CERTIFICATION REPORT

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Certified Reference Material

BAM-L102

TiN single layer on 100Cr6 steel

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Abbreviations and symbols

as used within the report in alphabetical order:

ABS	Arc Bond Sputtering
AES	Auger Electron Spectroscopy
AFM	Atomic Force Microscopy
c	phase velocity of surface acoustic waves
cps	counts per second
CRM	Certified Reference Material
DAP	Deutsches Akkreditierungssystem Prüfwesen GmbH
DIN	Deutsches Institut für Normung e.V.
d_a	average layer thickness measured by SEM
d_{SAW}	average layer thickness measured by SAW
d_{SiO_2}	average layer thickness of the SiO_2 reference coating
d_i	layer thickness at different points
d_{CRM}	certified layer thickness
E_{IT}	indentation modulus (can be correlated to Young's modulus)
EN	Euro-Norm
ESCA	Electron Spectroscopy for Chemical Analysis
f	frequency
F_{Ar}	Argon flow rate
F_{max}	maximum test force
F_{N2}	Nitrogen flow rate
GD-OES	Glow Discharge Optical Emission Spectroscopy
GIXRD	Grazing Incidence X-Ray Diffraction
H_{IT}	indentation hardness (can be correlated to Vickers' hardness)
h_{max}	maximum indentation depth
I_{coil}	magnetic coil current
i_n	absolute intensity of reflexes
I_{nx}	relative intensity deviation of identical reflexes with respect to the average of this reflex of all samples
ISO	International Organisation for Standardisation
P	electrical power
PI_n	relative intensity deviation with respect to the average of the sums of normalised reflex intensities of all samples
PVD	Physical Vapour Deposition
R_a	roughness average
R_{max}	maximum roughness depth
R_z	mean roughness depth
SAW	Surface Acoustic Waves
sccm	standard cubic centimeter per minute
SEM	Scanning Electron Microscopy
StAA	Standard Arbeitsanweisung (standard testing procedure)
T	temperature
U_{BIAS}	BIAS voltage
UBM	Unbalanced Magnetron

$U(d_{CRM})$	expanded uncertainty of certified layer thickness (k = 2)
$u(d_a)$	standard uncertainty of average layer thickness
$u_c(d_{CRM})$	combined standard uncertainty of certified layer thickness
$u(d_{SiO_2})$	standard uncertainty of layer thickness measurements for ideal samples
$u(d_{SEM})$	standard uncertainty of layer thickness measured by SEM
$u(d_{SAW})$	standard uncertainty of layer thickness of deposition levels measured by SAW
WLI	White Light Interferometry
Δ_{corr}	correction of layer thickness measured for ideal samples by SEM

1. Scope

This report describes the certification of the layer thickness of TiN coatings that are useful for the evaluation and calibration of depth measurement and depth resolution of surface analytical methods (e.g. GD-OES, AES, ESCA) and for the evaluation and calibration of metallographic preparation methods (e.g. cross-sectioning, ball-grinding).

TiN coatings with a nominal layer thickness of 2.5 µm have been deposited on polished 100Cr6 steel substrates (discs of 30 mm in diameter and 4 mm thickness) using a PVD UBM sputtering process. To improve adhesion, a Cr inter-layer with a layer thickness of approximately 100 nm was used.

For each CRM, a value of the averaged layer thickness d_{CRM} is certified with respect to deposition levels. The certified value d_{CRM} is valid for the central surface area of a diameter of 25 mm. The determination of the certified value was performed by means of a validated and calibrated scanning electron microscope (SEM) at cross-sections of batch reference samples.

The certification procedure was conducted in a laboratory of BAM accredited according to DIN EN ISO/IEC 17025 [1] (DAP-PL-2614.08). Wherever possible, BAM reference procedures [2] have been used.

2. Design and preparation

2.1 Substrate-related features

100Cr6 steel substrates (discs of 30 mm in diameter and 4 mm thickness) have been polished to a mirror finish (R_a = 0.03 µm; R_z = 0.2 µm according to DIN EN ISO 4287/4288 [3]) using metallographic standard procedures. The substrate material contains (besides iron) the following elements (weight %), [4]: C: 0.90-1.05 %; Si: 0.15-0.25 %; Mn: 0.25-0.45 %; Cr: 1.35-1.65 %; Cu < 0.3 %; Ni < 0.3 %).

2.2 Coating-related features

TiN coatings with Cr inter-layer have been prepared by means of PVD UBM sputtering in a commercial deposition system HTC 625 Multilab ABS™ (HAUSER Techno Coating) similar to that described in detail elsewhere [5].

Sputter targets were made from solid Ti- (99.99% purity) and Cr-plates (99.95% purity). Ar

(99.999% purity) and N_2 (99.999% purity) were used as working and reactive gases.

To avoid any influence of sample clamps on the homogeneity of the coatings, the substrates were mounted on special substrate holders (Fig. 1). These holders are fixed on a planetary rotational system (Fig. 2) which can rotate around two axes. The frequency of rotation around the first axis was 10 rev/min.

