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ORTHO-PARA CONVERSION PROCESS
IN HYDROGEN BUBBLES IN COPPER

1985

1. INTRODUCTION

The long-time heat release in copper, cooled down to a low or very low temperature, has often been observed [1-5]. According to [4], this heat release is due to autocatalytic ortho-para conversion in hydrogen bubbles precipitated in copper metal.

In our previous paper [5], we have reported the measurements of time dependence of power released at 1.3K and of the dependence of the total heat released on the equilibrium temperature, after cooling from this temperature down to 1.3K, in stock oxygen free copper (4N purity). Both dependences agree well with the assumption of 19 at. ppm impurity of molecular hydrogen, which undergoes the ortho-para conversion. (Afterwards, bubbles with the radius $R \approx 0.1\mu m$ and the mean distance between them about $2\mu m$ were seen on electron microphotographs.) This conversion goes generally like that in solid hydrogen specimens without external influence ("free hydrogen") according to

$$d\bar{x}/dt = -k\bar{x}^2. \tag{1}$$

where $\bar{x} = N_{ortho}/(N_{ortho} + N_{para})$ is the mean throughout the bubble orthohydrogen concentration, and $k = 0.0196$ h^{-1} which is in good agreement with the theory [6] and other experiments [4,7].

But there are two phenomena reported in [5], which we did not succeed to explain by the model of "free hydrogen":

First, relaxation at $T \geq 10K$ is essentially faster than at 1.3K.

Secondly, "rapid" heat release just after the cooling to 1.3K, dissapearing in several hours, was observed (see, for instance, figs.1,3).

The rate of the autocatalytic ortho-para process may in principle increase due to higher pressure at higher temperature [8]. In this case, equation (1) holds good, i.e., the power released is proportional to x^2, with a larger constant k only. Further we shall see that it is impossible to explain experimental data in this way. However, more intensive relaxation may also be due to catalytic influence of the surrounding atoms (copper or impurities) at the surface of the bubble. In this case additional power released in the surface layer ("surface power") is added to the power released in the bulk.
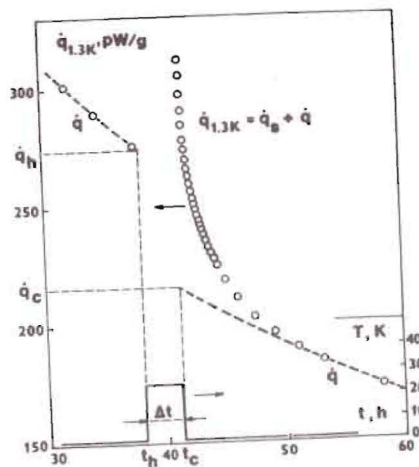
Fig.1. Heat release before and after a heating cycle. t – time, T – temperature, $\dot{q}$ – bulk heat release according to (1), $\dot{q}_s$ – "rapid" heat release, $\dot{q}_{1.3K}$ = $\dot{q} + \dot{q}_s$, t_h – the time of heating up, t_c – the time of cooling down, $\Delta t = t_c - t_h$, $\dot{q}_h = \dot{q}(t_h)$, $\dot{q}_c = \dot{q}(t_c)$. Lower solid curve – temperature; dashed curves – extrapolation for $\dot{q}_c$ and $\dot{q}_h$ determination.

Fig.2. A sketch of three types of the ortho hydrogen concentration distribution in the bubble for fixed $\bar{x}$. (1) – $x_R < \bar{x}$, (2) – $x_R = \bar{x}$, (3) – $x_R > \bar{x}$, R – the bubble radius, r – the distance from the centre of the bubble, $\bar{x}$ – ortho concentration.
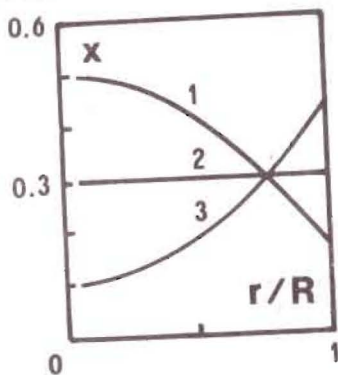
The surface power must be proportional to the concentration $x_R(t)$ at the surface. In an isolated surface layer, concentration $x_R(t)$ drops exponentially with the characteristic catalyser time constant τ_k after the cooling down. However, there is a ortho-hydrogen flow from the bulk to the surface due to concentration gradient $\partial x/\partial r$ (r is the distance from the centre of the bubble). The rate of the flow is controlled by the diffusion constant D , which strongly depends on temperature, being at 1.3K about four orders of magnitude smaller than at 10K [7].

What are the expected consequences of this model? First, $\bar{x}$ ceases to be the only determining factor of the total heat release, since concentration $x_R(t)$ at the surface is essential for the surface power. Quite different values of heat release may be observed for the same value of $\bar{x}$ due to various $x_R(t)$, i.e., due to various $\partial x(r,t)/\partial r$, depending on the "cooling history" of the specimen. In the usual course of experiment with specimen cooled from room temperature down to 1.3K and heated up to temperature T (10K or 25K) with the equilibrium concentra-

tion $x_g(T)$ lower than $\bar{x}$, we have $\partial x(r,t)/\partial r < 0$, $x_R(t) < \bar{x}$. If, at a certain t , heating is performed to such T , for which $x_g > \bar{x}(t)$, the inhomogeneity of the type $x_R(t) > \bar{x}(t)$ (Fig.2) may be realized.

Secondly, the temperature dependence of D necessarily implies the temperature dependence of the heat release. At lower temperature, D is smaller, and $x_R(t)$ decreases faster, due to the insufficient supply of ortho-hydrogen. Therefore at temperatures low enough, surface influence will take a form of the rapidly decreasing additional power, which is really observed at 1.3K. If the temperature is higher, D is larger and larger is the area influenced by the catalyser. Then the surface heat release is more intensive and takes longer time.

This work is an attempt to compare this model with the experimental behaviour of such system.

