Progress in Ultra-Low-Radioactive titanium production

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"ULR titanium" team :

Lomonosov MSU Skobeltsyn Institute of Nuclear Physics

Statement of the physical problem, data processing and R&D program development - "a customer" representing DarkSide collaboration and "glue" of the project

JSC "Solikamsk Magnesium Plant" and

VSMPO-AVISMA Corp. -

Industrial partners from Russian titanium industry

Institute of Solid State Physics of RAS and

Belgorod State Research University

Theory of titanium alloys, unique metallurgical cleaning methods and installations, melting, rolling, welding, mechanical tests

D. Mendeleyev University of Chemical Technology and

INFN LNGS

ICP-MC & HPGe U/Th measurements

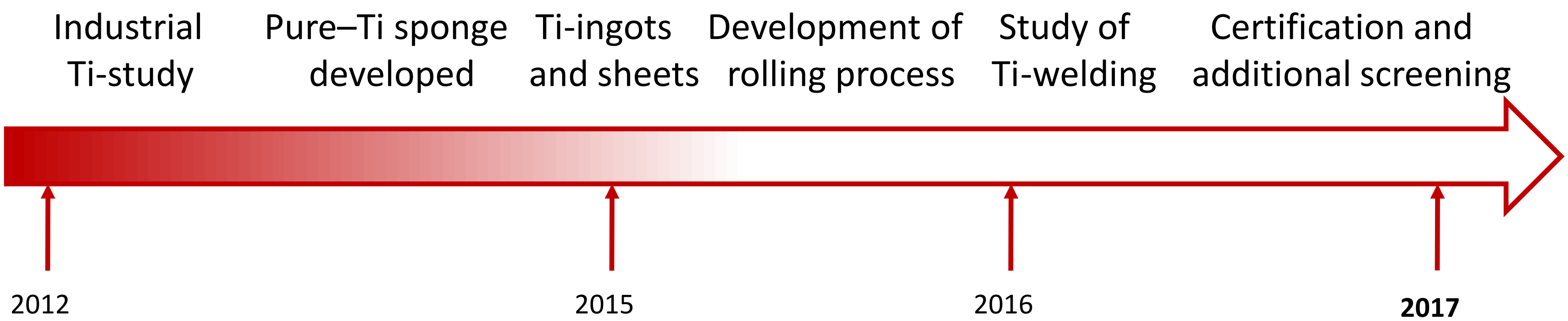
Ultra-Low-Radioactive (ULR) titanium roadmap and goals

- to develop industrial production cycle of ULR titanium and titanium parts

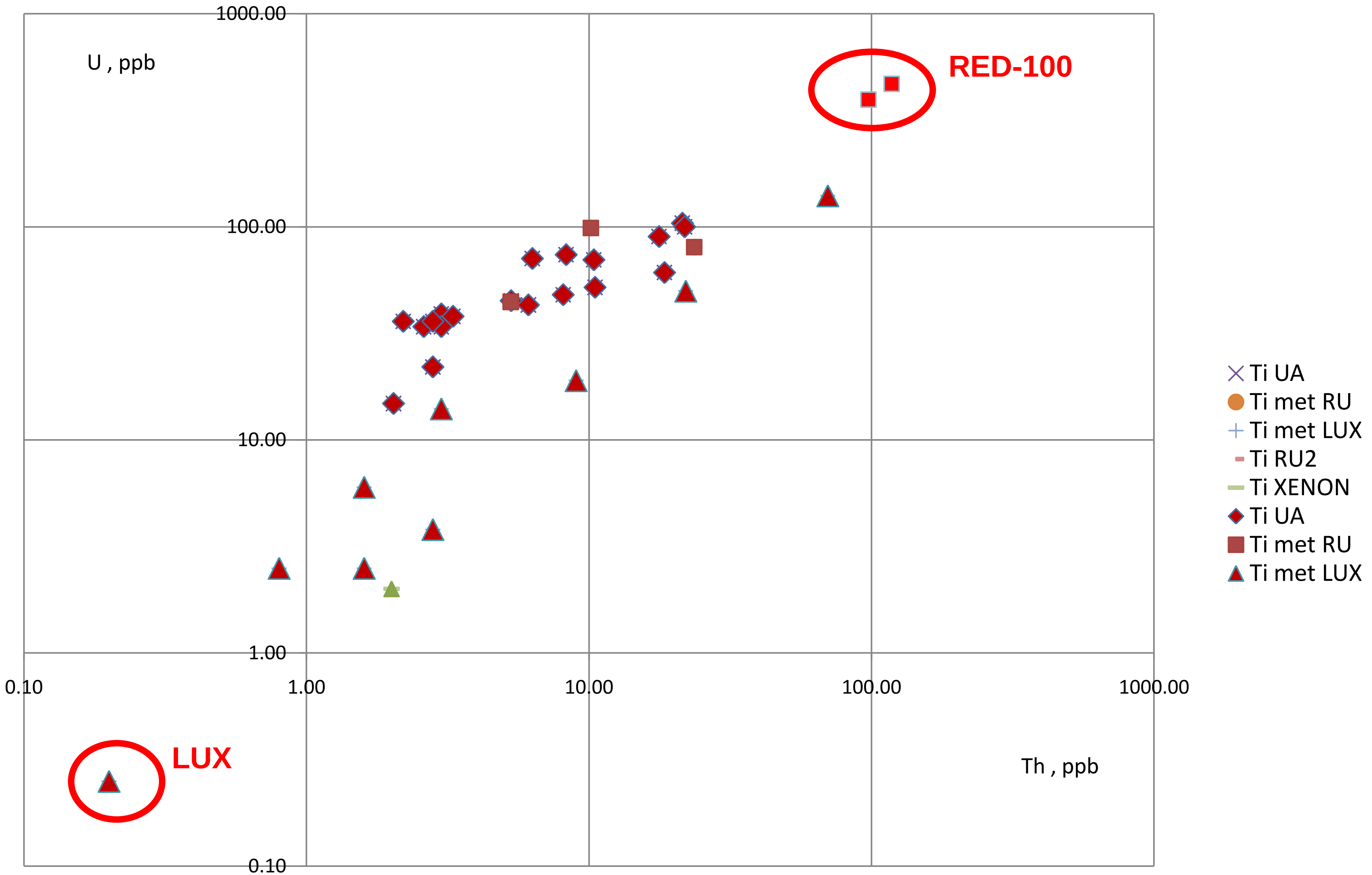
^{238}U & ^{232}Th <= 1 mBq/kg (equivalent to < 0,1 ppb U & < 0,25 ppb Th)

