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Migration of ^{210}Po in Lead to the Surface

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Measurements and analysis of the kinetics of the phenomenon of migration of polonium to the surface in lead are presented. Polonium atoms diffuse to surface because their thermodynamic potential on surface is lower than inside the lead of the raw production. The effect is very weak for the case of thermal diffusion at room temperature, but very strong when close-to-surface layer is plastically deformed for instance by cutting of the surface. After several vacuum-remelting processes all the effect decrease.

Introduction

In 1981 the effect of the increasing of surface alpha radioactivity of lead with time after rescraping of the surface was first noted (Wöjcik, 1981) and alpha radiation was identified as originating from ^{210}Po. Detail investigation were reported in Zastawny (1988) and Zastawny *et al.* (1989).

Usually lead of new production is contaminated by radioactive ^{210}Pb that decays in the sequence

$$^{210}\text{Pb}\xrightarrow[31\text{y}]{\beta 61.5}{>}\,^{210}\text{Bi}\xrightarrow[7.2\text{d}]{\beta 1161}{>}\,^{210}\text{Po}\xrightarrow[200\text{d}]{\alpha 5305}{>}\,^{206}\text{Pb}.$$

The kind and energy of decay (keV) are given above the arrow, the average life time below. If N_0 denotes the uniform density of polonium atoms in the steady state, τ is their mean life-time and R the range of polonium alpha particles in lead (10.6 μm), then the alpha radioactivity of a unit of surface in the steady state is equal to

$$A_0 = \frac{N_0 R}{4\tau}. \tag{1}$$

On account of short life-time of Bi and Po with respect to Pb, usually the steady state occurs i.e. $N_i/\tau_i = \text{const}$, where τ_i and N_i denote the mean life-times and densities of the radionuclides in the decay series.

Zastawny *et al.* (1989) presented the results of the measurements of the alpha radioactivity of the lead vs of the time after rescraping or etching of the lead surface. After rescraping the alpha radioactivity increased quickly at the beginning and later more slowly to a steady-state value higher then A_0. Further on, when the temperature was increased from room temperature to 100°C, the process activated itself and as before, the new higher steady-state value of radioactivity was reached. Next, when the temperature was decreased back to room temperature, the radioactivity was decreasing only with the rate corresponding to the radioactive decay of the ^{210}Po, to a steady-state value corresponding to room temperature. When the lead surface was etched, the increase of the alpha radioactivity in the measured time period of some days was so low that it was neglected.

According to interpretation in Zastawny *et al.* (1989), the free energy of the polonium atoms on non-oxidized lead surface is lower than in bulk material. Therefore, the polonium atoms can be accumulated on the surface in the diffusion process. When the surface of the lead is etched, only very low thermal diffusion occurs and increasing of the radioactivity is very slow and low. A high value of the diffusion coefficient in the material near the surface is stimulated by plastic deformation of the layer close to the surface, when the surface is rescraped or cut. The high value of the diffusion coefficient is caused by high density of the defects in the crystal lattice, generated in plastic deformation process. The experimental data presented in Zastawny *et al.* (1989) show that at temperature of 100°C, the effect of the alpha radioactivity increase was considerably higher then at room temperature. From this it was concluded that the difference between free energy of ^{210}Po atoms on surface and inside of the material is considerably higher than the thermal energy kT. The increasing of the radioactivity at higher temperature is a result of the increasing of the diffusion coefficient on account of thermal activation. The density of the polonium atoms in lead, near of the surface is a function of the time and the distance x from the surface and the radioactivity $A(t)$ of the surface unit is equal

$$A(t) = \frac{2A_0}{R}\int_0^R \left(1 - \frac{x}{R}\right) n(x, t)\,\mathrm{d}x \tag{2}$$

