

URANIUM DIFFUSION INTO FISSION CHAMBER ELECTRODES

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1. Introduction

In large boiling water reactor cores the local flux distribution is monitored continuously with in-core fission chambers [1]. These fission chambers are exposed to high neutron- and gamma-fluxes, high temperatures and high pressure and should be in operation as long as possible. Therefore high quality standards are necessary for all parts of the fission chamber in order to achieve an acceptable lifetime. One critical part of the fission chamber is the uranium coated electrode. The electrode is usually a titanium cylinder and may be coated by several methods with highly enriched ^{235}U . This process should result in an even uranium distribution on the surface and a high adhesive strength of the uranium to the titanium.

Because of the fission energy released in the uranium layer the temperature of the electrode will be considerably above the ambient temperature of the fission chamber. Therefore temperature-induced diffusion of uranium into the titanium is possible and will result in a decreased fission chamber sensitivity because of the short range of the fission fragments.

The aim of these investigations was to analyse the temperature- and time-dependence of diffusion of uranium atoms into titanium by different means.

2. Preparation of the samples

The electrodes consisted of a titanium cylinder of

25 mm length, 4.6 mm outer and 3.9 mm inner diameter. The 93% enriched metallic uranium layer with a thickness of $0.15\ \mu\text{m}$ was deposited by an entirely new method [2]. The electrodes were cut by a spark-erosion process into four pieces which were annealed afterwards for different times at different temperatures. Then the samples were mounted on a quartz glass stick and put into a steel tube together with depleted uranium which acted as a getter for small amounts of oxygen. The steel tube was evacuated before the annealing process and then filled with argon gas of 99.99% purity. Afterwards the whole experimental arrangement was inserted into a conventional resistance furnace, the temperature was measured with a NiCr–Ni thermocouple and could be held constant within $\pm 5^\circ\text{C}$. After the heat treatment the individual samples were polished perpendicular to the axis of the cylinder in order to observe a uranium profile in the titanium with X-ray fluorescence analysis. The results were negative because of the small diffusion depth of the uranium atoms compared with the diameter of the analysing electron beam ($\approx 3\ \mu\text{m}$). Therefore an attempt was made to spread this distance by polishing the cylinder under a very small angle to the cylinder axis. Accurate measurements showed that an angle of 2° could be achieved. The samples were embedded in a synthetic resin and polished in several steps with fine grain diamond paste. Between each step the surface was controlled with a light microscope.

3. X-ray fluorescence analysis

The polished electrodes were analysed with a scanning electron microscope and the uranium distribution was observed by X-ray fluorescence analysis. The investigations showed no presence of uranium in the polished surface of the samples 10/650 and 1/850. (The first digits indicate the annealing time in hours and the second group of digits indicate the annealing temperature in degrees centigrade.) The sample 1/950 revealed

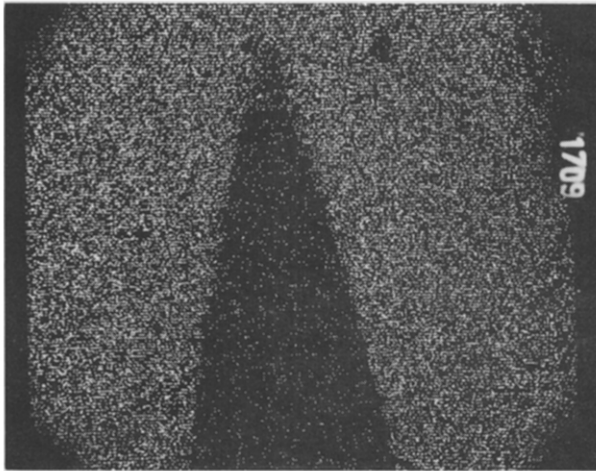


Fig. 1. Sample 10/650: annealing time 10h, annealing temperature 650°C; scale 1 cm \cong 0.3 mm.

