

## No Reduced Radioactivity of Tritium in Small Titanium Particles

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The experimental results of O. Reifenschweiler are explained by the known reactions between hydrogen and titanium under careful distinction of the effects at the surface and in the bulk.

In contrast to the remarks in [1], the following statements must be made.

- 1) The assertion that “it is not possible to distinguish between bulk absorption and chemisorption at the surface” is not true, neither for the PdH-nor for the TiH-system.

Concerning the PdH-system, the processes at the surface ( $H_2$ -dissociation, surface diffusion) have been described in [2] in two chapters, p. 84ff. and 134ff. At about the same time, Minnerup [3] showed that the entrance of the H atoms into the Pd-lattice does not start before the external surface is covered by a hydrogen monolayer. Minnerup further showed that the H-atoms between the surface layer and the bulk phase have to pass a “sub-surface state” [4]. This state, intermediate between adsorption on the surface and absorption in the bulk, was detected a few years earlier with LEED-investigations by Christmann et al. [5]. The enthalpy of desorption of hydrogen from the surface is much higher than the enthalpy of the decomposition of the PdH compound in the bulk; the potential wells of the H atoms at the surface are correspondingly deeper, and the vibration frequencies of the H atoms are higher. This is the reason why the surface will be covered before the H atoms enter the interior of the lattice.

Concerning the TiH-system, the differences between the surface and the bulk are similar. The measurements of the local modes  $h\omega$  by Hempelmann et al. [6] and Ross et al. [7] were performed by neutron scattering (as in the PdH-system) and are therefore not sensitive to the surface states but represent only the vibration modes of the hydrogen in the bulk.

Reprint requests to Prof. E. Wicke.

- 2) Reifenschweiler declares with respect to the Ti particles that “the time constant for the uptake of tritium is about  $10\text{ s}$ ”.

From what measurement, however, comes this value? Is this time constant not determined by the velocity of the transport of tritium in the inlet devices? Titanium is known to be a getter material, taking off  $H_2$ ,  $O_2$ , CO and other “vacuum contaminations” spontaneously. This, of course, means adsorption at the surface; the entering of H into the interior of the lattice needs the performance of the processes mentioned above and takes more time or requires higher temperatures. According to Maeland et al. [8], the reaction is extremely slow at room temperature and needs activation, typically by heating to several hundred degrees in hydrogen. In the case of the Ti particles the reactions, i.e.  $H_2$ -dissociation, surface diffusion and entering the lattice, became accordant Reifenschweiler apparent at about  $115^\circ\text{C}$ . At room temperature the arrangement of Ti particles, shown in Fig. 1 of [1], acts as a getter and takes off all the tritium added spontaneously by adsorption at the first layers of Ti particles. The surface of all Ti particles present could take off 20 times more tritium by adsorption, as calculated in [9] for smooth sphere surfaces; considering the surface roughnesses, the factor will be 40 to 60, i.e. the surfaces of about the first two particle layers only in Fig. 1 of [1] will be covered by gettering all the tritium added.

- 3) The statement that the arrangement of the Ti particles is “thus a homogeneous source of X-radiation” is irrelevant and misleading.

At about  $115^\circ\text{C}$  the tritium begins to spread out by surface diffusion over all Ti particles present and to enter their lattice. The X-radiation from the  $\beta$ -decay of tritium coming from the tube wall, Fig. 1 of [1], has to pass, according to the calculations of O. Reifenschweiler, about 80 monolayers of Ti particles, whereas its maximum energy is just adequate to pass 130 monolayers. There are, accordingly, quite a number of X-ray photons, the intensity of which, as a consequence of absorption and scattering, is no more sufficient to produce counts in the GM tube. (By the way: it is quite unusual – and by no means precise – to measure the intensity of X-radiation by the counts in a GM tube). This deficiency of X-ray photons, i.e. of counts produced in the GM tube, is in my opinion the

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main cause of the fictitious "Reduced radioactivity of tritium in small titanium particles" above about 115°C claimed in [10]. The intensity of the X-radiation, leaving the topmost layer of the Ti particles depends, due to the loss in energy by absorption and scattering, on the place, where its source is located; the statement that the titanium mass present is "a homogeneous source of X-radiation" is, therefore, misleading.

- 4) The author points out that "the enthalpy of formation of 1 mol of titanium oxide is nearly 2 times that of 2 mols of water." This is true for  $\text{TiO}_2$  as titanium oxide; I never have asserted, however, a reduction of  $\text{TiO}_2$  by hydrogen.

With regard to the access of oxygen I wrote [9] "that the evaporator of the Ti was removed from the glass vessel prior to the first addition of tritium, and on this occasion impurities, especially oxygen, will have had

access to the freshly deposited Ti layer." After all, the investigations in the groupe of Reifenschweiler have been done about 35 years ago, and the enormous modern developments and improvements of UHV-techniques were mostly still unknown in 1960. On the other hand, titanium is a very active getter, and there is no doubt that this material had some oxygen on its surface, from where ever this "contamination" had come. The sites of adsorption are primarily surface defects, and at some of these defects the oxygen molecules will dissociate. If now tritium is added, these molecules will be adsorbed, too, and will dissociate, also in the immediate neighbourhood of the oxygen atoms. It needs then a small step only to build up a TO molecule from the two atoms, and a second step to recombine with a further T atom in the surface defect to a  $\text{T}_2\text{O}$ . In this way,  $\text{T}_2\text{O}$  molecules are formed from oxygen and tritium, without any reduction of a Ti oxide, by catalysis through titanium surface defects.

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