- to provide DarkSide (DS-20k) experiment with ULR titanium in the required quantity

Laboratory scale stage is completed !!

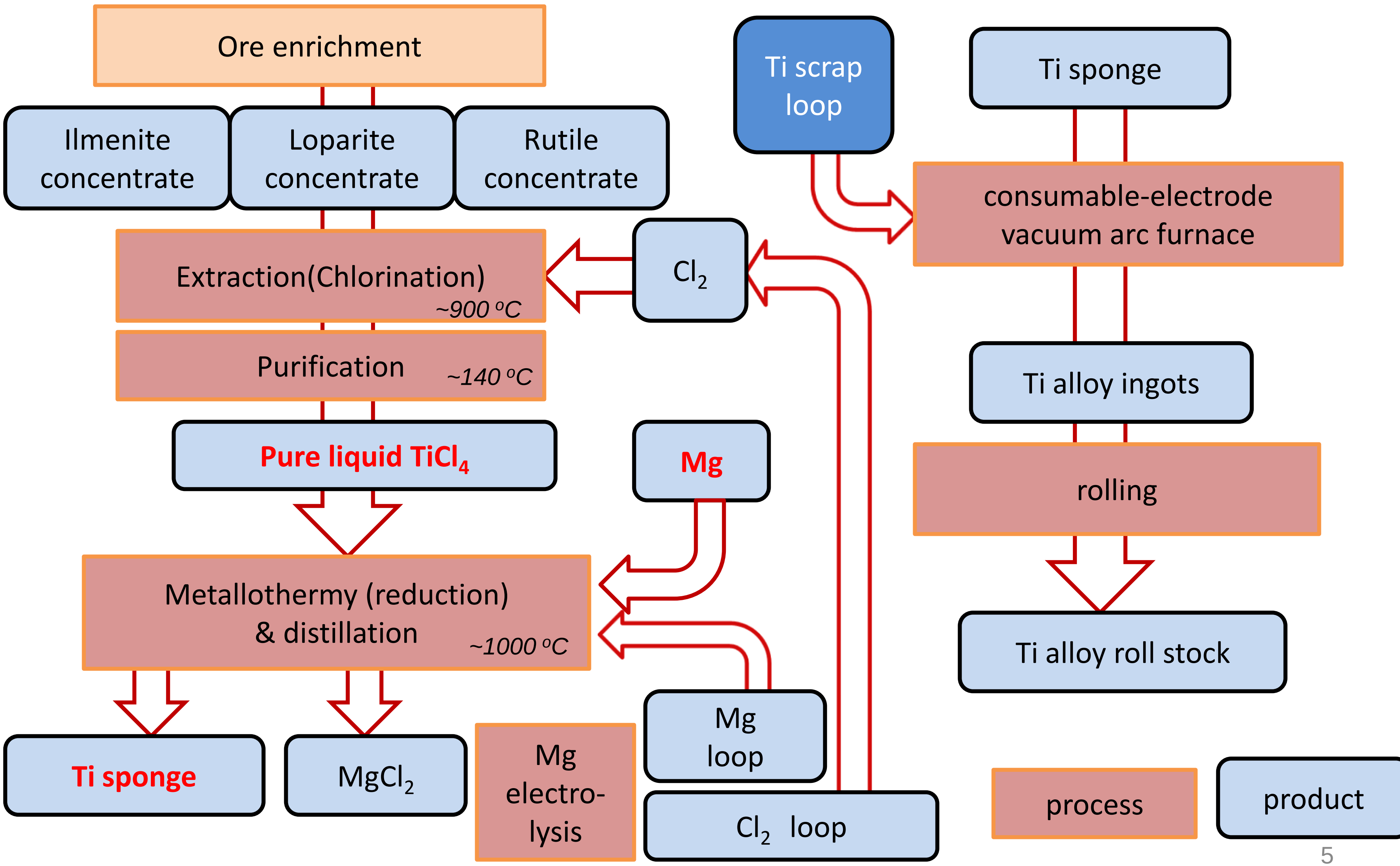


First stage results dated 2012 initiated the development of ULR-titanium
Ti metal samples from different sources (U/Th difference ~4 orders !)