2. EXPERIMENTAL

The apparatus and measuring procedure were the same as in [5]. Copper (4N purity) specimen (m = 485 g) with a germanium thermometer and a heater hangs in the calorimeter on 12 kapron threads (~ 0.13 mm in diameter, 31 mm long). Heat connection with the calorimeter is provided by a scissors-like switch.

The heat release was calculated from the drift of the specimen temperature with the heat switch off. The temperature T of the specimen was usually close to the temperature T_K of the body of the calorimeter which was stabilised to 10^{-4} K. The power released

$$\dot{Q} = \dot{Q}_m - \dot{Q}_A - \dot{Q}_B , \tag{2}$$

where

$$\dot{Q}_m = \dot{R}C/(\partial R/\partial T), \tag{3}$$

$$\dot{Q}_A = A(T_K - T), \tag{4}$$

$\dot{Q}_m$ is the measured power, $\dot{Q}_A$ - heat leak from the body of the calorimeter to the specimen, $\dot{Q}_B$ = (730 + 250) pW - thermal back-ground ($\dot{Q}_B/m$ = (1.5 + 0.5) pW/g), $\dot{R}$ - germanium thermometer resistance drift, C - heat capacity of the specimen, $\partial R/\partial T$ - sensitivity of the thermometer, A - coupling constant

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between the specimen and the body of the calorimeter with the switch off (experimentally measured $A/m = 0.24$ pW/gmK).*

Due to the high heat capacity of the specimen and the low sensitivity of the thermometer, it was difficult to measure directly the heat release above 4.2K. It is to be calculated from the measurements at 1.3K just before heating up and after cooling down. This trick is shown in fig.1. Excluding the time interval of the rapid relaxation, ortho-para conversion at 1.3K goes according to (1), and the power released

$$\dot{Q} = -Nu \, d\bar{x}/dt , \qquad (5)$$

where N is the mole number of molecular hydrogen in the specimen, $u = 1064$ J/mole – latent heat of ortho-para conversion. The time dependence of the heat release per gram is

$$\dot{q}(t) = \dot{q}_0/(1 + kx_0 t)^2 , \qquad (6)$$

where $\dot{q}(t) = \dot{Q}(t)/m$, and x_0, $\dot{q}_0$ are initial values. (Cooling very rapidly from room temperature, we may take $x_0 = 0.75$ – room temperature equilibrium concentration – and, according to /5/, $\dot{q}_0 = 10^3$ pW/g for our specimen). Under these circumstances, it is possible to determine the mean concentration $\bar{x}$ at the time t from the corresponding heat release as

$$\bar{x} = x_0 (\dot{q}(t)/\dot{q}_0)^{\frac{1}{2}} . \qquad (7)$$

The heat release $\dot{q}_T$ at $T > 1.3$K was calculated from

$$\dot{q}_T = (Nu/m)(\bar{x}_h - \bar{x}_c)/(t_c - t_h) , \qquad (8)$$

where t_h is the time of heating to T , t_c the time of cooling to 1.3K ($t_c > t_h$),

$$\bar{x}_h = x_0(\dot{q}(t_h)/\dot{q}_0)^{\frac{1}{2}}$$
$$\bar{x}_c = x_0(\dot{q}(t_c)/\dot{q}_0)^{\frac{1}{2}} \qquad (9$$
$$\bar{x} = (\bar{x}_h + \bar{x}_c)/2 ,$$

$\dot{q}(t_h)$ was determined by extrapolation from the time dependence of the form (7) for $t \to t_h$, $t < t_h$, $\dot{q}(t_c)$ by a similar extrapolation for $t \to t_c$, $t > t_c$. Fast heat release was not taken into account in $\dot{q}(t_c)$ calculation.

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* The symbols used differ from /5/.

It is more convenient to use the ratio of power released at T to the power released at 1.3K (without rapidly relaxed power) at the same $\bar{x}$; this ratio should be a function of the mean ortho concentration $\bar{x}$:

$$\dot{Q}_T/\dot{Q} = \dot{q}_T/\dot{q} = (1/kx^2)(\bar{x}_h - \bar{x}_c)/(t_c - t_h) . \qquad (10)$$

The heating up and cooling down must be rapid enough compared to $\Delta t = t_c - t_h$ for accurate determination of $\dot{q}_T$. As a rule, the heating from 1.3K to 25K (10K) was completed in 2 minutes (0.5 min), cooling down in 12 min (4 min).

The measuring method used implies an experimental uncertainty: on the one hand it is necessary to have a very short measuring interval at 1.3K to avoid distortion of the x -distribution in the bubble, on the other hand it is impossible to make it shorter than 10 hours because of additional "rapid" heat release $\dot{q}_s$ just after each cooling.

The measuring strategy chosen ought to prove successively the consequences of the model with catalytic influence of the surface. Five measuring series were completed in total; during each of them several short heatings to 25K (in the first, second and third series) or to 10K (in the fourth and fifth series) were performed. The series differ in the starting temperature or in the time of measuring at 1.3K before the first heating up, i.e., in initial conditions.

3. RESULTS

a. Heat Release at $T \geq 10$K

The data about all measuring series are shown in table 1. In the first series, the specimen was rather rapidly cooled down from room temperature to 1.3K (292K → 80K in 4 hours, 80K → 1.3K in 1.5 hour); then the heat release was measured during 40 hours untill the mean concentration $\bar{x}_{h1} = 0.41$ was achieved. Afterwards several fast heatings to 25K and coolings to 1.3K were performed. The first three cycles of this series are shown in Fig.3.

Ratios $\dot{q}_T/\dot{q}$ calculated from these data according to (10) are plotted in Figs.4 and 5 (curve 1). According to this curve, the power released at 25K is about 8 times larger than at 1.3K for large values of $\bar{x}$; the difference is insignificant for small $\bar{x}$. This contradicts the assumption of more intensive heat release due to higher k at higher temperatures: in the case of the bulk autocatalytic heat release only, the concentration x is homogeneous throughout the bubble, the heat release is proportional to x^2 and $\dot{q}_T/\dot{q} = k(T) \cdot x^2/k(1.3K) x^2 = k(T)/k(1.3K)$ does not depend on concentration.