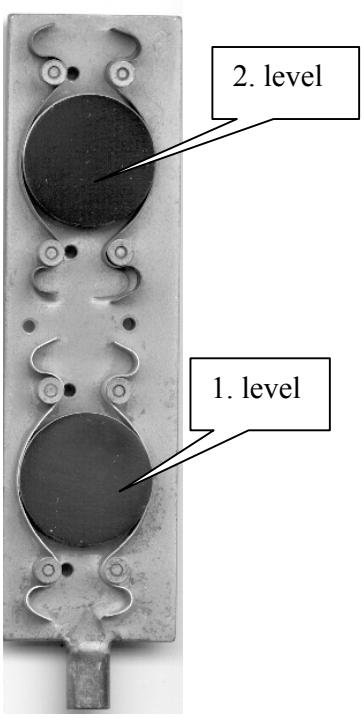


Fig. 1: Lower substrate holder with clamps and mounting levels 1 and 2

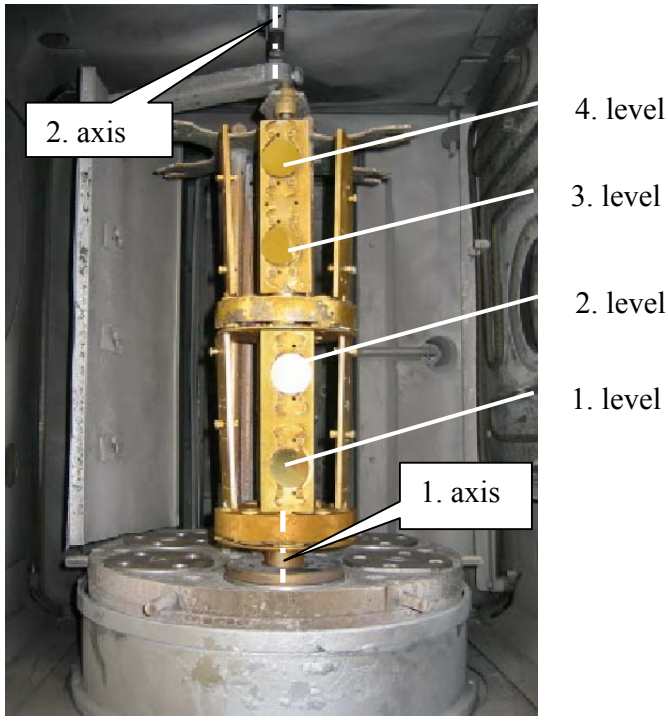


Fig. 2: Planetary rotational system with one pair of upper and lower substrate holders

By rotation around the second axis, the sample holders move automatically in fixed positions in front of the Cr-target for Cr deposition or the Ti-target for TiN deposition. Argon flow rate (F_{Ar} =150 sccm), nitrogen flow rate (F_{N2}=60 sccm), source power (P = 5 kW), bias voltage (100V), coil current (5A) and temperature (T = 380°C) were kept constant for the TiN deposition period.

In this case, and as proved for this set-up, deposition rate and corresponding layer thickness depend only on the mounting level of the substrates in the deposition chamber. Three sets of

samples (deposition batches 639, 641, 666) have been prepared, using four mounting levels for substrates (Fig. 2). An example of a complete deposition sequence is provided in the appendix.

Each set of samples includes 16 reference materials (L102/#) for non-destructive testing by SAW and GIXRD and 4 batch reference samples (BL102/#) for additional destructive testing (cross-sections) and SEM inspection. Prior to cross-sectioning, batch reference samples (BL102/#) have been additionally coated with a Cr coating using PVD UBM sputtering.

The position of all individual samples on different mounting levels is given in Table 1.

Table 1: Sample positions and mounting levels

batch 639

4. level	L102/010	L102/012	L102/014	L102/016	BL102/647
3. level	L102/009	L102/011	L102/013	L102/015	BL102/664
2. level	L102/002	L102/004	L102/006	L102/008	BL102/650
1. level	L102/001	L102/003	L102/005	L102/007	BL102/685

batch 641

4. level	L102/026	L102/028	L102/030	L102/032	BL102/678
3. level	L102/025	L102/027	L102/029	L102/031	BL102/687
2. level	L102/018	L102/020	L102/022	L102/024	BL102/655
1. level	L102/017	L102/019	L102/021	L102/023	BL102/688

batch 666

4. level	L102/042	L102/044	L102/046	L1020/48	BL102/689
3. level	L102/041	L102/043	L102/045	L102/047	BL102/696
2. level	L102/034	L102/036	L102/038	L102/040	BL102/691
1. level	L102/033	L102/035	L102/037	L102/039	BL102/693

3. Certification

3.1 Strategy of certification

The average layer thickness d_a was measured according to StAA-No. VIII.23-5 [6] and StAA-No. VIII.23-PM [7] at cross-sections using a calibrated SEM. The certification strategy was as follows:

1. All reference materials and batch reference samples have been tested non-destructively by means of surface acoustic waves (SAW). So, a fingerprint of layer thickness, Young's modulus, Poisson's ratio and density was taken. SAW data are sensitively correlated to the mounting level of samples in the deposition chamber.
2. For batch reference samples, destructive testing has been performed additionally. Preparation method (cross-sectioning) and measurement method (SEM) have been validated using reference SiO_2 coatings on Silicon. Prior to destructive testing, the layer thickness of SiO_2 coatings has been determined non-destructively and independently by spectroscopic ellipsometry (SE), BAM reference procedure [2], according to StAA-Nr. VIII.2901-V.2.01 [8]. Further details are given in sec. 3.2 and in the certification report BAM-L101.
3. The average layer thickness d_a of TiN was calculated from measurements at 5 points along the cross-section of the batch reference samples using validated and calibrated preparation and measurement methods described before.
4. The average layer thickness d_a determined for the batch reference samples of each mounting level was identified as the certified value of layer thickness d_{CRM} for samples of identical mounting levels.

3.2 Validation of the certification method

The preparation method (cross-sectioning) and the measurement method (SEM) have been additionally validated and re-calibrated using SiO_2 reference coatings on Silicon. An example of a cross-section of a SiO_2 reference coating on Si, coated with a TiN hard top coating, is shown in Fig. 3.

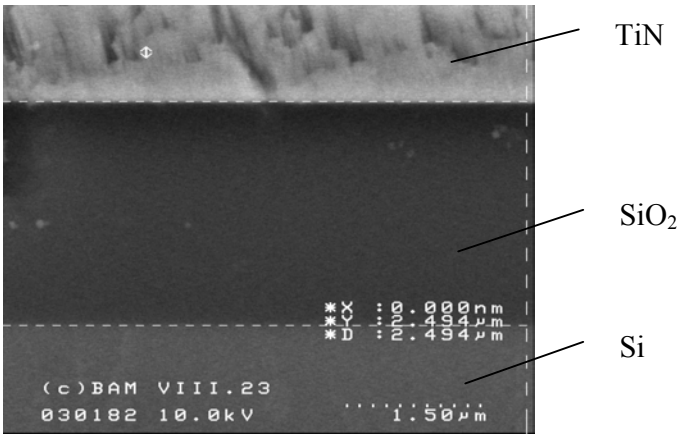


Fig.3: Cross-section of a SiO_2 reference coating on Si with TiN hard top coating

Table 2 provides 12 measurements of the layer thickness of SiO_2 at different points along the cross-section. The evaluation length was 5 µm for each measurement.