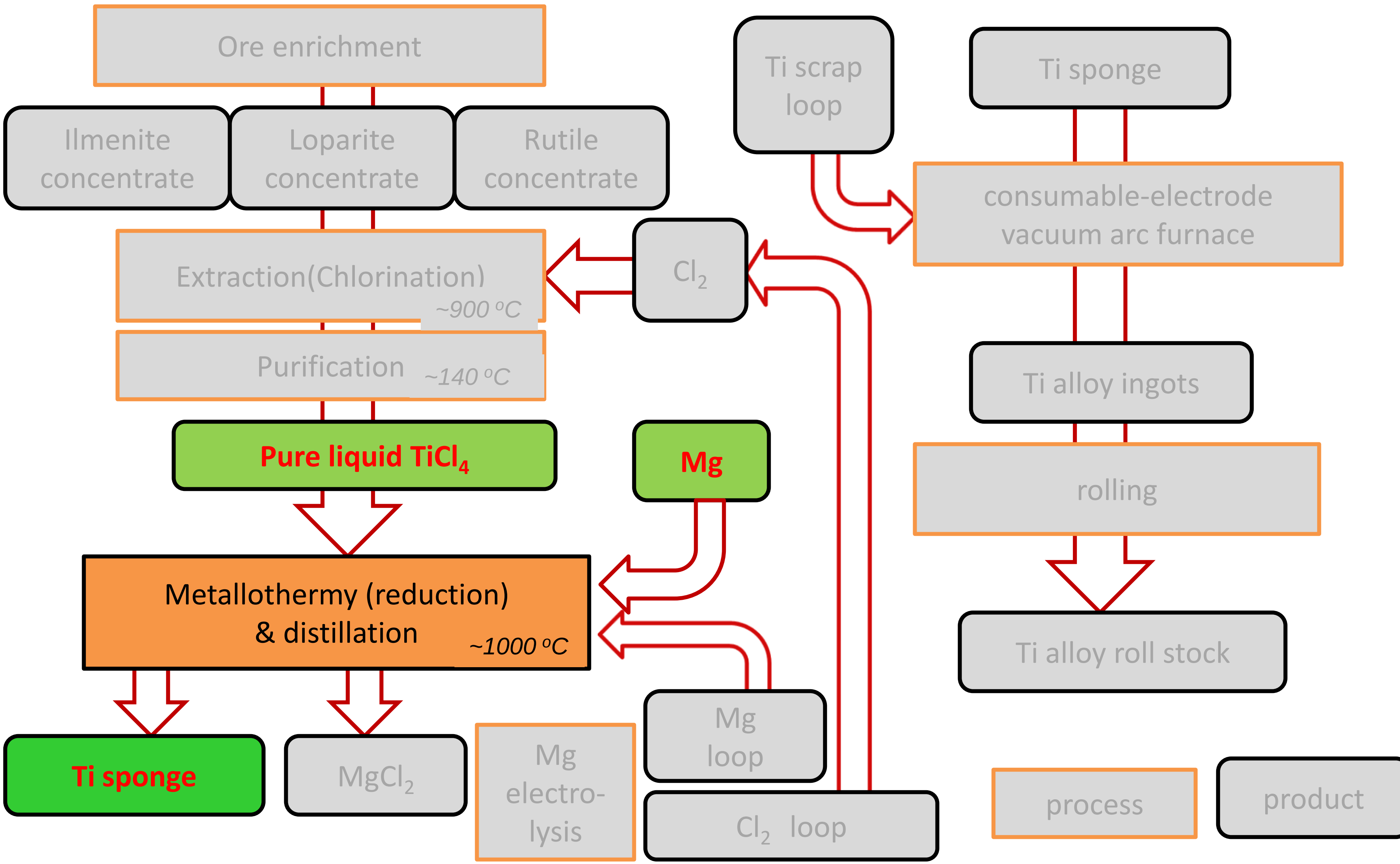
REMEMBER THE GOAL: ^{238}**U < 0,10 ppb ~ 1 mBq/kg**
^{232}**Th < 0,25 ppb ~ 1 mBq/kg**

Kroll-based industrial titanium production cycle



Kroll-based industrial titanium production cycle

Two simple substances are used to produce Ti sponge !!!



JSC "Solikamsk Magnesium Plant“

Nonstop operation since 1936
54% of Russian Mg and Mg alloys
100% of Russian rare earth & Nb, Ta

