Research Article

Response to Comment on the Article 'Simulation of Crater Formation on LENR Cathodes Surfaces'

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Abstract

In Ref. [1] the kinetics of heat transfer during the heat bursts at the origin of the formation of the micro-craters on Pd cathodes during electrolysis are discussed. It is assumed that LENR is the source of energy. In Ref. [2], M. Tsirlin made several comments. The present paper answers these comments. Tsirlin thinks it is premature to accept the fact that craters result from LENR events. Other less exotic phenomena should be considered first to explain the crater formation, before nuclear reactions. Tsirlin proposes three potential heat sources:

(A) Recombination (molarization) of atomic hydrogen.
(B) Oxidation of the hydrogen at the cathode surface by oxygen evolved at the anode.
(C) Sudden emissions of the absorbed gas.

The three phenomena are examined and discussed here.

  – The energy balance involved during hydrogen recombination does not match the energy required to create a crater.
  – The oxidation process of the cathode is too slow to produce eruptions.
  – Craters may result from the breakout of some of the many micro-cavities filled with hydrogen at high pressure. Mechanism C might explain some features observed on Pd cathodes, such as craters gathered along surface defects. However, this mechanism alone cannot explain the presence of frozen debris.

It seems that depending on the experimental setup, different types of craters may be obtained. Craters with a smooth internal wall could be developed by fast and very energetic heat bursts, while craters with a rough internal wall would be formed by the breakout of micro-cavities. More investigations are needed.
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1. Introduction

In Ref. [1], the kinetics of heat transfer during heat bursts that form micro-craters on Pd cathodes during electrolysis are discussed. In Ref. [2], Tsirlin made several comments about this. The present paper answers these comments.

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Many authors reported the presence of small size craters on the surface of palladium cathodes after LENR electrolysis experiments. Their structure, observed by scanning electron microscopy, seems to indicate they result from micro-eruptions. In some cases, a fraction of the metal is frozen, as if the metal were melted during the eruption. It is conjectured the craters result from violent reactions [3–7].

In Ref. [1], the kinetics of heat transfer are investigated. The main teachings are summarized in a subsequent section. In the article, it is assumed, as a starting hypothesis, that the violent reactions are of nuclear origin.

This assumption prompted comments from Tsirlin [2], summarized below. For Tsirlin, accepting that craters result from LENR events is clearly premature. He proposes some non-nuclear phenomena which should be considered first in order to find out their potential contribution to crater formation.

These comments and suggestions are quite interesting. As an answer to Tsirlin's comments, the phenomena proposed are briefly examined.

2. Simulation of heat Flow During Crater Formation – A Summary of Ref. [1]

The crater diameters generally range between 2 and 50 μm. A few are larger. In most cases, the craters are circular. Some of them exhibit evident signs of fusion of a fraction of the solids. Kim [3] and Nagel [4] proposed a correlation between the crater diameters and the energy involved in their formation. Starting from the corresponding assumption, it can be derived that the enthalpy released raises the temperature of the crater content to about 2000 K.

The purpose of Ref. [1] was to examine the heat transfer between a small quantity of metal at 2000 K and the surroundings by cooling via conduction and radiation. The aim was to determine within an order of magnitude the maximum duration of the event before complete cooling. The simulation considers an initial sphere of metal at 2000 K embedded in the bulk of metal. The model calculates the temperature evolution by conduction.

Because of the small dimensions of the objects considered, the cooling rate is extremely fast. For example, a 50 μm diameter crater is cooled in less than 1 μs.

If the metal piece at 2000 K is located at the surface of the cathode, some heat is lost by radiation. It is shown that radiative cooling has little influence.

The model does not need a physical explanation of why the temperature of a metal piece is suddenly brought at 2000 K. The same model can be used to simulate heat bursts other than LENR. On the other hand, the model does not give any hint about the origin of the energy. It teaches only that if heat bursts occur, the lifetime of the hot spots is very short.

