rn permeability at low T_H ($\leqslant 0.32$) in Au, pre-annealed at different temperatures. It may be pointed out that the possibility of formation of any surface (oxide) layer on the specimen or its rupture due to the TCNM is precluded in case of Au specimen, and hence, these experiments may provide a better insight into the influence of TCNM.

2. Experimental

Au foil of 26 μm thickness used in the present investigation was prepared from high purity Au (99.995%) by cross rolling at room temperature with intermediate annealing at 700°C. After the last rolling pass, a portion of the cold worked Au foil was annealed at 700°C for 1 h (Au700), while for another portion the annealing temperature was 850°C (Au850). After annealing, both the foils were furnace cooled to 600°C (in ~0.5 h) followed by air cooling to room temperature. The average grain size of the Au700 and Au850 foils was 42 ± 9.9 μm and 53 ± 5.5 μm, respectively. These foils were initially (Phase-I) used to study isothermal permeability and the results have been reported elsewhere [3,5]. Immediately after that the same specimens have been used in the

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present investigation in Phase-II to investigate the effect of TCNM.

The description and working principle of the modified Rn permeability measuring equipment capable of measuring radon flux (N_{Rn}) < 2300 atoms m^{-2} s^{-1}, have been given earlier [2,3,6]. The temperature of the specimen was controlled to ±0.05°C by means of a Julabo RC-12 thermostated bath circulator. As shown in Fig. 1 of Ref. [2,3], an independently controlled electrical booster heater in conjunction with the bath circulator was able to change the specimen temperature at a rate of ~10°C/min during introduction of the thermal cycles. A thermocouple was placed in a vicinity of the foil sample and connected to a strip-chart recorder to keep a record of the thermal schedule of the specimen in course of permeation.

3. Results

Since the ^{222}Rn permeability in Au is known to depend on the thermal history in course of permeation [1,3,6], it is necessary to present the entire thermal schedule in course of permeation. The thermal schedule in Phase-I for isothermal permeability experiments with virgin Au700 and Au850 specimens were reported in [3,6], respectively. There the permeability was measured in course of heating up to 150°C with intervening prolong (⩾160 h) isothermal holding at 100°C and 130°C. During isothermal holding at 150°C (⩾160 h) in Phase-I, the ^{222}Rn permeability in Au700 gradually increased to a steady state value $N_{Rn(steady)} = 5.45$ atoms mm^{-2} s^{-1} [3], while in Au850 it reached a maximum level $N_{Rn(max)}$ of 0.042 atoms mm^{-2} s^{-1} [6]. At that stage the same specimens have been subjected (in Phase-II) to the TCNM as per the schedule in Figs. 1 and 2, following which the ^{222}Rn permeability is measured at $T_P = 150$°C. Here, in treatments h_{10A}, h_{11A} and h_{12A} (Fig. 1), h_{10B}, h_{11B} and h_{12B} (Fig. 2), the TCNM of amplitude ΔT_n (20–60°C) has been introduced, which comprises of cooling the specimen at a rate of ~5°C/min to ($T_P - \Delta T_n$) followed by isothermal holding for 30 min and reheating (~5°C/min) to T_P. The treatments h_{13A}, h_{15A}, h_{13B} and h_{15B} represent the step heating treatments of short duration (~12 h) at different T_P, while in treatments h_{14A} and h_{14B} the specimen is held at 30°C for 72 h.

Fig. 3 shows the variation of N_{Rn} in Au700 with the cumulative number of thermal cycles (Z) in h_{10A}, h_{11A} and h_{12A} (cf. Fig. 1). After prolonged equilibration at 150°C in h_{9A} (Phase-I), when the Au700 specimen was subjected to one TCNM of $\Delta T_n = 20$°C (in treatment h_{10A} of Fig. 1), N_{Rn} at 150°C increased from the $N_{Rn(steady)}$ value of 5.45–5.63 atoms mm^{-2} s^{-1}. The N_{Rn} enhanced gradually with Z of same ΔT_n (20°C), and reached a peak value, $N_{Rn(peak)} = 7.81$ atoms mm^{-2} s^{-1} after 23 thermal cycles, beyond which N_{Rn} diminished gradually. With the increase in the magnitude of ΔT_n to 40°C in treatment h_{11A} (Fig. 1), the N_{Rn} once again displayed a peak and this time $N_{Rn(peak)} = 8.18$ atoms mm^{-2} s^{-1}. It is found that $N_{Rn(peak)}$ obtained in

