***Work package number WP14** - JRA6 - EURISOL*

Task 2: Development of chemically reactive nuclear beams - BEAMLAB

Subtask 2: Material compatibility in reactive gas atmospheres

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Materials used in oxidation studies

-Tantalum plates were cut from 100μm Ta foil in two dimensions: 10 x 10 mm and 7 x 10 mm

-These plates were washed in tetrachloromethane for one hour and in acetone for half an hour using a ultrasonic cleaner

-After washing the Ta surface were cleaned with Sontara „MicroPure100” wipes using acetone

-Quartz tubes were washed with hot concentrated nitric acid and then washed with deionized water

-The inner diameter of quartz tubes was: 11mm and 8 mm

-Tantalum plates were placed in a quartz tube parallel to the tube walls

-The oxygen used had a purity 99,999% and a dewpoint of about -29^{0}C (moisture content - 0,3 mg/L)

Oxidation kinetics of Ta at atmospheric pressure

Tantalum plates were oxidized for 5 to 60 minutes at temperatures between 790 and 990 K. A flow rate of oxygen - 3.6 mL/min was controlled by Brooks Mass Flow Meter. The oxidation kinetics were measured by gravimetry. In all cases the results represent averages of 2 or 3 different runs at each set of experimental conditions. The weight gain (in g/cm^2) during oxidation was evaluated using the original geometrical dimensions of tantalum plates. The reproducibility was between ±5 and ±10%.

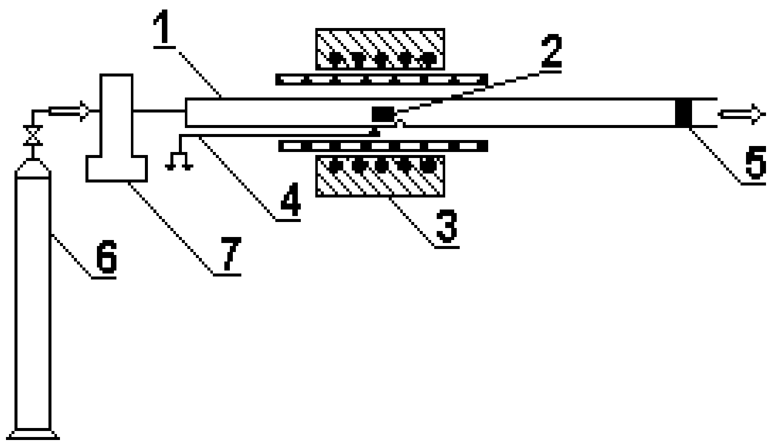


Figure 1. Apparatus for oxidation of Ta foil at atmospheric pressure: 1 - quartz column (inside diameter 11 mm); 2 – Ta plate (10x10x0,1 mm;); 3- resistance oven; 4 – thermocouple; 5 – quartz plug; 6 - O_2 gas; 7- Brooks Mass Flow Meter.

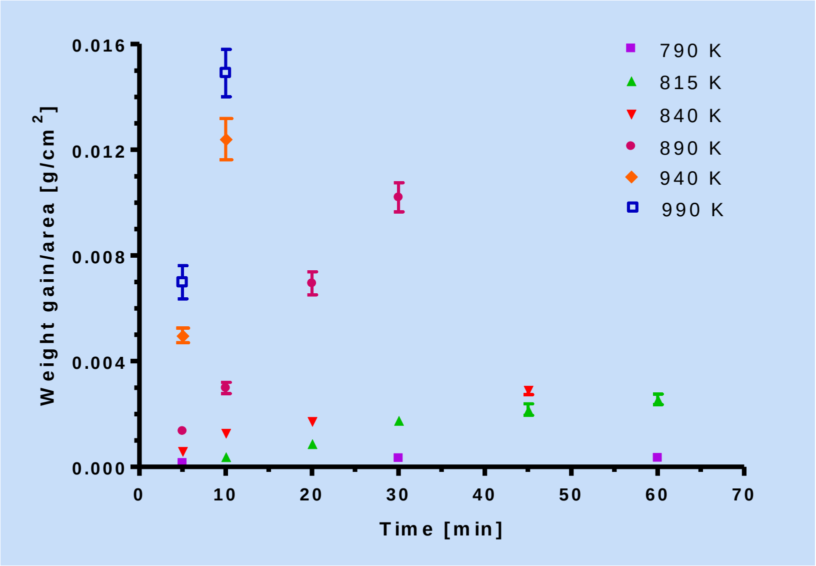


Figure 2. Weight gain/area *vs.* oxidation time for different temperature.