Table 2: Thickness of cross-sections of SiO_2 reference coatings (coated with TiN) on Si

measurement - ID	d/µm
30170	2.57
30172	2.45
30173	2.47
30174	2.45
30175	2.47
30177	2.47
30178	2.46
30179	2.46
30180	2.44
30181	2.54
30182	2.49
30183	2.48
average value	2.48
standard uncertainty $u(d_{SiO_2})$	0.05

The average layer thickness d_{SiO_2} of SiO_2 reference coating was derived to

$$d_{SEM,SiO_2} = (2.48 \pm 0.05)\ \mu\text{m}. \qquad (1)$$

For the validation of the preparation method (cross-sectioning) and the certification method (SEM), this result was compared with the layer thickness of SiO_2 derived from SE using the BAM reference procedure [2] spectroscopic ellipsometry according to StAA-No. VIII.2901-V.2.01 [8]. From the analysis of ellipsometric data, the average layer thickness of the SiO_2 reference coating was derived to

$$d_{SE,SiO_2} = (2.51 \pm 0.01)\ \mu\text{m}. \qquad (2)$$

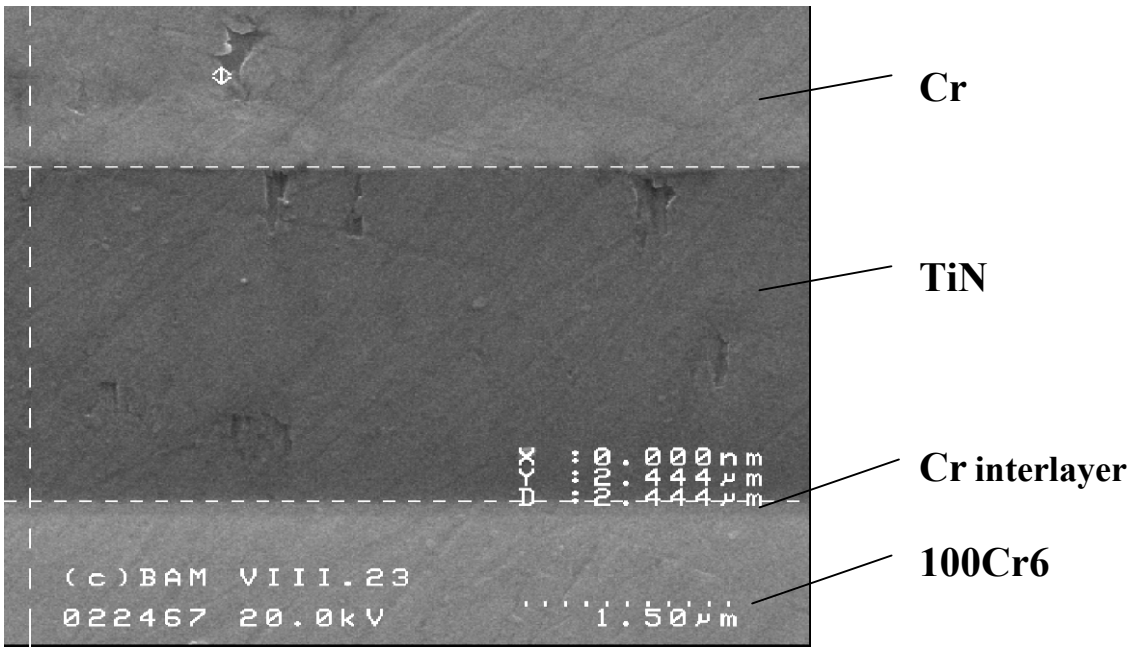
For the calculation of the certified layer thickness of TiN, the difference $(d_{SEM,SiO_2} - d_{SE,SiO_2})$ was taken as a constant correction ($\Delta_{corr} = 0.03$ µm) for the TiN layer thickness measured by SEM .

3.3 Certification measurements

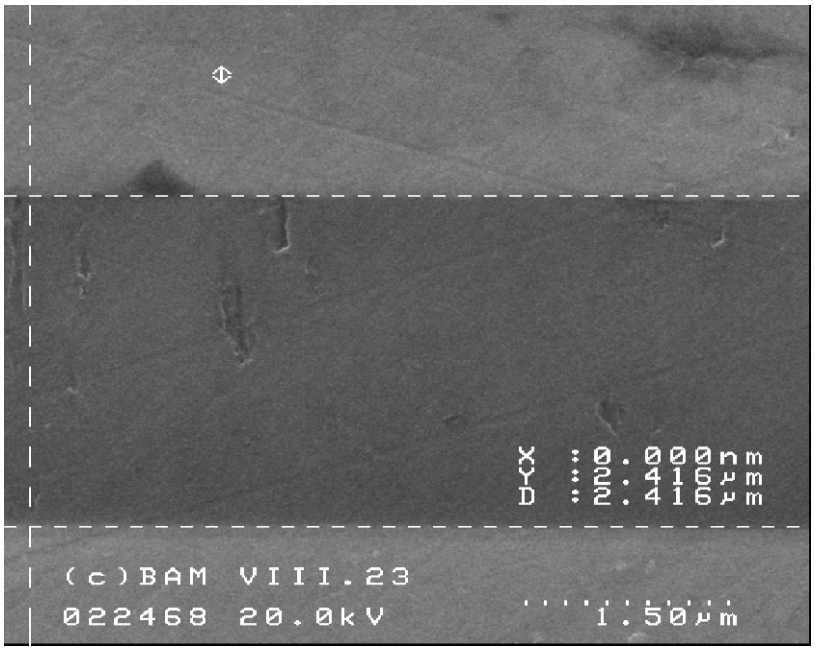
3.3.1 Average layer thickness of batch reference samples

As a result of the standard calibration procedure of the SEM, it was shown that the uncertainty of the length measurements $u(d_{SEM})$ is 10 nm for ideal samples. As an example, for the measurement of layer thickness by SEM, a cross-section of a TiN batch reference sample (coated with a Cr top coating) is shown in Figs. 4 a-b. The average layer thickness d_a and the standard uncertainty $u(d_a)$ were calculated from measurements at 5 different points (d_{1-5}) along the cross-section.