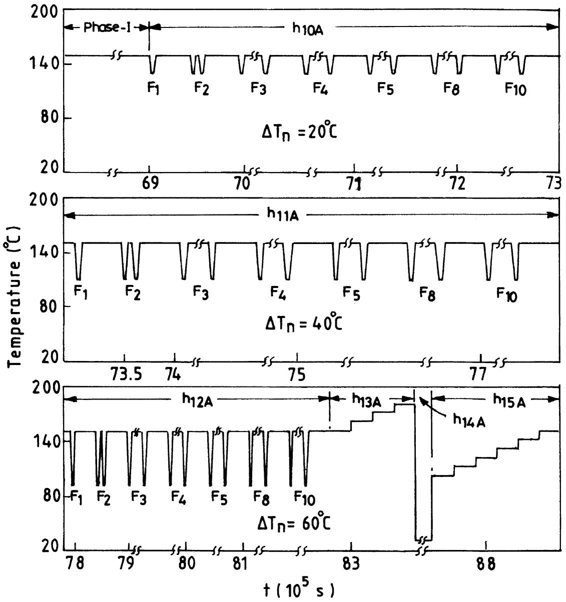

Fig. 1. Thermal schedule of Au700 specimen in course of permeation including that of TCNM. Subscript of F represents the number of TCNM.

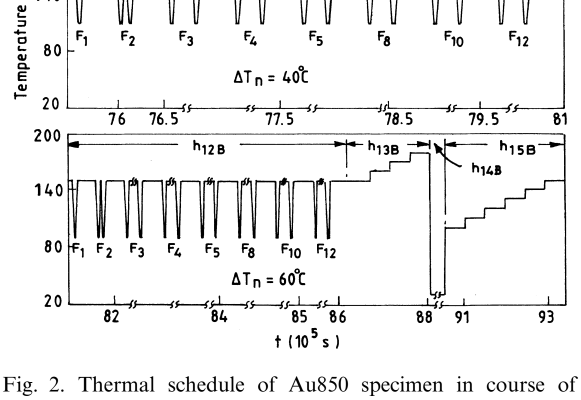

Fig. 2. Thermal schedule of Au850 specimen in course of permeation including that of TCNM. Subscript of F represents the number of TCNM.

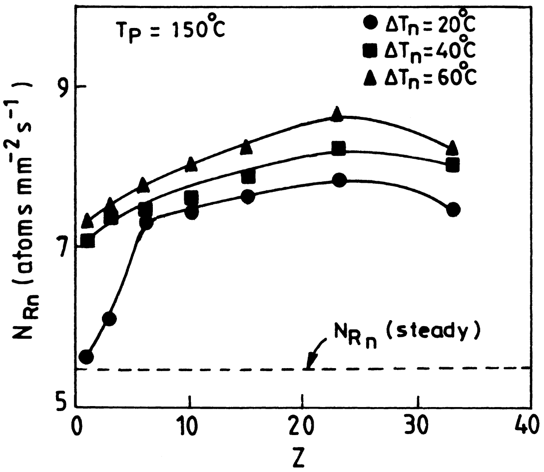

Fig. 3. N_{Rn} vs. Z for Au700 in course of treatment h_{10A}, h_{11A} and h_{12A} of Fig. 1.

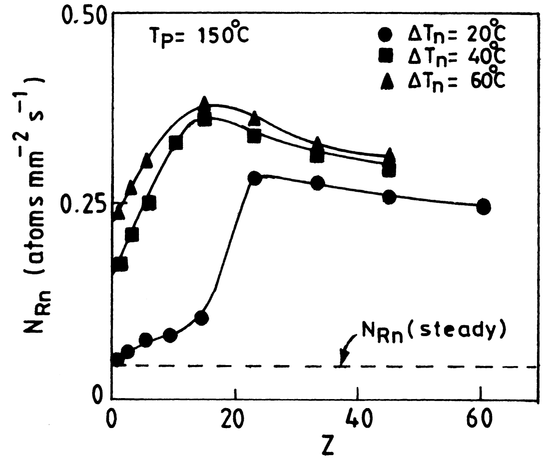

Fig. 5. N_{Rn} vs. Z for Au850 in course of treatment h_{10B}, h_{11B} and h_{12B} of Fig. 2.