Several difficulties are raised by the simulation, which are listed in paragraph §5 of [1]. A paradox appears, because if LENR phenomena develop on particular structures of the solids (Nuclear Active Environment), these structures should be destroyed as the solid melts down, so that the reaction should stop immediately.

3. Summary of the Comments Made by Tsirlin [2]

Tsirlin took the opportunity to comment my paper to stress that the origin of craters is a subject which deserves caution. In LENR literature, it is widely believed that the origin of cratering is of some form of nuclear energy. In Tsirlin's view, many arguments in favor of this assertion are questionable.

Tsirlin discusses the detection of transmutation products. My own competences do not allow me to make any comment in this field, so I leave it to others to address this point.

Regarding the craters, Tsirlin is in the best position to comment on the pictures in Ref. [1], as he was involved in the project which published the pictures reproduced in Figs. 3 and 4. The studies performed at Energetics Technologies allow Tsirlin to make important statements which are taken into consideration here:

– The craters arise on palladium cathodes in electrolytes made with light or heavy water.

Table 1. Basic hypotheses.

Hypothesis 1	The solids involved in the crater formation are PdH_x hydrides, with $x \approx 1$
Hypothesis 2	The crater is formed by a sudden heat burst originating from the solids contained within the crater volume before the eruption
Hypothesis 3	The matter is ejected at high temperature (2000 K)

– Craters are observed with or without generation of excess heat.
– The surface density of craters is relatively low. Summing up all the energy related to the craters formed on the cathode gives an insignificant power. Whatever the origin of the crater energy, excess heat, when present, is much larger and must be produced by other processes.

Tsirlin considers the assertion about the nuclear origin of the craters premature, and invites us to consider first less exotic sources of heat as cause of the phenomenon.

Three potential sources are proposed:

(A) Recombination of atomic hydrogen (deuterium).
(B) Reaction of oxygen coming into contact with the hydrogen loaded cathode because of vigorous stirring of the electrolyte.
(C) Sudden emission of the absorbed gas.

4. Basic Assumptions

The three possible phenomena are examined below. In this discussion, we consider the hypotheses listed in Table 1. They are similar to the assumptions in Ref. [1]. We shall see later that this set of hypotheses may have to be revised.

The three hypotheses are sufficient to retain the main teaching of the model presented in Ref. [1], i.e. the crater formation is very fast. For instance, the heat release and the ejection are completed in less than 1 μs for a 50 μm diameter crater.

## 5. MECHANISM A : Atomic Hydrogen Recombination

The recombination of atomic hydrogen into molecules yields a large quantity of heat:

$$2H \rightarrow H_2, \quad \Delta H = -217 \text{ kJ g}^{-1}.$$
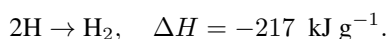
In fact, the hydrogen contained in the palladium cathode is not in a free atomic form, but it is instead dissolved in the metallic matrix or combined as hydride. When hydrogen gas is put in contact with palladium, the sequence of reactions summarized in Fig. 1 takes place:

According to the literature [8], the complete sequence corresponds to the formula:

$$Pd + X/2\,H_2 \rightarrow PdH_x, \quad \Delta H = -X\,18.6 \text{ kJ mol}^{-1}(X < 0.7).$$
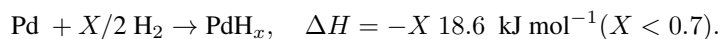
The above diagram shows the schematic sequence of palladium hydride formation.

The reaction is exothermic, indicating that palladium hydride is a stable compound. Then too, if we consider the reverse reaction, some heat must be brought to the system to dissociate the hydride and release the hydrogen.

The formation enthalpy of palladium hydride PdH_x depends on the loading quantity X.