Youngest and most modern in Russia titanium-sponge production plant

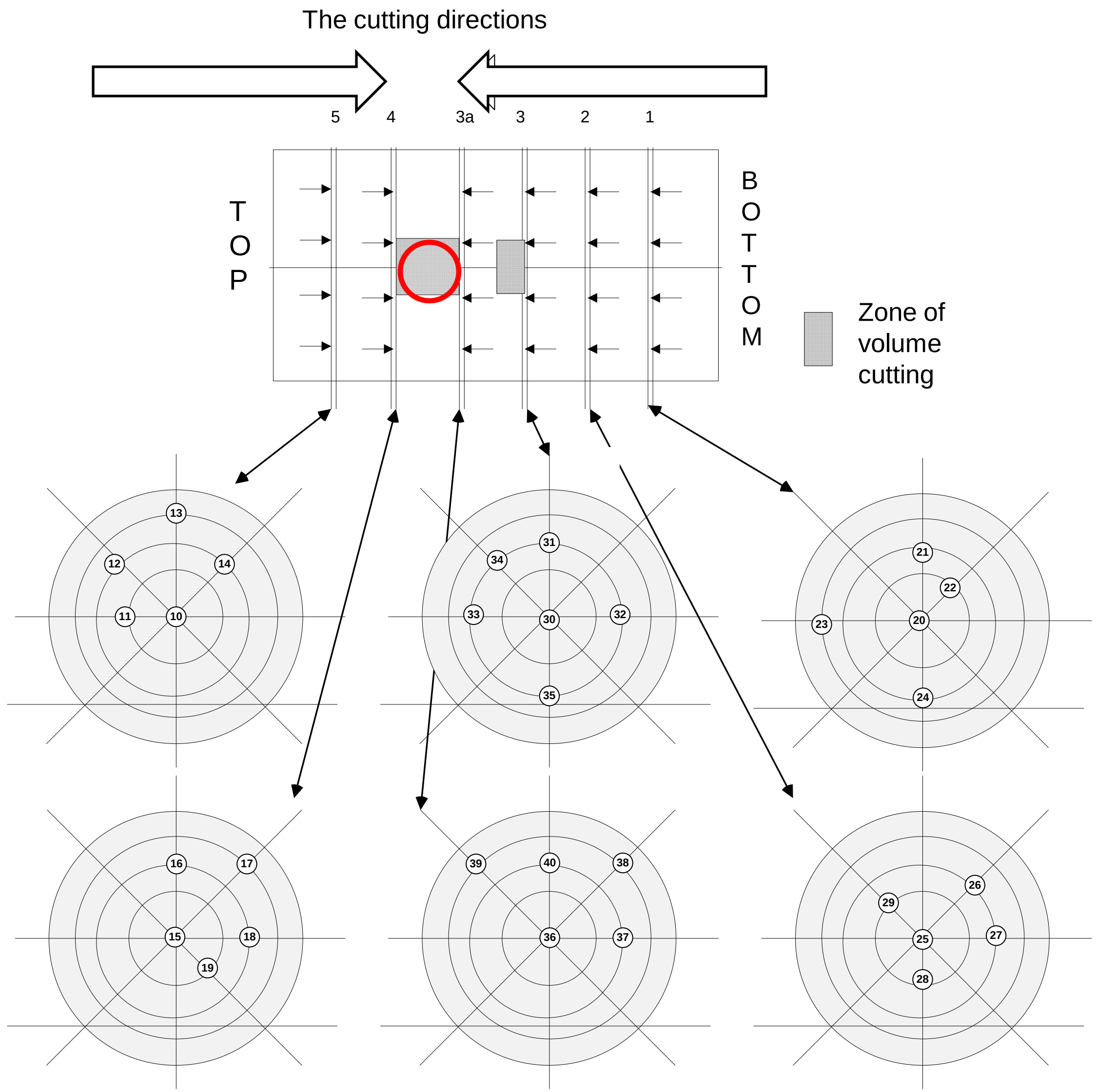

Titanium sponge vacuum distillation


Block of titanium sponge before cutting


Ti-sponge Dendrites

Solikamsk Magnesium Plant
titanium sponge block analysis program

titanium ~6t sponge block

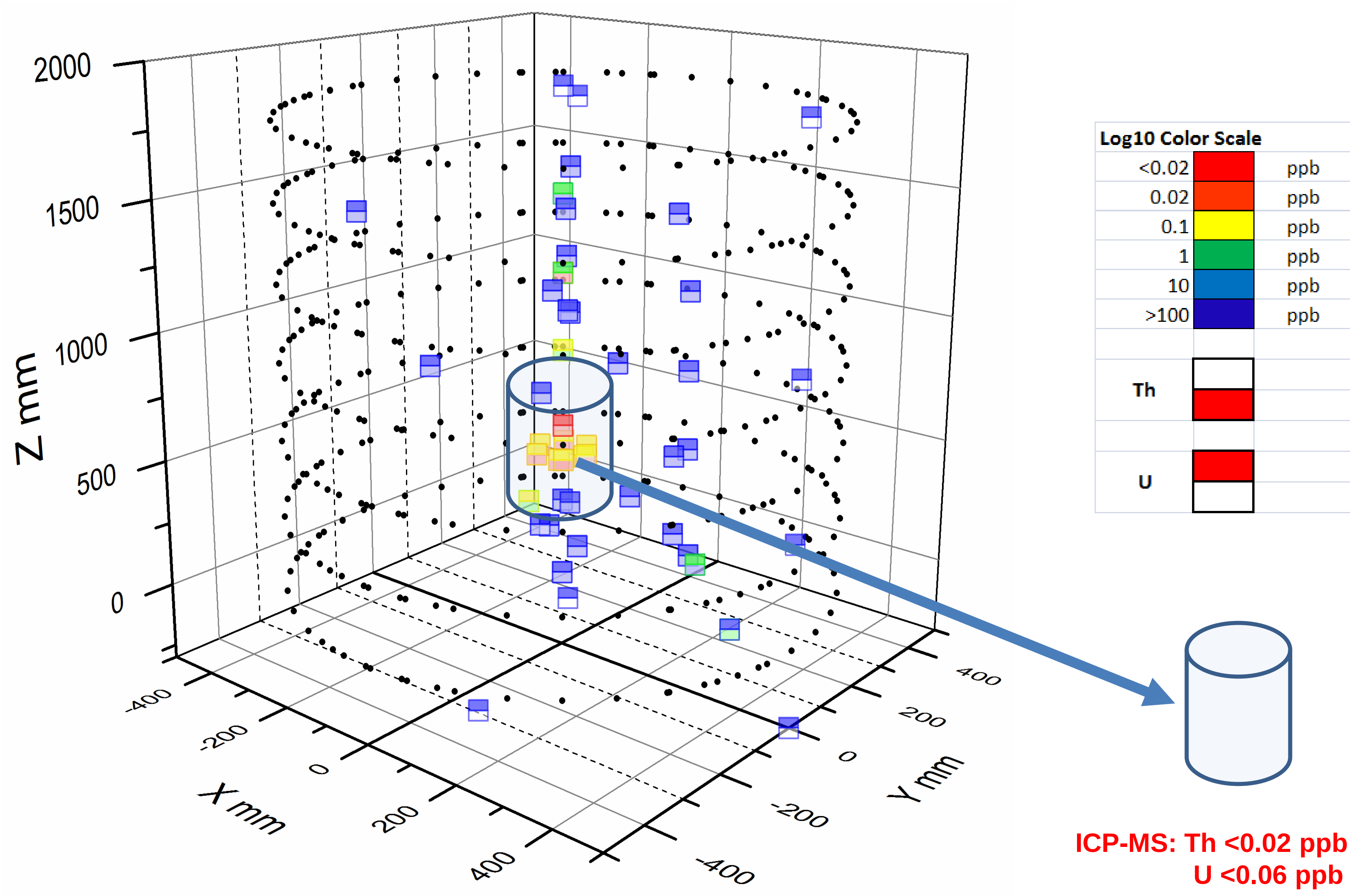


Scheme of Ti sponge block cutting and sampling

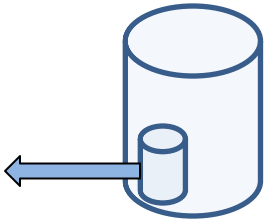
Solikamsk Magnesium Plant
titanium sponge block analysis program

titanium ~6t sponge block

Confirmation of principal hypothesis about ULR-area of titanium sponge block



LNGS HPGe test



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sample: Ti sponge, Solikamsk, March 2015, DS50
weight: 2927 g
live time: 3587352 s
detector: GeMPI2

radionuclide concentrations:

Th-232:				
Ra-228:	< 0.41 mBq/kg		<==>	< 1.0 E-10 g/g
Th-228:	(0.23 +- 0.07) mBq/kg	<==>	(6 +- 1) E-11 g/g	
U-238:				
Ra-226	(0.34 +- 0.06)mBq/kg	<==>	(2.8 +- 0.5) E-11 g/g	
Th-234	< 9.4 mBq/kg	<==>	< 7.6 E-10 g/g	
Pa-234m	< 9.3 mBq/kg	<==>	< 7.5 E-10 g/g	
U-235:	< 0.28 mBq/kg		<==>	< 5.0 E-10 g/g