Table 1

Data on experimental series

Series	$\dot{q}_h$ pW/g	$\dot{q}_c$ pW/g	t_c-t_h h	$\bar{x}_h$	$\bar{x}_c$	$\dot{q}_T/\dot{q}$	$\bar{x}$
1 $T_0=292$ K $\bar{x}_1=0.617$ $T=25$K	300.5	244.5	1.72	0.4110	0.3710	7.8	0.3910
	134.2	113.4	2.15	0.2750	0.2530	7.6	0.2640
	83.3	59.5	8.15	0.2160	0.1830	5.3	0.2000
	48.5	35.2	15.15	0.1650	0.1407	3.2	0.1530
	27.9	20.9	29.15	0.1253	0.1084	2.2	0.1170
	7.1	5.0	118.15	0.0630	0.0530	1.3	0.0580
2 $T_0=292$ K $\bar{x}_1=0.594$ $T=25$ K	458.0	398.6	1.22	0.5076	0.4735	5.9	0.4906
	274.3	215.6	3.13	0.3928	0.3482	5.3	0.3705
	162.3	120.7	7.62	0.3022	0.2606	3.5	0.2814
	99.6	65.2	20.18	0.2368	0.1915	2.5	0.2141
3 $T_0=60$ K $\bar{x}_1=0.265$ $T=25$ K	111.2	81.3	1.11	0.2500	0.2210	31.2	0.2350
	73.4	50.4	3.10	0.2030	0.1680	16.7	0.1860
	47.0	29.5	9.11	0.1627	0.1287	9.1	0.1457
	27.4	18.6	20.11	0.1242	0.1024	4.35	0.1133
4 $T_0=70$ K $\bar{x}_1=0.342$ $T=10$ K	179.3	147.7	1.02	0.3180	0.2880	16.0	0.3030
	133.5	100.1	2.52	0.2740	0.2370	11.4	0.2560
	88.3	72.3	3.02	0.2230	0.2016	8.0	0.2123
	66.6	43.3	11.02	0.1936	0.1560	5.8	0.1750
5 $T_0=110$ K $\bar{x}_1=0.570$ $T=10$ K	440.8	371.6	1.02	0.4980	0.4570	9.0	0.4776
	312.5	250.0	2.02	0.4190	0.3750	7.1	0.3970
	213.6	160.5	4.02	0.3466	0.3005	5.6	0.3235
	143.0	90.5	11.02	0.2836	0.2257	4.2	0.2546
	82.6	58.2	13.02	0.2156	0.1810	3.5	0.1983

T_0 – the temperature before the cooling; $\bar{x}_1$ – the initial mean concentration after the cooling from T_0 to 1.3K; T – the heating temperature; t_h – the time of the heating to T; t_c – the time of cooling from T to 1.3K; $\bar{x}_h$ – the mean concentration at t_h; $\bar{x}_c$ – the mean concentration at t_c; $\dot{q}_T$ – heat release at T; $\dot{q}$ – heat release according to (1), (?); $\dot{q}_h = \dot{q}(t_h)$; $\dot{q}_c = \dot{q}(t_c)$.
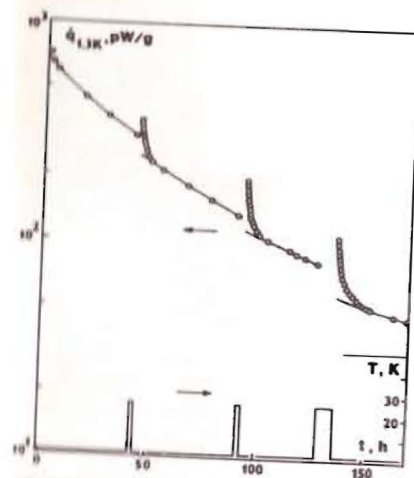
Fig.3. The first three cycles of the first experimental series ($x_R(0) < \bar{x}$). Dots – $\dot{q}_{1.3K} = q + \dot{q}_s$; upper curves – bulk heat release; lower curve – temperature.
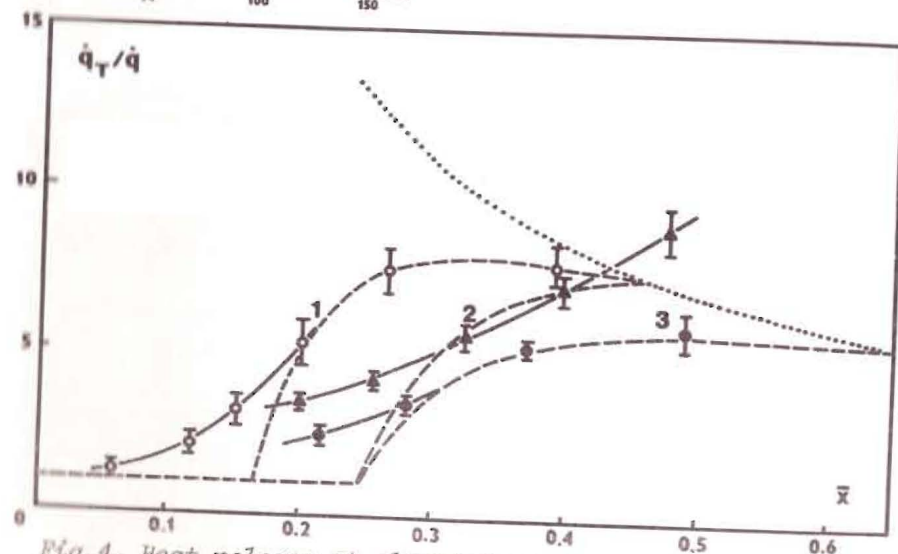