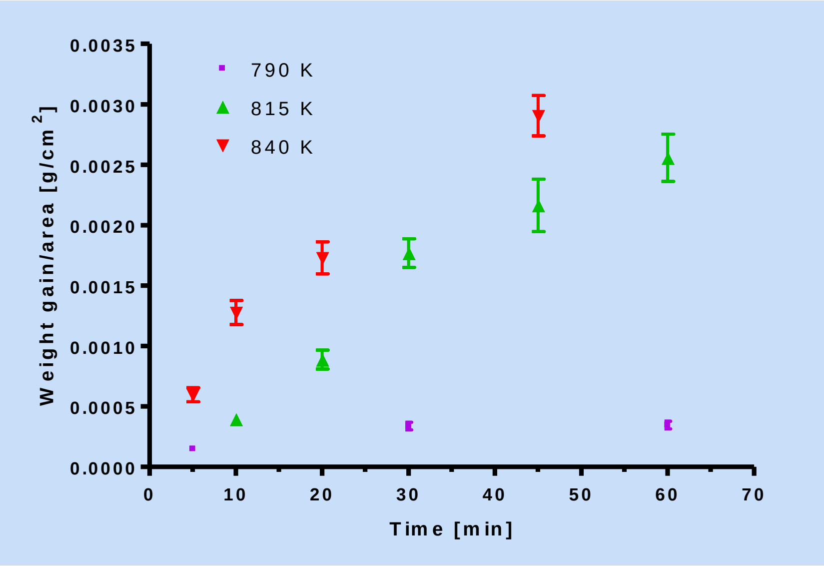


Figure 3. (Weight gain/area) *vs.* oxidation time for different temperature.

In Fig. 2 results of reaction rate measurements on tantalum are plotted as a function of oxidation time. The curves on Figure 3 shows a parabolic oxidation.

$$\left(\frac{\Delta W}{A}\right)^2 = k_g t \qquad [1]$$

where:

ΔW - is weight gain, *A* is the sample surface area,

k_g - is the parabolic rate constant, and *t* is the oxidation time.

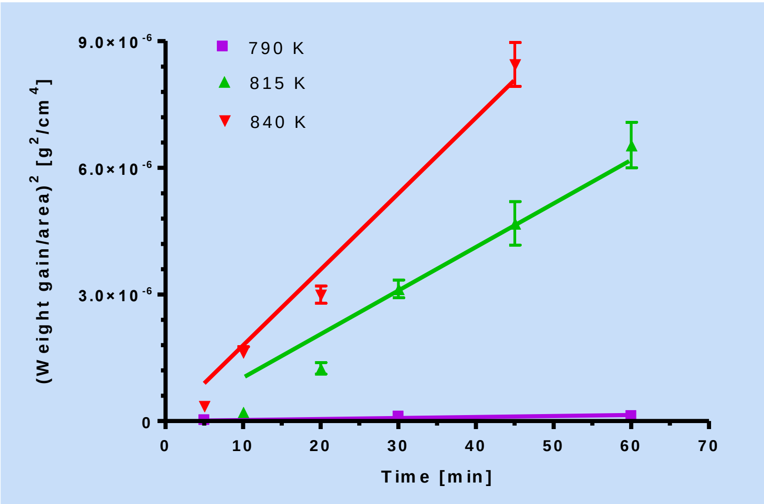


Figure 4. (Weight gain/area)^2 *vs.* oxidation time for different temperature.

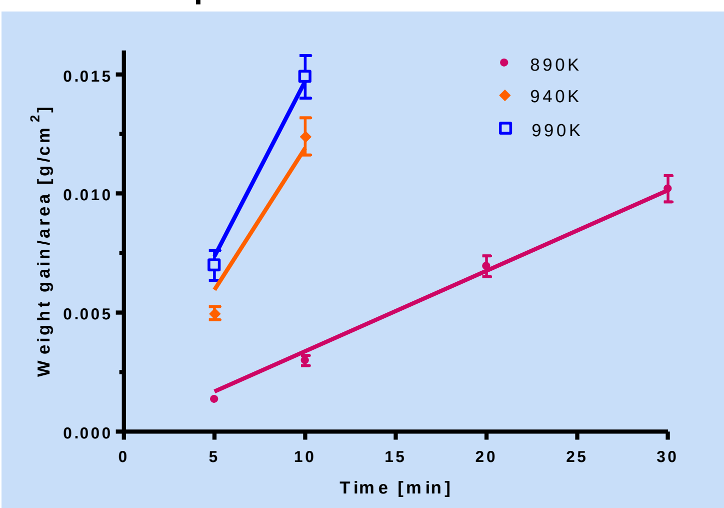


Figure 5. (Weight gain/area) *vs.* oxidation time for different temperature.

At temperatures from 890 K to 990 K the oxidation follows a linear rate law (Fig. 5), Eq. 2:

$$\frac{\Delta W}{A} = k_l t \qquad [2]$$

The obtained parabolic oxidation rate constants k_g at temperature range of 790 to 840K (Fig. 4) and linear oxidation rate constants k_l at temperature range of 890 to 990K (Fig. 5) were used for determination of an activation energy –*Q* by Arrhenius equation-