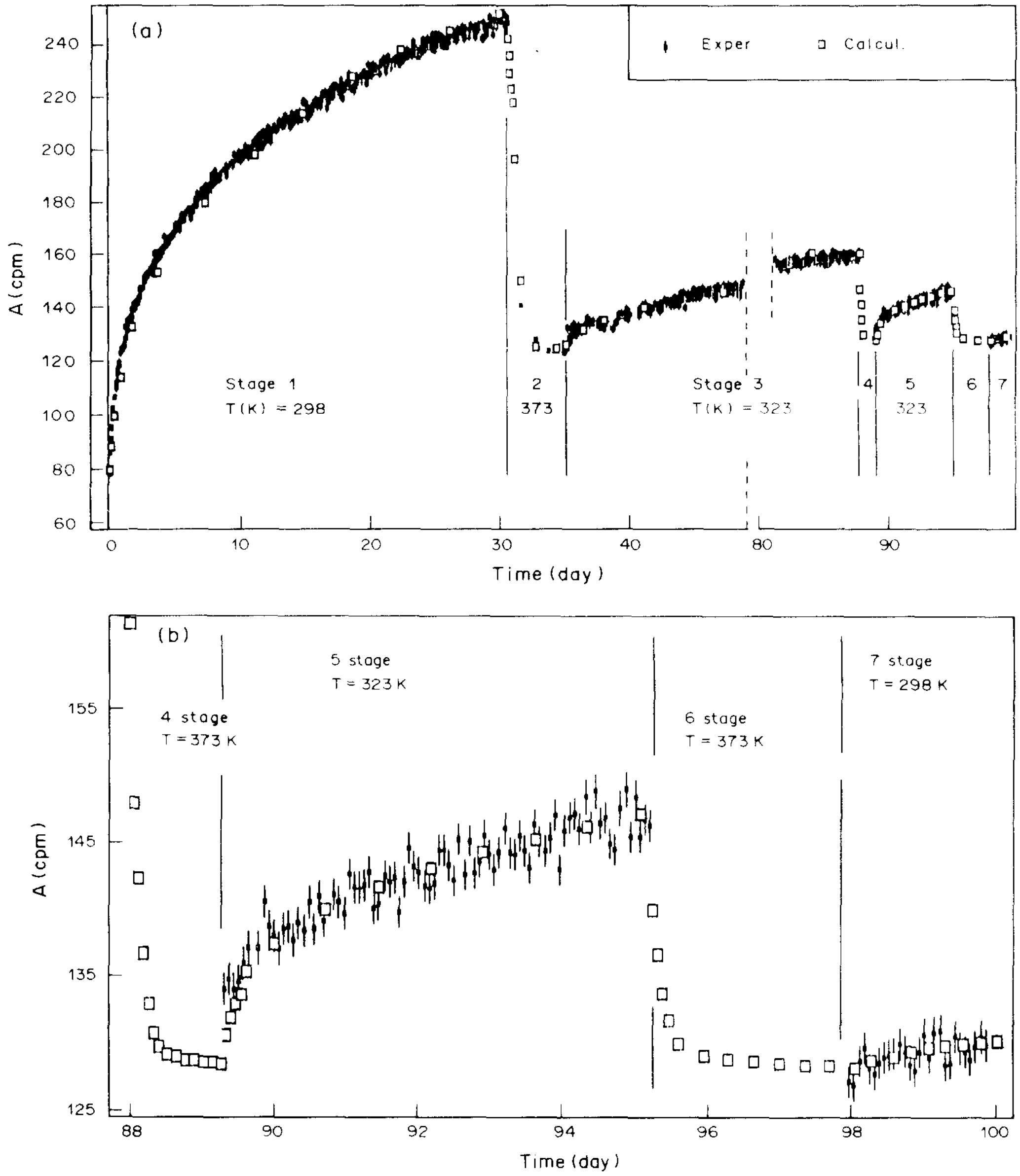

Fig. 1. Results of the measurements and some theoretical calculation of the alpha radioactivity vs time of the rescraped lead. The experiment was divided into stages from 1 to 7 with different temperature of storage of lead. Part (b) of the figure is an enlarged picture of the stages 4–7.

where $n(x, t)$ is the relative density of the polonium atoms with respect to non-disturbed density N_0.

The sample of lead used in [3] was prepared from raw materials by remelting in the air. In further experiments, it was discovered that after remelting of the lead in a vacuum (followed by a strong outgassing process) the sample has demonstrated differences of the effect with respect to earlier results. Also some attempts of measuring of the effect without plastic deformation of the near-surface layer and looking for the effect of the increasing beta radioactivity were undertaken.

