Fuel Retention in ITER

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The fuel for ITER will be a combination of tritium and deuterium

Deuterium occurs naturally and comprises 0.015% of all hydrogen.

Tritium is radioactive, and only trace amounts of tritium occur naturally from cosmic-ray interactions. The half life of tritium is 12.3 years. Tritium is a pure beta emitter, producing no gammas during the decay.
Why Care??

Why do we care about the retention/release of deuterium and tritium from ITER??’

The answer is COST and RADIOACTIVITY
Costs

In the US, a 1A bottle of deuterium (6400 liters at STP) cost approximately $7000.

The price of tritium (from Canada) is approximately $80,000/gm. The same 1A bottle of tritium* would cost $128,000,000. Actually, that only represents about 1.6 kg of tritium. ITER will use 7 to 16 kg of tritium during it lifetime.

*Tritium isn’t transported in 1A bottles. It is transported on metal hydride beds for safety reasons.
ITER will use 120 grams of tritium for each 400 second pulse. Each gram of tritium represents 10,000 curies:

1 pulse = 1,200,000 curies of radioactivity

Permissible release = 1 curie/day

Assuming 10 pulses per day => release fraction must be less than 1 in 10^7!!!
Availability

Again, ITER will use 7 to 16 kg of tritium during its lifetime.

Canada presently has approximately 15 kg of tritium from the CANDU reactors. Due to new reactors coming on line, this inventory will increase to approximately 25 kg before starting to decrease (if the number of reactors goes down).

(Data from Scott Willms, Los Alamos National Laboratory)
What Happens With Plasma Facing Materials?

- Incident Flux
- Recycling, Reflection and Recombination ($K_{\text{re}}C_n$)
- Enhanced Trapping in Implant Zone
- Intrinsically Generated Traps
- Permeation, Isotopic Exchange or Recombination ($K_{\text{re}}C_n$)

Plasma | First Wall | Continuum
What are the parameters that determine tritium release and retention?

**Diffusivity:** For hydrogen isotopes, this is the rate at which it moves through another material. For the different isotopes, the diffusivity is inversely proportional to the square root of the mass. The units are m$^2$/s. The diffusivity is given by $D = D_0 \exp(-E_D/kT)$.

**Solubility:** Solubility is the concentration of hydrogen at the boundary resulting from exposure to hydrogen gas at a certain pressure. The concentration at a boundary is given by $C = S p^{1/2}$ where $S$ is the solubility and $p$ is the pressure. The units are mol H$_2$ m$^{-3}$MPa$^{-1/2}$. Solubility is given by $S = S_0 \exp(-E_S/kT)$. 
Parameters

Permeability: Permeability is defined as the product of solubility time diffusivity (number of atoms or moles per unit volume times the velocity). \( P=SD \). Units are \( \text{mol H}_2 \text{ m}^{-1}\text{s}^{-1}\text{MPA}^{-1/2} \).

Trapping: Hydrogen can become trapped (fall into an energy well) as it migrates through a material. Traps can be defects such as grain boundaries, vacancies, dislocations, voids or chemical bonds (such as O-H or C-H bonds). To determine the effects of traps, you must know the density of the traps and the energy of the traps. Hydrogen can be both trapped and detrapped.
The change in concentration of mobile hydrogen with time at any location is equal to the change due to atoms moving in and out of location plus any sources minus the rate at which they are caught in traps.

This is more detail than you probably want, but this is the equation used in finite difference computer programs to calculate permeation and uptake of tritium in fusion reactor materials. Examples of these codes are PERI, DIFFUSE, and TMAP.
Boundary Conditions for the Diffusion Equation

The most common boundary condition is that determined by Sievert’s Law. Sievert’s Law simply states that the concentration at a boundary is determined by its solubility:

\[ C = Kp^{1/2} \quad \text{or} \quad C = Sp^{1/2} \]

where \( K \) or \( S \) is the solubility.

The other important boundary condition is that associated with recombination rate limited release.
Recombination Rate Limited Release

The boundary condition for this case is:

\[ J = K_R c^2 \]

where \( K_R \) is defined as the recombination rate constant and has the units of \( m^4/s \) and \( c \) is in atoms/m\(^3\) (or mols/m\(^3\)).