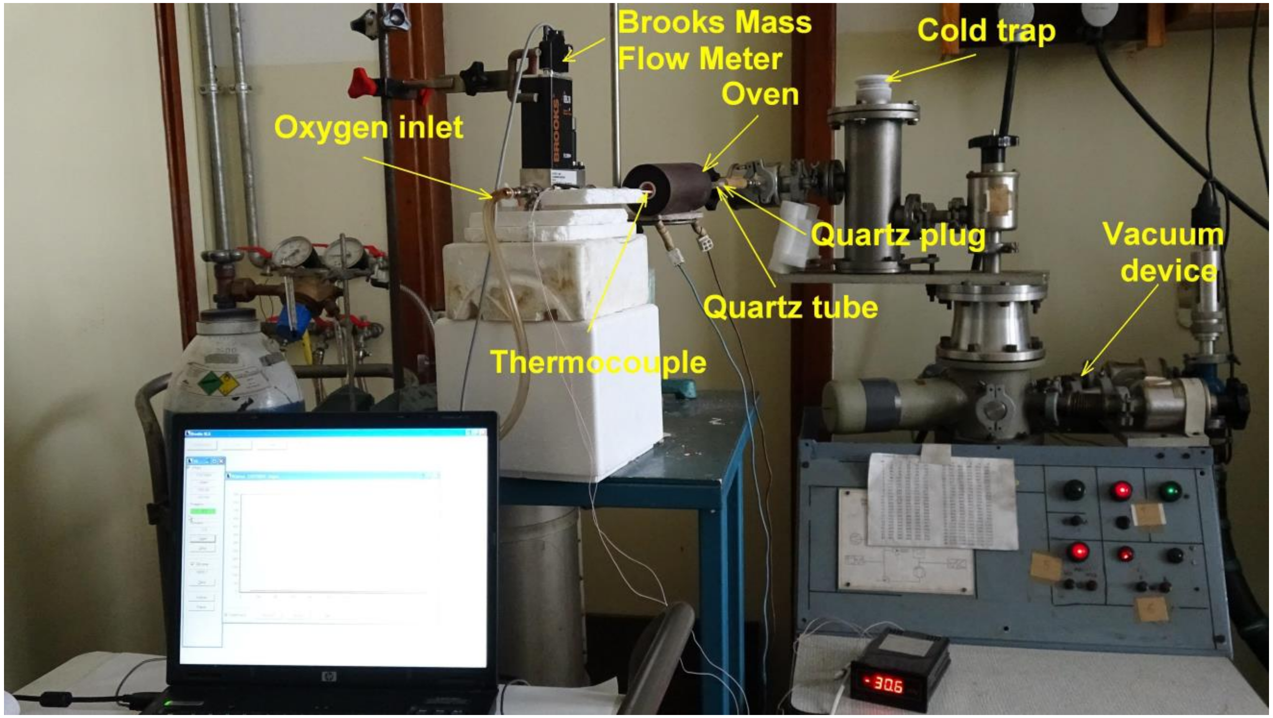
$$k_g = k_o \exp\left(\frac{-Q}{RT}\right)$$

where: *R* is the gas constant,
T is the temperature and
k_o is the pre-exponential factor.

Activation energies (kJ/mol) for oxidized Ta for two different temperature ranges.

790 to 840 K	890 to 990 K
480,0 ± 44,0	110,0 ± 10,0

Oxidation kinetics of Ta at low oxygen pressures



Oxidation of tantalum has been studied at 1003-1363 K and at oxygen pressures from $1x10^{-3}$ mbar to $2,5x10^{-4}$ (which corresponds to the flow rate of oxygen from 7,2 mL/min to 1,8 mL/min).

Oxidation kinetics of Ta at low oxygen pressures

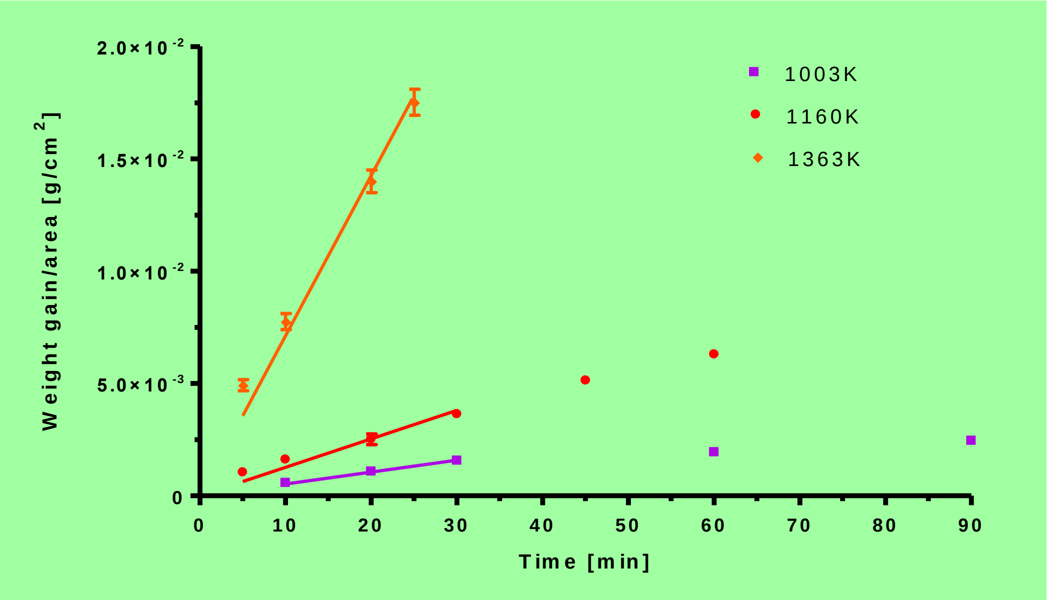


Figure 6. Weight gain/area *vs.* oxidation time for different temperature at the flow rate of oxygen 3,6 mL/min .

The results of the gravimetric oxidation rate measurements on tantalum are shown in Fig. 6. The linear oxidation rate constants k_l at temperature range of 1003 to 1363 K (Fig. 6) were used for determination of an activation energy –Q by Arrhenius equation. Activation energy for oxidized Ta at pressure 6x10^{-4} mbar was 81,7 ± 8,9 kJ/mol.