Fig.4. Heat release at elevated temperatures. o – first series (heating temperature 25K, $x_{h1} = 0.411$, $x_R(t_{h1}) < \bar{x}_{h1}$); • – second series (25K, $\bar{x}_{h1} = 0.508$, $x_R(t_{h1}) < \bar{x}_{h1}$); ▲ –fifth series (10K, $x_{h1} = 0.498$, $x_R(t_{h1}) > \bar{x}_{h1}$); dashed curves – eq. (25): $1 - \tau = 11 h$, $\bar{x}_{min} = 0.165$; $3 - \tau = 11 h$, $\bar{x}_{min} = 0.245$; $2 - \tau = 8 h$, $\bar{x}_{min} = 0.245$; dotted curve – $(\dot{q}_T/\dot{q})|_{t_{h1}}$ for $x(\tau,0) = x_i$ according to (28); $\bar{x}$ – mean ortho concentration.

In the second series after cooling as in the first one, the specimen was held at 1.3K for 15 hours only (till the mean concentration $\bar{x}_{h1} = 0.51$) before the first heating was performed. The resulting curve 3 (Figs.4,5, table 1) lies below the curve 1.
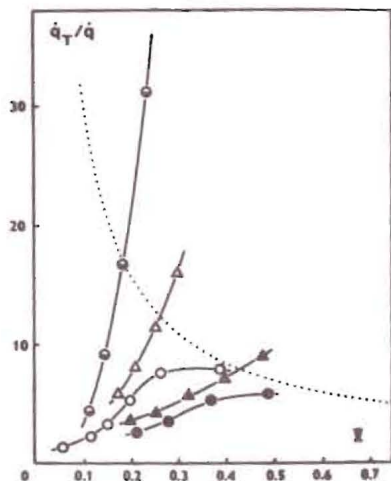
Fig.5. Heat release at elevated temperatures (experimental summary). o – first series (heating temperature 25K, $x_{h1} = 0.411$, $x_R(t_{h1}) < \bar{x}_{h1}$); • – second series (25K, 0.508, $x_R(t_{h1}) < \bar{x}_{h1}$) ; ◐ – third series (25K, 0.250, $x_R(t_{h1}) > \bar{x}_{h1}$) ; △ – fourth series (10K, 0.318, $x_R(t_{h1}) > \bar{x}_{h1}$) ; ▲ – fifth series (10K, 0.498, $x_R(t_{h1}) > \bar{x}_{h1}$). Dotted curve – $(\dot{q}_T/\dot{q})|_{t_{h1}}$ for $x(r,0) = x_1 = \bar{x}$ according to (28); $\bar{x}$ – mean ortho concentration.

Fig.6. The first three cycles of third experimental series $(x_R(t_{h1}) > \bar{x}_{h1})$. Dots – $(500/\dot{q}_{1.3K})^{1/2}$; upper straight lines – extrapolation for $\dot{q}_c$ determination; lower curve – temperature; t – time.
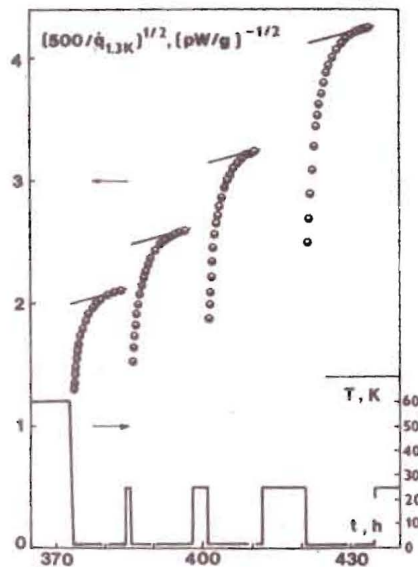
Before the third series, the specimen stayed at 60K ($x_g = 0.35$) during 90 hours. Because of increasing $\bar{x}$ in the reversed process during the heating to the temperature with $x_g > \bar{x}$, possible inhomogeneity is of the type $x_R(t) > \bar{x}$. The heat release should be larger under these initial conditions. The resulting time dependence of $\dot{q}$ for several cycles is shown in Fig.6 (as a time dependence of more convenient expression $(\dot{q}_0/\dot{q})^{1/2}$); according to the data in table 1 and curve 3 in Fig.5, the power released at $\bar{x} = 0.235$ is in this case 31 times larger than at 1.3K.

Because of such strong dependence on initial conditions, more detailed study – including the study of temperature depen-

dence of the heat release – is rather difficult. Yet we performed – for getting an information about this dependence – analogous experiments with heating up to 10K, trying to form definite and simple initial conditions. At the beginning of the fourth (fifth) series, the specimen stayed at 70K during 27 hours (at 110K during 110 hours). The results are plotted as heating to 70K (110K) in Fig.4 and 5. The mean concentration $\bar{x}$ before value x_g (70K) = 0.44 (x_g (110K) = 0.65). Enchanced heat release agrees with the surface effect at 10K, too.

b. "Rapid" Heat Release

The power relaxing with a characteristic time of the order of several hours after each cooling was calculated as

$$\dot{q}_s(t') = \dot{q}_{1.3K}(t') - \dot{q}(t') \tag{11}$$

from the experimental heat release $\dot{q}_{1.3K}(t')$ and the extrapolated power release $\dot{q}$, where $t' = 0$ at the time of cooling down ($t' = t - t_c$).