K-40:	(2.1 +- 0.3) mBq/kg		<==>	(6.8 +- 0.9) E-8 g/g
Cs-137:	< 0.13 mBq/kg			
Co-60:	< 0.049 mBq/kg		@ start of measurement: 12-JUN-2015	
Sc-46:	(2.48 +- 0.21) mBq/kg		@ start of measurement: 12-JUN-2015	
V-48:	(0.38 +- 0.06) mBq/kg		@ start of measurement: 12-JUN-2015	
Ti-44:	< 0.10 mBq/kg		@ start of measurement: 12-JUN-2015	

upper limits with k=1.96,
uncertainties are given with k=1 (approx. 68% CL);

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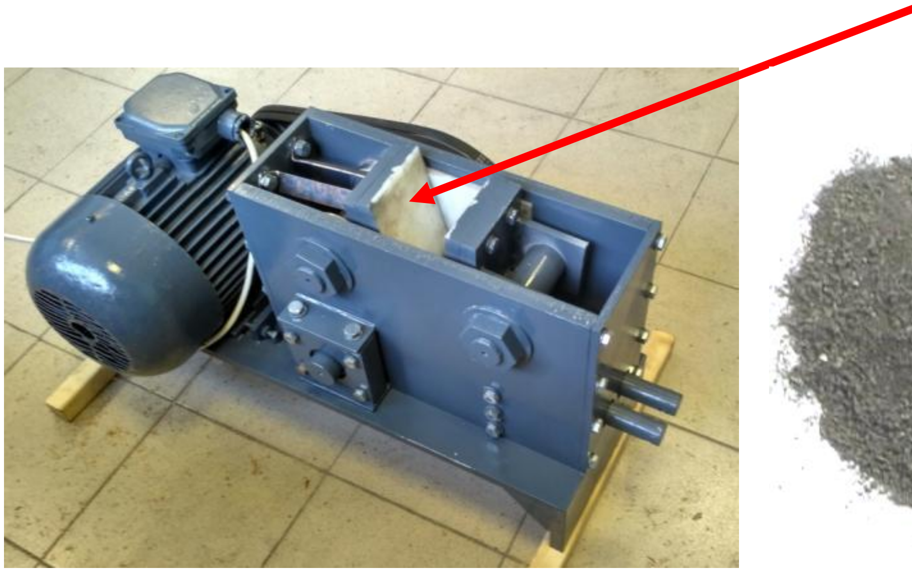
Many thanks to Matthias Laubenstein

HOW TO PRODUCE PARTS FORM THE ULR-SPONGE AND AVOID RECONTAMINATION ?

Special “ULR-Mill” lined with ULR titanium

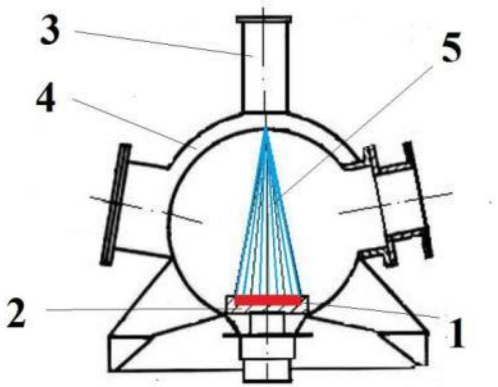


~ 50x200 mm

Isostatic compacting of the ULR titanium sponge

Electron Beam Vacuum Melting

Mass of each ingot is ~5 kg thickness - 18-20 mm, material losses during the melting up to 15-20% of the load. **Th <0.02ppb, U <0.06ppb**



1-liquid metal,
2-mould,
3-EB axial gun,
4-vacuum vessel,
5-electron beam

&

Cylindrical consumable electrodes are melted by electric arc into a water-cooled mold. The weight of each ingot is 1.9 kg.

