AEOI
Atomic Energy Organization of Iran

IAEA
International Atomic Energy Agency

AEOI Activities Report in the Framework of CRP ATF-TS

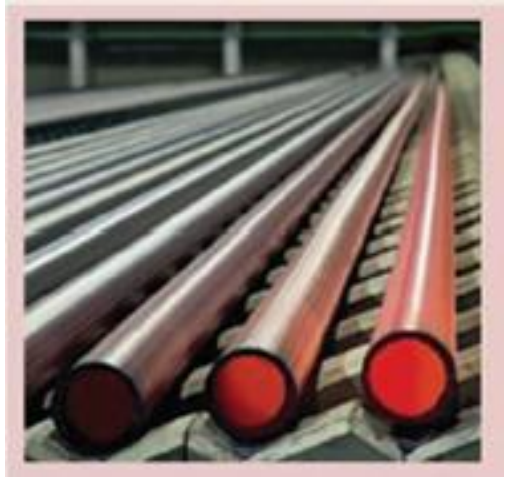
A. Riahi, A. Zareidoost

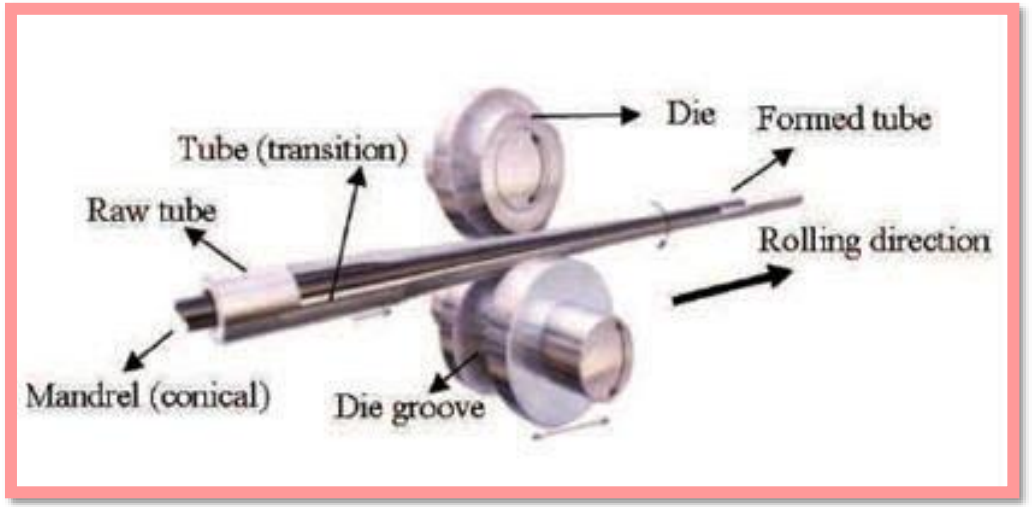
Contents

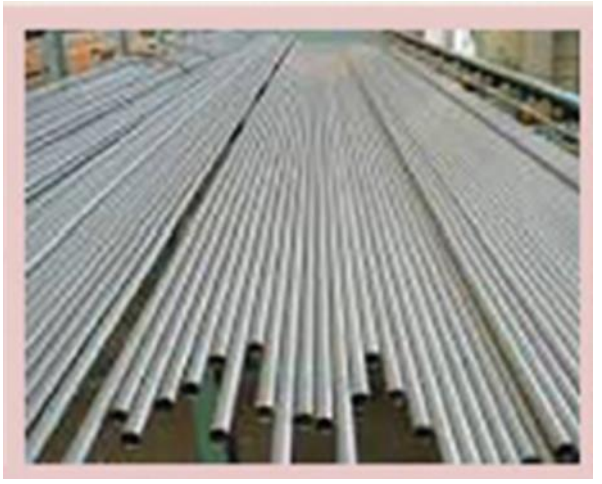
- WT1-Provided ATF samples;
- Used coating technology and some investigations into the studied samples;
- Oxidation experiments on samples and corresponding results;
- Summary

WT1-Provided ATF samples

Nuclear Reactors Fuel (NRF) company







WT1-Provided ATF samples

- **The first step of the provided ATF samples**

September 2021

Provider	Shared with	Material	Geometry	Size (mm)	Num. (each group)
AEOI	JRC (Karlsruhe)	Reference-Cr, CrN and Multilayer Coated	Tube	D: 9.1, L: 250	1
AEOI	INCT	Reference-Cr, CrN and Multilayer Coated	Tube	D: 9.1, L: 250	2
AEOI	UPM	Reference-Cr, CrN and Multilayer Coated	Tube	D: 9.1, L: 250	5
AEOI	CTU/UJP	Reference-Cr, CrN and Multilayer Coated	Tube	D: 9.1, L: 250	5
AEOI	EK	Reference-Cr, CrN and Multilayer Coated	Tube	D: 9.1, L: 250	5
AEOI	KIT	Reference-Cr, CrN and Multilayer Coated	Tube	D: 9.1, L: 250	4
AEOI	JRC (Petten)	Reference-Cr, CrN and Multilayer Coated	Tube	D: 9.1, L: 250	3
AEOI	VTT	Reference-Cr, CrN and Multilayer Coated	Tube	D: 9.1, L: 250	3

WT1-Provided ATF samples

November 2022

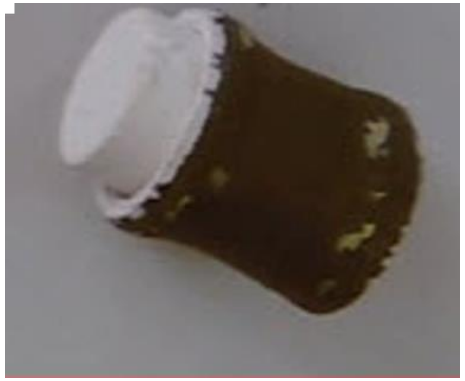
- **The second step of the provided ATF samples**

Provider	Shared with	Material	Geometry	Size (mm)	Num.
AEOI	UPM	Reference	Tube	D: 9.5, L: 250	5
		Cr Coated			5
		CrN Coated			5
		Multilayer Coated			4
AEOI	CTU/UJP	Reference	Tube	D: 9.1, L: 300	10
		Cr Coated			10
		CrN Coated			3
		Multilayer Coated			2
AEOI	INCT	Reference	Tube	D: 9.1, L: 250	3
		Cr Coated			5
		CrN Coated			5
		Multilayer Coated			3
		Reference	Sheet	50 * 50	3
		Cr Coated			5
		CrN Coated			5
		Multilayer Coated			5

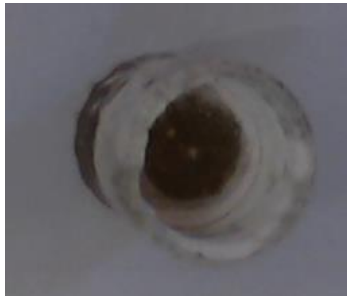
Preparation and shipment of the prepared samples

Bar Inside the clad

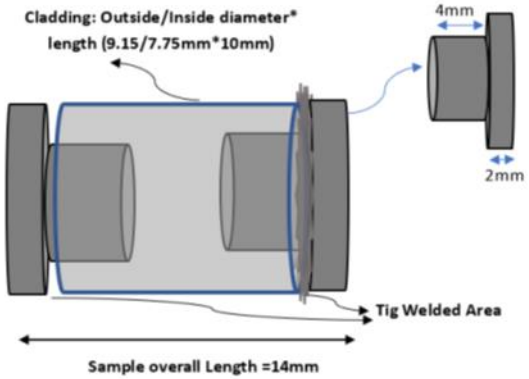
Ceramic pellet Inside the clad



One-Side Capped



Both side welded



Preparation and shipment of the prepared samples

Samples arrangement for coating

CNPRI-China

陈蒙腾
to Ki, fangzexin, Amir, Martin, 陈蒙腾, yan.jun, 刘洋, me

Dear Abdollah,

Thanks for your kindly remind. Considering the operability and airtightness, we actually hope the outer diameter of samples are D
test and creep test with D=9.1mm samples from CTU. So I think it is ok for the mechanical tests with D=9.1mm or D=9.5mm samp
before.

