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Letter to the Editors

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

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Abstract

The effect of the thermal cycles of negative magnitude (TCNM) on the ^{222}Rn permeability in Pb was studied at 150°C, after prolonged equilibration at the same temperature. It was found that TCNM enhance the permeability and reduce the activation energy of permeation to an insignificant level of 1.2 kJ/mol. The results have been explained in terms of capture of vacancies by large ^{222}Rn atoms and/or opening up of small 'channels' of atomic dimensions. These defects tend to annihilate during prolonged (72 h) isothermal holding at ambient temperature. © 1997 Elsevier Science B.V.

1. Introduction

Permeation of inert gases at low partial pressure is of particular interest in nuclear technology. The extremely small permeation flux in case of inert gases, however, precludes the possibility of using conventional permeation measuring methods. The development of a highly sensitive α-spectroscopic method by Pabi and Hahn [1] for measuring the ^{222}Rn permeation flux on atomic scale ($\sim 10^4$ atoms/m^2 s) has enabled the time modulation of permeability at low partial pressure ($\sim 10^{-7}$) to be tracked over a long period of time (e.g., months). In this method there is no externally impressed force to cause ionization of Rn atoms during its incorporation in metal lattice. Recently, Bhattacharya and Pabi [2,3] have used a modified version of this α-spectroscopic method to study the ^{222}Rn permeability in Pb at high homologous temperatures T_H (≥ 0.68) and in Au at low T_H (≤ 0.32). It was found that virgin annealed Au specimen was impermeable to ^{222}Rn during prolonged (4.5–35 d) isothermal holding up to 150°C; but the permeation was triggered when the specimen was subjected to a thermal cycle of negative magnitude (TCNM), and naturally, the effect cannot be attributed to the rupture of any surface layer on the specimen [3]. In the present investigations, the effects of TCNM of varying amplitude on the ^{222}Rn permeability in Pb at higher T_H (≥ 0.68) have been studied with a view to explore the possible effects of temperature fluctuation on the inert gas permeability in reactors, using ^{222}Rn as a probe.

2. Experimental

A cross-rolled, well annealed (in oil at 130°C for 3 h) 67 μm thick Pb (99.99%) foil specimen having average grain size of 12 μm, that has been used earlier to study isothermal permeability [2], is also used in the present investigation. The description and working principle of the modified Rn permeability measuring equipment capable of measuring radon flux (N_{Rn}) down to the order of 5000 atoms/m^2 s have been given earlier [2,3]. 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 Refs. [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 the 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 Pb is known to depend on the thermal history in course of permeation [2], it is

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necessary to present the entire thermal schedule in course of permeation. Fig. 2 of Ref. [2] displayed the thermal history of the Pb specimen in the phase-I of the investigation. Here the permeation flux in the virgin Pb specimen was measured in course of heating up to 150°C with intervening prolonged ($\geq$ 135 h) isothermal holding at 100°C and 130°C. During isothermal holding at 150°C for 135 h in phase-I, the ^{222}Rn permeability in Pb gradually increased to a steady state value $N_{Rn(steady)} = 255$ atoms/mm^2 s [2]. At this stage, the present set of experiments (i.e., phase-II) commences, where the same specimen has been subjected to thermal cycle of negative magnitudes (TCNM) as per the schedule in Fig. 1 following which the ^{222}Rn permeability is measured at T_P = 150°C. Here, in treatments h_7, h_9, h_{10} and h_{11}, the TCNM of amplitude ΔT_n (20°C–80°C) has been introduced, which comprises 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_8 and h_{13} represent step heating of short duration (~ 12 h) at different T_P, while treatment h_{12} signifies isothermal holding at 28°C for 72 h.

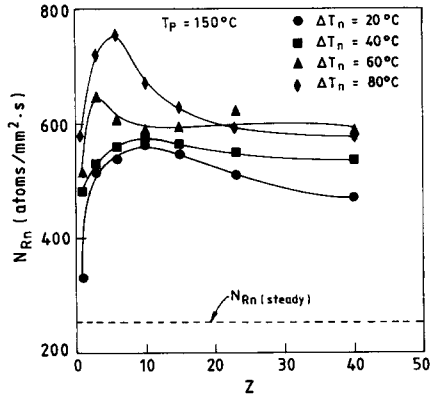

Fig. 2. N_{Rn} vs. Z in course of treatment h_7, h_9, h_{10} and h_{11} of Fig. 1.