Oxidation kinetics of Ta at low oxygen pressures

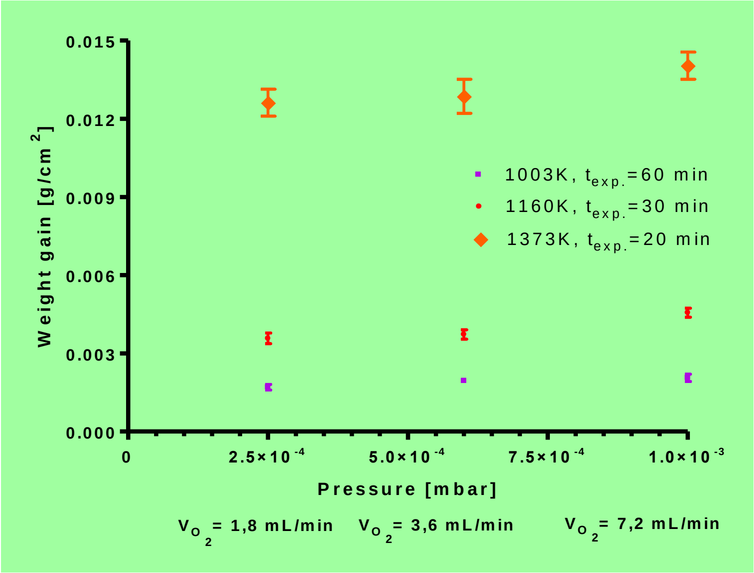


Figure 7. Effect of oxygen pressure on the oxidation of tantalum.

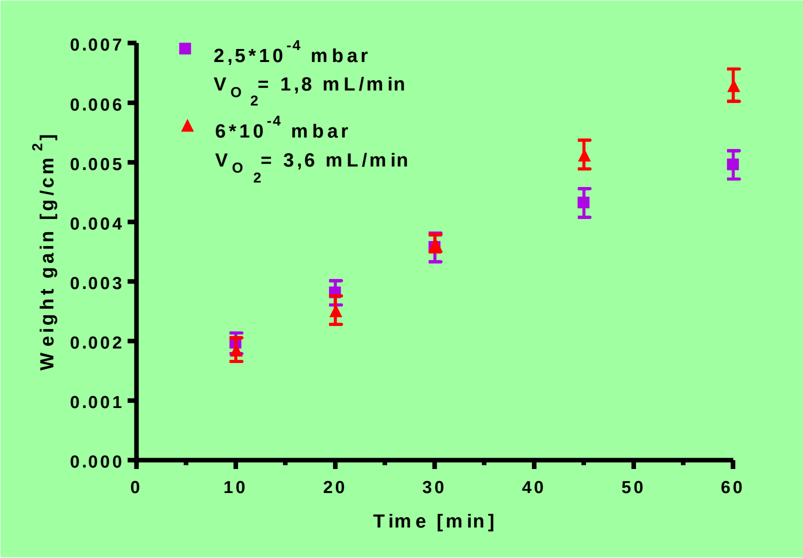
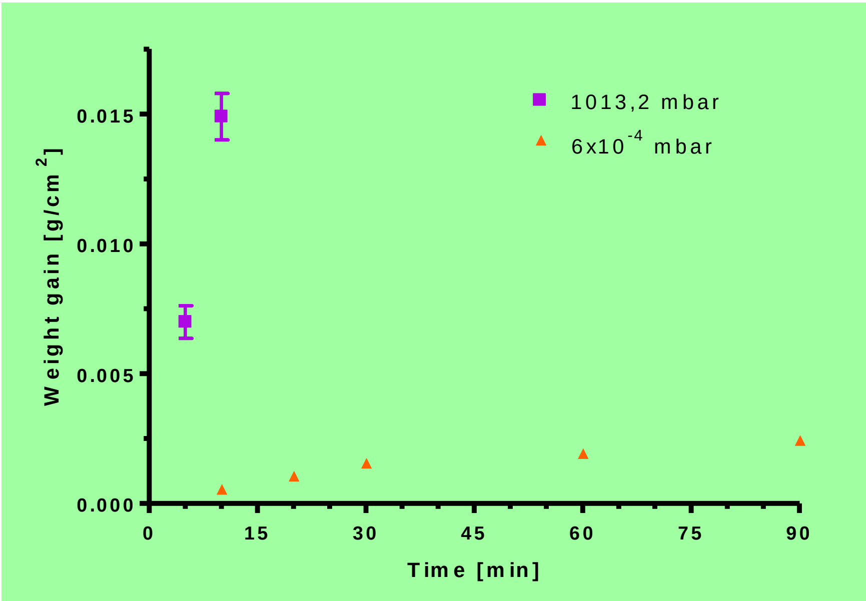
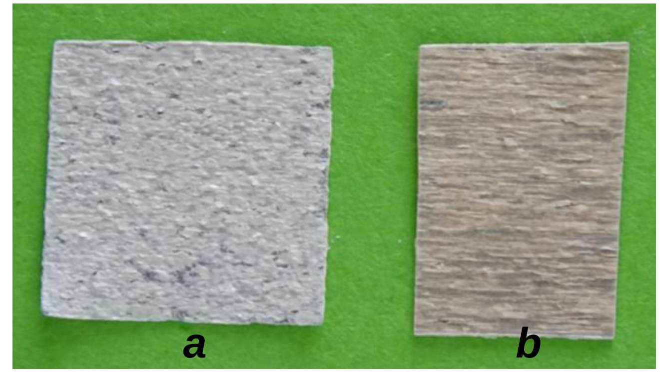


Figure 8. Weight gain/area *vs.* oxidation time for 1160 K.