There are various equations for the recombination rate constant (Pick and Sonnenberg, Baskes, Wampler, etc), but in reality, the experimental data never agrees with the models due to surface impurities. Surface impurities, especially oxide layers, strongly reduce the recombination rate constant.
The recombination rate boundary condition can be important for PFCs when they are exposed to intense plasma bombardment. Consider the following figure:

In this figure, hydrogen is implanted to a depth $L$ in a metal of thickness $A$. If the concentration at the both boundaries is zero, the ratio of hydrogen exiting the boundaries is proportional to the slopes of the lines. That means the fraction of hydrogen exiting the rear of the sample is $L/A$. Because the range of energetic hydrogen in metals is small (microns or less), permeation is typically small.
Recombination Rate Continue

High Recombination Rate Constant  Moderate Recombination Rate Constant  Low Recombination Rate Constant

Concentration Profile
Back in the days of old (well, actually it was in the 1980’s), there was much work focused on the recombination rate of materials. The fear was that a low recombination rate constant would not only lead to high permeation rates, but would also lead to high inventories of tritium in the plasma facing materials. If the recombination rate constant is high, most of the implanted tritium simply diffuses back out of the front face. A low recombination rate coefficient drives the tritium inward.

Dire predictions of excessive inventories of tritium in beryllium were made! Did it come true? We’ll see.
Let's Now Look at the Planned ITER Materials

It is now anticipated that the first wall of the DT burning ITER will be made from beryllium and the divertor made from tungsten.

Still, the initial phase of ITER will have carbon fiber composites in the divertor, and many say that the carbon will have to remain if ITER is to be successful.

Therefore, we will now look at carbon, beryllium, and then tungsten.
Graphite is manufactured using the Acheson process. Coke is produced by heating coal and/or petroleum (900 to 2000 C) to remove the volatile constituents (water, coal-gas, and coal-tar). The material is then crushed, milled, and sized through screens into various sizes. The various sizes are then recombined according to the desired properties of the final product. After mixing with coal tar pitch, the product is heated and then formed into shape by extrusion or molding. As the properties depend on the orientation of the grains, the molding or extrusion can affect the properties of the final material. Nuclear graphites are typically isotropic. The formed material is baked at 750 to 900 C for 30 to 70 days to coke the pitch binder (drive off water and impurities). This process removes about 1/3 of the pitch, resulting in porosity in the graphite. Typically, the graphite density is increased by a sequence of coal tar pitch impregnations and heating cycles. The final graphitization is carried out in Acheson furnaces where the product is heated to 2600 to 3000 C. An Acheson furnace uses carbon bricks heated by water cooled electrodes. This process usually takes about 15 days.
The process just described falls into two distinct phases. The first part is the carbonization process where volatile materials are removed. The second part is the graphitization where the graphite grains coalesce and grow. Hydrogen, and its removal, play an important role in the production of graphite. The carbon chains are typically terminated by hydrogen, and the extension of the chain (or the graphite crystallite) depends on the hydrogen being removed and replaced by a carbon. As the temperatures of the various processes are increased, the interlayer spacing of the material decreases and the crystallite size increases.

A typical nuclear grade graphite is relatively pure, has a density of about 1.8 g/cm³, a microcrystallite size of about 50 nm, and a grain size of 5 to 500 microns. The grains are determined by the starting coke sizes while the microcrystallite size is determined by the degree of graphitization.

Graphite has the hexagonal closed pack structure (layers of hexagonal structures)
Carbon Composites

Carbon composites begin with carbon fibers or filaments. A common method of making carbon filaments is the oxidation and thermal pyrolysis of polyacrylonitrile (PAN), a polymer based on acrylonitrile used in the creation of synthetic materials. Like all polymers, polyacrylonitrile molecules are long chains, which are aligned in the process of drawing continuous filaments. A common method of manufacture involves heating the PAN to approximately 300 °C in air, which breaks many of the hydrogen bonds and oxidizes the material. The oxidized PAN is then placed into a furnace having an inert atmosphere of a gas such as argon, and heated to approximately 2000 °C, to graphitize the material. When heated in the correct conditions, these chains bond side-to-side (ladder polymers), forming narrow graphene sheets which eventually merge to form a single, jelly roll-shaped or round filament. The result is usually 93–95% carbon. Lower-quality fiber can be manufactured using pitch or rayon as the precursor instead of PAN.
Interaction of Tritium with Carbon

We will discuss the interaction of tritium with carbon in the following order:

• Saturated layer
• Surface diffusion
• Intergranular diffusion
• Codeposition

The plot to the left is typical in measurements of the retention of deuterium or tritium in graphite or carbon composites exposed to energetic ions. Initially, 100% of the hydrogen is retained. At a certain fluence, the retention fraction strongly decreases.