For the oxidation test, we can conduct the test on simultaneous thermal analyzer (picture below). In my opinion,the both sides cap
would be better for high temperature steam oxidation test. The length of samples is about 10mm. If we conduct HT steam oxidatio
could be made ourselves.(e.g. A L=30cm sample can be cuted 20cm for mechnical test and the rest can be divided for HT steam
If you have any suggestion, please feel free to contact me. Thanks.

Best regards,
Mengteng

CNPE-China


Refrence CNPE
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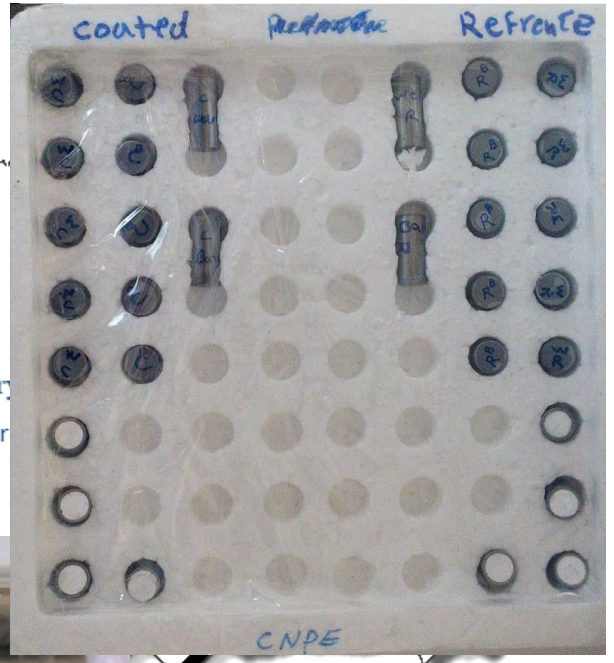
Coated
Refrence
CNPE


M-Coated CNPE
M-Coated CNPE
M-Coated CNPE
M-Coated CNPE
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M-Coated CNPE


CNPE-China
Coated samples

WT1-Provided ATF samples

CRIEPI-Japan

Kinya Nakamura (中村 勤也) <kinya@criepi.denken.or.jp>
to Amir, me

Dear Riahi,

Thank you for your quick response. Your reply satisfied me.

Could you please provide the following samples for the ballooning and burst test?

- Two coated cladding with one end welded and the other open, cladding length 235 mm
- One coated cladding with about 50 mm length for characterization prior to the burst test
- One uncoated cladding with one end welded and the other open for reference, cladding length 235 mm
- One uncoated cladding with about 50 mm length for characterization prior to the burst test

The shipping address is as follows. If you have any questions, please feel free to contact me.

Address: 2-6-1 Nagasaka, Yokosuka, Kanagawa 240-0196, Japan

Recipient: Kinya Nakamura

Organaization: Central Research Institute of Electric Power Industry (CRIEPI)

Best regards,

Kinya

WT1-Provided ATF samples

JRC-Germany

VLAHOVIC Luka <Luka.VLAHOVIC@ec.europa.eu> Wed, Mar 15, 5:00 PM

to me, Martin, Amir

Dear Riahi,

You can send us your samples. You have to be aware that we have some delays in our lab. In my lab, JRC.G in Karlsruhe (Germany), we measure thermophysical properti
If you wish to have corrosion and mechanical tests, please contact my colleague NOVOTNY Radek from JRC.G-PETTEN, Radek.NOVOTNY@ec.europa.eu, and ask him if h
can do it. Please leave Martin in copy of your email.

I will send you a form for the German customs that you will have to join to your shipping, but I need from you following information:

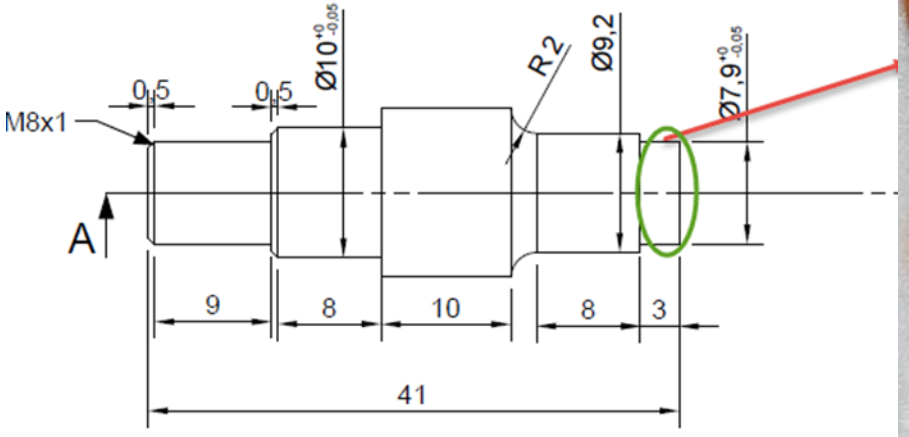
- Full name and address of your institute
- Short description of the samples
- Approximate value of the samples

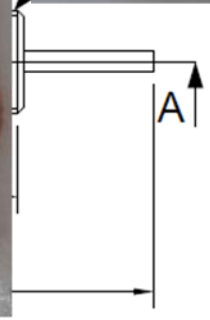
I will provide you the shipping address with the form for the custom.

Best regards,
Luka

VTT-Finland

- The biaxial creep testing of AEOI samples have been postponed to early 2023 due to mechanical plugging system failure. We could use material specification info and feedback on the parameter specifications of these experiments from the mechanical modelling point-of-view.





VTT-Finland

Toivonen Aki <Aki.Toivonen@vtt.fi> Apr 7, 2023, 2:32 PM

to Peltonen, Martin, me, Amir

Dear Abdollah,

The oxidation samples are 10 mm long (=very short) due to space limitations. What we would need is that steam can not enter th … nough

I forwarded the question to my colleagues who are doing mechanical/creep tests on the tubes, but I have not yet received any an … a more plugging. We'll return to the subject.

Best regards,

WT1-Provided ATF samples

❑ The third step of the provided ATF samples

Provider	Shared with	Material	Geometry	Length (mm)	Num.	Comment
AEOI	CRIEPI	Reference and Multilayer Coated	Tube	L: 237	2	One-side capped (welded)
				L: 250	1	Open sample
AEOI	KIT	Reference and Multilayer Coated	Tube	L: 130	5	One-side capped (welded)
AEOI	VTT	Reference and Multilayer Coated	Tube	L: 10	5	One-side capped (mechanical)
					5	Capped with ceramic
					2	Capped with welded plug
					7	Capped with Zr rod
				L: 20	1	Capped with welded plug
					1	Capped with Zr rod
				L: 50	4	Capped with VTT plug
				L: 250	6	Open sample
AEOI	CNPRI	Reference and Multilayer Coated	Tube	L: 10	8	Capped with Zr rod
					12	Capped with ceramic
				L: 20	4	Capped with ceramic
				L: 100	2	Capped with welded plug
				L: 250	14	Open sample
AEOI	CNPE	Reference and Multilayer Coated	Tube	L: 10	5	Capped with Zr rod
					4	Capped with ceramic
				L: 14	5	Capped with welded plug
				L: 20	1	Capped with welded plug
					1	Capped with Zr rod
				L: 100	4	One-side capped (welded)
				L: 250	7	Open sample

May 2023

INCT (Poland)

Table 1.