	38-3	39-3	40-3
	ppb	ppb	ppb
Th	<0.02	<0.03	<0.02
U	<0.01	<0.02	0.005

Vacuum Arc Melting

Study of the rolling conditions and the mechanical properties of titanium sheets

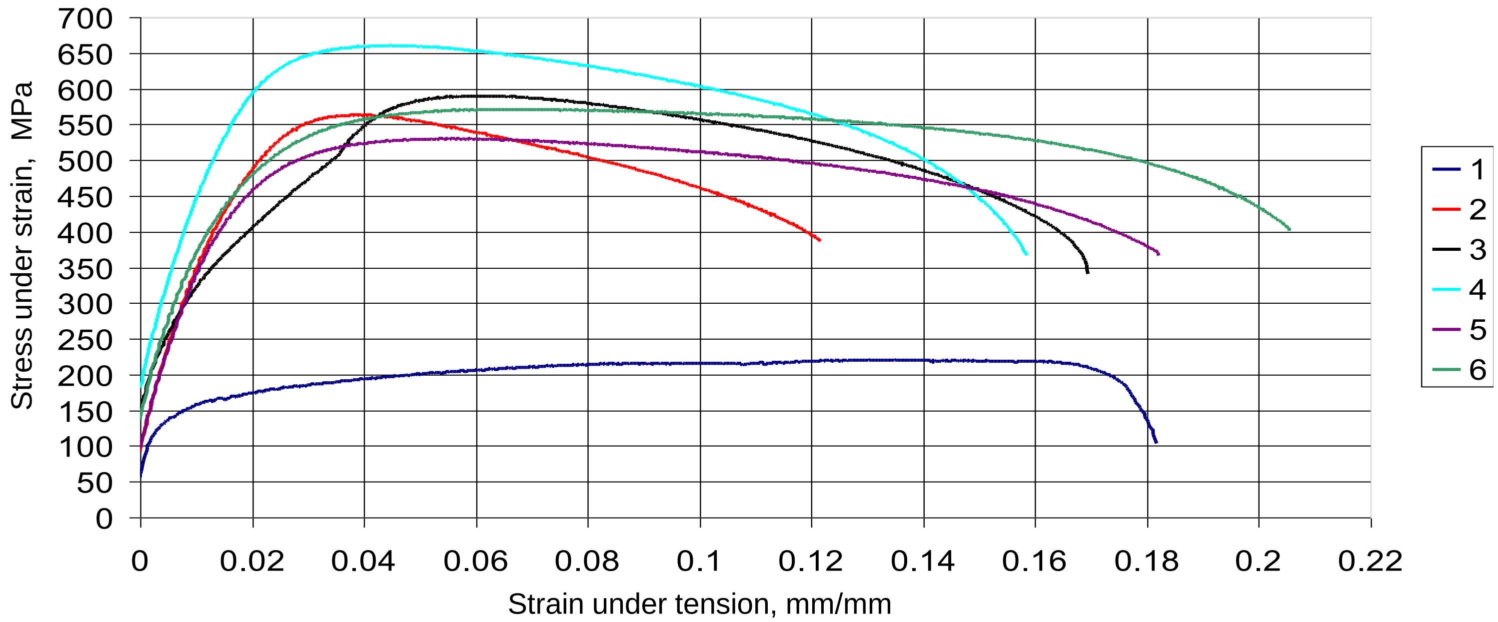
- The goal was to produce Ti sheets with optimal mechanical properties at cryogenic temperatures, which means uniform fine-grained (~5 mkm) structure and keep low radioactive properties.

- The task is complicated by the fact that the original ingots contain large grains and have a low level of impurities. Since a high-purity Ti undergoes polymorphic conversion of the diffusion path during cooling there is no obstacle for the growth of deformation twins. The twinning and slipping in titanium are two competing processes of plastic deformation. Changes in temperature can be controlled by the intensity of these processes. The twinning process is the primary mechanism to the 1 mkm structure, and twins are the large internal stress concentrators and thus lead to cracking. The modes have been developed to prevent the occurrence of cracks through the timely removal of stresses arising in the formation of mechanical twins and thus achieve an uniform and maximum structure.

Furnace for vacuum annealing

ULR titanium sheets rolling equipment

Results of mechanical tests of rolled titanium



№1. The initial state. Cast after melting.

№2. 25% rolling, vacuum annealing at 700°C.

№3. Warm rolling with a total degree of deformation of 80% by 6-8% per pass.

№4. Variable warm/cold with a cross-rolling of the ingot with a total degree of deformation of 80% by 6-8% per pass.

№5. Warm rolling with a cross-rolling of the ingot with a total degree of deformation of 80% by 6-8% per pass, followed by annealing at 450°C.

№6. Variable warm/cold cross-rolling with a total degree of deformation of 80% by 6-8% per pass, followed by annealing at 450°C.

Mechanical and U/Th properties

Optimal rolling process which gives necessary mechanical and keeping ULR properties was selected.