treatment h_{11A} is higher than that in treatment h_{10A} (Fig. 3). With further increase in ΔT_n to 60°C in treatment h_{12A}, the N_{Rn} vs. Z plots (Fig. 3) again exhibit $N_{Rn(peak)}$, the magnitude of which is higher than that in h_{10A} and h_{11A}. Fig. 3 demonstrates, that the $N_{Rn(peak)}$ attained after TCNM of $\Delta T_n = 60$°C is ~2.0 times the $N_{Rn(steady)}$ measured at the same T_P. The step-heating treatment from 150°C to 180°C introduced at this stage in treatment h_{13A} (Fig. 1) yielded an activation energy for permeation $Q_P = 23.1 \pm 0.2$ kJ/mol (Fig. 4). After completion of TCNM and step-heating experiments, the Au700 specimen was cooled to room temperature (30°C) and held for 72 h (in treatment h_{14A}) before subjecting it to the step-heating treatment from 100°C to 150°C in treatment h_{15A} (Fig. 1). The N_{Rn} recorded in the treatment h_{15A} yielded $Q_P = 27.12 \pm 0.3$ kJ/mol (Fig. 4).

The variation of N_{Rn} in Au850 with Z for different values of ΔT_n in treatments h_{10B}, h_{11B} and h_{12B} (cf. Fig. 2) is shown in Fig. 5. After prolonged equilibration at 150°C, when the Au850 was subjected to one TCNM with $\Delta T_n = 20$°C (in treatment h_{10B} of Fig. 2), N_{Rn} at 150°C increased from the $N_{Rn(max)}$ value of 0.042–0.048 atoms mm^{-2} s^{-1}. The N_{Rn} increased with Z, and attained a peak value, $N_{Rn(peak)} = 0.29$ atoms mm^{-2} s^{-1} following it showed a gradual decline. With further increase in ΔT_n to 40 and 60°C in treatment h_{11B} and h_{12B}, respectively, the N_{Rn} vs. Z plots (Fig. 5) again exhibit $N_{Rn(peak)}$, the level of which increases with the magnitude of ΔT_n. Fig. 5 shows that at $T_P = 150$°C, the $N_{Rn(peak)}$ obtained after TCNMs of $\Delta T_n = 60$°C is about an order of magnitude higher than the $N_{Rn(max)}$ recorded during prior isothermal treatment at the same T_P (i.e., in treatment h_{9B}). The step-heating treatment from 150°C to 180°C, that followed in treatment h_{13B} (Fig. 2) gave $Q_P = 14.7 \pm 0.2$ kJ/mol (Fig. 6). Similar to Au700, here also after completion of TCNM and step-heating experiments, the specimen was cooled to room temperature (30°C) and held

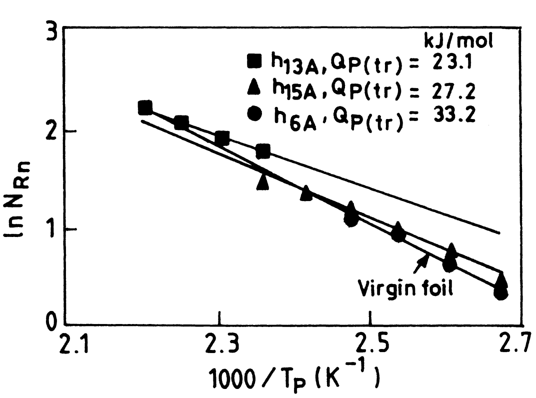

Fig. 4. Arrhenius plots of ln N_{Rn} vs. $(1000/T_P)$ for Au700.

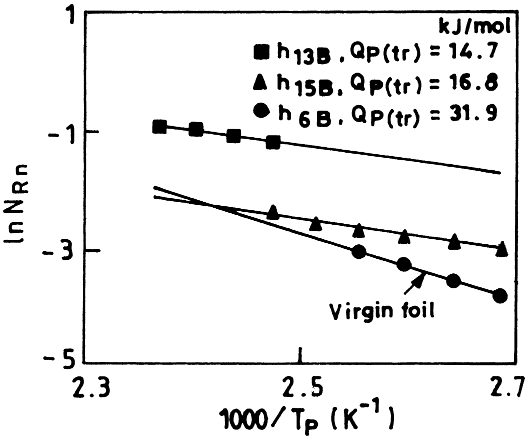

Fig. 6. Arrhenius plots of ln N_{Rn} vs. $(1000/T_P)$ for Au850.

for 72 h (in treatment h_{14B}). Subsequent step-heating treatment from 100°C to 150°C in treatment h_{15B} (Fig. 2) yielded $Q_P = 16.8 \pm 0.1$ kJ/mol (Fig. 6).