Elemental composition of investigated zirconium alloys samples obtained with Instrumental Neutron Activation Analysis (INAA) method

Sample number:	Zr_1	Zr_2	Zr 3	Zr 4
Zirconium isotope	Zr1Nb (AEOI) plate [ppm]	Zr1Nb (AEOI) tube [ppm]	ZIRLO (tube) CTU [ppm]	Zry-4 (tube) KIT [ppm]
Ag	0,464	1,077	0,497	0,598
Au	5,808	2,475	0,091	
Au	0,003	0,001	0,003	
Ba	9,939	78,812		0,995
Br	30,233	33,886	107,149	62,914
Ca	4047,148	2638,438		
Cd				
Ce	0,498		0,063	0,535
Co	1,326	0,553	0,259	0,293
Cr	10,254	146,830	7,134	11,603
Cs				0,090
Cu	208,079	186,124	139,453	116,405
Dy			0,114	6,692
Eu	0,048	0,189	0,006	0,063
Fe	2256,640	2680,808	1740,117	1262,490
Ga	1,364	0,893	0,936	0,903
Gd	0,754	0,525	3,966	
Ge	41,368			
Hf	7,933	19,690	27,027	5,387
Hg	38,861			
Ir	0,000	0,004	0,013	0,002
K	18,228			
La	0,669	0,497	0,413	0,628
Lu	0,003	0,004		
Mn	35,134			
Mo	1,286		0,070	
Na	72,894	47,226	41,611	49,498
Nd	18,916	3,182	9,260	
Ni(Co-58)	17,189	4,495	319,585	23,542
U-238	0,581	0,643	0,365	0,378
Th		0,214	0,126	0,113
Tr	3,570	1,580		
Tb		12,394		
Sb	0,998	1,247	0,830	0,599
Sc	0,069	0,059	0,066	0,073
Se	3,069	0,211	1,502	0,231
Si	167,175	30,304	13,196	10,320
Sm	0,087	0,085	0,071	0,078
Sn	67,775	7360,085	2910,786	196,261
Ta	0,327	0,251	3,358	0,895
Tb	0,165	0,116	0,194	0,064
Tm	0,038	0,001	0,053	0,125
W	0,125	0,358	0,261	0,143
Yb	0,069	0,340	0,180	0,202
Zn	121,543	92,683	97,600	86,484
Zr	999990,702	994466,446	974466,446	993710,675

ON GOING WORKS – elemental composition for references (INAA)

INFO from INCT
according to plates Zr1Nb

I wonder the results obtained for Zr1Nb plate material.

can you comment difference in zirconium content between
* AEOI plate 66.7% and
*AEOI tube 90.5%

I plan to confirm detailed elemental analysis using the other analytical method

INFO from AEOI

The results are not consistent with the real elemental analysis.
Please kindly note that there is no difference between plate and tube material.
So, I would appreciate it if you could change your method….

INFO from INCT

of course we can discuss this point.
In general each analytical method has it's own limits.
INCT plan:
* to discuss this subject I'll talk about our INAA specialists
* to use the other analytical method

Most important:
* Zr concentration:Zr1Nb plate: 66.7%
Zr1Nb tube: 90.5%
ZIRLO: 97.5%
Zry-4 tube: 99.4%
* 46 isotopes analysed

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RCM 2 in the frame of ATF-TS 5-9.12.2022

Neutron Activation Analysis of tube and sheet samples

Reactor and Nuclear Safety Research School
Nuclear Science and Technology Research Institute
Atomic Energy Organization of Iran

MNSR Facility, ENTC, Roshan-Dasht, Isfahan, Iran, P.O. Box 81465/158

Date: May 31, 2023

Subject of report: INAA of tube and strip samples of NRF Company

Two Zr1Nb samples, tube and strip, have been received from NRF Company to the NAA laboratory of Isfahan MNSR for analysis. In this laboratory, the INAA is done using standard reference materials (SRMs) and the maximum neutron flux at full power of reactor (30 kW) is 1E+12 n/cm^2/s. Based on the received request, different irradiation times and analysis conditions were used to identification of desired elements. The results are tabulated below.

	Tube	Strip
Element	Concentration	Concentration
Co	0.70 ± 0.04 ppm	1.20 ± 0.07 ppm
Hf	35.00 ± 2.17 ppm	32.0 ± 1.8 ppm
Al	10.0 ± 0.7 ppm	6.1 ± 0.4 ppm
Mn	7.1 ± 0.6 ppm	5.0 ± 0.4 ppm
Fe	412 ± 25 ppm	512.0 ± 34.8 ppm
Nb	1.02 ± 0.02 %	0.99 ± 0.03 %
*Ta	available	available
**Zr	available	available

* Lower than detection limit.
** Due to high concentration of Zr in samples, it is recommended to use the "rest method" to exact determination of Zr. In this method, all trace elements are identified and the total concentration of them subtracted from 100 (total mass of sample). The NAA technique is not suitable for analysis of high concentration elements, e.g. > 10% that is more than 1E+05 ppm. On the other hand, NAA cannot analyze some samples like H, O, C, B, Pb, etc.

NAA (Neutron Activation Analysis) is a powerful analytical technique used for determining the elemental composition of various materials. However, like any other method, it also has some drawbacks and limitations:

- Detection limits: NAA can detect very low levels of elements, but it may not be sensitive enough for trace analysis of some elements. Additionally, it is not suitable for elements with low neutron capture cross-sections.
- Sample preparation: The sample preparation process for NAA is time-consuming and requires careful handling to prevent contamination or loss of sample material.
- Interference from matrix effects: Matrix effects, such as the presence of other elements in the sample, can interfere with the accuracy of the analysis.

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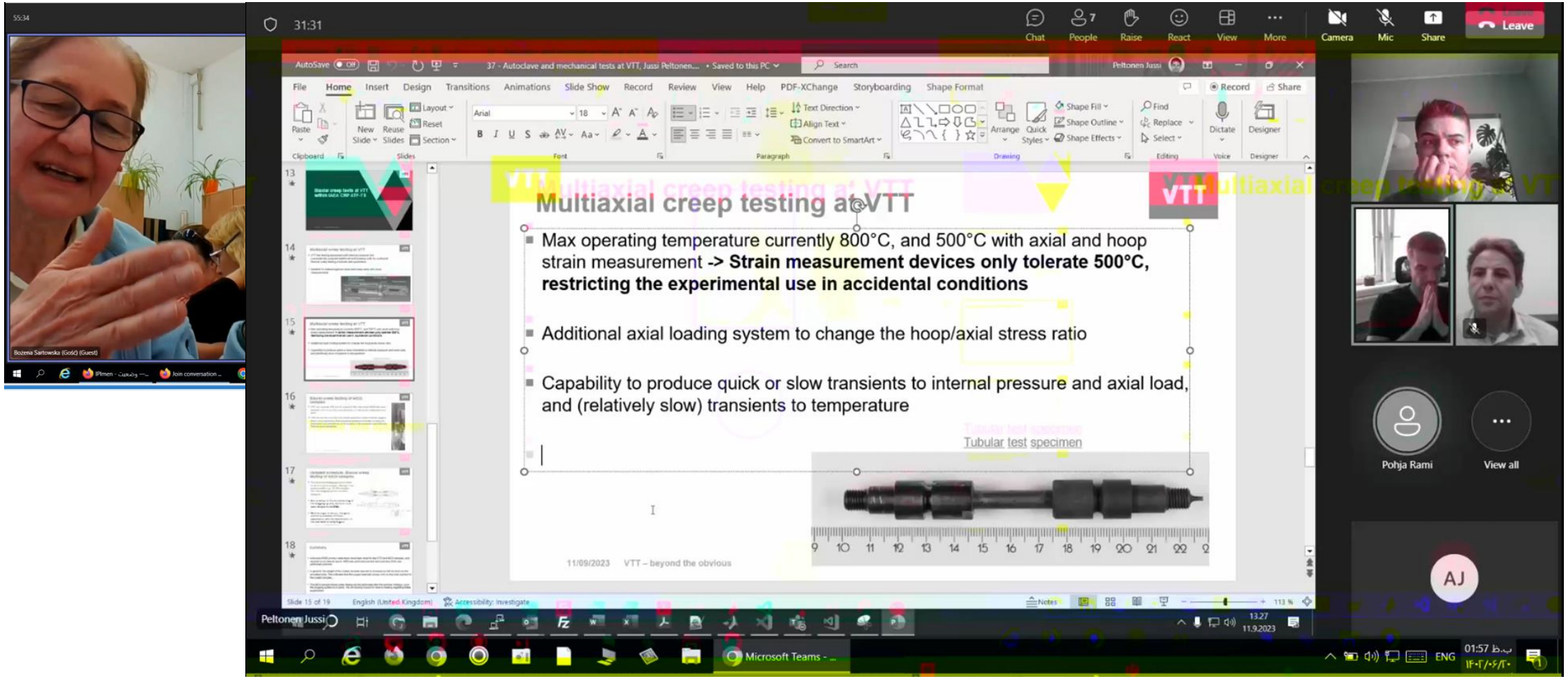
Bilateral Meetings