It was the experimental result from the work of Langley, Blewer, and Roth on the interaction of energetic deuterium with pyrolytic graphite that led to an understanding of the saturated layer. Initially, all deuterium was retained in the area of where it was deposited. As more deuterium was implanted, the concentration initially increased and the area of retention broadened. Once a certain concentration was achieved, the peak concentration no longer increased, but the peak continued to broaden until it spread to cover the entire area of implantation.

It is now understood that hydrogen is insoluble in crystalline graphite. When hydrogen isotopes are implanted into graphite, the atoms immediately come out of solution. As more hydrogen is implanted, the graphite becomes amorphous (the grain structure is destroyed).

While the structure opens up as it becomes amorphous, significant amounts of hydrogen remain in the layer due to weak chemical bonding between the carbon and the hydrogen. At temperatures below about 800 K, the H/C ratio in the saturated layer is about 0.4
If saturation is achieved, then why does the deuterium concentration continue to increase with fluence after saturation is achieved?

**Saturation**

The reason is that graphite (and carbon composites) are porous, and surface diffusion occurs.

Surface Diffusion

Once the implant zone of the graphite is saturated, there is an excess of atomic hydrogen sitting at the edge of that zone. It simply diffuses along the surface of the pores. Remember that graphite has a BET surface area of 0.2 to 1.0 m$^2$/g.
The diffusion coefficient of hydrogen along carbon surfaces has been measured by several groups:

Robell et al.\textsuperscript{1} and Olander and Balooch\textsuperscript{2} used the rate of uptake on carbon surfaces decorated with platinum deposits to measure the diffusion rate. The platinum serves to dissociate the hydrogen molecules into diffusive atoms. Robell et al. reported an activation energy of 1.7 eV. Olander and Balooch gave 0.38 eV for the basal plane and 0.66 eV for the prism plane. Causey et al.\textsuperscript{3} used the measured profiles of tritium in POCO AFX-5Q graphite exposed to a tritium plasma in his measurements to determine a surface diffusion coefficient of $D=1.2\times10^{-4} \exp(-0.9 \text{ eV/kT}) \text{ m}^2/\text{s}$.

\begin{itemize}
\item \textsuperscript{1} AJ Robell, EV Ballou, M Boudart, J. Phys. Chem. 68 (1964) 2748
\item \textsuperscript{2} DR Olander and M Balooch, J. Catal. 60 (1979) 41
\end{itemize}
An excellent example of this surface diffusion of tritium in graphite is given in the work reported by Penzhorn et al.\textsuperscript{1}. Mechanical sectioning of graphite tiles removed from the JET reactor after the tritium run was completed showed tritium profiles extending all the way through some of the tiles. The tritium levels were determined by oxidizing the graphite powder resulting from the mechanical sectioning and collecting the resulting tritiated water.

\textsuperscript{1}RD Penzhorn, N. Bekris, U Berndt, et al., J. Nucl.Mater. 288 (2001) 170
Surface Diffusion

Quiz time: If you exposed a graphite block to a tritium plasma at 100 C and another at 300 C, both for the same length of time, which would have the most tritium? Wouldn’t the sample at 300 C have tritium diffuse further in, and therefore retain more tritium???
The answer is “no”. Above are the results from a set of my tritium experiments years ago with Papyex (Graphoil). All of the data points above were for the same length of time. The overall retention drops because the “effective” solubility drops with increasing temperature. If the retention is due to a chemical bond, the ability to remain bonded drops with increasing temperature.
Remember the first few viewgraphs on graphite? We talked about how graphite was made, and talked about its structure. Graphite has grains, but these grain are not like the grains in a metal. Grains in metals are more or less crystals. For graphite, the grain size was determined by the grinding of the coke particles. These grains are not the crystals, but are composed of nanocrystallites of graphite. It is the diffusion of tritium along the surface of these nanocrystallites that we call transgranular diffusion.
Transgranular Diffusion

• Transgranular diffusion only occurs at high temperatures (750 C and above).