4. Discussions

Annealing the Au specimens at 700°C or 850°C, well above the recrystallization temperature of pure Au (200°C) [7], prior to the permeability measurements ensured recrystallization and annihilation of any deformation induced excess vacancies in the specimens. Moreover, after annealing both Au700 and Au850 were furnace cooled to 600°C, so that there is no significant difference in the impurity segregation pattern at the grain boundaries in the two specimens. During isothermal treatments in Phase-I with the same Au specimens, respective Q_P values for Au700 and Au850 were 33.2–35.6 and 31.9–35.4 kJ/mol [3,6]. These values of Q_P are much smaller than the activation energy of diffusion (Q_D) of Rn in cold worked Ag (~130 kJ/mol) determined by high energy ion bombardment technique [8]; but it is higher than Q_D of Rn in Ta (~8 kJ/mol) yielded by the data of nuclear recoil experiments [9]. Moreover, these values of Q_P in annealed Au are much smaller than the lattice self diffusion energy in Au (176.6 kJ/mol) [10] or grain boundary self diffusion energy, $Q_{D(g,b)}$ of Au, (84 kJ/mol) [11]. Since a neutral radon atom occupies ~3 times the volume of a Au ion, it has been suggested earlier that ^{222}Rn permeates in annealed Au mainly through the structural defects like grain boundaries by capturing vacancies [3,6], which conforms to the earlier proposition of Rimmer and Cottrell [12]. The present values of Q_P obtained in treatment h_{13A} and h_{13B} after the introduction of TCNM of amplitude $\Delta T_n = 60$°C are 23.1 and 14.7 kJ/mol in Au700 and Au850, respectively. These values are comparable to the Q_P in cold worked Au (18.0–22.5 kJ/mol) measured during isothermal permeation measurements [3]; but these are substantially lower than the activation energy of migration of monovacancies (80.6 kJ/mol) and divacancies (68.16 kJ/mol) in Au lattice [13,14].

The enhancement of permeability in Au at lower T_H ($= 0.32$) caused by the introduction of TCNM cannot be attributed to the rupture of any surface layer (e.g., oxide) or redistribution of impurities during the TCNM, because the possibilities of formation of any surface oxide layer or considerable redistribution of impurities by volume diffusion during TCNM may be precluded in Au. The heating and cooling rates (~5°C/min) are unlikely to enhance the dislocation density in a well annealed Au foil. Besides, similar enhancement of N_{Rn} in annealed Pb cannot be attributed to such dislocation generation at high T_H ($\geqslant 0.63$) [4]. The TCNM was introduced only after prolong isothermal holding ($\geqslant 160$ h) at 150°C, when the contribution of pre-existing dislocations (if any) to the permeation process would reach a steady state. Moreover, there cannot be any quenched-in excess (lattice) vacancies at T_P due to the TCNM, since the magnitudes of the thermal cycles are negative.

The inert gases are normally insoluble in metal lattice [15]; but the imperfection like grain boundaries in polycrystalline metals may be more receptive to larger solute atoms like ^{222}Rn due to the existence of a wider spectrum of interatomic distances in these regions [16,17]. It is plausible that during TCNM when the specimen temperature is varied between T_P and $(T_P - \Delta T_n)$, the local strain around the large ^{222}Rn atoms residing at the structural imperfections like grain boundaries or grain boundary triple points may play an important role during this TCNM. Fig. 7(a) and (b) illustrate one possible mechanism by which TCNM can enhance the permeability. Some of the lattice vacancies present at T_P prior to TCNM (Fig. 7(a)) would tend to escape to the grain boundaries in its attempt to attain the equilibrium concentration in course of cooling down during TCNM. In the process some of these vacancies can be captured by the large Rn atoms (Fig. 7(b)) residing at the boundaries, which can promote the mobility of the Rn atoms during subsequent heating. The process is likely to be enhanced with the increase in magnitude of ΔT_n in TCNM. When the TCNM is repeated, more and more vacancies would be captured, that can gradually increase the free volume at these structural defects. Therefore, TCNM in annealed Au may also act as a 'vacancy pump' resulting in an increase