In Ref. [8], values are given for different values of X at a temperature of 298 K:

$$X < 0.7 \; : \Delta H = -18.6 \pm 0.3 \text{ kJ mol}^{-1}H(\text{plateau } \alpha - \beta \text{ of the Pd} - H_2 \text{ diagram})$$
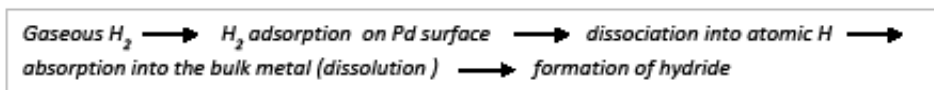
Figure 1. Schematic sequence of palladium hydride formation.

$$0.7 < X < 0.86 : \Delta H = X . 46.71 - 50.38 \text{ kJ mol}^{-1} \text{H} .$$

Figure 2 shows the corresponding relationships. It can be concluded that the hydride stability decreases when the loading factor increases. However, up to $X = 1$ the formation remains fundamentally exothermic.

To simplify the calculations, one can consider the average enthalpy of formation when $X = 1$. To do this and for the ease of the calculation, it is assumed that $\Delta H = 0$ for $X = 1$ (see Fig. 2). The average value obtained is:

$$\Delta H = - 16 \text{ kJ mol}^{-1} \text{ for PdH}_x \text{ with } X = 1.$$

This is an approximation, but it is sufficient for the present discussion.

In Ref. [1], Fig. 5 shows that the heating of palladium metal up to 2000 K requires 640 kJ.kg^{-1}, or 68 kJ mol^{-1}. This value includes the latent heat of fusion of palladium (16.7 kJ mol^{-1}), and the sensible heat of the solid and liquid metal.

In fact, these values correspond to the enthalpy of metallic palladium only and do not take into account the presence of the hydrogen dissolved or combined with the metal, which is also involved in the eruption. This should be taken into account. If we assume that the crater results from the melting of PdH up to 2000 K, the overall energy requirement is the sum of:

PdH dissociation	16.0 kJ mol^{-1}	
Pd enthalpy at 2000 K	68.0 kJ mol^{-1}	
$^1/_2$ H$_2$ enthalpy at 2000 K	25.4 kJ mol^{-1}	(6)
Total	109.4 kJ mol^{-1}	

Several authors showed that hydrides may contain a large amount of vacancies, so-called super abundant vacancies (SAV) [9,10]. The total energy of the ordered defect hydride corresponding to the formula Pd$_3$VacH$_4$ is lower than
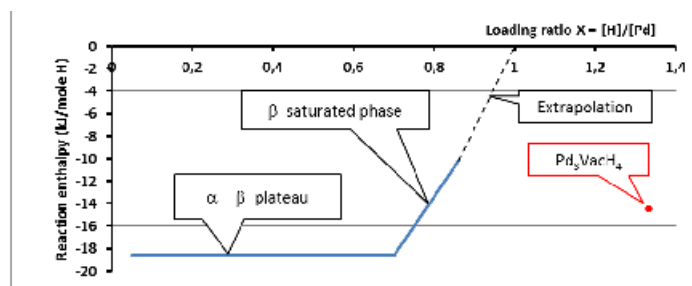

Figure 2. Pd–H$_2$ reaction enthalpy – the relationship up to $X = 0.86$ is from Ref. [8] – the extrapolation between $X = 0.86$ and 1.0 is from the author – Value for Pd$_3$VacH$_4$ is from Ref. [10].

the ideal defect-free PdH hydride. The calculated formation enthalpy of the SAV hydride is -0.15 eV, or -14.49 kJ mol^{-1} H. This value is plotted in Fig. 2 for H/Pd = 4/3 = 1.33

Hydrogen absorption is exothermic up to high hydrogen loading rates. As a consequence, the outgassing of the hydride following the sequence opposite to the one shown in Fig. 1 must consume heat to proceed.

According to this pure thermodynamic analysis, it appears unlikely that a sudden and spontaneous release of hydrogen could generate the heat bursts able to melt the metal accompanied by a flux of hot hydrogen.