Fig.4: Measurement of the layer thickness of a TiN batch reference sample (coated with a Cr top coating)



a) 1. measurement of layer thickness BL102/693: d_1 = 2.44 µm



b) 2. measurement of layer thickness BL102/693: d_2 = 2.42 µm

3.3.2 Evaluation of batch homogeneity

Batch homogeneity has been evaluated non-destructively for each reference material by means of surface acoustic waves (SAW).

For coated materials, the phase velocity of surface acoustic waves depends on the elastic parameters and the density of both the coating and substrate material and the layer thickness [9]. Since the penetration depth of the surface acoustic wave decreases with increasing frequency, the higher frequency range is primarily influenced by the coating whereas the lower frequency range is dominated by the substrate. This results in a dispersion of phase velocity c(f) of the surface acoustic wave. A laser-acoustic technique measures the dispersion of phase velocity as a function of frequency (experimental dispersion curve). By means of a parameterised model (theoretical dispersion curve), the modulus of the coating is derived by fitting the theoretical on the experimental dispersion curve.

Fig. 5 shows the dispersion curves for batch reference samples BL102/689, BL102/693, and BL102/691 (batch 666) with a layer thicknesses of 2.14 µm, 2.45 µm and 2.88 µm. They look similar but their ascend is getting steeper for higher layer thickness. In addition, a comparison is made with the dispersion curve for bare 100Cr6 steel. In case of the uncoated substrate, the phase velocity of the surface acoustic is nearly constant within the bandwidth of 20 MHz to 60 MHz.

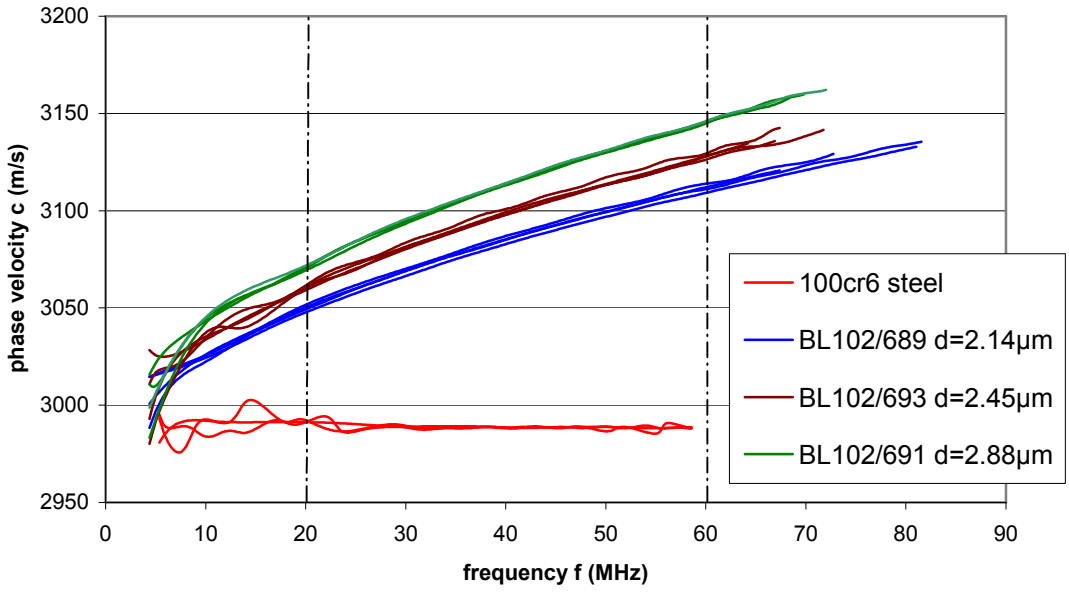


Fig.5: Dispersion curves of TiN coatings (batch 666) and bare 100Cr6 steel

Young's modulus E_{SAW} and the average layer thickness d_{SAW} of the TiN coating, deduced by fitting the theoretical dispersion curve [9] on the experimental one within the bandwidth of 20 MHz to 60 MHz, are given in Table 3.

Table 3: Evaluation of the reproducibility of overall coating quality

batch / level	d_a / µm	E_{SAW}/ GPa	average value of d_{SAW} / µm	$u(d_{SAW})$ / µm
batch 639				
4	2.44	471	2.44	0.093
3	3.12	505	3.11	0.021
2	3.14	517	3.14	0.017
1	2.53	520	2.50	0.092
batch 641				
4	2.37	457	2.36	0.046
3	3.10	490	3.09	0.033
2	3.24	474	3.23	0.014
1	2.68	469	2.68	0.108
batch 666				
4	2.14	458	2.14	0.048
3	2.74	504	2.71	0.022
2	2.88	496	2.87	0.036
1	2.45	486	2.45	0.076

The model parameters for the fit are summarised in Table 4.

Table 4: SAW model parameters

	Young's modulus/ GPa	Poisson's ratio	density g/cm³
TiN coating		0.210	5.40
100Cr6 steel	210	0.293	7.80
Cr coating	270	0.210	7.19

The layer thickness d_{SAW} for each sample is given in Fig. 6 in dependence on the mounting level and compared to SEM measurements.