Fig. 2 shows the variation of N_{Rn} with the cumulative

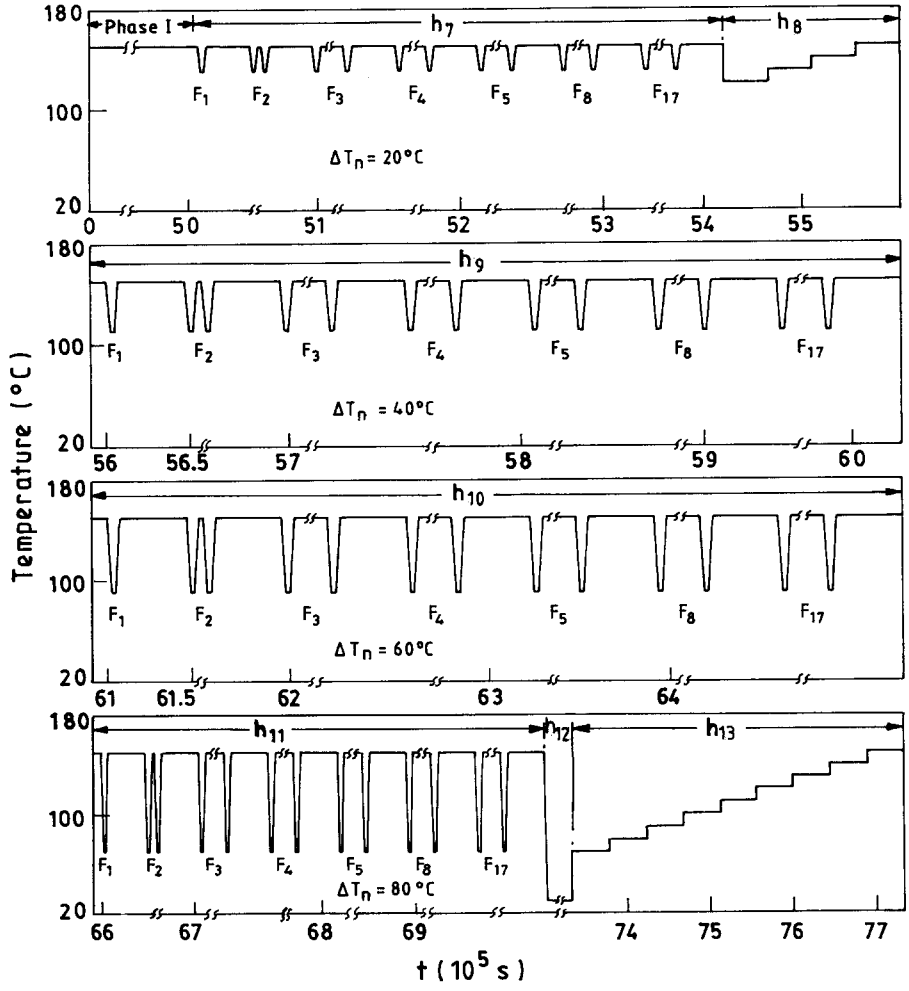

Fig. 1. Thermal schedule of Pb specimen in course of permeation including that of TCNM. Subscript of F represents the number of TCNM.

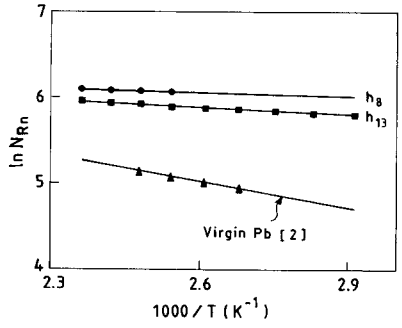

Fig. 3. Arrhenius plots of ln N_{Rn} vs. $(1000/T)$.

number of thermal cycles (Z) for different values of ΔT_n in treatments h_7, h_9, h_{10} and h_{11} (cf. Fig. 1). After prolonged equilibration at 150°C in phase-I, when the Pb specimen was subjected to one TCNM with $\Delta T_n = 20$°C (in treatment h_7 of Fig. 1), N_{Rn} at 150°C increased from the $N_{Rn(steady)}$ value of 255 atoms/mm^2 s to 330 atoms/mm^2 s. The N_{Rn} increased gradually with Z of same ΔT_n (20°C), and reached a peak value, $N_{Rn(peak)} =$ 567 atoms/mm^2 s, after 10 thermal cycles, beyond which N_{Rn} showed a gradual decline. The step-heating treatment from 120 to 150°C introduced at this stage in treatment h_8 (Fig. 1) yielded an activation energy for permeation $Q_P =$ 1.2 kJ/mol (Fig. 3). With the increase in the magnitude of ΔT_n to 40°C in treatment h_9 (Fig. 1), the N_{Rn} once again attained a peak value $N_{Rn(peak)} = 578$ atoms/mm^2 s in a manner similar to that in treatment h_7 (Fig. 2). It is found that $N_{Rn(peak)}$ obtained in treatment h_9 is higher than that in treatment h_7 (Fig. 2). With further increase in ΔT_n to 60 and 80°C in treatment h_{10} and h_{11}, respectively, the N_{Rn} vs. Z plots (Fig. 2) again exhibit $N_{Rn(peak)}$, the level of which increases with the magnitude of ΔT_n. Fig. 2 shows that at $T_P = 150$°C, the $N_{Rn(peak)}$ attained after TCNM of $\Delta T_n = 80$°C is about three times the value of $N_{Rn(steady)}$ measured earlier at the same T_P (i.e., 150°C) in absence of thermal fluctuation.