6. MECHANISM B: Reaction with Oxygen

Tsirlin invites us to consider the situation in an electrolysis experiment. Oxygen bubbles are generated on the anode, part of the oxygen is dissolved in the electrolyte, and because of the vigorous stirring of the bath, some oxygen bubbles can come close to the cathode. The bubbles are considered to be the major source of oxygen available to drive the oxidation process.

Let us imagine that some bubbles of oxygen come into contact with the cathode and stick to it (Fig. 3).

The following chemical reaction may arise:

$$H_{2g} + {}^{1}\!/\!_{2}\,O_{2g} \rightarrow H_2O, \qquad \Delta H = -285.8 \ \text{kJ mol}^{-1}.$$
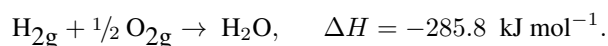
The reaction must logically take place at the cathode surface. The hydrogen may be hydrogen adsorbed on the cathode before the approach of the oxygen bubble, or hydrogen absorbed within the palladium migrating to the surface.

Let us consider the case of a 50 μm diameter crater. The energy for the formation is 3.2×10^{-5} J if we keep the value of 68 kJ mol^{-1} considered in [1]. According to the discussion in the above, the crater formation energy should rather be 109.4 kJ mol^{-1} . The energy of formation of this 50 μm crater is then 5.1×10^{-5} J.

If we make the rough and optimistic assumption that all the heat produced by oxidation of hydrogen is transferred without any loss to the metal, the volume of oxygen required to generate the desired heat burst is at least $V = 2 \times 10^{-12}$m^3. This corresponds to a 160 μm diameter spherical bubble at standard conditions. The reaction spot is supposed to have the final crater diameter, 50 μm in this case, with a surface $S = 2 \times 10^{-9}$m^2.
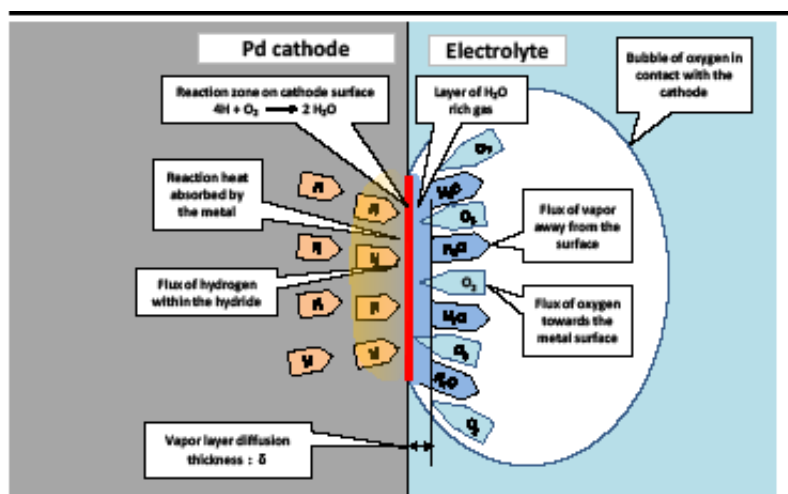

Figure 3.   schematic interpretation of an oxygen bubble in contact with the cathode.

Let us further assume that the reaction between hydrogen and oxygen is instantaneous. The reaction rate is then governed by the diffusion of the reactant species:

- – Diffusion of oxygen within the bubble towards the cathode surface.
- – Diffusion of hydrogen within the metal towards the surface.

The H_2O formed on the metal surface must go away from the surface. The water molecules can only migrate into the oxygen bubble. Inside the bubble attached to the cathode, a layer of vapor-rich gas is formed over the reaction spot. The oxygen must then diffuse across this layer to reach the metal.

Let us consider for example that the vapor layer attached to the metal over the reaction spot has a thickness of $\delta = 10~\mu$m. The diffusion coefficient of oxygen is about $D = 0.3$ cm^2 s^{-1} or $D = 3 \times 10^{-5}$ m^2 s^{-1} .