• The diffusion process is really a process of jumping from one chemical bond to another. The activation energy is 2.5 to 3.0 eV.
The transgranular diffusion coefficient has been measured by many. The values vary considerably, because the results depends on which type of carbon is used, how one performs the measurements, and how the data is interpreted. The diffusion length (distance the tritium must diffuse to reach equilibrium) is the grain radius. This is typically on the order of a few microns.
Transgranular Diffusion

The grain radius is the diffusion length because the porosity associated with graphite occurs around the grains, not in the grains. When you expose graphite to tritium gas at elevated temperatures, all of the grains are effectively exposed to the gas that readily enters the porosity.

Fig. 13. Hydrogen transgranular diffusivity in carbon.
Now let me confuse you even more. There is one other property that must be taken into consideration to understand the uptake and diffusion rate. There is also hydrogen trapping in graphite.

What? Didn’t you already say that the diffusion process for graphite is a process of jumping from one chemical bond site to another? Isn’t that the same as trapping?

Yes.

What is the difference?

Well, the site we call a trap site for graphite is about 4.3 eV whereas the diffusional trap sites are only about 2.8 eV. Additionally, the density of the 2.8 eV traps seems to be consistent from one graphite and composite to another while the 4.3 eV site is not. As an example, radiation damage changes the density of the 4.3 eV trap but not the other.
A good nuclear grade graphite has a 4.3 eV trap density of approximately 20 appm. Radiation damage can increase that trap density to over 1000 appm. Likewise, high temperature annealing can reduce the density of high energy traps.
The other parameter that one needs to model the uptake data of tritium in graphite is an effective solubility. The solubility here has the normal definition. When the solubility coefficient at a certain temperature is multiplied by the square root of gas pressure, you then know the concentration of mobile atoms at the outer boundary of the graphite grains.

For modeling the tritium uptake, I recommend using Atsumi’s solubility coefficient and my “best estimate” diffusivity.

\[ S = 6.4 \times 10^{-5} \exp(+0.2 \text{ eV/kT}) \text{ H/C atm}^{-1/2} \]


\[ D = 9.3 \times 10^{-5} \exp(-2.8 \text{ eV/kT}) \text{ m}^2/\text{s} \]

How Does This Work?

When you expose graphite to tritium at elevated temperatures, tritium gas is able to quickly enter the porosity of graphite and expose the grains to the gas. At the higher temperatures, dissociation can occur, and atomic tritium begins to migrate along the microcrystallite surface into the grains. The rate the tritium moves is given by the transgranular diffusion coefficient, and the mobile concentration is given by the solubility. As the tritium moves inward, it decorates the traps. Typically, the trap density is greater than the mobile concentration, and the tritium profile moves inward like a square wave.
So, if you model the uptake of tritium in graphite using the Atsumi solubility and the Causey “Best Estimate” diffusivity, and use the correct grain size and correct trap density, you will get an answer that duplicates reality.

If instead, you took a graphite sample that had already been saturated with tritium and elevated it to a high temperature for release, you would see results that are dominated by the trapping and not the real diffusivity. This is the primary reason that the diffusion data shown earlier has all the scatter:
Graphite is Not Simple!

If all the researchers had modeled tritium uptake and not desorption, then all the data would agree.

No one ever said that graphite is simple.
The sputtering rate (erosion rate) of graphite by energetic hydrogen particles is very high.

So what? Graphite is relatively cheap. Just replace the graphite tiles every year or so.

But what happens to the carbon? Where does it go, and what goes with it?

Unfortunately, it codeposits in cool areas with the deuterium and tritium from the plasma.

Plasma-wall interaction: a complex combination of surface processes critical for thermo-nuclear fusion
Roth, J.; Tsitrone, E.; Loarte, A.
What Do We Know About the Erosion and Redeposition?

This figure shows us that it is not just carbon that is being emitted during the erosion process. Note the different species.

Chemical erosion of pyrolytic graphite by low-energy H+ and D+ impact
Mech. BV; Hagez, AA; Davis, JW
What Do We Know About the Erosion and Redeposition?