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Used coating technology and some investigations into the studied samples

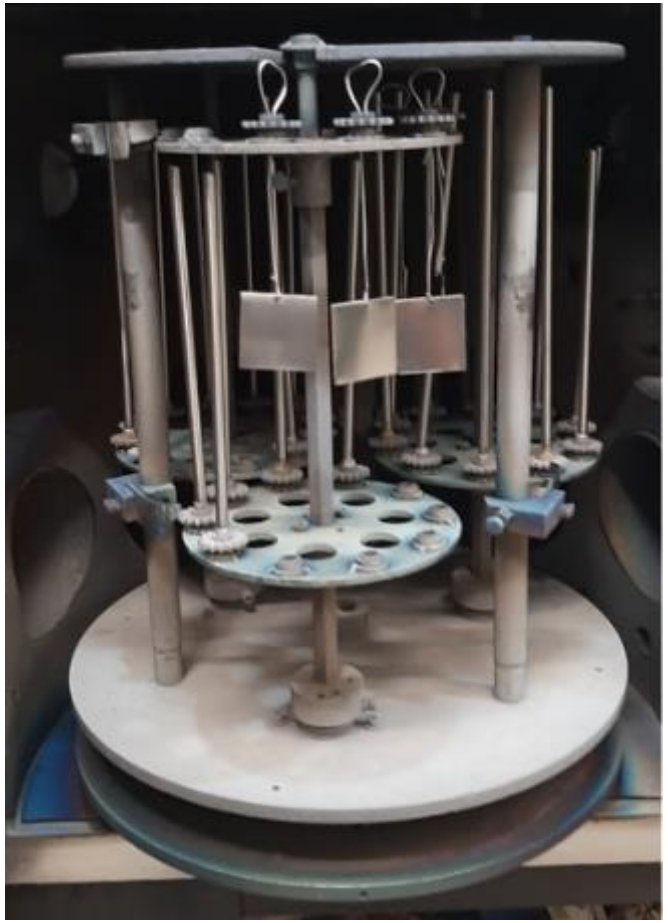
Coating Technology

- AEOI prepared Cr, CrN, and multi layer Cr/CrN-coated Zr-1%Nb and one group as a reference

- The Arc-PVD coating parameters used for preparing theses coatings

Type of coating / Parameter	Multi-layer (Cr/CrN)	CrN	Cr
Coating thickness (micron)	7 - 10	7 - 10	6 - 10
Number of the targets	2	2	4
Bias voltage (V)	100	100	100
Substrate temperature (°C)	300 ± 2	300 ± 2	300 ± 2
Ar gas pressure (sccm)	15	15	60
Periodic injection of Nitrogen gas (min)	~4.0	~55.0*	0.0
Coating duration (hr)	~8.5	~7.0	~4.5

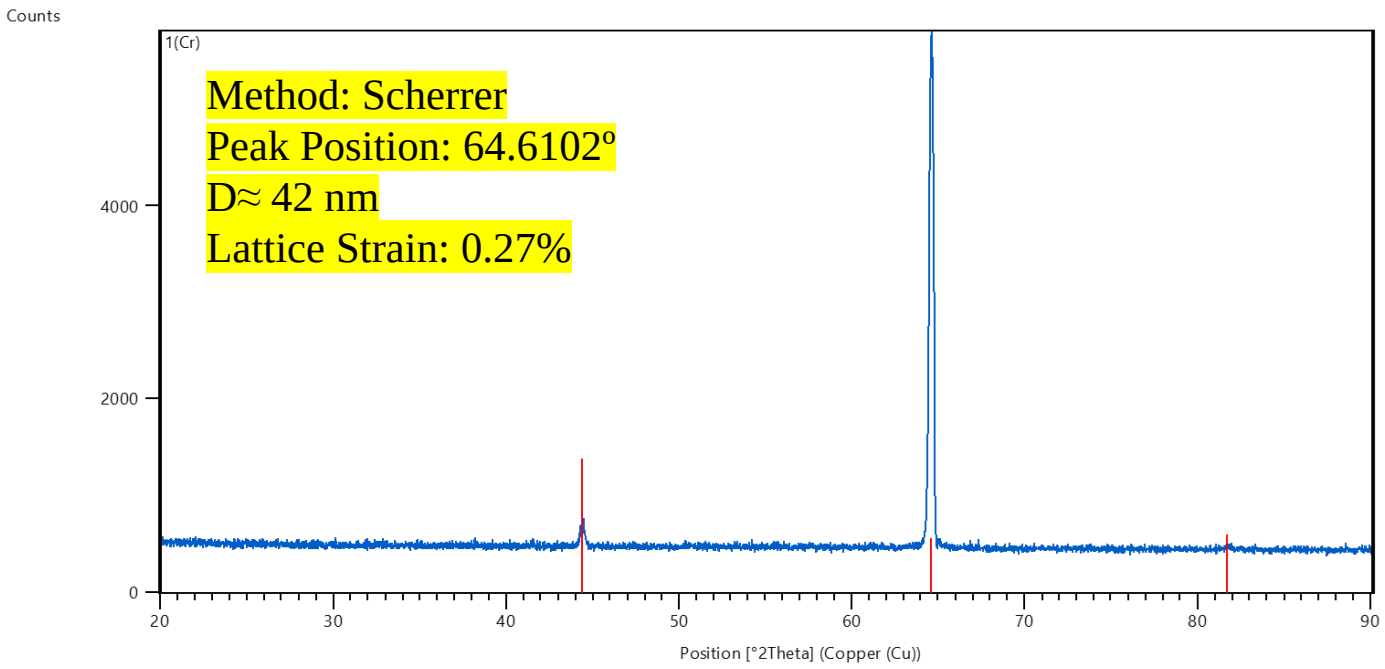
* To control the shedding and decreasing the residual stress of the CrN coating



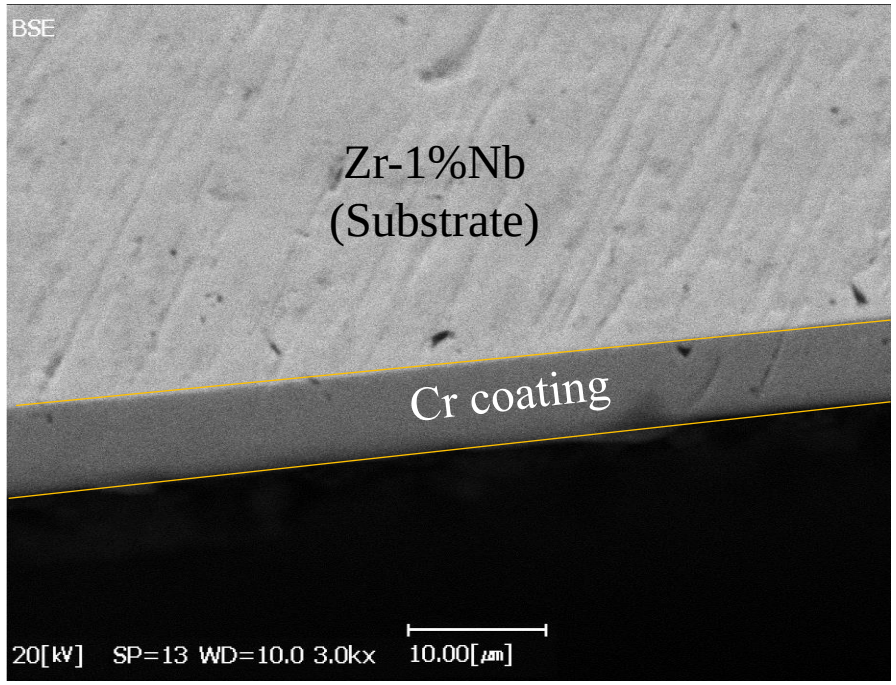
The inside view of the ARC-PVD coating chamber.