The order of magnitude of the transfer rate of oxygen is:

$$Q = \frac{DS}{\delta}.$$

The time required to transfer the volume of oxygen V is:

$$t = \frac{V}{Q}, \quad t = \frac{V\delta}{DS}.$$

With the values used here, we obtain $t = 330~\mu$s

This is only accurate to within an order of magnitude. As the reaction proceeds, the temperature rise can accelerate the diffusion. On the other hand, the vapor layer grows and the oxygen diffusion slows down. In any case, this value is clearly much longer than the crater formation, by almost three orders of magnitude. As a result, the oxidation mechanism is relatively slow and cannot explain alone the fast formation of the craters as they are observed on the surface of cathodes.

7. MECHANISM C: Sudden Emission of Absorbed Gas

The third mechanism proposed by Tsirlin is a sudden emission of the hydrogen absorbed in the cathode.

It is known that in palladium loaded with hydrogen, many cavities appear under the influence of the stresses resulting from the hydrogen introduction into the metal lattice [11]. The cavities are filled with hydrogen gas at a pressure which can be very high.

Super abundant vacancies (SAV) can also generate micro-voids. In Ref. [12], experiments are reported with palladium loaded at high hydrogen pressure at 800°C. The vacancies coalesce together to form pores 20–30 nm in size when present in the interior of the metal, and 1–3 μm when condensed at the surface. Moreover, the pores are dispersed homogeneously across the surface.

We can imagine the following scenario (Fig. 4):

- – The hydrogen combines with the palladium to form the β phase hydride.
- – Many small cavities appear, as a result of mechanical stresses and dislocations, or as a result of SAV formation. The micro-cavities are filled by hydrogen at high pressure.
- – At a given moment, a cavity close to the surface breaks out and the gas content is released into the environment. The local hydrogen pressure is suddenly relieved.
- – The pressure of hydrogen is still high in the surrounding hydride and micro-cavities. The distribution of the stresses in the solid becomes non-uniform. This drives the disintegration of the solid locally. Small debris are ejected by the gas flow, leaving a crater.
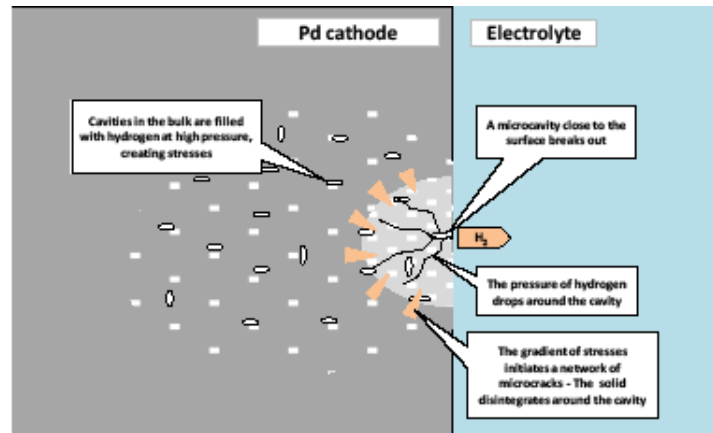
Figure 4. Schematic view of hydride disintegration.

- The order of magnitude of the disintegration propagation is the sound velocity in the solid, in the range of 10^3 m s^{-1}. A small crater can be formed in the very short time calculated in the paper.

This is only an outline of a possible mechanism. More studies would have to be made to refine the process, in particular the mechanical behavior of the solids during the disintegration.

The initial breakout may preferentially occur where the surface presents pre-existing defects. This may explain why craters are sometimes seen aligned along surface defects. See for example Fig. 5, reproduced from Ref. [5].