The graphs on the previous page gave us the knowledge we need to predict the erosion rate of the carbon and the generation rate of the different CH species. The chart to the left here gives us the information we need to generate the deposition rate of the various CH species.

Reposition of hydrocarbon layers in fusion devices
Jacob, Wolfgang
SPEC. ISS., p.839-846
What Do We Know About the Erosion and Redeposition?

This is what the codeposited layer looks like.

Fig. 5. Structure of co-deposits from the neutraliser plates.
Okay, we now know the production rate of the different CH radicals and the sticking coefficient for each of them. Remember that the radicals were $\text{C}_1\text{H}_x$, $\text{C}_2\text{H}_x$, and $\text{C}_3\text{H}_x$ where $x$ was bigger than 1.

What would you expect the H/C ratio to be in the thick deposited films?

Well, it turns out it depends on where it deposits and at what temperature. If it deposit in a plasma interactive area, the layer is actively bombarded by energetic hydrogen ions as it is deposited.

It is not difficult to imagine that such an actively bombarded layer might be very similar to the saturated layer.
What Do We Know About the Erosion and Redeposition?

From the plot to the left, the dissociation rate of the saturated layer and the redeposited layer are identical (the referenced data points were for saturated layers and the “Present Study” was for a codeposited layer). Both layers have the identical H/C ratio of 0.4 at lower temperatures.

If the two layers have identical thermal properties, how are they different? The difference is that the saturated layer is only as thick as the implantation layer of the hydrogen ions. The codeposited layer thickness is only limited by the length of time that it is allowed to accumulate.
What Do We Know About the Erosion and Redeposition?

Much of the data to the left agrees with the thermal desorption plot shown earlier (begins to drop off from the H/C saturation value of 0.4 as the temperature exceeds about 700 K).

What about the JET flakes shown to the left??

**Codeposition of deuterium with ITER materials**

Doerner, RP; Baldwin, MI; De Temmerman, G; Hanna, J; Nishijima, D; et al.

NUCLEAR FUSION (MAR 2009) Vol.49
What Do We Know About the Erosion and Redeposition?

The codeposited film from JET that had the C/H ratio of 1 was special. It resulted from rather intense plasma interaction with a spot on the carbon divertor that was very close to the louvers at the bottom. The louvers were indeed cool, but more importantly, were shaded from interaction with the plasma. I have heard people refer to films deposited in the plasma interactive area as being “coimplanted”. This JET film represented the first example of a real codeposited film. Once JET shut down after the DT operational phase and the machine was exposed to air, the film actually began to flake off of the louvers. This layer contained over 1 gram of tritium.
How Bad Is It Going to be With Carbon?

You can see that predictions are that the tritium inventory in the carbon codeposited layer will exceed the 700 gram limit by the time ITER reaches several hundred discharges. What can be done to get rid of this layer?

Unfortunately, ITER cannot be heated to 573 K in air or oxygen.

The removal of codeposited layers from TFTR tiles by O\(_2\) gas exposure
Haasz, A.A.; Davis, J.W.
Ablate it with a laser


Various other techniques have been proposed (UV, Flashlamps, etc). In reality, the best way is just not to use carbon at all. It is presently the plan to have the tritium burning ITER use only beryllium and tungsten. Lets hope it stays that way!
Beryllium

• Beryllium is a low Z material (good for plasma performance).

• It has a good thermal conductivity and relatively high melting point (1278 C).

• Unfortunately, approximately 6 to 10% of the people are allergic to beryllium. Those allergic can become very ill (similar effect as that caused by asbestos). At present, there is no way to know who is allergic to beryllium.

• Beryllium will compose the first wall of ITER. Blanket modules to be added to ITER later will use beryllium as a neutron multiplier.
When the diffusion codes were run for beryllium in the early days, the apparent uptake of tritium exposed to intense plasmas looked quite high. Why?

The apparent diffusivity looked fairly low.
The apparent solubility also looked fairly low as well (based on average measured value).
Beryllium

The lofty uptake predicted by the computer codes was driven by a low recombination rate constant. The codes predicted the beryllium would fill up like filling a bath tub.

To begin to understand why later data would prove those computer prediction to be wrong, let’s go back and look at the solubility data.