Fig.7. "Rapid" heat release $\dot{q}_s(t')$ for various $\dot{q}_c$ in the first series (T = 25K). Dots and solid curves – experimental $\dot{q}_s(t')$; dashed curves – $\dot{q}_s(t')[pW/g] = 10\exp(-t[h]/1.9)$, $t' = t - t_c$; lower left corner: cooling before "rapid" heat release observation.
1 – $\dot{q}_c$ = 244.5 pW/g,
2 – $\dot{q}_c$ = 113.4 pW/g,
3 – $\dot{q}_c$ = 59.5 pW/g,
4 – $\dot{q}_c$ = 35.2 pW/g,
5 – $\dot{q}_c$ = 20.9 pW/g,
6 – $\dot{q}_c$ = 9.1 pW/g,
7 – $\dot{q}_c$ = 5.0 pW/g,
8 – $\dot{q}_c$ = 1.0 pW/g.
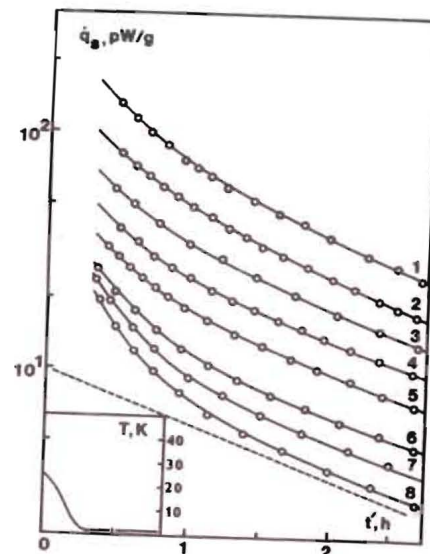
Values $\dot{q}_s(t')$ and $\dot{q}(t')$ of all cycles of the first series (cooling down from 25K to 1.3K for various $\dot{q}$ ($t' = 0$) = $\dot{q}_c$) are shown in Fig.7. With decreasing $\dot{q}_c$ values of $\dot{q}_s$ get smaller: even $\dot{q}_s$ is due to hydrogen conversion.

For $t' > 1$ h $\dot{q}_s(t')$ varies in time approximately as

$$\dot{q}_s(t') = \dot{q}_s(0) \exp(-t'/r_s) \tag{12}$$

with the relaxation time $r_s \simeq (1.6 \div 2.4)$ h. Although $\dot{q}_s(0)$ falls down with decreasing $\bar{x}$ at large $\bar{x}$, it becomes independent of concentration for $\bar{x} < 0.075$ ($\dot{q}_c < 10$ pW/g). There probably exists a residual concentration independent heat release $\dot{q}_{so}(t')$ with relaxation time of the same order. It is interesting that $\dot{q}_s(t')$ becomes independent of concentration in the region of $\bar{x}$ where the heat release $\dot{q}_T$ becomes independent of temperature ($\dot{q}_{25K}/\dot{q} = 1$, see Fig.4).

In addition, $\dot{q}_s(t')$ depends on initial conditions: at the same $\bar{x}$ values $\dot{q}_s(t')$ of the second series are smaller than those of the third one (Fig.8). Values of $\dot{q}_s(t')$ after cooling from different temperatures (viz. 25K and 10K) differ only for small $\bar{x}$, where $\dot{q}_s(t') = \dot{q}_{so}(t')$. With large $\bar{x}$ both values of $\dot{q}_s(t')$ are approximately the same (Fig.9).
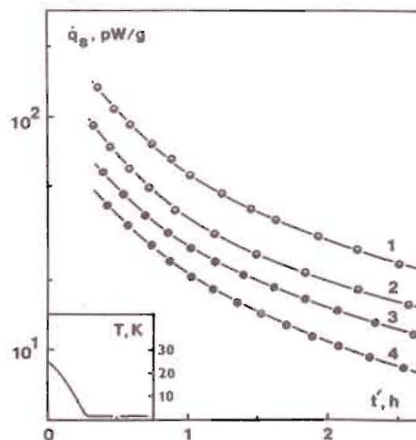
Fig.8. The influence of initial conditions on "rapid" heat release: comparison of the second ($x_R(t_{h1}) < \bar{x}_{h1}$) and third ($x_R(t_{h1}) > \bar{x}_{h1}$) series. 1 - third series, $\dot{q}_c = 81.3$ pw/g, 2 - third series, $\dot{q}_c = 50.4$ pW/g, 3 - second series, $\dot{q}_c = 120.7$ pW/g; 4 - second series, $\dot{q}_c = 65.2$ pW/g; lower left corner - cooling before the measurements.
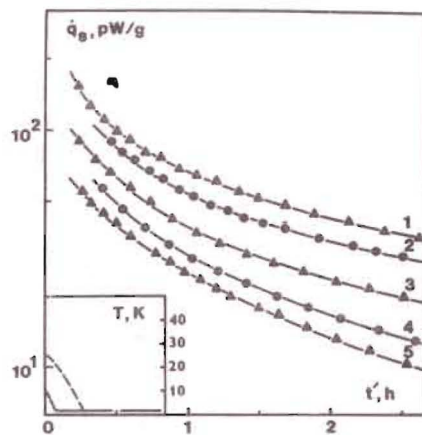
Fig.9. "Rapid" heat release after cooling from different temperatures.
● - T = 25K (second series),
▲ - T = 10K (fifth series);
1 - $\dot{q}_c = 250.0$ pW/g,
2 - $\dot{q}_c = 215.6$ pW/g,
3 - $\dot{q}_c = 160.5$ pW/g,
4 - $\dot{q}_c = 120.7$ pW/g,
5 - $\dot{q}_c = 90.5$ pW/g. Lower left corner: cooling before the measurements.

4. DISCUSSION

a. Influence of the Surface and the Diffusion

Strong dependence of the heat release $\dot{q}_T$ on the initial conditions at elevated temperature is clear evidence of the catalytic influence of surrounding atoms (ions) at the bubble surface. Due to the catalyser with the time constant r_K the ortho concentration in the surface layer satisfies the following equation:

$$4\pi R^2 \Delta n \frac{dx_R(t)}{dt} =$$

$$-4\pi R^2 \Delta n \frac{x_R(t)}{r_K} - 4\pi R^2 n D \left.\frac{\partial x(r,t)}{\partial r}\right|_{R-\Delta} - 4\pi R^2 \Delta \cdot n k x_R^2(t) \tag{13}$$

with the initial condition $x(r,0) = x_1$. R is the radius of the bubble, Δ - the depth of the catalyser influence ($\Delta \ll R$), n - hydrogen density. On the left-hand side of (13), there is a decrease of the number of ortho molecules in the surface layer, on the right-hand side the number of catalytic ortho-para conversions at the surface, the number of ortho molecules diffused to the surface layer, and the number of autocatalytic conversions in this layer.