These results obtained at 2,5 x 10^{-4} mbar and 6,0 x 10^{-4} mbar (Fig. 8) confirm that the difference of rate of oxidation increases with growth of experimental time.

Oxidation kinetics of Ta at low oxygen pressures





Photography of appearance of tantalum specimens after oxidation at flow rate of O_2 – 3,6 mL/min and 1003 K :
a) 1013,2 mbar; 7 min b) $6x10^{-4}$ mbar; 90 min.

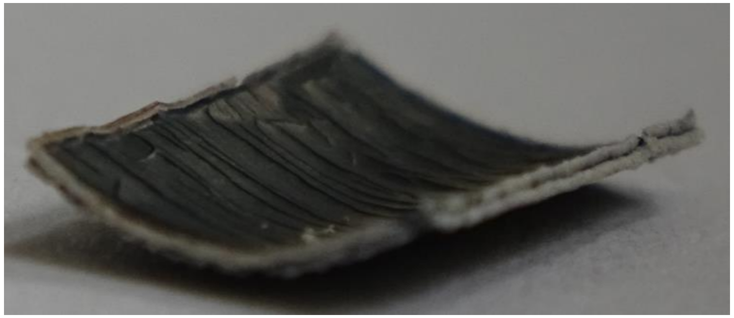
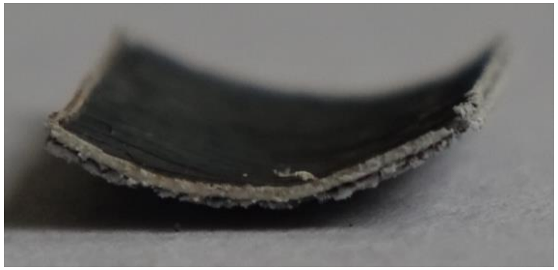
*Fig. 9. Dependence of weight gain [g/cm^2*min] on concentration of oxygen under the same experimental conditions: 10 minutes, $T_{experiment}$ = 1003 K and flow rate of O_2 – 3,6 mL/min.*

	Pressure [mbar]		Ratio
	1013,2	$6x10^{-4}$	
Weight gain/area*time [g/cm^2*min]	$1,4 \times 10^{-3} \pm 8,9 \times 10^{-5}$	$5,8 \times 10^{-5} \pm 5,5 \times 10^{-6}$	≈25

Oxidation kinetics of Ta at low oxygen pressures

*Dependence of total and edges weight gain [g/cm^2*min] on concentration of oxygen under the same experimental conditions: 20 minutes and $T_{exp.}$ = 1363 K (area of the edges only 2,5% from total area of Ta plate).*

Flow rate of O_2 [ml/min] (Preassure [mbar])	Weight gain- total [g]	Weight gain- edge [g]	Ratio edge/total	Weight gain/area [g/ cm^2] total	Weight gain /area [g/ cm^2] edge	Ratio edge/total
1,8 (2,5 x 10^{-4})	0,019 ±0,0003	0,004 ±0,0003	≈22 %	0,0126 ±0,0005	0,12 ±0,008	≈10,0
3,6 (6,0 x 10^{-4})	0,02 ±0,0003	0,005 ±0,0003	≈25 %	0,0135 ±0,0007	0,14 ±0,009	≈10,0
7,2 (1,0 x 10^{-3})	0,022 ±0,0003	0,013 ±0,0003	≈60 %	0,014 ±0,0005	0,37 ±0,019	≈26

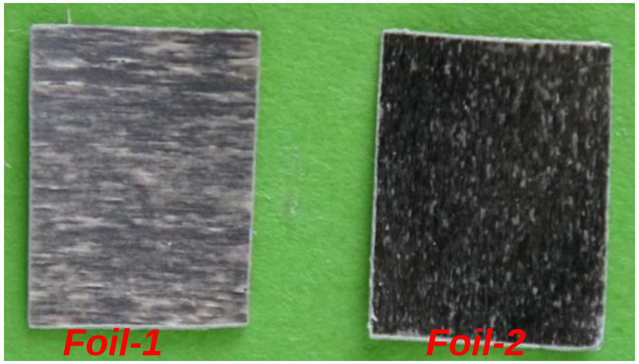



Photographies of results of 20 min oxidation of tantalum at 1363 K and 1,0 x 10^{-3} mbar.