The apparent activation energy for the solubility varied by as much as 1 eV (96 kJ/mol) but the measured values differed by less than an order of magnitude over temperature range of the experiment.
It is my contention that the solubility experiments were not done incorrectly, but simply gave the wrong answers. In his report, Swansiger\textsuperscript{1} hinted that oxides might be playing a role in the results. Many (certainly including me) now believe that the solubility of hydrogen in beryllium is effectively zero. The measured values were simply hydrogen being trapped on and in surface oxides.

What would happen if you implanted hydrogen into a material that has almost zero solubility? Remember what happened to carbon in the last section?

Beryllium

The answer is that the hydrogen would simply come out of solution, and normally generate an open amorphous layer.

Well, that is almost what happened. The hydrogen certainly came out of solution and created an open structure. The rest is mostly conjecture, but I say that beryllium hydrides (beryllanes??) are at least partially volatile and re-condense in this “worm-like structure.”

Note the similarity of the above ion exposed beryllium to the ion exposed aluminum to the right. Allanes (aluminum hydrides) are known to be volatile.

As one would expect for a material that has virtually a zero solubility for hydrogen, the uptake during extended exposure to energetic particles came to a relatively low saturation value.
So, beryllium has no tritium retention problems, right?

What are we missing?

Bonding of beryllium to hydrogen?

Bonding of beryllium to oxygen and hydrogen?

Where does that lead us?

What about codeposition (like carbon)
The are two sets of data for sputtering yields, high vacuum accelerator experiments and more realistic plasma experiments.


PISCES Experiments

Speculation is that the difference is due to vacuum conditions (oxide films?)
The codeposition data (below right) was calculated using some average sputtering yield. It puts the problem into perspective with that of carbon.

**Fig. 6.** Retained deuterium concentration in C, Be and W deposits under co-deposition conditions [75].

J. Roth et al., J. Nucl. Mater. 390-391 (2009) 1
So, beryllium in place of carbon significantly extends the lifetime of ITER before the 700 gram tritium limit is reached. In the case of beryllium, it is not apparent that heating in air will help reduce the retention as it does for carbon codeposits. Below is for a vacuum bake.

Does beryllium have any other interesting tritium problems?

Yes, the following interactions will affect the long term operation of beryllium in a DT burning machine (not ITER).

\[ ^9\text{Be} + n \rightarrow ^7\text{Li} + ^3\text{H} \]
\[ ^7\text{Li} + n \rightarrow ^4\text{He} + ^3\text{H} + n' \]
\[ ^9\text{Be} + n \rightarrow ^6\text{He} + ^4\text{He} \]
\[ ^6\text{He} \rightarrow ^6\text{Li} + \beta^- \]
\[ ^6\text{Li} + n \rightarrow ^3\text{H} + ^4\text{He} \]

A fusion reactor with 50 Mg of beryllium exposed to 3MWy/m² results in the production of 5.5 kg of tritium. This is a sizeable quantity of tritium. Because the tritium ends up inside the beryllium grains, it is more difficult to remove this tritium. Temperatures in excess of 700 °C will be needed for removal.

The divertor of ITER is made of tungsten. If you look at the diffusivity and solubility, tungsten looks pretty good!
Tungsten

The retention of hydrogen isotopes in tungsten exposed to intense plasmas consistently show the retention to be low at low and elevated temperatures. The maximum retention occurs at 500 to 700 K.

Causey et al., J. Nucl. Mater. 266-269 (1999) 467
Computer modeling of the hydrogen isotope retention due to plasma exposure of tungsten using known diffusivities, solubilities, recombination rate coefficients, and trap conditions do not reproduce the experimental results. As both the modeling and the experimental data show, the high temperature retention should drop as trapping becomes ineffective (traps can not continue to hold the hydrogen). It is the low temperature retention that does not seem to make sense. What is causing the retention to be low instead of peaking??

Fig. 6. Comparison of the measured hydrogen isotope retention in lanthanum oxide doped tungsten versus that predicted by a model utilizing accepted values for migration parameters.