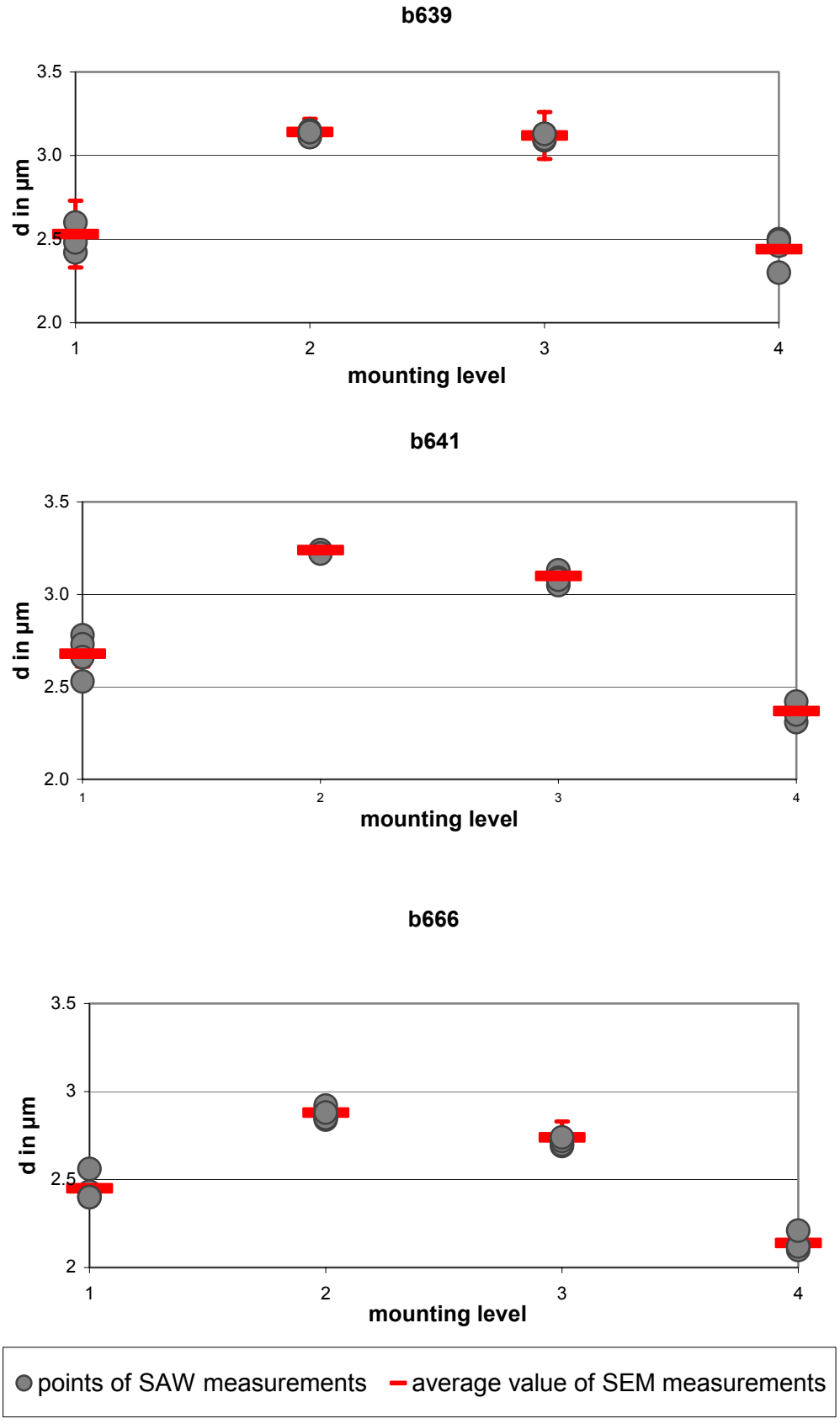


Fig. 6: Layer thickness for TiN coatings in dependence on the mounting level

3.4 Summary of certification results

1. The standard calibration procedure of the SEM Hitachi S4100 (BAM StAA-No. VIII.23-PM1) results in an uncertainty of length measurements of $u(d_{SEM}) = 10$ nm.
2. The additional evaluation of the certification method SEM by means of SE as a standard-free reference method results in a constant correction $\Delta_{corr} = +30$ nm.
3. From cross-sections of the batch reference samples, the average layer thickness d_a and the standard uncertainty $u(d_a)$ have been derived by SEM.
4. The average layer thickness d_a with the standard uncertainty $u(d_a)$ of batch reference samples has been identified as the certified layer thickness for reference samples of the same mounting level.
5. Consequently, the certified value for the layer thickness can be written as follows:

$$d_{CRM} = d_a + \Delta_{corr} \qquad (3)$$

$$u_c(d_{CRM}) = \sqrt{[u(d_a)]^2 + [u(d_{SiO_2})]^2 + [u(d_{SEM})]^2 + [u(d_{SAW})]^2} \qquad (4)$$

$$U(d_{CRM}) = k * u_c(d_{CRM}), \qquad (k = 2) \qquad (5)$$

All certification results are summarised in Table 5.

Table 5: Certification results

sample ID	batch	level	d_{CRM} / µm	$U(d_{CRM})$ / µm, k=2
L102/001	639	1	2.53	0.45
L102/002	639	2	3.14	0.19
L102/003	639	1	2.53	0.45
L102/004	639	2	3.14	0.19
L102/005	639	1	2.53	0.45
L102/006	639	2	3.14	0.19
L102/007	639	1	2.53	0.45
L102/008	639	2	3.14	0.19
L102/009	639	3	3.11	0.30
L102/010	639	4	2.44	0.22
L102/011	639	3	3.11	0.30
L102/012	639	4	2.44	0.22
L102/013	639	3	3.11	0.30
L102/014	639	4	2.44	0.22

L102/015	639	3	3.11	0.30
L102/016	639	4	2.44	0.22
L102/017	641	1	2.68	0.28
L102/018	641	2	3.24	0.12
L102/019	641	1	2.68	0.28
L102/020	641	2	3.24	0.12
L102/021	641	1	2.68	0.28
L102/022	641	2	3.24	0.12
L102/023	641	1	2.68	0.28
L102/024	641	2	3.24	0.12
L102/025	641	3	3.10	0.13
L102/026	641	4	2.37	0.14
L102/027	641	3	3.10	0.13
L102/028	641	4	2.37	0.14
L102/029	641	3	3.10	0.13
L102/030	641	4	2.37	0.14
L102/031	641	3	3.10	0.13
L102/032	641	4	2.37	0.14
L102/033	666	1	2.45	0.19
L102/034	666	2	2.88	0.13
L102/035	666	1	2.45	0.19
L102/036	666	2	2.88	0.13
L102/037	666	1	2.45	0.19
L102/038	666	2	2.88	0.13
L102/039	666	1	2.45	0.19
L102/040	666	2	2.88	0.13
L102/041	666	3	2.74	0.21
L102/042	666	4	2.14	0.19
L102/043	666	3	2.74	0.21
L102/044	666	4	2.14	0.19
L102/045	666	3	2.74	0.21
L102/046	666	4	2.14	0.19
L102/047	666	3	2.74	0.21
L102/048	666	4	2.14	0.19

4. Stability testing

The stability of the reference material has been evaluated by repeated SAW measurements after 500 days. Samples have been stored under ordinary laboratory conditions. One example of these measurements is shown in Fig. 7.