This model does not explain why the temperature can rise to very high values, or why some craters exhibit frozen material.
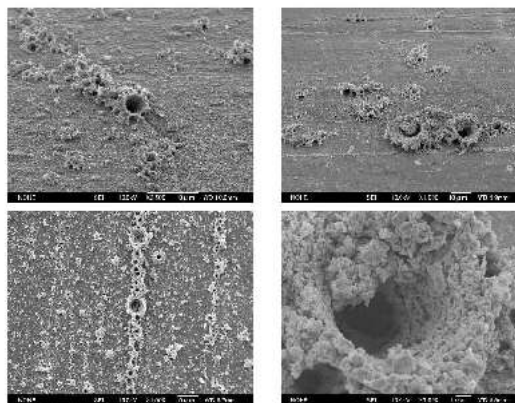

Figure 5. SEM photographs of craters on palladium cathode surfaces after 10 days of electrolysis in a light water based electrolyte. Scale lines are shown at the bottom of each photograph. Ref. [5].
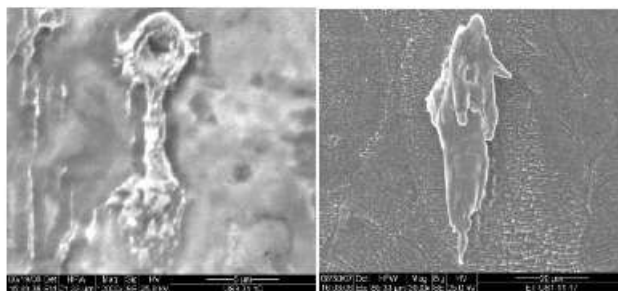
Figure 6.   Example of craters found on the surface of palladium cathodes that were subjected to intermittent application of ultrasound cavitation during electrolysis in an heavy water based electrolyte, Ref. [6].

8. Rough Craters and Smooth Craters

All craters are not alike. A review of the different morphologies is given in Ref. [4]. Two different examples are shown in Figs. 5 and 6.

Figure 5 is taken from a paper by Toriyabe, Mizuno and Ohmori [5]. The craters were observed on palladium after 10 days of electrolysis in light water. The craters whose maximum size is over 10 μm are located along pre-existing scratches on the surface. The crater walls are very rough, with many small pieces of fractured metal. No evident sign of fusion can be seen. Mechanism C described above could explain the rough structure observed in this case.

Figure 6 reproduces two micrographs obtained at Energetic Technologies during experimentation with ultrasonic excitation [6]. The picture on the left shows a crater with a diameter of 3 μm. Apparently, molten matter spouted out of the crater and formed a kind of "micro-lava flow" about 10 μm long. It seems that the cathode surface was vertical during the test, and the flow is in the downward direction. Tsirlin could confirm this.

The picture on the right shows another microscopic lava flow. It extends 40 μm downwards. The crater at the origin of the flow cannot be seen, probably because it is hidden behind the frozen eruption.

These two examples exhibit smooth crater walls and lava flow shapes.

Let us suppose that the "micro lava flows" were formed by a flow of fused matter which dripped along the surface before cooling down. For cathodes immersed in water, the cooling is very fast. However, if the eruption takes place when a bubble of hydrogen is present at the same location, the cooling may take more time. Heat flow calculations could be made to clarify the phenomena, although this is not done here.

We can calculate the minimum duration of the flow of melted matter as follows:

– The matter located at the tip of the "lava flow" follows a trajectory with a speed which can only be smaller than the free fall velocity of an object induced by gravity
– The distance traveled under the influence of gravity is given by the formula:

$Z = \frac{1}{2}gt^2$ with $g = 9.81\ \mathrm{m\,s^{-2}}$ acceleration of gravity

– Considering the flow lengths shown in Fig. 6 (10–40 μm), the duration of the free fall is 1.4×10^{-3} s to 2.8×10^{-3} s.

The actual duration of the flow is probably longer, because the velocity has to be slower than a free fall. The important point is that the phenomena at the origin of the flows visible on the microphotographs lasts several milliseconds. This order of magnitude is completely different from the one considered before (10^{-6} s), which resulted from the set of

hypotheses listed in Table 1.