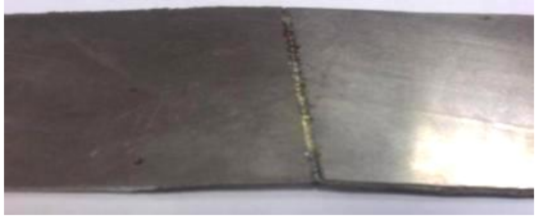
Material	HV (hardness)	$\sigma_{0,2}$, Mpa (conventional yield limit)	$\sigma_в$, Mpa (tensile strength)	ISP-MS data	
Industrial materials					
AISI 304		210	510		
VT1-00 / GRADE 1	**110-140**	**250-380**	**300-450**		
AISI 316	180-250	250-450	450-800		
VT16 (Al, V)	170-400	600-1000	1000-1500		
Ingots/sheet from pure Ti-sponge				U, ppb	Th, ppb
Original ingot from pure Ti-sponge	140 std.dev 30	150	220	**<0.003**	**< 0.05**
Sample №2	160 std.dev 53	410	565	**0.83**	**0.67**
Sample №3	**165 std.dev 10**	**420**	**590**	**<0.003**	**< 0.05**
Sample №4	155 std.dev 15	250	390	**0.16**	**0.14**
Sample №5	160 std.dev 45	280	400	**<0.003**	**0.017**

Study of ULR titanium welding

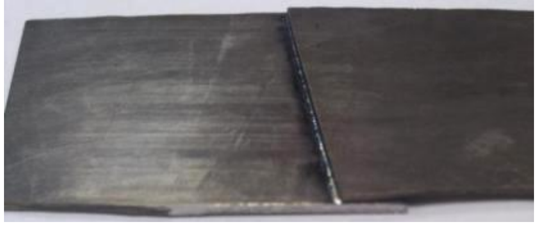
An essential step in the manufacture of the cryostat is welding. The welding process should not lead recontamination by radioactive impurities, and the mechanical properties of the welds should not impair the mechanical strength of the assembly. To investigate the possibility of creating a weld sheets radiation pure titanium welding process three were selected:

1. Argon arc welding of non-consumable tungsten electrode with the location details of the butt, without the use of additives, with double-sided weld penetration.

2. Laser welding arrangement butt parts without using additives with bilateral weld penetration.



3. Laser welding with overlapping, without the use of additives with a bilateral joint penetration.



Mechanical properties and U/Th of the welds

Mechanical properties show that the laser and argon welding allow to use UHP Ti as a structural material in the manufacture of a cryostat. The strength of the welded joint was about 400MPa. An advantage of laser welding is a small heat-affected zone.

Samples	Max strength MPa
Laser welding (butt)	450
Laser welding (overlap)	355
Argon arc welding (butt)	390
Original material	590

Ti 1-X - argon arc welding;
Ti 2-X - laser welding.

Task		Ti 1-1			Ti 1-2	Ti 2-1	Ti 2-2
ppb		ppb	St dev ppb	St dev %	ppb	ppb	ppb
<0.25	Th	<0.02			<0.02	**<0.01**	**<0.01**
<0.10	U	0.69	0.04	6.4	<0.03	**<0.01**	**<0.01**

The laser welding keeps U/Th level low. Contamination with argon arc welding by U requires further study and may be associated with a contamination from the tungsten electrode.

Low radioactivity of the original material was confirmed again.

Ultra Low Radioactive titanium samples manufactured from industrial titanium sponge

Step 1. Production of low-radioactive sponge.
Step 2: Crushing sponge. Step 3: Isostatic compacting of the sponge.
Step 4: Vacuum arc- melting or Step 5: Vacuum e-beam-melting.
Step 6: Rolling with annealing. Step 7: Laser welding.

	ppb
Th	<0.02
U	<0.03

LABORATORY-SCALE STAGE RESULTS

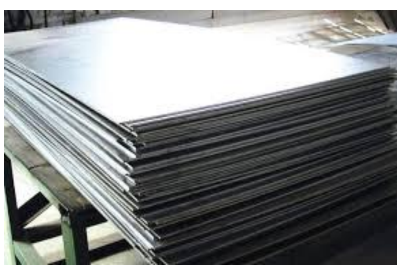
1. It is confirmed, that ULR-titanium sponge could be produced by Kroll process
2. EBV-melting in water cooled crystallizer & VA-melting (most widely used in industry) keep the material clean.
3. Mechanical properties of processed ULR-titanium could be equal or better than commercial VT1-00 alloy due to specially developed rolling/annealing process
4. Laser welding is preferable welding method to keep ULR titanium clean
5. ICP-MS screening on all stages confirms the target levels of U/Th

Ultra-Low-Radioactive (ULR) titanium future

Laboratory scale stage is completed !!
Industrial scale stage (tons of titanium) is started !!

Is it possible to reach the level below 0.1 mBq/kg (of U/Th)?
Yes, the way to 0.1 and below is visible but it needs to do additional R&D

2017 2018 2019 **2020**



Is it possible to purchase ULR titanium now ?
Not yet. Please wait until the end of 2017.

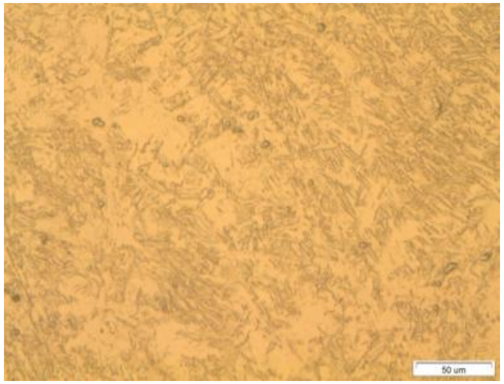
Thank you for your attention !

The project was financially supported by a program of the ministry of education and science of The Russian Federation for higher education establishments, project №14.578.21.0192 (RFMEFI57816X0192).