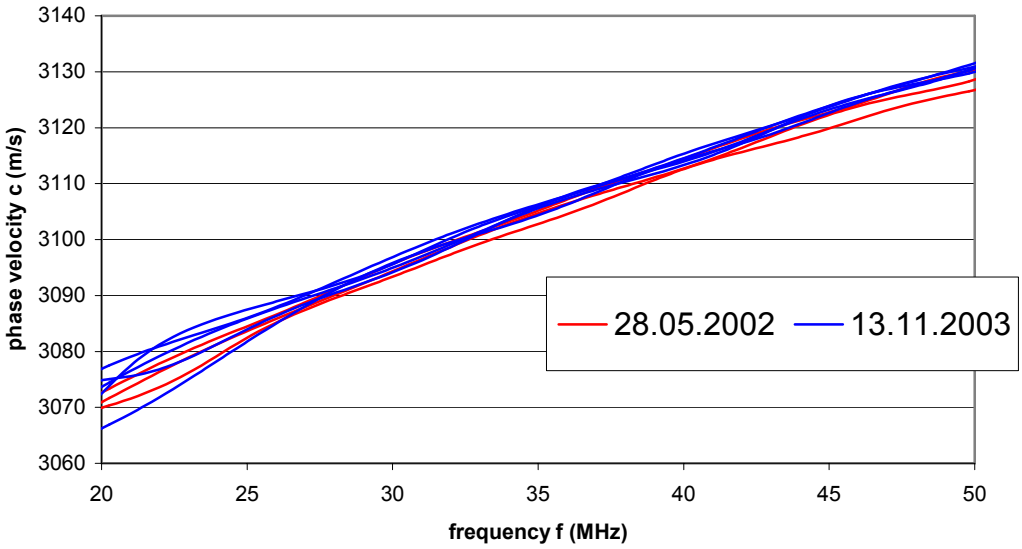


Fig.7: Repeated SAW measurements of samples L102/047 after 500 days of storage

From the agreement of both measurements, i. e. no significant difference in the derived SAW ratios, it was concluded that the samples are stable under ordinary laboratory conditions.

5. Instruction for use

For each CRM, a value of the TiN layer thickness, valid for the central surface area of a diameter of 25 mm, was certified. In case of use, it is a prerequisite to avoid any mechanical (such as scratching) or chemical treatment (such as aggressive agents) of the surface. Storage under ordinary laboratory conditions results in an unavoidable native oxide film of some nanometer film thickness.

6. Additional information

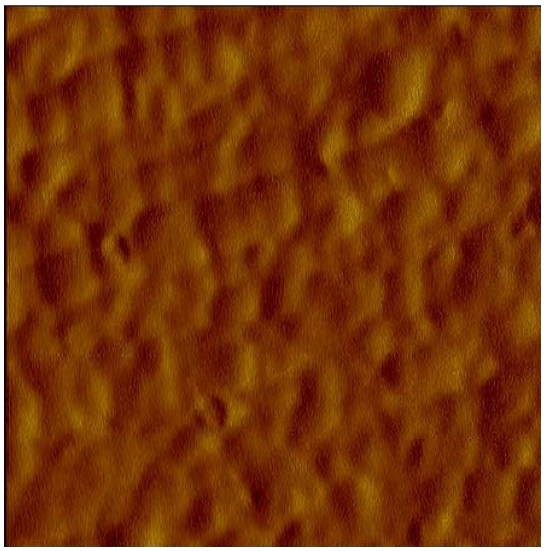
6.1 Topography and roughness

The TiN coatings have a columnar but relatively dense structure with minor defects and droplets.

The evaluation of roughness according to DIN EN ISO 4288 [3] with a mechanical

profilometer has shown that there is no measurable difference in surface roughness between the coated and uncoated samples (R_a = 0.03 µm; R_z = 0.2 µm).

Moreover, the topography of the CRM was investigated by AFM for the characterisation of smaller surface areas (evaluation area was (5 x 5) µm^2). An example is given in Fig. 8.



R_a = 8.0 nm

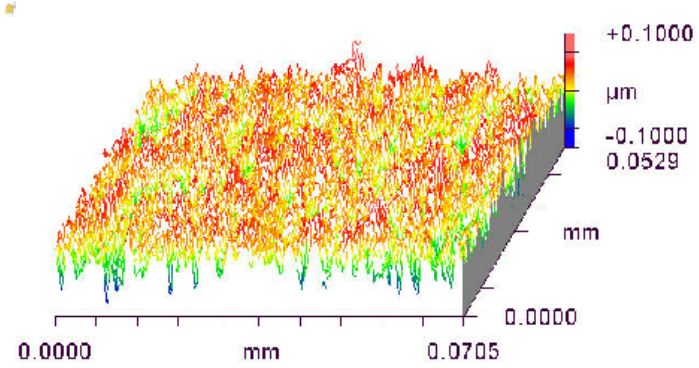
R_{max} = 60.5 nm

R_z = 50.7 nm

area : (5 x 5) µm²

Fig. 8: AFM-topography (BAM-L102/041)

In addition, WLI (evaluation area was (70 x 50) µm^2) has been used for the characterisation of larger surface areas. An example is shown in Fig. 9. Table 6 summarises the results of WLI measurements.