Causey et al., J. Nucl. Mater. 266-269 (1999) 467
There are two possible reasons for the hydrogen isotope retention in plasma exposed tungsten to be low at low temperatures. One possibility is that there is some type of enhanced diffusion in the implant zone. The penetration depth of 100 eV deuterons is only a few nm. Most of the data shown is for samples exposed to particle fluxes greater than $10^{21}$ D/m$^2$-s. An alternative idea is that a version of blistering, which occurs at moderate temperatures (as shown to the right) is occurring at the lower temperatures. Solubility and diffusion are both lower at low temperatures. Trapping is in full force. I think the deuterium simply comes out of solution at low temperatures, creating near-surface roughening.

What about this blistering?


Fig. 2. SEM photographs of blisters on a powder metallurgy tungsten sample exposed to a hydrogen plasma at 550 K. The ion incident energy and the fluence are 90 eV and $3.4 \times 10^{18}$ m$^{-2}$, respectively; (b) is a cross section of (a).
What about this blistering?

There are two theories on the blister formation. One theory is that microvoids collect the migrating hydrogen. Because the hydrogen is implanted into the tungsten, the concentrations that result are the equivalent to concentration generated by exposure to gaseous hydrogen at thousands of atmospheres. Diffusing hydrogen encountering such a void would continue to come out of solution until the pressure inside the void is thousands of atmospheres. The resulting stresses would be sufficient to deform the tungsten into blisters or equivalent surface features.

The alternate explanation is that migrating hydrogen is trapped at dislocations. The trap site density is much higher than the mobile hydrogen concentration. Once the trapped concentration reaches a certain level, the stresses cause the near surface to partially delaminate into blisters.
What about this blistering?

As the two figures to the right show, there are pockets of molecular deuterium in the plasma exposed tungsten samples.
What about this blistering?

Does the existence of gas filled voids prove one theory over the other?

No, I don’t think so. Either theory would have these gas filled voids.

The picture I showed earlier of a blister cap with a void directly under it supports one theory (stress generated delamination). When the void is initially created, there would be no gas in it. Hydrogen permeating through the blister cap would soon fill the void.

A recent set of experiments by J. Roth and others at Garching on recrystallized tungsten seem to support the other theory. For recrystallized tungsten, the dislocation density is so small that trapping is almost non-existent. In that case, micro- or nano-voids on grain boundaries may eventually capture sufficient gas to generate large gas filled voids, pushing up volumes similar to blisters.
Neutron irradiation of tungsten generates dislocations of all forms including micro-voids. The computer codes say that long term exposure of radiation damaged tungsten at about 600 K will eventually generate sizable tritium inventories. The DIFFUSE code generates results suggesting that tritium will move through this tungsten like a wave front, decorating traps as it comes through.

Is there a problem with this picture?

I contend that bubbles and blisters in the near-surface region will steal all the tritium as it passes through, protecting the inner area. Bursting blisters and bubbles may cause erosion, but inventory should be limited.
It is difficult for me to see how, but there are studies showing that tungsten also codeposits with hydrogen isotopes.

As can be seen, the implications of codeposition of tritium with eroded tungsten are not nearly as scary as that of carbon and beryllium!

Summary

Carbon:

At low temperature plasma exposure, the saturated layer is formed. Surface diffusion along porosity can take tritium deep into the graphite or composite. Tritium retention is small, but certainly non-zero.

At high temperatures, tritium diffuses into the grains of the graphite. Molecular tritium will freely enter the porosity, uniformly loading the grains with tritium. After long term exposure at high temperatures, the tritium retention is moderate. Radiation damage over long periods can lead to “significant” inventories. Difficult to drive out by heating!

Codeposition is BAD. Inventories can be very high. Learn how to remove, or don’t use carbon!
Beryllium:

Hydrogen is basically insoluble in beryllium. Exposure to a hydrogen plasma generates a saturated layer that is deeper than the depth of penetration of the energetic plasma particles. Tritium does permeate through the beryllium via grain boundaries.

Neutron irradiation produces tritium in the beryllium. It is difficult to remove that tritium.

Codeposition of beryllium with tritium is bad, but not as bad as carbon. Heating to 600 K will remove most of this codeposited material. Disruption discharges might work??
Tungsten:

Tritium inventory in tungsten is controlled by trapping. Keep the tungsten hot or cold will minimize the uptake. Blistering and bubble formation will likely lead to increased erosion, but it is difficult to believe that tritium inventory for tungsten will ever be a problem.