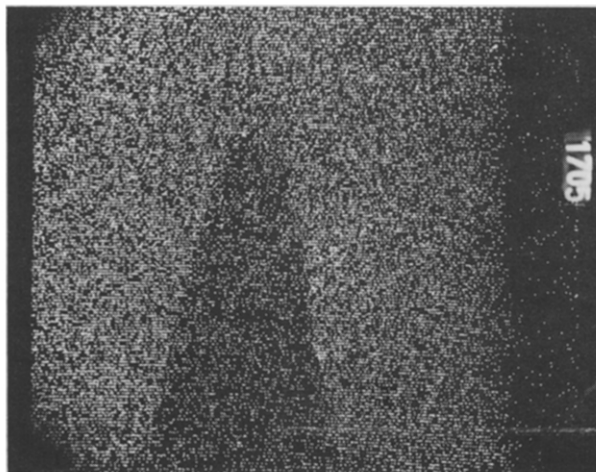


Fig. 2. Sample 10/850: annealing time 10h, annealing temperature 850°C; scale 1 cm \cong 0.3 mm.

no uranium at the surface at all while the samples 100/650, 10/850 and 3/850 showed some uranium in the polished surface. Figs. 1 and 2 show the uranium distribution in samples 10/650 and 10/850. Sample 10/650 shows a sharp decrease of uranium in the polished surface; only at the upper end of the parabolic area can a distinctive uranium concentration be observed. Sample 10/850 shows a high uranium concentration in the polished area especially at the upper end of the parabolic area.

At the Ti-U interface several discrete uranium particles were observed which may have been broken off during the polishing process. Therefore quantitative measurements of the uranium profile in the Ti are not possible with this method. Better results have been achieved by measuring the α -activity of the sample which will be shown below. The main difficulty in observing the uranium diffusion is the increase of the diffusion velocity at temperatures above 890°C, marked by the α - β -phase transition of Ti and the end of the resistance of TiU_2 , which results in a rather even uranium distribution in titanium.

Annealing experiments performed at temperatures above the phase transition will have no practical feedback into chamber technology because these temperatures will be far above the operating temperature of current in-core fission chambers.

4. Measurement of the α -activity

The α -activity of the samples was measured in a Packard Tri-Carb 3800 liquid scintillation spectrometer. Liquid scintillation can be well used for measuring α -rays in the presence of low-energy β -rays [3]. If the energy of the β 's is too high, pulse-shape discrimination has to be used [4]. The scintillating liquid used was conventional toluene scintillator (12.5 g PPO = 2.5 diphenyloxazole; 0.6 g POPOP = 1.4-bis-2-(5-phenyloxazolyl)-benzene; 2.5 l toluene).

Measurement of the α -activity was chosen because the range of α -particles with an energy of 4.7 MeV in Ti is only a factor 2-3 greater than the range of the fission products. Thus by measuring the α -activity one gets a good result correlated to the efficiency of the fission chamber.

In the spectrometer the sample enclosed in a plastic or glass bulb is seen by two photomultipliers mounted

opposite to each other. Only coincidence pulses are detected for suppressing noise. For maintaining a standard geometry the samples were held vertically in the bulbs. The main α -activity is due to the α -emission of ^{234}U having an energy of approximately 4.7 MeV.

Using this liquid scintillation spectrometer it was possible to measure the pulse height spectrum. The total α -activity of the samples was also measured.

5. Results of the α -activity measurements

As mentioned above the samples were annealed at 650°C for 1–100 h, at 850°C for 1–10 h and at 950°C for 1 h. Fig. 3 shows the pulse-height spectrum of the sample annealed for 3 h at 850°C. It can be seen that the α -peak becomes smaller and broader because of the diffusion process. The mean α -energy is also shifted to lower energies because the α -particles coming from nuclei diffused into the Ti lose much of their energy before reaching the surface of the sample. The pulse-height spectrum can be obtained by folding the appropriate solution of the diffusion equation

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}, \quad (1)$$

Table 1
Decrease of the integrated α -activity of the electrodes at different temperatures for the longest annealing times. The values of the after-annealing times agree within experimental error with an exponential law (eq. (3)).

$T(^{\circ}\text{C})$	I/I_0	$K [\text{h}^{-1}]$
650	0.93 after 100 h	7.3×10^{-4}
850	0.45 after 10 h	7.7×10^{-2}
950	0.017 after 1 h	–

initial conditions $C = C_0$ for $0 \leq x < h$,

$C = 0$ for $h < x$,

boundary conditions $\frac{\partial C}{\partial x} = 0$ for $x = 0$ and all t ,

with the energy distribution of the α -particles coming from a fixed source at a certain depth below the surface of the electrode. Because of the small thickness of the U-layer (0.15 μm) at the beginning of the diffusion compared to the thickness of the diffusion medium (250 μm), the solution for the infinite diffusion medium can be used with good approximation. This solution is [5]

$$C(x, t) = \frac{1}{2} C_0 \left[\text{erf} \left(\frac{h-x}{2\sqrt{Dt}} \right) + \text{erf} \left(\frac{h+x}{2\sqrt{Dt}} \right) \right], \quad (2)$$