Experimental

All measuremements of alpha radioactivity were carried out with one sample the same as in the experiments presented in Zastawny *et al.* (1989).

The sample had the shape of a disc with a surface area of 200 cm^2. A photomultiplier with a diameter a little larger than the diameter of the sample, covered on top with directly activated zinc sulphite was situated 3 mm above the sample surface. The sample with the photomultiplier was placed in an air-tight chamber rinsed by inert gas. The heating of the

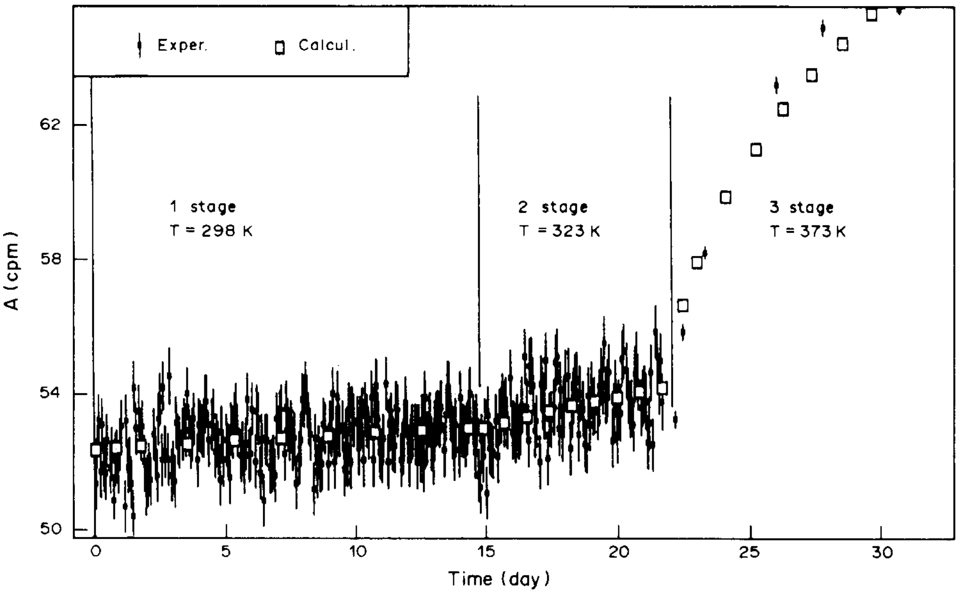

Fig. 2. Results of the measurements and some theoretical calculation of the alpha radioactivity of the sample stored after etching at different temperatures.

sample could be controlled up to 50°C. In another vacuum heating chamber the sample could be stored at a temperature of up to 100°C. In such case, for measurements the sample was cooled, placed in the measuring chamber for the time of the measuring, and next placed back in the heating chamber.

The counts were recorded every 100 min. The background of the measuring stand amounted to about 4.0 cpm. The results of these measurements are presented in diagrams with their Poisson errors.

The surface of the sample was scraped by machining or etched by electrolytic pickling in electrolyte mixtures; 35% of perchloric acid and 65% of acetic anhydride.

The measurements of the beta radioactivity for looking for the possible increase of the ^{210}Bi radioactivity were performed by means of a needle gas counter with the small samples prepared from the same material. Zastawny and Rabsztyn (1986).

Results and Their Analysis

The first part of the investigation deals with the measurements of alpha radioactivity of a sample, after twice-vacuum-remelting process, stored at different temperatures after cutting. The essential results are presented in Fig. 1. The results are from a single sample stored after scraping at different temperatures. The decreasing of the alpha radioactivity when the temperature is increased to 100°C (stage 2), is a new result compared to Zastawny *et al.* (1989), when a significant increase of radioactivity was observed. The results on Fig. 1 firmly show that for different temperatures the different equilibrium states are reached. The equilibrium states result from opposed processes—thermal activating of the diffusion coefficient and thermal disturbance of the atoms collected on surface. This means that the difference between the free energy of ^{210}Po atoms on the surface and inside the material is not considerably higher than the thermal energy kT and consequently the simplified equation used in Zastawny *et al.* (1989) for current density of the Po atoms can not be accepted in full form i.e.