Characterization of the coated samples

❑ Phase characterization of the Cr coating



The XRD pattern of the Cr coating

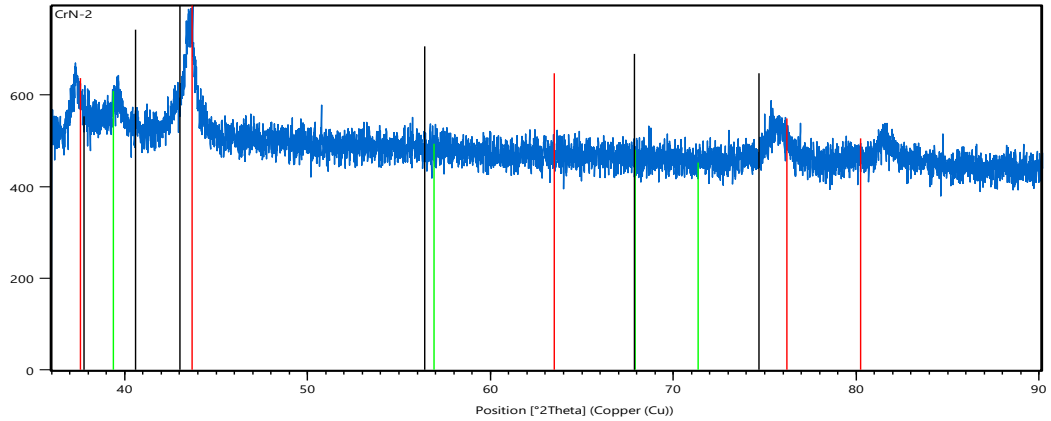


The SEM-BSE image of the Cr coating

- ✓ Cr coating shows a strong crystallographic orientation
- ✓ The Cr layer is uniformly coated on the Zr-1%Nb substrate

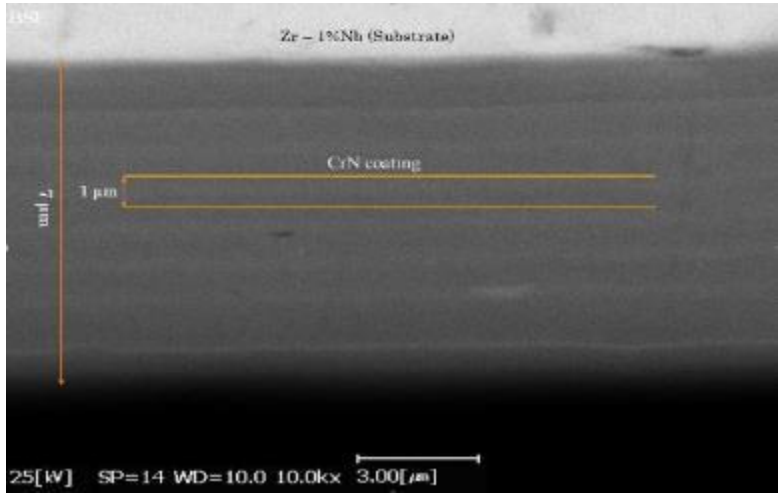
Characterization of the coated samples

❑ Phase characterization of the CrN coating



The XRD pattern of the CrN coating

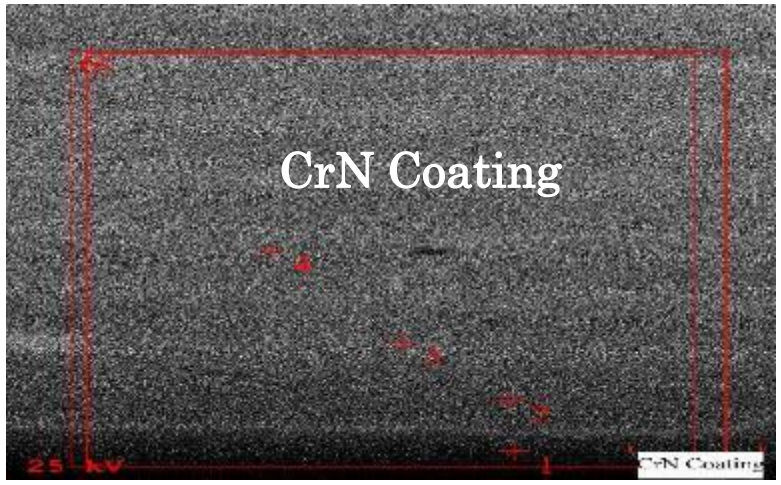
Method: Scherrer
Peak Position: 43.56º
D ≈ 17 nm
Lattice Strain: 0.62%



The SEM image of the CrN coating.

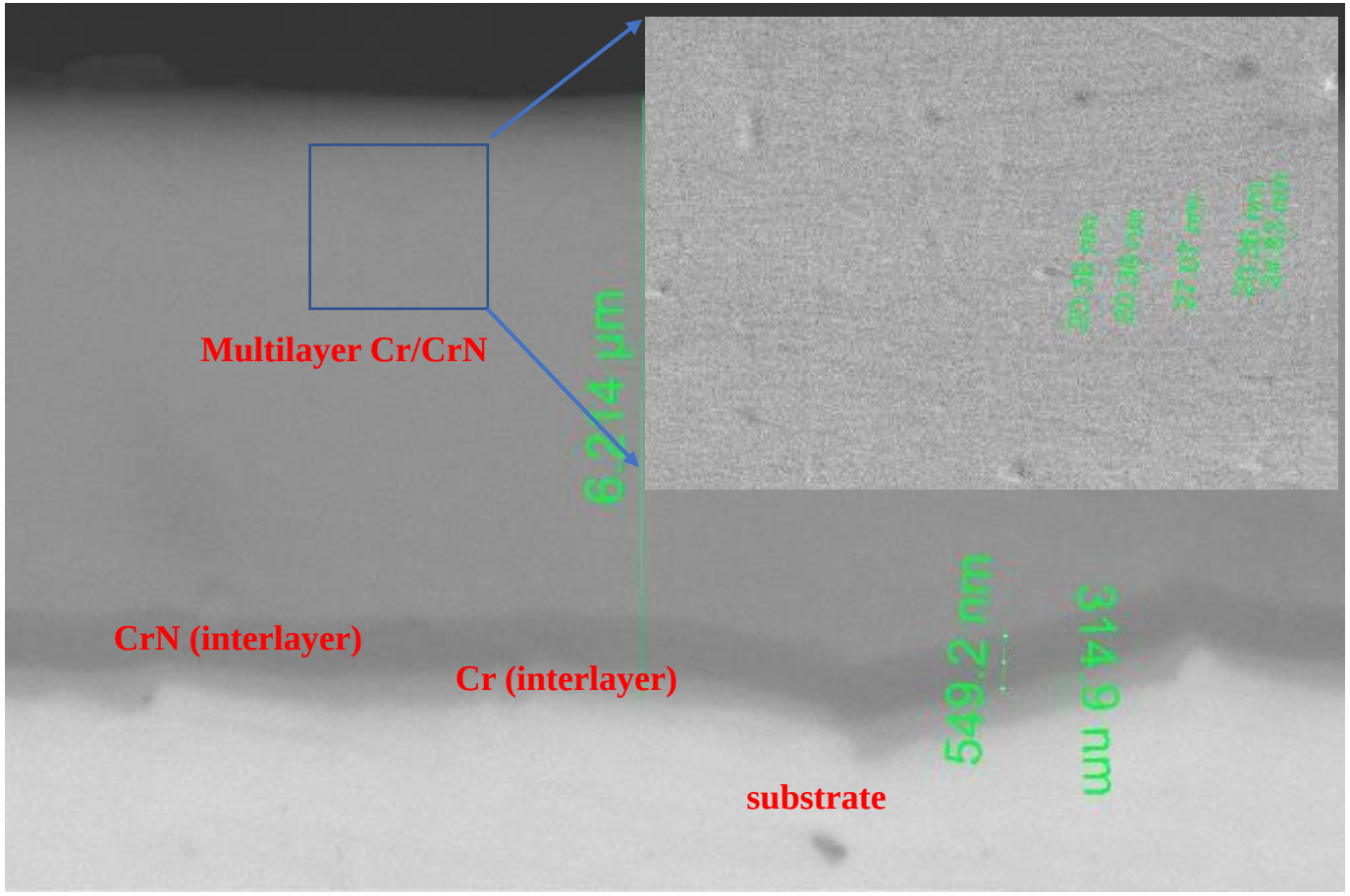
The elemental composition from different points of the CrN coating by EDS analysis