R_a= 0.02 µm

R_{max} = 0.47 µm

R_z = 0.24 µm

area : (70 x 70) µm²

Fig. 9: WLI-topography (BAM-L102/041)

Table 6: Summary of the WLI – measurements

no.	sample ID	batch / level	R_z / µm
1	L102/002	639/2	0.44
2	L102/003	639/1	0.56
3	L102/009	639/3	0.22
4	L102/010	639/4	0.33
5	L102/025	641/2	0.39
6	L102/041	666/3	0.24
		average value	**0.36**
		standard deviation	**0.13**

6.2 Mechanical properties

Mechanical properties (H_{IT}, E_{IT}) of BAM- L102/030 were determined by instrumented indentation tests (F_{max} = 10 mN, h_{max} = 130 nm, 100 indentations averaged over an area of (20 x 20) mm^2) according to DIN EN ISO 14577 [10] and StAA VIII.2901-V.1.11 [11] as follows:

H_{IT} = (33.3 ± 5.7) GPa

E_{IT} = (497.3 ± 75.6) GPa

6.3 Microstructure

Microstructure and texture of TiN coating have been evaluated for each reference material and all batch reference samples by means of grazing incidence X-ray diffraction (GIXRD). A typical GIXRD diagram is shown in Fig.10.

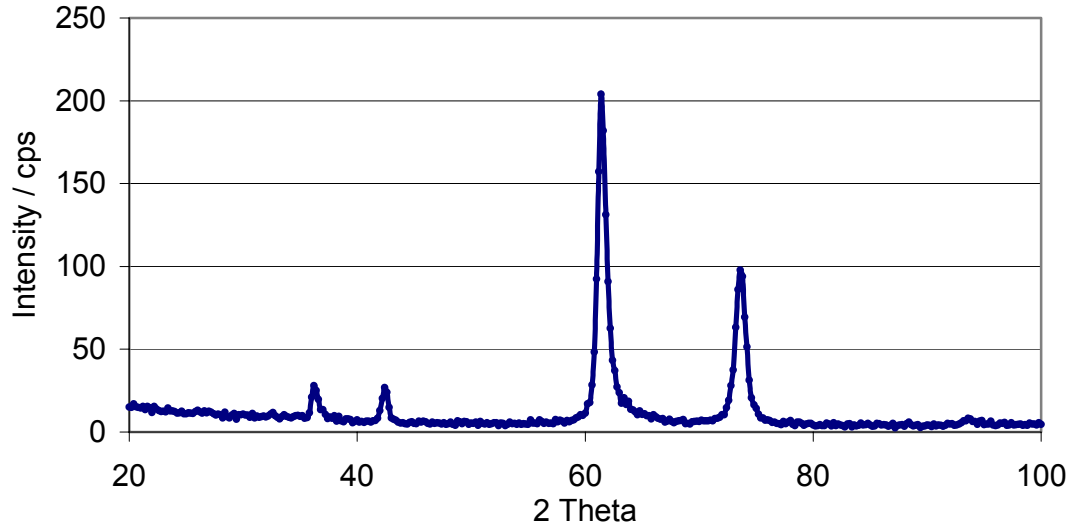


Fig. 10: GIXRD-diagram of sample L102/008

As described in more detail earlier [12], normalised intensity ratios were calculated for evaluation of the reproducibility of overall coating quality (Table 7).

Table 7: GIXRD-intensity ratios (batch 666)

level	sample ID	PI_n TiN	i_n TiN (111) (36.2°)	i_n TiN (200) (42.3°)	i_n TiN (220) (61.4°)	i_n TiN (311) (73.5°)
1	L 102/33	0.89	39.7	12.6	45.5	35.1
2	L 102/34	0.76	20	9.8	35.3	34.8
3	L 102/41	0.77	24.6	9.0	34.6	38.2
4	L 102/42	1.42	131.5	27.2	83.8	32.7
1	L 102/35	0.83	35.1	11.4	42.2	34.3
2	L 102/36	0.75	21.5	8.8	38.5	34.0
3	L 102/43	0.81	24	11.0	39.2	35.3
4	L 102/44	1.47	151.3	26.7	92.3	33.5
1	L 102/37	1.07	59.4	16.6	61.7	34.7
2	L 102/38	0.83	23	10.8	40	37.1
3	L 102/45	0.86	26.1	11.4	41.4	37.6
4	L 102/46	1.65	195.6	32.2	97.2	36.8
1	L 102/39	0.98	53.6	13.8	53.6	37.5

2	L 102/40	0.80	17.8	9.7	38.2	37.9
3	L 102/47	0.88	26	11.6	43.4	38.5
4	L 102/48	1.22	99.3	18.8	77	35.0
1	L 102/33	0.89	39.7	12.6	45.5	35.1
2	L 102/34	0.76	20	9.8	35.3	34.8
3	L 102/41	0.77	24.6	9.0	34.6	38.2
4	L 102/42	1.42	131.5	27.2	83.8	32.7

A Seifert X-ray diffractometer XRD 3000 TT was used for GIXRD measurements. Each sample was analysed at an angle of incidence of 2° to the surface with sample rotation. The evaluation area was 1.5 cm². From the absolute intensity of reflexes (i_n in cps), the relative intensity deviation I_{nx} of identical reflexes was calculated with respect to the average of this reflex of all samples (equation 6), and the relative intensity deviation PI_n was calculated with respect to the average of the sums of normalised reflex intensities of all samples (equation 7). The data for each sample of batch 666 are given in Table 8.

$$I_{nx} = \frac{i_{nx} n}{\sum_{n} i_{nx}} \qquad (6)$$

$$PI_n = \frac{\sum_{x} I_{nx} n}{\sum_{n}\sum_{x} I_{nx}} \qquad (7)$$

The relative intensity deviations PI_n for each sample are shown in Fig. 11 in dependence on the mounting level for batch 666.