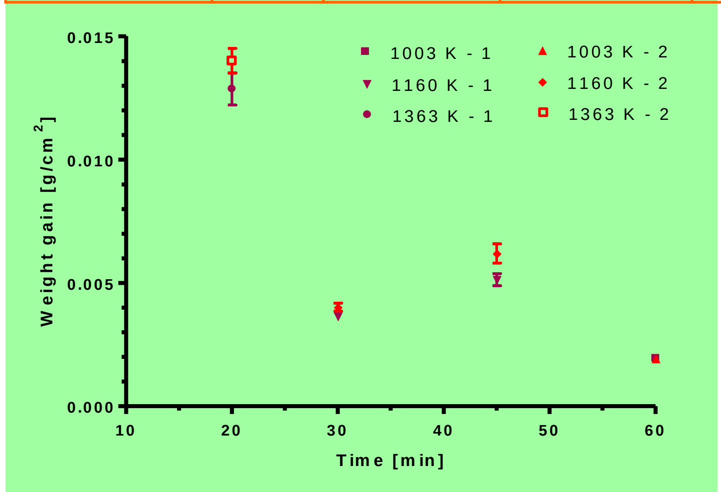
Oxidation kinetics of Ta at low oxygen pressures

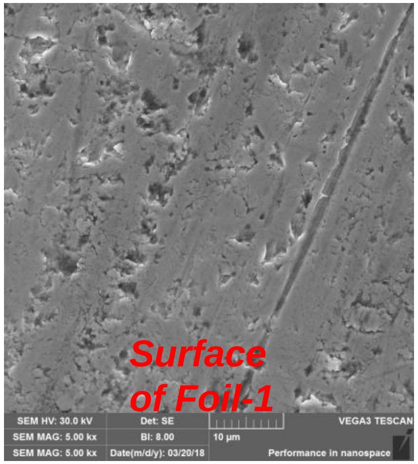
Comparison of weight gain [g/cm^2] for two tantalum foils of different origin at flow rate of oxygen - 3,6 mL/min (which corresponds to preasure in apparatus $6x10^{-4}$ mbar)

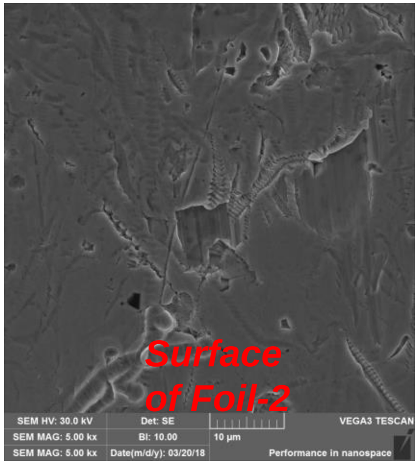
Temperature [K]	Time [min]	Weight gain /area [g/cm^2]		Weight gain /area*min [g/cm^2*min]	
		Foil 1	Foil 2	Foil 1	Foil 2
1003	60	$1,95 \times 10^{-3} \pm 1,3 \times 10^{-4}$	$1,93 \times 10^{-3} \pm 1,3 \times 10^{-4}$	$3,24 \times 10^{-5} \pm 2,2 \times 10^{-6}$	$3,22 \times 10^{-5} \pm 2,1 \times 10^{-6}$
1160	30	$3,64 \times 10^{-3} \pm 1,4 \times 10^{-4}$	$4,01 \times 10^{-3} \pm 1,7 \times 10^{-4}$	$1,21 \times 10^{-4} \pm 4,7 \times 10^{-6}$	$1,34 \times 10^{-4} \pm 5,5 \times 10^{-6}$
	45	$5,13 \times 10^{-3} \pm 2,4 \times 10^{-4}$	$6,20 \times 10^{-3} \pm 3,9 \times 10^{-4}$	$1,14 \times 10^{-4} \pm 5,4 \times 10^{-6}$	$1,38 \times 10^{-4} \pm 8,7 \times 10^{-6}$
1363	20	$1,29 \times 10^{-2} \pm 6,5 \times 10^{-4}$	$1,40 \times 10^{-2} \pm 5,0 \times 10^{-4}$	$6,43 \times 10^{-4} \pm 3,2 \times 10^{-5}$	$7,0 \times 10^{-4} \pm 2,5 \times 10^{-5}$



Photography of results of 30 min oxidation of tantalum at 1160 K and 6,0 x 10^{-4} mbar.

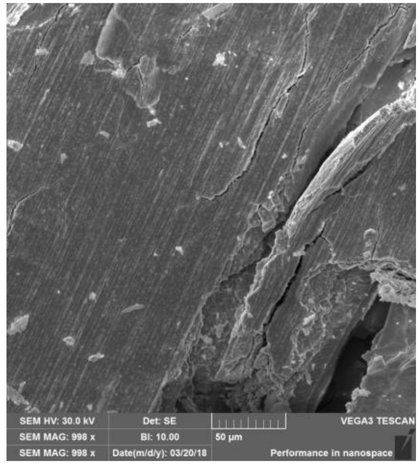






Magnification 5 kx

Investigations of oxidized specimens by means of SEM and EDS



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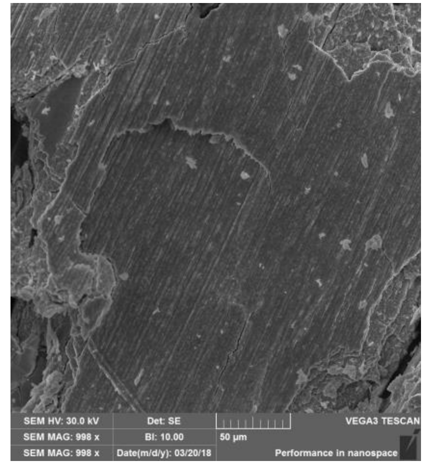
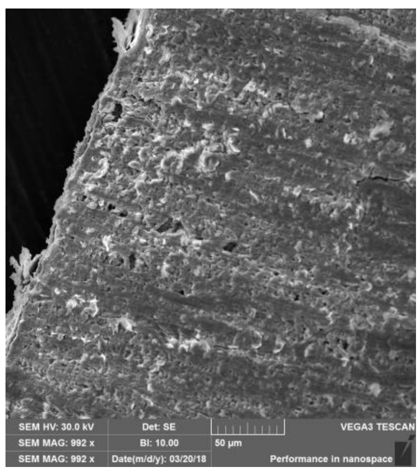