In the limit of $D = 0$,

$$x_R(t) = x_i \exp(-t/r_K). \tag{14}$$

With r_K small enough, ortho concentration at the surface decreases very fast and a large concentration gradient originates. However, the corresponding energy released in the surface layer is small: for $R = 10^{-5}$ cm, $\Delta = 5\cdot10^{-9}$ cm (Bohr's radius),

$$\frac{Q_{surface}}{Q_{bulk}} = \frac{4\pi R^2 \Delta n x_i}{(4/3)\pi R^3 n x_i} = \frac{3\Delta}{R} \approx 1.5\cdot10^{-3}. \tag{15}$$

On the contrary, at $D \to \infty$, there is no concentration gradient and - due to the catalytic influence of the surface - ortho concentration, homogenious throughout the bubble, is

$$x(r,t) = x_1 \exp(-t/r_\infty), \tag{16}$$

$$r_\infty \simeq (R/3\Delta) r_K \simeq 670 r_K. \tag{17}$$

For sufficiently small r_K , the contribution of the surface dominates for any concentration value.

According to [7], D strongly depends on temperature. Thus, for our specimen ($R \approx 10^{-5}$ cm), depending on D , relaxation time may differ by about $2 - 3$ orders of magnitude, though for medium D the power released may be not pure exponential in time.

At 10K and 25K, the surface contribution is dominant for not too small $\bar{x}$, with slight dependence on T . That means that we are in the region of large D , and solution of (13) - after setting up a quasiequilibrium, when the flow of ortho molecules to the surface is near to the number of conversions per second at the surface - should be close to the exponential, since with increasing D the solution should approach the limit (16). Thus,

$$x_{T,R}(t) = x_{T,R}(0)\exp(-t/r) \tag{18}$$

with an additional heat release

$$\dot{q}_T - \dot{q} = (\dot{Q}_T - \dot{Q})/m = (N_B u/N_A m)\cdot n\, 4\pi R^2 \Delta (x_{T,R}(0)/r_K) \times \tag{19}$$
$$\times \exp(-t/r) = (\dot{q}_0/kx_i^2)(3\Delta/R)\,x_{T,R}(t)/r_K,$$

where N_B is the number of the bubbles, N_A - Avogadro number. Here, the relaxation time r and the initial ortho concentration $x_{T,R}(0)$ depend (in contrary to the limit $D \to \infty$) on D . From the condition of quasiequilibrium we can get the relation between $x_{T,R}(0)$ and x_i :

$$\Delta \cdot x_{T,R}(0)/r_K \gtrsim -D(\partial x/\partial r)\big|_{R-\Delta} \approx D(x_i - x_{T,R}(0))/\Delta, \tag{20}$$

$$x_{T,R}(0)/x_i \gtrsim D/(D + \Delta^2/r_K). \tag{21}$$

At $T \gtrsim 10K$, $D \gtrsim 10^{-16}$ cm^2/s [7] , and - as will be shown - $\Delta^2/r_K = 2.5\cdot10^{-19}$ cm^2/s. Then $x_{T,R}(0) = x_i$ in this temperature region.

b. Dependence on $\bar{x}$

With the help of (18), we can calculate the ratio of the power release at $T \gtrsim 10K$ to that at 1.3K as a function of the mean ortho concentration $\bar{x}$. For the surface process only, the rate of the decrease of the number of ortho molecules in bubbles equals the number of ortho-para conversions at the surface per second, and

$$(4/3)\pi R^3 (x_i - \bar{x}(t)) = 4\pi R^2 \Delta \cdot \int_0^t (x_R(t)/r_K)\,dt; \tag{22}$$

the time dependence of the mean concentration

$$\bar{x}(t) = x_i - (3\Delta/R)(r/r_K)x_i (1 - \exp(-t/r)) \tag{23}$$

implies that the influence of the surface takes place only for concentrations higher than a certain $\bar{x}_{min}$,

$$\bar{x}_{min} = x_i(1 - (3\Delta/R)(r/r_K)). \tag{24}$$

From (5), (23) we finally get (for $\bar{x} \geq \bar{x}_{min}$), taking into account the power released in the bulk:

$$\dot{Q}_T/\dot{Q} = \dot{q}_T/\dot{q} = -(d\bar{x}/dt)\big|_T /kx^2 = 1 + (\bar{x} - \bar{x}_{min})/r k \bar{x}^2. \tag{25}$$

There is a maximum in (25) for $\bar{x} = 2\bar{x}_{min}$, which is observable, if $2\bar{x}_{min} \leq x_i$. It is demonstrated in Fig.4 that this model fits experimental points of first and second series fairly well, if we choose $r = 11$ hours, $\bar{x}_{min} = 0.165$ and 0.245 consequently.

c. Catalyser Relaxation Time r_K

Relaxation time r_K of the catalyser can be estimated either with the help of $\bar{x}_{min}$ (equation (24)) or from the initial value of the additional release $\dot{q}_T - \dot{q}$ (eq. (19)).

Using (24), we meet two sources of error: (1) the changes of $\bar{x}_{min}$ due to the reduction of ortho inhomogeneity during the measurement at 1.3K, (2) the decrease of x_i during cooling from room temperature to 1.3K and measuring at 1.3K before the first heating cycle.

Since $x_i > x_{h1}$, ($x_{h1} = \bar{x}(t_{h1})$, t_{h1} - the time of the first heating), then, according to (24), $r_K < 3\Delta r/(\bar{x}_{h1} - \bar{x}_{min})R$, we get $r_K < 121$ sec from the first series, $r_K < 104$ sec from the second one.