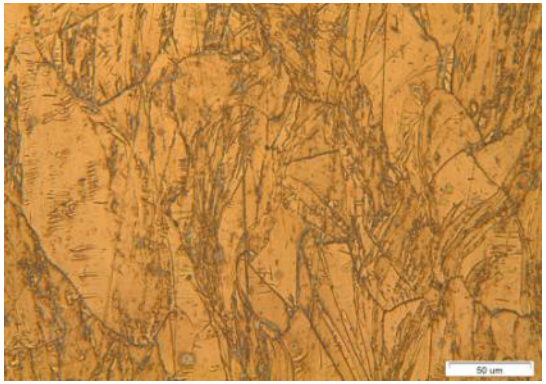
Titanium monument above
Moscow museum of space research
http://москва-россия.рф/muzey-kosmonavtiki-v-moskve/

- Additional slides

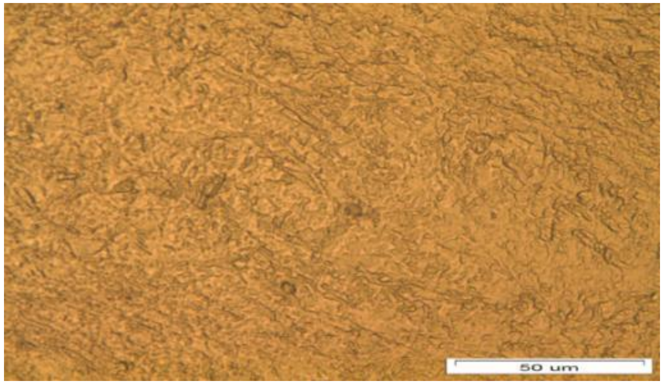
Microstructure of titanium sheets depending of the rolling modes



№3. Warm rolling (300°C) with a total degree of deformation of 80% by 6-8% per pass.



№2. 25% rolling, vacuum annealing at 700°C.



№6. Variable warm/cold with a cross-rolling of the ingot with a total degree of deformation of 80% by 6-8% per pass, followed by annealing at 450°C/

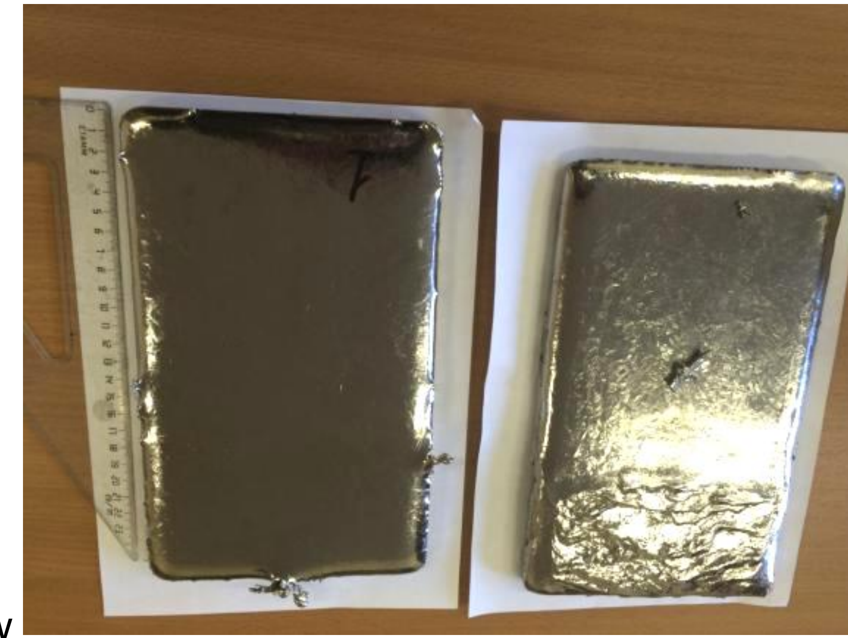
Variable warm/cold rolling and subsequent annealing at 450̊C (N6) yielded a more homogeneous structure with the size of 3 microns fragments. Warm rolling contributed a slip deformation, allowing to relax stresses caused by formed in cold rolling twins, as evidenced by the uniformity of microhardness. This cold deformation, due to activation of the twinning process, contributed to intensive fragmentation pattern.

Melting 1: Electron Beam Vacuum Melting

The thickness of the bars - 18-20 mm.
The operations were carried out in the ISSP RAS.
Melting was carried out in a specially constructed water-cooled copper mold with multiple coup of ingot when the ingot melted through the entire depth. Power 60 kW axial gun, with a magnetic deflection of the beam and electron beam focus from acute to scattered.
Material losses during the melting - 15-20% .

Data analysis ICP-MS of both flat bars for “Remelting 1" showed that the recontamination doesn’t happen, U and Th concentrations are below the detection limit.

Th <0.02ppb, U <0.06ppb



Mass of each ingot is ~5 kg

WHILE THE GOAL IS: U < 0,10 ppb ~ 1 mBq/kg
Th < 0,25 ppb ~ 1 mBq/kg

Melting 2: Vacuum Arc Melting

The process was done according to the standard test-process on “VSMPO-AVISMA" Co. The pressed cylindrical consumable electrodes were made by crushing and compacting of ULR Ti sponge. Then the consumable electrodes were rmelted by electric arc into a vertical water-cooled mold.
Three ingots were produced with numbers 38, 39 and 40. The weight of each ingot was ~1.9 kg.
The ingots were cut to the segments, as shown in Figure.
Results of ICP MS analysis is presented below

Demands		38-3	39-3	40-3	St dev	Rel St dev
ppb		ppb	ppb	ppb	ppb	%
<0.25	Th	<0.02	<0.03	<0.02	-	-
<0.10	U	<0.01	<0.02	0.005	0.0048	88.4