Magnification 1 kx

Oxide surface after oxidation of tantalum for 7 min at 990 K and 1013,2 mbar (*at flow rate of oxygen - 3,6 mL/min).*



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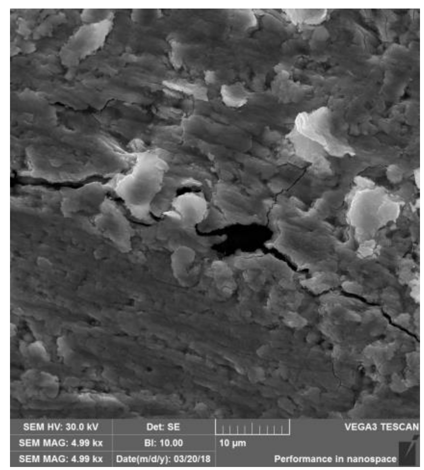
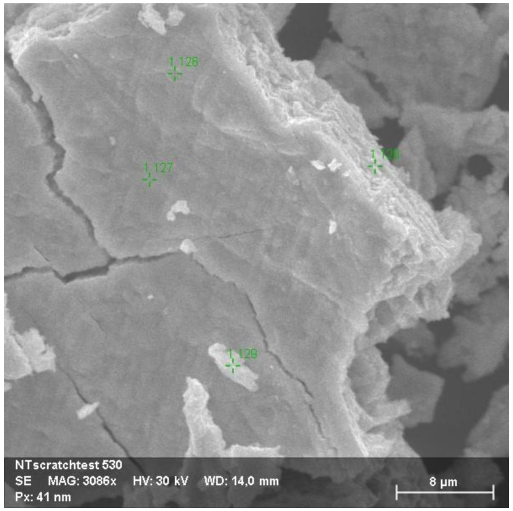


Magnification 5 kx

Oxide surface after oxidation of tantalum for 20 min at 1000 K and 6x10^{-4} mbar (*at flow rate of oxygen - 3,6 mL/min)*

Investigations of oxidized specimens by means of SEM and EDS



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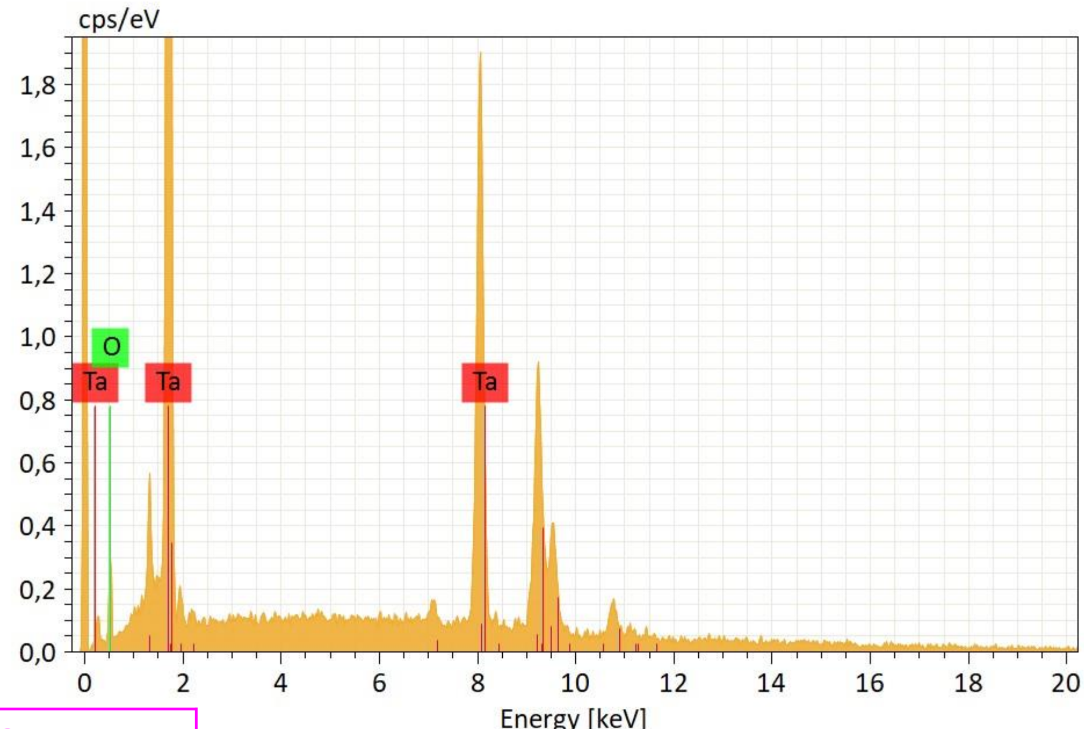
T_{exp} = 990 K, $t_{exp.}$=10 min,
p= atmospheric pressure
(flow rate of oxygen 3,6 mL/min)