$$i(x,t) = -D\frac{\partial n(x,t)}{\partial x} - \frac{D}{kT}\frac{\partial U(x)}{\partial x}n(x,t). \quad (3)$$

Here $i(x,t)$ is the quotient of the current density by N_0, D is the diffusion coefficient, $U(x)$ is the free energy of the polonium atoms, T is the temperature and k is the Boltzmann constant. Consequently the transport equation [as opposed to Zastawny *et al.* (1989)] has the form

$$\frac{\partial n}{\partial t} = D\frac{\partial^2 n}{\partial x^2} + \left(\frac{\partial D}{\partial x} + \frac{D}{kT}\frac{\partial U}{\partial x}\right)\frac{\partial n}{\partial x}$$
$$+\frac{1}{kT}\left(\frac{\partial D}{\partial x} + \frac{\partial U}{\partial x} + D\frac{\partial^2 U}{\partial x^2}\right)n + \frac{1-n}{\tau}. \quad (4)$$

In the second part of the experimental investigation, an attempt to determine the values of the thermal diffusion coefficient of the polonium atoms in lead was made. A big sample was etched in order to obtain a plastically undeformed layer near the surface and then measurements were begun at room temperature and then at higher temperatures. From several series of measurements only ones with the lowest increase of the rate of alpha radioactivity (equal 0.093% per day for $T = 298$ K and 0.37% per day for 323 K) are presented in Fig. 2.

The third part of the experiment were carried out in a similar fashion to the first one but after additional twice-vacuum-remelting process of the sample. From the results it follows that all the effects of the increasing of the alpha radioactivity disappear. So it can be concluded that higher free energy of the ^{210}Po atoms inside of the lead with respect to surface is caused by gases dissolved in lead or other effects removed in the vacuum remelting process and after successive vacuum remelting the difference of the free energy decreases to zero.

The last part of the experiment concerns the possible increasing of the ^{210}Bi beta radioactivity in a mechanism similar to ^{210}Po. After measurements during one month with a sample prepared as in Zastawny *et al.* (1989) it may be concluded with an accuracy of about 0.2% that no effect occurs and therefore it is found that the single result cited in Zastawny *et al.* (1989) in this matter was a mistake.

Some preliminary numerical calculations were undertaken. The terms $U(x)$ and $D(x)$ were approximated by expressions

$$U(x) = -U_0 \exp(x/\lambda) \tag{5}$$

and

$$D(x) = D_0 \exp(x/L) + D_t. \tag{6}$$

In equation (5) U_0 is the decrement of the free energy on surface with relation to the inside of the material. The first term in equation (6) describes the diffusion activated by lattice defects, the second term corresponds to the thermal diffusion. Parameter λ was accepted as equal to one step of the iteration along the coordinate x, equal to 0.5 μm. Constants U_0, D_0, L, D_t were chosen for the best agreement of the calculated results with experimental data. An agreement with the experimental results was obtained for the values $U_0 = 0.05$ eV, $L = 5\,\mu$m and $D_0 = 200\,\mu\text{m}^2$/d for stage 1, 60 μm^2/d for stages 2, 4, 6, 10 μm^2/d for stages 3, 5 and 2.5 μm^2/d for stage 7. Decreasing of the D_0 in stage 2 can be explained by the thermal soaking of the greater part of the crystal defects. From results presented in Fig. 2 similar to the above, numerical calculations for $D_0 = 0$ give the values of D_t equal to about 0.05, 0.2 and 1 μm^2/d for temperatures 25, 50 and 100°C respectively.

Conclusions

In lead of the row production, contaminated by radioactive ^{210}Pb, atoms of the radioactive derivative product ^{210}Po migrate to the surface due to the lower value of the free energy of the polonium atoms on non-oxidized lead surface than in bulk material. Kinetics of this effect is limited by diffusion coefficient, difference in free energy and mean life-time of the polonium atoms. In some cases increment of the surface alpha radioactivity connected with this process is a few times greater values corresponding to the uniform density of the polonium atoms in lead.

Remelting process of the lead in vacuum, followed by a strong outgassing process decreases the difference of the mentioned free energy and after several remelting processes all effect disappears.

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