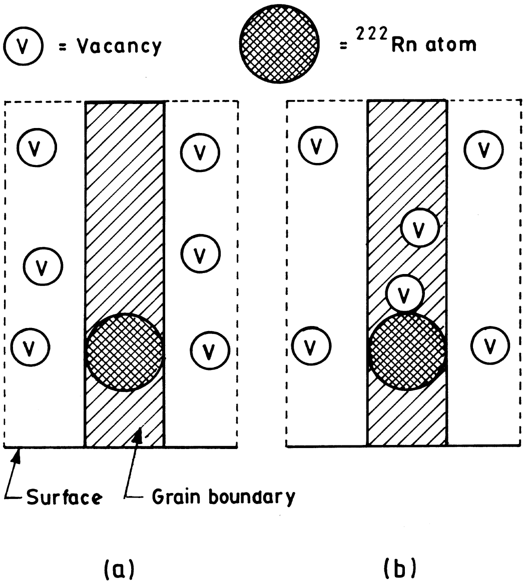

Fig. 7. Schematic presentation of ^{222}Rn atom migration process through a grain boundary. Here (a) and (b) depict the situation before and after cooling down in TCNM, respectively.

in radon transport through imperfections like grain boundaries, in a manner analogous to that in annealed Pb [4]. In fact, many of the defects introduced by TCNM in annealed Au seems to get annihilated during holding at ambient temperature, as evidenced by (Figs. 4 and 6) a reduction of N_{Rn} and increase in Q_{P} in treatments $h_{15\mathrm{A}}$ and $h_{15\mathrm{B}}$. For instance, in Au700 Q_{P} in virgin foil (33.2 kJ/mol) was reduced to 23.1 kJ/mol in $h_{15\mathrm{A}}$ due to TCNM, and it recovered to 27.12 kJ/mol during subsequent holding at room temperature for 72 h (Fig. 4).

Finally, it may be noted that the effects of TCNM on the ^{222}Rn permeability in Au at low T_{H} $(=0.34)$ observed in present study is qualitatively similar that in Pb at high T_{H} $(=0.72)$, excepting that Q_{P} in Pb dropped to an insignificant level of 1.2 kJ/mol due to TCNM, while for Au it was quite significant (27.12 kJ/mol). This also can be accounted for by the vacancy pump model [4] presented in Fig. 7, as follows. The non-equilibrium concentration of vacancies in the ^{222}Rn permeation paths should depend on the number of ^{222}Rn atoms migrating through those paths, because radon atoms tend to capture vacancies [2–4]. At the same measuring temperature ($T_{\mathrm{P}} = 150$°C), the $N_{\mathrm{Rn(steady)}}$ in Au700 (cf. Fig. 3) is about two orders of magnitude lower than that observed in Pb [2]. Therefore, during TCNM that excess vacancy concentration in case of Pb can attain a level enough to open up ‘channels’ of atomic dimension to diminish Q_{P} to an unusually low value ($\sim$1.2 kJ/mol) for any solid state diffusion, while it not so in case of Au due to smaller magnitude $N_{\mathrm{Rn(steady)}}$. It may be recalled that the deformation induced vacancies and/or structural change of the grain boundaries caused by cold working the Au specimen also manifested similar relaxation and reduction in N_{Rn} during isothermal holding at room temperature [3], that is well below the recrystallization temperature of pure Au (i.e., 200°C) [7].

5. Conclusions

Thermal cycle of negative magnitude can significantly enhance the ^{222}Rn permeability in Au at low T_{H} $(=0.34)$ and reduce Q_{P} moderately. These effects may be explained in terms of capture of vacancies by large Rn atoms vis-a-vis enhancement of the free volume of the effective permeation paths, like boundaries. It appears that these defects tend to annihilate during prolong isothermal holding at ambient temperatures.

Acknowledgements

The work is sponsored by Department of Atomic Energy, Govt. of India, vide grant nos. 34/7/89-G and 34/4/95-R&D-II/678. S.K.B. is grateful to CSIR, Govt. of India, for offering him a SRF in support of this work. The authors are thankful to Dr Srikumar Banerjee for stimulating discussions and constant encouragement.

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