From (19), we have

$$(\dot{q}_T/\dot{q})\big|_{t=t_{h1}} = 1 + (1/k\bar{x}_{h1}^2)(3\Delta/R)(x_{T,R}(0)/r_K). \tag{26}$$

Since $x_{T,R}(0) \approx x_{i,R}(0) < \bar{x}_{h1}$ in the first and second series, and $x_{T,R}(0) \approx x_{i,R}(0) > \bar{x}_{h1}$ in the third, fourth and fifth series, equation (26) gives us the upper and lower limit of r_K as

$$70 \text{ sec} < r_K < 105 \text{ sec}. \tag{27}$$

In what follows, $r_K = 100$ sec will be used. Then $\Delta^2/r_K = 2.5\cdot10^{-19}$ cm^2/sec and $r_\infty = 18.5$ hours, which is not far from the measured $r(25K) \approx 11$ h (Fig.3).

d. The Influence of Initial Conditions

If the ortho concentration in the time t_{h1} of the first heating is homogenious throughout the bubble, i.e., $x_R(t_{h1}) = x(r, t_{h1}) = \bar{x}_{h1}$, then – according to (26) –

$$(\dot{q}_T / \dot{q})|_{t_{h1}} = 1 + 3\Delta / (Rk\bar{x}_{h1} \, r_K) - \qquad (28)$$

ratio $\dot{q}_T / \dot{q}$ increases with decreasing $\bar{x}_{h1}$. The dependence (28) is shown in Fig.4 and 5 as a dotted curve ("homogeneity curve"). According to the model, the experimental points with $x_R(t) = \bar{x}(t)$ should lie on it. The first and second series are the nearest upon these conditions – and their first points (for largest $\bar{x}$) are rather close to (28), indeed, and the first point of the first series lies above that of the second one, which is also consistent with (28).

We have discussed (section 3a) the influence of the inhomogeneity $x(r, t)$ throughout the bubble. The curves of third, fourth and fifth series indicate it is possible to displace the first points far beyond the homogeneity curve and to increase considerably the heat release, producing $x_R(t) > \bar{x}(t)$.

e. Temperature Dependence of the Heat Release

The initial power released at 25K and that at 10K differ a little, corresponding to (21). According to our model, lower temperature implies shorter r, and – according to (24) – higher $\bar{x}_{min}$. Then, according to (25), the ratio $\dot{q}_T / \dot{q}$ diminishes more rapidly with reducing $\bar{x}$ at lower temperatures. One can see this tendency in Fig.3 comparing curves for 25K and 10K. For 10K, $r(10K) \simeq 8$ h.

At 1.3K the diffusion constant D is about four orders of magnitude smaller than at 10K [7], and the surface heat release should relaxe more rapidly. We shall show that the observed "rapid" relaxation can be explained by this hypothesis.

f. Rapid Heat Release

In case of lowering the temperature from 10K to 1.3K, the relaxation time r becomes only 4 times smaller: its dependence on the diffusion constant is rather slight even in this case. Essential reduction of D may imply $D \ll \Delta^2 / r_K$; then the ortho concentration at the surface before reaching quasiequilibrium falls down with catalyser time constant r_K, and the surface heat release should be lower than at $T = 25K$ or 10K just before the cooling. Thus, in the vicinity of t_{c1},

$$(\dot{q}_T(t_{c1}) - \dot{q}(t_{c1})) / \dot{q}_s(t_{c1} + t^*) = x_{T,R}(t_{c1}) / x_{1.3K,R}(t_{c1} + t^*), \qquad (29)$$

where t^* is the time necessary for reaching quasi equilibrium ($t^* \simeq 20$ min).

Experimental values of $(\dot{q}_T(t_{c1}) - \dot{q}(t_{c1})) / \dot{q}_s(t_{c1} + t^*)$ (table 2) range between 10.4 and 15.4. The mean value, 13, corresponds (according to (21)), to $D = 2 \cdot 10^{-20}$ cm^2/sec in agreement with other experimental data, 10^{-20} cm^2/sec and $4 \cdot 10^{-20}$ cm^2/sec [7]; this is in contradiction to the theory [9].

Thus, we have a qualitative change after cooling from 10K to 1.3K; not only r is smaller, but also $x_{T,R}(0)$ is significantly reduced, $x_{T,R}(0) \ll x_{iR}(0)$, and the amount of the heat, released under the catalytic influence of the surface, is much smaller. For sufficiently low temperatures $D \ll \Delta^2 / r_K$ and – according to (21) – $x_{T,R}(0) / x_i \sim D$, which can be used for finding temperature dependence of D. But here more accurate calculation would be necessary.

Moreover, exact calculation may explain the lowering of the ratio $x_{T,R}(0) / x_{1.3K,R}(0)$ with increasing ortho inhomogeneity (the ratio is five times smaller for the fourth point of the fifth series than for the first point of the same series) and the non exponential behaviour of $q_s(t')$ for $t' < 1$ h.

Table 2

Connection between the heat release at elevated T and the "rapid" heat release

Series No.		1	2	3	4	5
T, K		25	25	25	10	10
$\dot{q}_T(t_{c1}) - \dot{q}_{c1}$	, pW/g	1687	1953	2033	1994	2750
$\dot{q}_s(t_{c1} + t^*)$	, pW/g	162	129	135	148	178
$\dfrac{\dot{q}_T(t_{c1}) - \dot{q}_{c1}}{\dot{q}_s(t_{c1} + t^*)}$		10.4	15.1	15.1	13.5	15.4

T – the heating temperature; $\dot{q}_T(t_{c1})$ – the heat release at T in the time $t = t_{c1}$ at the end of the first heating cycle; $\dot{q}_{c1}$ – the bulk heat release at 1.3K, $t = t_{c1}$; $\dot{q}_s(t_{c1} + t^*)$ – "rapid" heat release at the time of setting of quasiequilibrium after the first heating cycle, $t^* = 0.3$ h.