This means that these hypotheses are not valid ways to simulate the phenomena at play during the formation of the craters shown in Fig. 6. Moreover, the shape of the "lava flows" seems to indicate that the gas velocity during the eruption was relatively modest. Otherwise the molten metal would have been ejected away from the cathode surface.

9. Further Research is Needed

The conclusion of this investigation is that additional observations should be undertaken.

In the case of "smooth craters", it would be important to determine the elemental composition of the "micro lava flows", to check the influence of a possible contamination.

If a partial melting actually occurs during the formation of some craters, a high temperature is reached during a short time. Molten metal at 2000 K must emit photons in the visible range. The presence of impurities on the surface may lower locally the metal melting temperature, but the peak temperature is still probably sufficient to emit photons in the visible range. A simple method to assess the peak temperature of hot spots is to observe the surface of the cathode during electrolysis. An experiment could be conducted in a dark chamber. A photon detector or a photographic camera with a long exposure time would detect the tiny light flashes emitted by the craters, if any.

In Ref. [7], an infrared camera was used to record the evolution of the temperature of a Pd film co-deposited on a Ni screen during electrolysis in heavy water. Hot spots were detected. The maximum temperature could not be assessed, because it exceeded the IR camera range. It is proposed here to perform similar experiments with photon detectors in the visible range. If the observations are made at two different wavelengths, the ratio of the light energies may give an indication of the temperature level reached.

It is conjectured that no photons in the visible range will be observed under the experimental conditions producing rough craters. In contrast, the formation of smooth craters should be characterized by light emissions, if the morphology of these craters results from partial melting.

10. Conclusions

Tsirlin considers that the assertion about the nuclear origin of craters is premature and that other prosaic sources of energy should be investigated first. He proposes three potential phenomena that should be evaluated. As an answer, this paper presents a first approach of the three proposed mechanisms:

- *A- Recombination of atomic hydrogen:* The hydrogen dissolved in the metal is in monoatomic form. The hydrogen absorption in palladium is exothermic. From a pure thermodynamic point of view, the reverse reaction (dissociation of the hydride, followed by the recombination of the hydrogen molecule) can only consume heat. Therefore, this mechanism cannot explain the spontaneous heat bursts observed.
- *B- Reaction with oxygen:* The hydrogen on the palladium surface can react with oxygen present in the bath. However, the reaction velocity is limited by the diffusion of the reactant species. This mechanism cannot proceed at the rate required to generate the heat bursts able to form craters.
- *C- Sudden emissions of absorbed gas*: Palladium loaded with hydrogen contains many micro-cavities filled with hydrogen at high pressure. Some cavities located close to the surface can break-out and initiate the formation of craters. This mechanism can explain the role of surface defects in the crater localization. However, it cannot explain the presence of melted matter found in some cases.

While some craters have a rough surface, which might be explained by mechanism C, others exhibit smooth shapes, indicating that melting takes place during the eruption. The origin of the fast and strong heat bursts remains unexplained.

It is suggested to confirm the temperature level reached during cratering. This can be done by monitoring the emission of visible photons during electrolysis in an experiment designed for this purpose. A temperature level of 2000 K must be accompanied by the emission of photons in the visible range, which can be easily detected.

In any case, it is important to keep in mind the fact that craters are only one aspect of the phenomena taking place. When an experiment yields some excess heat, the energy involved in the crater eruptions is a small fraction of the total heat measured. This means that the source of the excess heat is not directly linked to the craters. The craters are intriguing objects, which attract attention. It is tempting to draw a relationship between these micro-explosions and the excess heat, but other phenomena must be responsible for the major part of the excess heat.

I want to express my thanks to Tsirlin for his comments. My initial paper was not intended to discuss the LENR phenomenon, but only to have a look at the kinetics of crater formation. His invitation to consider less exotic explanations attracted my interest. For the moment, it does not seem that the potential mechanisms proposed can explain all the features of the craters.

More research is needed.

Acknowledgement

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