After completion of TCNM, the specimen was cooled to room temperature (28°C) and held for 72 h (in treatment h_{12}) before subjecting it to the step-heating treatment from 70 to 150°C in treatment h_{13} (Fig. 1). The N_{Rn} measured at this stage (i.e., h_{13}) fall on a straight line in an Arrhenius plot (Fig. 3) to yield $Q_P = 2.3$ kJ/mol.

4. Discussions

Annealing the Pb specimen at 130°C, well above the recrystallization temperature of pure Pb (33°C) [4], prior to permeability measurements ensured complete recrystallization and annihilation of any deformation induced excess vacancies. Earlier experiments [2] in phase-I with the same Pb specimen have yielded $Q_P \sim 8.2$ kJ/mol for ^{222}Rn permeation in virgin Pb sample (Fig. 3). This value of Q_P is quite close to the activation energy of diffusion (Q_D) of Rn in Ta (~ 8 kJ/mol) yielded by the data of nuclear recoil experiments [5]; but it is much smaller than the Q_D of Rn in Ag (~ 130 kJ/mol) determined by the high energy ion bombardment technique [6]. Moreover, this value of Q_P in Pb (8.2 kJ/mol) is smaller than the Q_P of hydrogen in annealed iron (48.5 kJ/mol) [7] or in Ni-base alloys (~ 30 kJ/mol) [8], or the activation energy for grain boundary diffusion $Q_{D(g.b.)}$ of Pb in Pb (17 kJ/mol) [9]. Since a neutral radon atom occupies ~ 1.5 times the volume of a Pb ion, it has been suggested earlier that ^{222}Rn permeates in annealed Pb mainly through the structural defects like grain boundaries by capturing vacancies [2], which conforms to the earlier proposition of Rimmer and Cottrell [10]. The present value of Q_P obtained in treatment h_8 after the introduction of TCNM of amplitude $\Delta T_n = 20$°C is only 1.2 kJ/mol, which is of the order of Q_D (1 kJ/mol) for liquid phase interdiffusion along ⟨001⟩ tilt grain boundary during its wetting in (Fe–10 at.% Si)–Zn bicrystal [11]. However, these values are unusually small for any diffusion in solid metals. For instance, even the $Q_{D(g.b.)}$ of hydrogen in Fe (6.355 kJ/mol) [12] is much higher than 1.2 kJ/mol, although the hydrogen atoms are much smaller than ^{222}Rn atoms [13]. Such a low value of Q_P at this stage (i.e., in treatment h_8) of ^{222}Rn permeation possibly indicates that the conventional thermally activated diffusion may not be dominant here.

The enhancement of permeability in Pb at higher T_H ($= 0.72$) 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 a similar result has also been obtained in Au at much lower T_H (≤ 0.32) [3], where the possibilities of formation of any surface oxide layer or considerable redistribution of impurities by volume diffusion may be precluded. Contribution of pre-existing dislocations (if any) to the permeation in Pb is also expected to reach a steady state during prolonged (135 h) isothermal holding at T_P ($= 150$°C) prior to the introduction of TCNM. Besides, 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. A possible mechanism of the enhancement of permeability by TCNM may be put forward as follows.

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 might provoke the capture of vacancies by the Rn atoms residing at the structural defects like grain boundaries or grain boundary triple points. 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 and/or open up 'channels' of atomic dimension across the foil. Under this situation, the transport of ^{222}Rn atoms through the specimen would take place by vacancy-aided thermally activated transport ($Q_P \approx 8.2$ kJ/mol), as well as by flow

through these 'channels'. If the latter one is dominant, the resultant value of Q_P would be marginalized (e.g., 1.2 kJ/mol in treatment h_8).

After completion of TCNM when the specimen is cooled to room temperature ($T_H = 0.5$) in treatment h_{12}, the 'channels' or captured vacancies get a chance to gradually collapse/annihilate. As a consequence, in treatment h_{13} a reduction of N_{Rn} and increase in Q_P (e.g., to 2.3 kJ/mol), as compared to the N_{Rn} and Q_P (1.2 kJ/mol) obtained in treatment h_8, might have resulted (cf. Fig. 3).

Further study is, however, warranted to understand why N_{Rn} declines beyond a certain number of thermal cycles (cf. Fig. 2). In this respect it may be pointed out that study of the isothermal permeability in cold worked Au [3] has indicated that the maxima in thermally activated ^{222}Rn permeability may be associated with some particular state of the defects (vacancies) in the grain boundaries. Probably, the permeation peaks in Fig. 2 may also be attributed to similar reason. Nevertheless, the present study demonstrates for the first time that small thermal fluctuations in reactor environment may have a pronounced influence on the inert gas permeability in materials.

5. Conclusions

Thermal cycles of negative magnitude can remarkably enhance the ^{222}Rn permeability in Pb at high T_H ($= 0.72$) and reduce Q_P to a trivial level. The results may be explained in terms of capture of vacancies by large Rn atoms vis-à-vis opening up of small 'channels' of atomic dimension. Probably, these defects tend to annihilate during prolonged (72 h) isothermal holding at lower T_H ($= 0.5$).

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