Chemical composition / Element	1	2	3	4	5
Cr	87.6	92.2	94.4	94.2	92.4
N	12.4	7.8	5.6	5.8	7.6



Characterization of the coated samples

❑ Phase characterization of the Multi-layer Cr/CrN coating

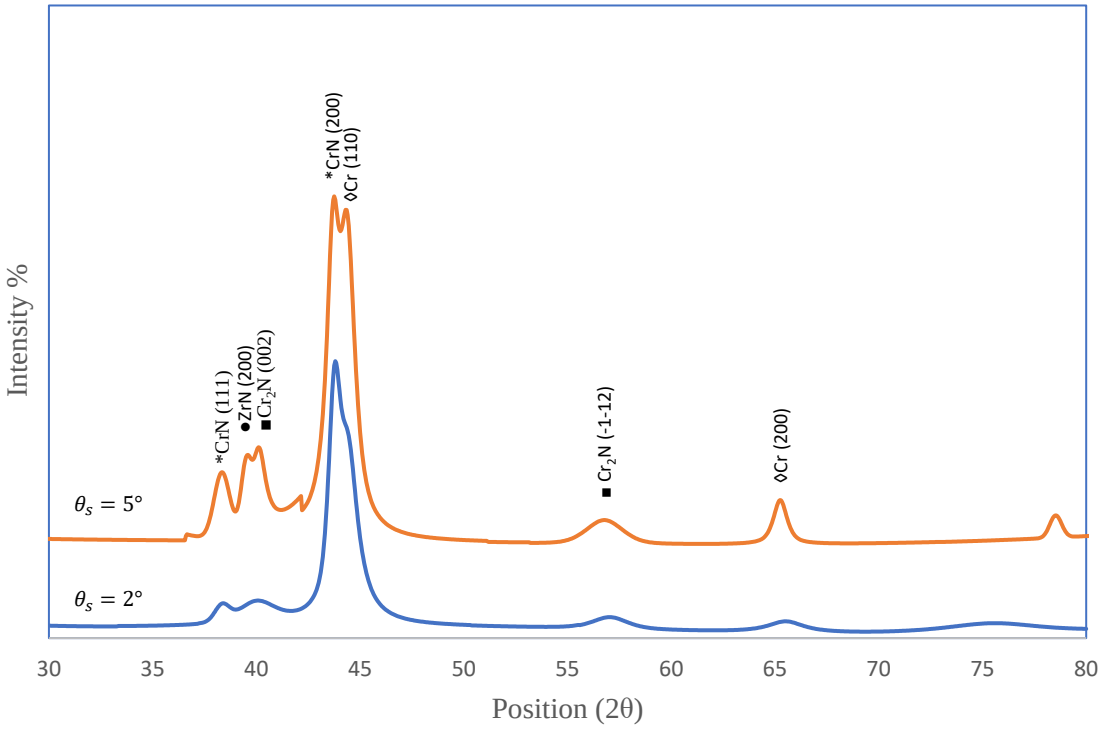


- ✓ The interface between the coating and the Zr–1Nb substrate appears uniform and smooth, with no visible defects or delamination.
- ✓ Two distinct transition layers are evident in Figure: the Cr layer adjacent to the substrate is approximately 300 nm thick, while the overlying CrN layer measures about 550 nm in thickness.
- ✓ the layer-by-layer structure of the Cr/CrN multilayer coating is clearly resolved in the high-resolution FE-SEM image, where individual layers exhibit thicknesses in the range of 20–30 nm.

✓ **Elemental composition and microstructural characterization**

Characterization of the coated samples

❑ Phase characterization of the Multi-layer Cr/CrN coating



✓ **Phase characterization via XRD analysis**

- ✓ GI-XRD (Grazing Incidence Angle XRD) configuration at two grazing angles of 2 and 5 degree was used for characterizing the phase analysis of the multilayer coating.
- ✓ Three crystalline phases are identified: Cr, CrN, and Cr_2N.
- ✓ The presence of the Cr_2N phase is likely attributed to the cut-off and connect the nitrogen gas flow during the coating process.
- ✓ The deposition technique and process stability significantly influence phase composition.

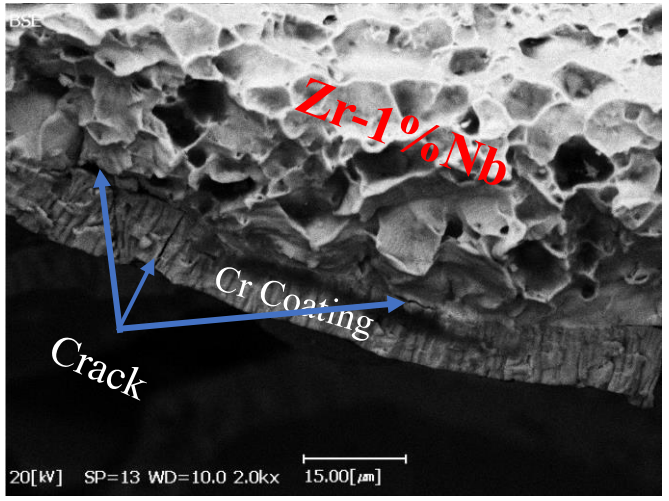
Characterization of the coated samples

❑ Mechanical Properties of the Cr and CrN coatings

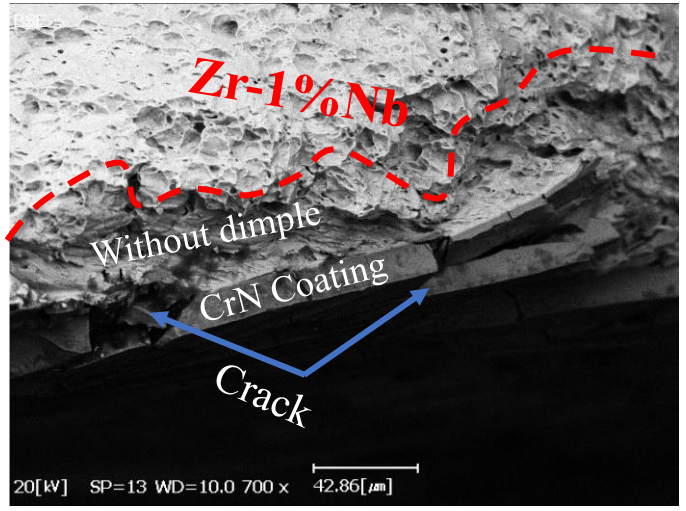
The Mechanical properties of the coated and uncoated Zr-1%Nb at room temperature.

Sample	Yield Stress, (MPa)	Ultimate Tensile Strength, (MPa)	Elongation (%)	Young's Modulus (GPa)
Reference (Uncoated Zr-1%Nb)	280	423	50	82
Cr-coated (Zr-1%Nb)	266	430	43	86
CrN-coated (Zr-1%Nb)	269	430	35	84

- ✓ There is no significant deference between Ys, UTS, and YM;
- ✓ After coating, the elongation is decreased (It is probably owing to the incoherency of the deformation behavior for the CrN coated sample).
- ✓ There are the non-dimple regions in the near of the CrN coating and substrate interface, affecting the elongation parameter of the sample.
- ✓ For Cr coating, the non-dimple regions are less than that of the CrN coating.