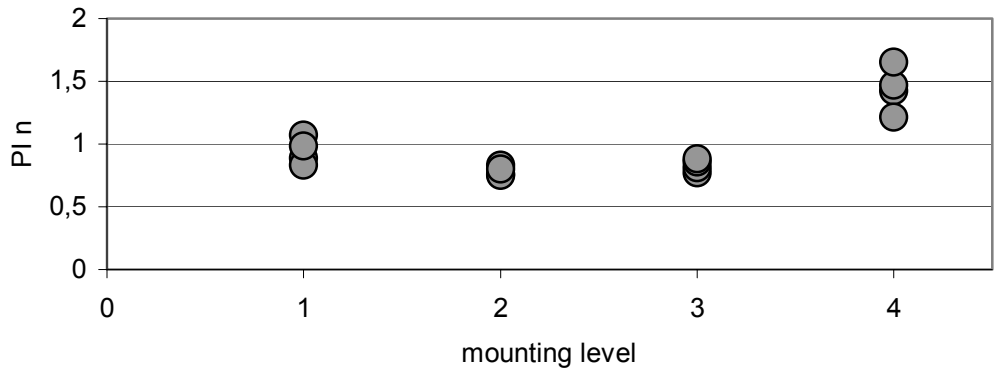


Fig. 11: Relative intensity deviations PI_n in dependence on the mounting level (batch 666)

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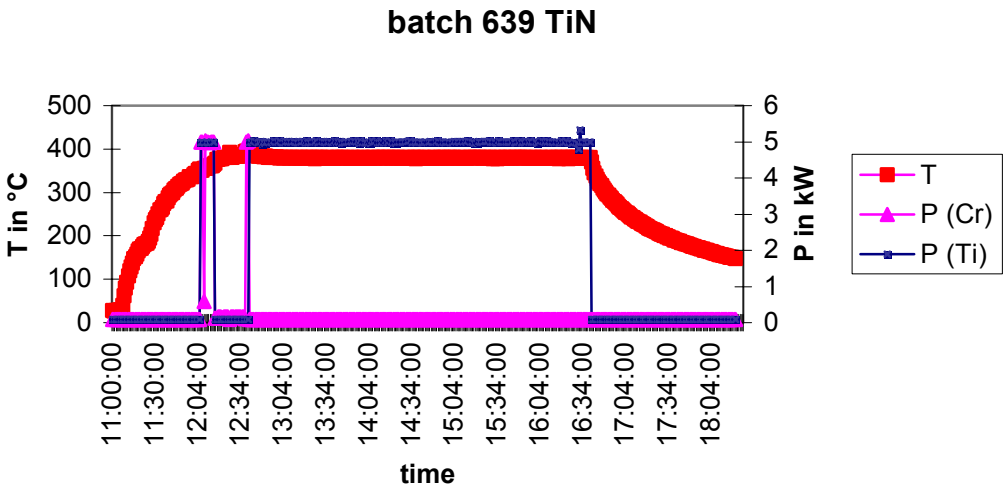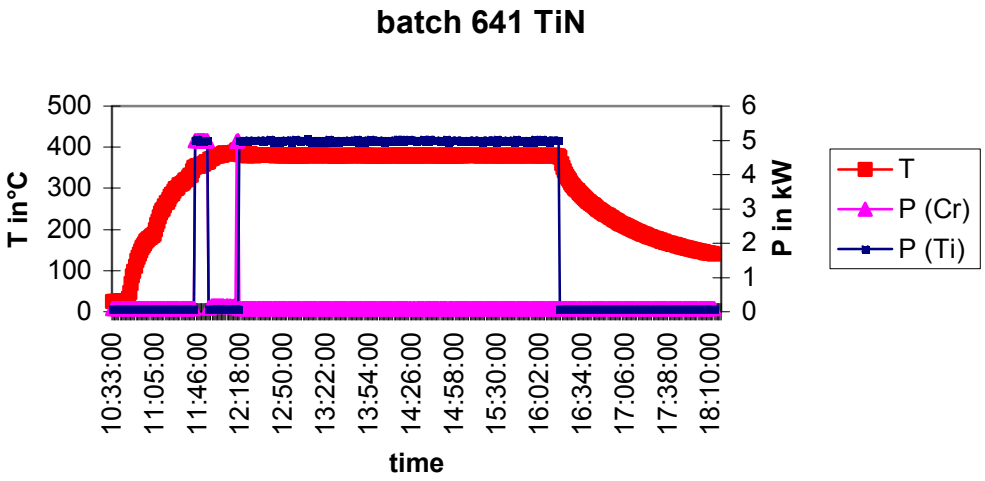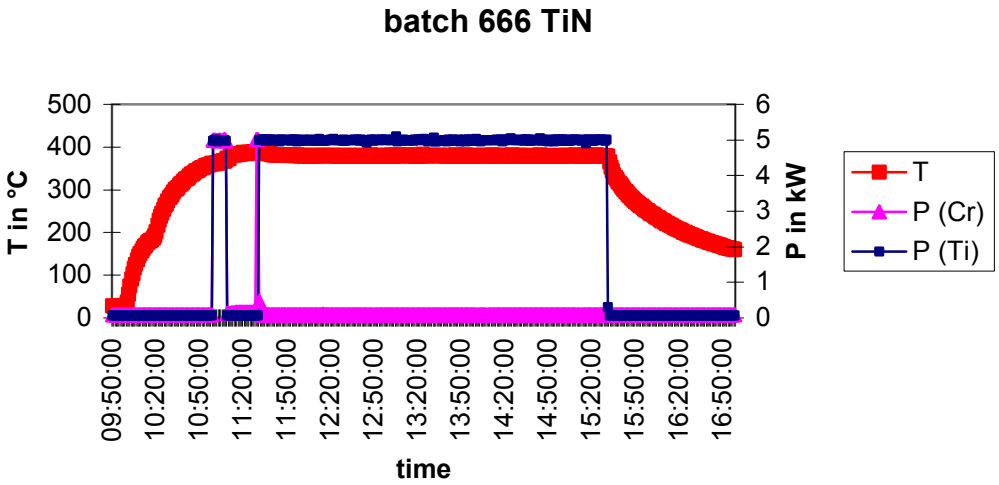
Appendix: Information on preparation