Since all values of $\dot{q}_{25K}$ and $\dot{q}_{10K}$ are calculated with the help of (7), they include the heat released in the surface layer at 1.3K,

$$\epsilon = \int_0^\infty \dot{q}_s(t')dt'; \qquad (30)$$

this additional term being less than 10 per cent of the full energy change for all our points.

If the "rapid" heat release is the result of surface influence, it must depend on initial conditions like the heat release at 10K and 25K. And it is just the case shown in Fig.8. Initial $\dot{q}_s(0)$ is determined by the concentration in the neighbourghood of the surface and does not depend directly on the temperature before the cooling down (Fig.9).

Residual heat release $\dot{q}_{so}(t')$ may be explained very simple in this model. At an elevated temperature, say 25K, surface heat release stops after reaching the equilibrium concentration x_g (x_g (25K) = 0.01) at the surface. At 1.3K, x_g is many orders smaller, and during cooling to 1.3K conversion at the surface starts again. Using (19) with $x_{T.R}(0) = x_g$ (25K), the upper limit of the corresponding initial heat release may be found:

$$\dot{q}_{so}(0) < 53 \text{ pW/g}. \qquad (31)$$

The experiment gives $\dot{q}_{so}(0) \simeq 10$ pW/g (Fig.7). The dependence of $\dot{q}_{so}$ on the heating temperature is due to the strong temperature dependence of x_g.

g. Another Copper Specimen

In conclusion, let us see, what we can expect in the case of another copper with molecular hydrogen bubbles.

First, the power released due to ortho-para conversion is proportional to the amount of hydrogen, precipitated in bubbles [4].

Table 3

Heat release in various-size bubbles

R, μm	$(\dot{q}_T - \dot{q})/\dot{q}\|_{t=0}$	$\bar{x}_{min}$	$\dot{q}_s(0)/\dot{q}(0)$
0.1	4.0	0.30	0.29
0.4	1.0	0.64	0.07
1.0	0.4	0.72	0.03

R - the bubble radius; $(\dot{q}_T - \dot{q})/\dot{q}\|_{t=0}$ - the ratio of the surface power release and the bulk one at T = 10K or 25K just after the infinitely rapid cooling from room temperature; $\bar{x}_{min}$ - the mean ortho concentration, at which the influence of the surface stops; $\dot{q}_s(0)/\dot{q}(0)$ - the ratio of initial values of the surface and bulk heat release at 1.3K just after the infinitely rapid cooling from room temperature.

Secondly, the mean radius of the bubble may differ. Wampler et al. [10] observed bubbles with radii from 0.4 μm to 6 μm (in a single crystal) depending on conditions of hydrogen precipitation and on the amount of lattice defects. The bulk conversion does not change, and the relaxation time τ should not be influenced significantly by the mean radius variations. The contribution of the surface should vary inversely as the mean radius; with $R \geq$ $\geq 1 \mu$m , it should be negligible (see table 3). For large R the surface heat release may be observed for $x_R(0) \gg \bar{x}(0)$ only.

Thirdly, other impurities may give another τ_K . A smaller τ_K implies both increasing $\dot{q}_T(0)$ and decreasing τ which is proportional to τ_K for large D . Heat releases more intensively, but in shorter time; the full energy released and $\bar{x}_{min}$ do not change significantly.

5. CONCLUSION

The experimental results indicate that the bubble surface acts as a catalyser of hydrogen ortho-para conversion. The power released in the surface layer depends on the catalyser time constant τ_K , on initial ortho concentration distribution throughout the bubble (which implies strong dependence on initial conditions), and on the value of the hydrogen diffusion constant D .

Due to a strong temperature dependence of D , the catalytic contribution to the total heat release depends on T . The surface

heat release dominates at elevated temperatures (10K, 25K) in a rather broad interval of ortho concentrations.

At a low temperature (1.3K), the influence of the surface catalyser manifest itself as rapidly relaxing power with a rather small contribution to the total energy released. Afterwards, the mechanism of the heat release at 1.3K is the same as in free solid hydrogen.

It is possible to determine the catalyser relaxation constant r_K and the diffusion constant D of hydrogen ortho molecules studying the temperature dependence of the heat release. Specimens with small bubbles are probably preferable for examination of the influence of the bubble surface.

If the catalytic influence of the bubble surface is taken into account, the model of molecular hydrogen bubbles [4] is able to explain all experimental data on low-temperature heat release in copper [1-5].

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Колач М. и др.   E8-85-404

Процесс орто-пара превращения в пузырьках водорода в меди

Экспериментальные результаты показывают, что поверхность пузырька действует как катализатор орто-пара превращения водорода. Мощность, выделяемая в поверхностном слое, зависит от постоянной времени катализатора r_K, начального распределения ортоконцентрации внутри пузырька /откуда следует сильная зависимость от начальных условий/ и от значения коэффициента диффузии в водороде. При низкой температуре /1,3K/ влияние поверхностного катализатора проявляется как быстро затухающая мощность, довольно мало влияющая на общую выделяемую энергию. После этого механизм тепловыделения при 1,3K такой же, как и в свободном твердом водороде. Если учесть каталитическое влияние поверхности пузырьков, то модель пузырьков молекулярного водорода способна объяснить все экспериментальные данные по низкотемпературному тепловыделению в меди.

Работа выполнена в Лаборатории ядерных проблем ОИЯИ.

Koláč M. et al.   E8-85-404

Ortho-Para Conversion Process in Hydrogen Bubbles In Copper

The low-temperature heat release in copper due to ortho-para conversion in hydrogen bubbles has been investigated. Deviations from the model of "free solid hydrogen" were observed: more intensive power release at $T \gtrsim 10K$ and "rapid" (10 hours) heat release after the cooling to 1.3K. The experimental results can be explained by the assumption of the autocatalytic conversion in the bulk and catalytic influence of the bubble surface.

The investigation has been performed at the Laboratory of Nuclear Problems, JINR.