Ta_2O_5		TaO_2	
Element	Stoichiometric composition [%]	Element	Stoichiometric composition [%]
O	28,6	O	33,3
Ta	71,4	Ta	66,7

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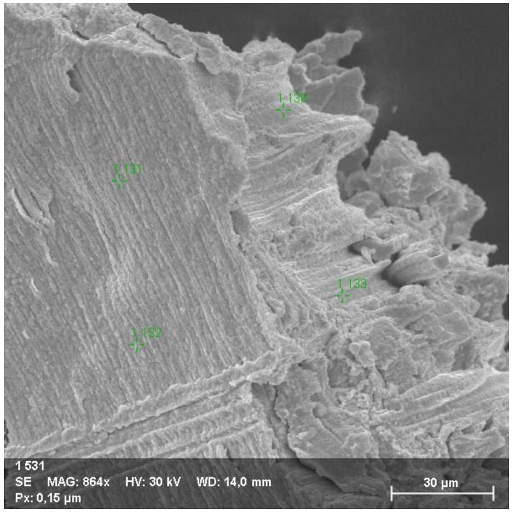
Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)	rel. error [%] (1 sigma)
O	8	460	8,93	18,46	71,92	2,58	28,92
Ta	73	8935	39,43	81,54	28,08	1,09	2,76
		Sum	48,36	100,00	100,00		

Investigations of oxidized specimens by means of SEM and EDS

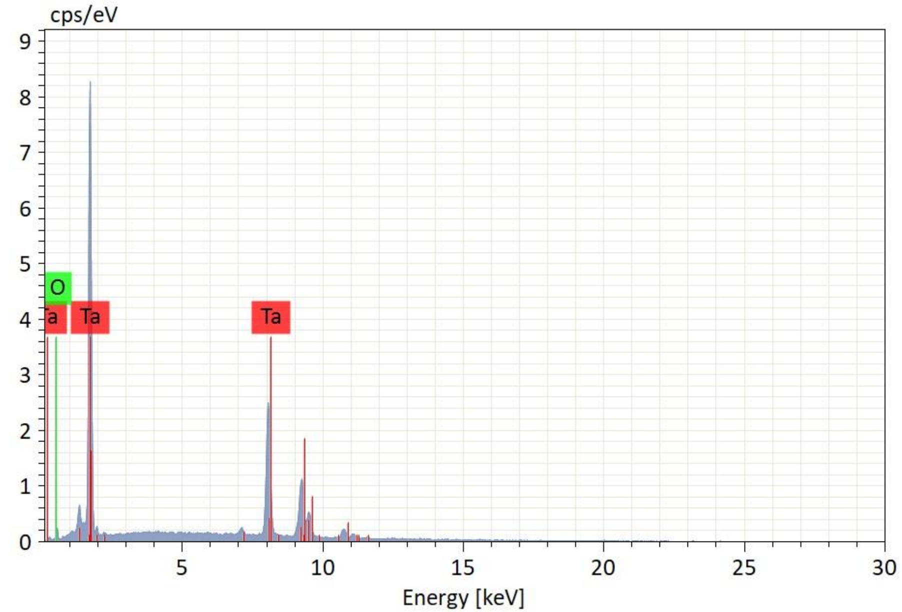


Magnification 864x

T_{exp} = 1363 K, $t_{exp.}$=30 min,

p= 6x10^{-4} mbar (flow rate of oxygen 3,6 mL/min)

Ta_2O_5		TaO_2	
Element	Stoichiometric composition [%]	Element	Stoichiometric composition [%]
O	28,6	O	33,3
Ta	71,4	Ta	66,7



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Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)	rel. error [%] (1 sigma)
O	8	454	7,79	14,62	65,95	2,27	29,09
Ta	73	12044	45,49	85,38	34,05	1,22	2,68
		Sum	**53,28**	**100,00**	**100,00**		

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Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)	rel. error [%] (1 sigma)
O	8	456	8,43	16,17	68,58	2,45	29,03
Ta	73	10589	43,67	83,83	31,42	1,18	2,71
		Sum	**52,10**	**100,00**	**100,00**		

Conclusions

- The rate of oxidation of tantalum has been studied in the temperature range 790K – 990K at atmospheric pressure and 1003K – 1363K at low oxygen pressures. At atmospheric pressure and above 940K the rapid oxidation was observed. At oxygen pressure - 6x10^{-4} mbar and above 1160K the rate of oxidation increased rapidly with temperature.

*- The results of total and edges weight gain [g/cm2*min] measurements on tantalum plate at $T_{exp.}$ = 1363 K and oxygen pressure - 1,0 x 10^{-3} mbar indicated that the rate of oxidation of edges area was almost 25 times higher than the rate of oxidation of total area.*

- The difference of the rate of oxidation for two batches of Ta foil at $T_{exp.}$ = 1363 K and oxygen pressure - 6x10^{-4} mbar is not more than 10%.

- In general the oxide surface had a very uneven appearance and exhibited a large number of cracks. The oxide scales at atmospheric pressure were white. At lower oxygen pressures the colour of the scale tanded to grey and dark grey. At 1363 K the colour of the scale was dark grey to black.

Thank you for your attention

Acknowledgements to prof. M. Parlińska and G. Gruzeł from Department of Soft Matter Research IFJ PAN for SEM-EDS measurements.