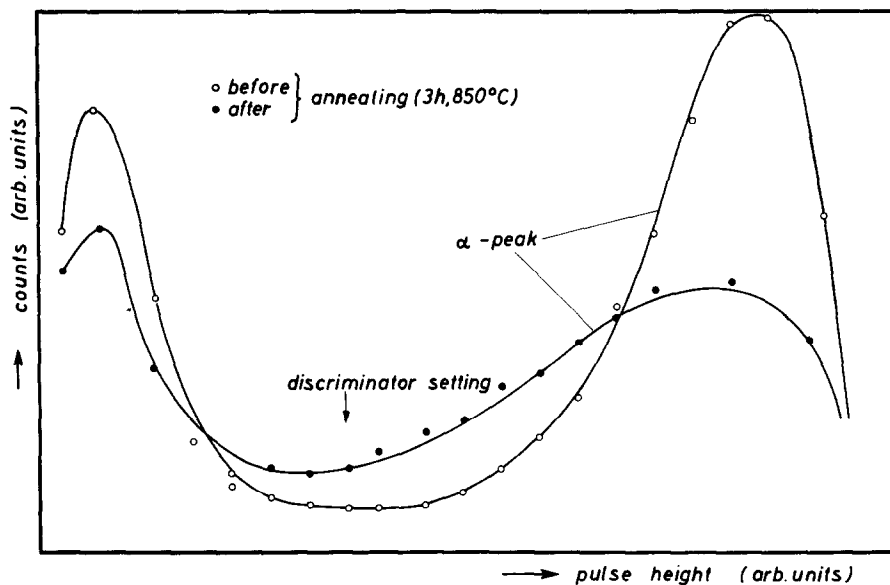


Fig. 3. Pulse-height spectra measured by liquid scintillation of sample 3/850 before and after annealing.

where h is the thickness of the uranium layer at the beginning of the diffusion. This means that it is in principle possible to determine the diffusion coefficient from the form of the pulse-height spectrum. Work on this problem is in progress. For measuring the integrated α -activity the discriminator level was set as indicated in fig. 3.

Annealing the samples led to a diminution in the integrated α -activity to values as indicated in table 1. The results measured at 650°C and at 850°C can be well fitted by an exponential law

$$I = I_0 e^{-Kt}, \quad (3)$$

where I_0 is the integrated α -activity before annealing and I the integrated α -activity after annealing for t h.

It follows from general arguments that for a broad band of diffusion times the constant K is related linearly to the diffusion coefficient. The activity of the sample 1/950 shows that uranium nearly totally disappears in the titanium. Pavlinov et al. [6] found that the diffusion coefficient of U in Ti measured at temperatures from 915 to 1200°C is extremely high. These authors propose that this anomaly is due to the $\alpha \rightleftharpoons \beta$ phase transition in Ti at 882°C, which causes atomic effects and therefore an increased diffusion mobility. It could also be assumed that the existence of the intermetallic compound TiU_2 is hindering the diffusion at lower temperatures. At the above-mentioned temperature Adda et al. [7] observed a marked increase in the diffusion velocity with increasing temperature.

Using our values of K for annealing temperatures of 650°C and 850°C and inserting them into an equation of the form

$$K = K_0 e^{-C/T}, \quad (4)$$

where C is a parameter proportional to the activation energy and T is the temperature in kelvin, it can be es-

timated that at an electrode temperature of 500°C it would take about 1000 days for a 10% reduction in α -activity. At 400°C this reduction would take about 200 years.

6. Conclusion

The time- and temperature-dependent behaviour of thin uranium layers on titanium were analysed by different methods. Qualitative results were obtained by X-ray fluorescence analysis. Better and quantitative results were achieved by α -spectroscopy and liquid scintillation counting of the samples. It could be shown that the uranium diffusion velocity into titanium increases rapidly after the phase transition at 890°C.

Estimations showed that the electrode sensitivity decreases for 10% after 1000 days at 500°C. This is however much smaller than the actual fission chamber sensitivity decrease (about 3% per month at $7 \times 10^{13} \text{ n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$) during reactor in-core irradiation due to the continuous fissioning of uranium atoms.

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