Fracture surface of Cr-coated Zr-1Nb cladding tube

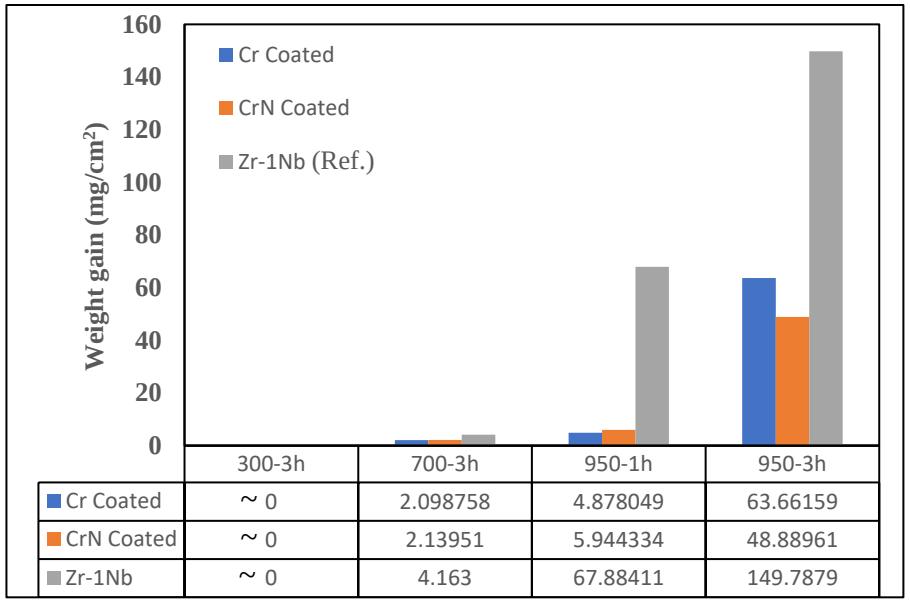


Fracture surface of CrN-coated Zr-1Nb cladding tube

Oxidation experiments on samples and corresponding results

Oxidation experiments on samples and corresponding results

- With Thermogravimetric Apparatus
  (Continual weighing of sample while heating)



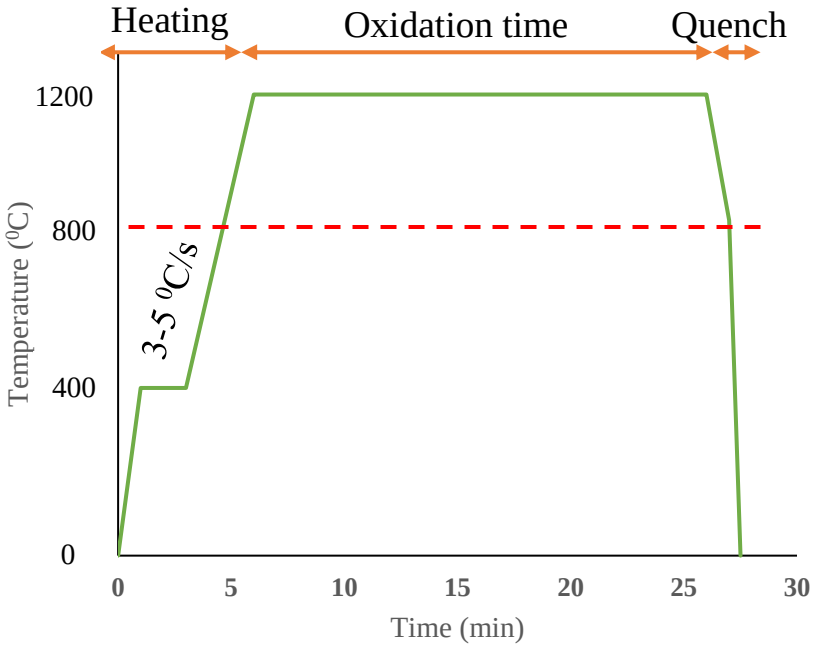
	300-3h	700-3h	950-1h	950-3h
Cr Coated	~ 0	2.098758	4.878049	63.66159
CrN Coated	~ 0	2.13951	5.944334	48.88961
Zr-1Nb	~ 0	4.163	67.88411	149.7879

- ✓ No obvious weight gain was observed for all samples in low temperatures (300 and 700 ^{0}C)
- ✓ With an increase in temperature up to 950 ^{0}C for 1 hour, the weight gain of the uncoated samples was significantly higher than that of the coated samples (about 10-15 times).
- ✓ The oxidation rate of the Cr and CrN coated samples was similar

- ✓ With further increases in time (i.e., 3 hours), the difference between the coated and uncoated samples in terms of weight gain became 2-3 times owing to the predominant oxidation of the internal surface.

H.T. Oxidation experiments on samples and corresponding results

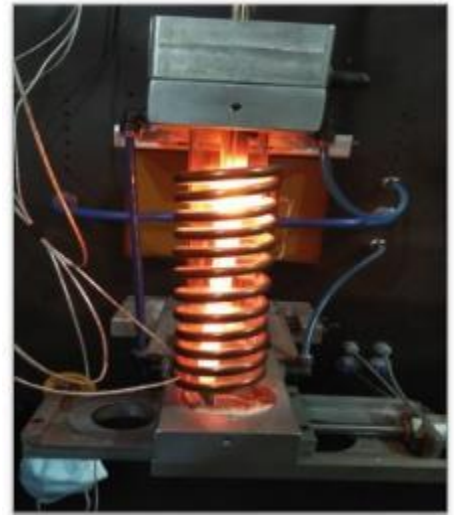
- With Induction Furnace



Test Scenario

Parameters for high-temperature oxidation tests

Sample	Condition	Heating Rate (⁰C/s)	Max. Temp. (⁰C)	Duration of oxidation (sec)	Cooldown
Multilayer Coated & Ref.	Air	5	1200	120	water
Multilayer Coated & Ref.	Air	5	1200	140	water
Multilayer Coated & Ref.	Air	5	1200	180	water
Multilayer Coated & Ref.	Air	5	1200	300	water



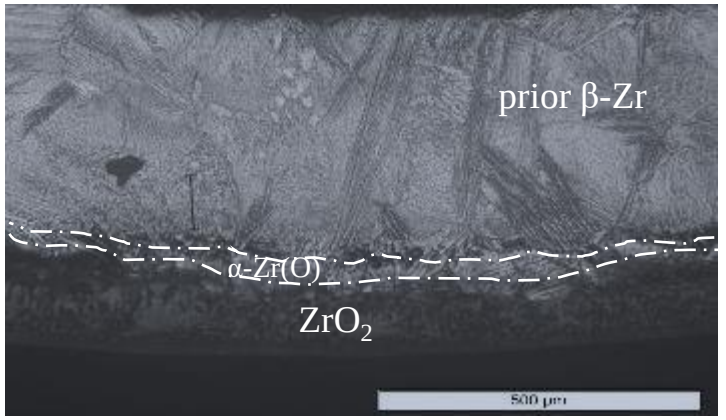
High frequency induction furnace (180 kHz)

H.T. Oxidation experiments on samples and corresponding results

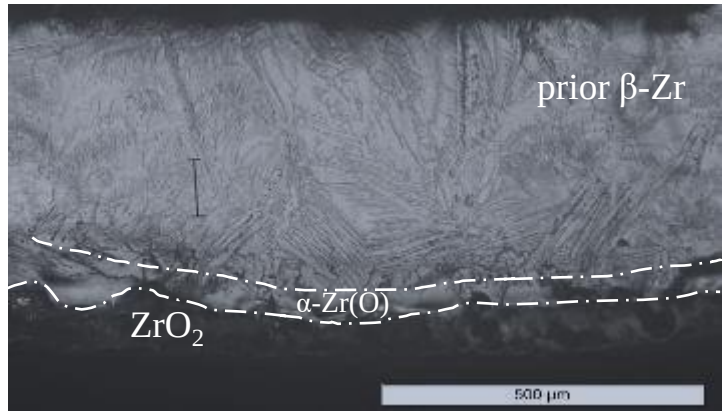
❑ The effect of time on oxidation of **<u>reference</u> (un-coated)** sample

- Both the oxide layer and the underlying α-layer thicken with increasing oxidation time
- Beneath the α-layer, a prior β-Zr phase layer remains, which retains ductility
- Likely due to the distinct surface preparation methods, the oxide layer formed on the outer surface is consistently thicker than that on the inner surface
- During the short oxidation times, the oxide scale remained intact without spallation.
- after 300 seconds of oxidation in air, microdefects were observed in the oxide layer. The formation of such microdefects can accelerate the corrosion rate by providing additional pathways for oxygen diffusion into the underlying metal.

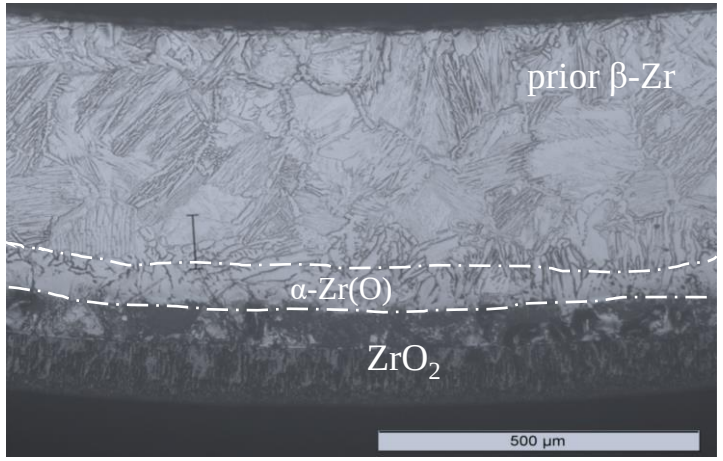
1200 ^{0}C, 120 sec, Air



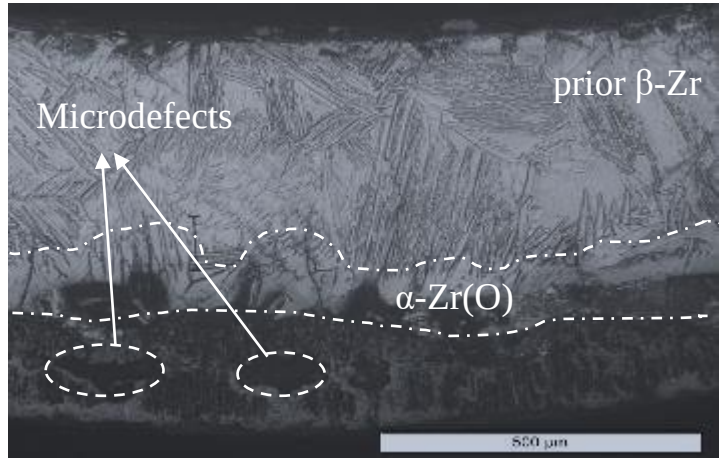
1200 ^{0}C, 140 sec, Air



1200 ^{0}C, 180 sec, Air



1200 ^{0}C, 300 sec, Air

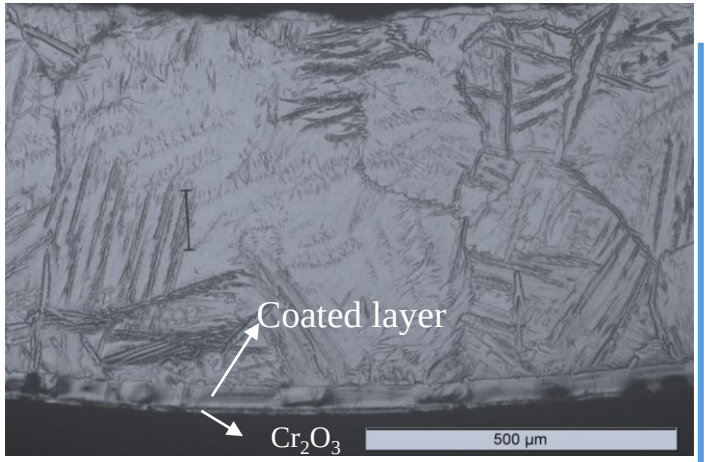


H.T. Oxidation experiments on samples and corresponding results

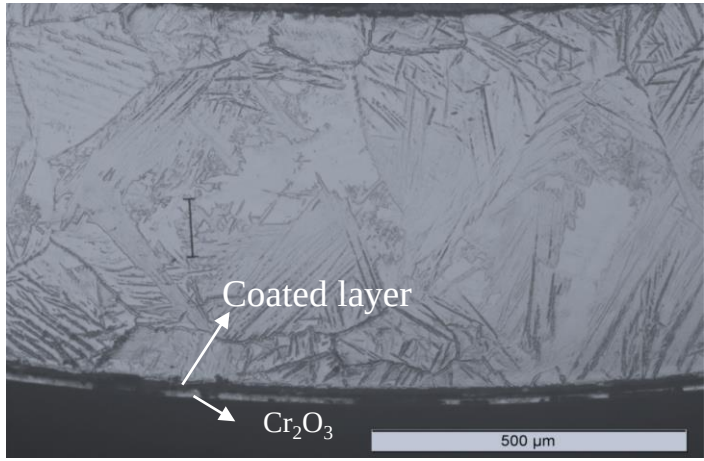
- The effect of time on oxidation of **multilayer Cr/CrN coated** samples

- The coated samples show no evidence of an oxygen-stabilized α-layer beneath the Cr/CrN multilayer coating, even after exposure to high temperatures for varying durations.
- The Cr/CrN multilayer coating effectively acts as a diffusion barrier, significantly inhibiting oxygen ingress into the Zr–1Nb substrate

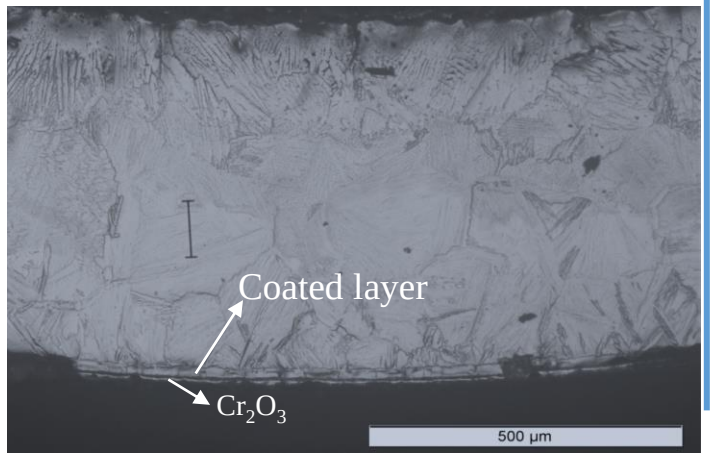
1200 ^{0}C, 120 sec, Air



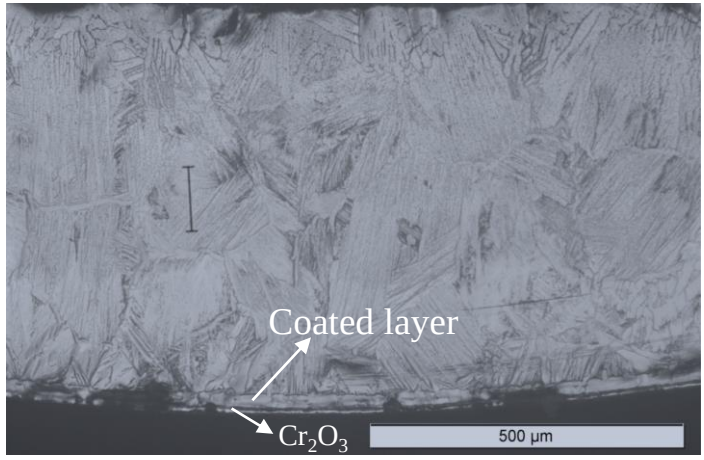
1200 ^{0}C, 140 sec, Air



1200 ^{0}C, 180 sec, Air



1200 ^{0}C, 300 sec, Air



Conclusions and Outlook

- Four groups of samples—comprising Cr-coated, CrN-coated, Cr/CrN multilayer-coated specimens, and uncoated reference tubes—were prepared and distributed to participating institutes.
- For CrN and the Cr/CrN multilayer coating a layer by layer structure is clearly observed, as each layer has the thickness of 1 µm and 20-30 nm, respectively.
- The presence of the Cr_2N phase in Cr/CrN multilayer coating is likely attributed to the cut-off and connect the nitrogen gas flow during the coating process—which can promote Cr_2N formation.
- Mechanically, the elongation of coated samples is decreased, probably due to incoherency of the deformation behavior for CrN coated sample.
- The difference between the coated and uncoated samples in terms of weight gain became lower after 3 hours of oxidation, owing to the predominant oxidation of the internal surface.
- At 1200 ^{0}C, for 300 seconds of oxidation in air, microdefects appeared in the middle part of the oxide layer accelerating the corrosion rate.
- Considering the oxidation of the inner surface of the coated samples, determining the meticulous mass gain has been difficult; so our future studies would be focused on the single-sided oxidation tests.

Thank you for your attention!