

Bundesanstalt für Materialforschung und -prüfung (BAM)

in cooperation with the Chemists' Committee of the GDMB
Gesellschaft der Metallurgen und Bergleute e.V.

Certified Reference Material

BAM-S012

Titanium Diboride Powder

Certified Values

Parameter	Mass fraction ¹⁾ in %	Uncertainty ²⁾ in %
Ti	68.3	0.8
B	30.71	0.15
B ₂ O ₃ ³⁾	0.359	0.024
	in mg/kg	in mg/kg
Al	12.0	1.3
Ca	44	4
Cr	97	4
Fe	640	40
Mg	1.6	0.4
Mn	3.8	0.4
Mo	11.7	0.7
Ni	23.5	1.1
V	10.2	0.8
Zr	121	4

¹⁾ Unweighted mean value of the means of accepted sets of data (consisting of at least 5 but usually 6 single results), each set being obtained by a different laboratory and/or a different method of measurement.

²⁾ Estimated expanded uncertainty U with a coverage factor of $k = 2$, corresponding to a level of confidence of approximately 95 %, as defined in the Guide to the expression of uncertainty in measurement, (GUM, ISO/IEC Guide 98-3:2008).

³⁾ The conventional "Method M1" described in the attachment can be used for the determination of total mass fraction of boron oxide.

Informative Values

Parameter	Mass fraction ¹⁾ in %	Uncertainty ²⁾ in mg/kg
C	0.169	0.008
N	0.120	0.007
O	0.480	0.08
R _{acid} ³⁾	0.22	0.03
	in mg/kg	in mg/kg
Si	11	5
Na	< 10	
Nb ⁴⁾	1700	
S ⁴⁾	2	
W ⁴⁾	114	

¹⁾ Values were not certified, but given for information, when the number of accepted data sets was too low (< 5) or when the uncertainty from the inter-laboratory certification was considerably larger than the expected range.

²⁾ Estimated expanded uncertainty U with a coverage factor of $k = 2$, corresponding to a level of confidence of approximately 95 %, as defined in the Guide to the expression of uncertainty in measurement, (GUM, ISO/IEC Guide 98-3:2008).

³⁾ R_{acid}: acid insoluble residue. The conventional "Method M2" described in the attachment shall be used.

⁴⁾ Mean value of the dataset from one laboratory.

End of Validity

This certificate is valid until May 2034.

Sample Description

The reference material BAM-S012 consists of a titanium diboride powder. The material is supplied in glass bottles containing 50 g each. Additionally, the remaining volume of the bottle is filled with argon.

Particle size distribution determined by laser light diffraction method:

D ₉₇	33.8 μm
D ₅₀	12.3 μm
D ₀₆	2.3 μm

Recommended Use

The reference material is intended to be used for the calibration of analytical instruments and for the validation or verification of analytical methods suitable for the analysis of titanium diboride materials.

Means of Accepted Data Sets

Certified Values

Line No.	Mass fraction in %			Mass fraction in mg/kg									
	Ti	B	B ₂ O ₃	Al	Ca	Cr	Fe	Mg	Mn	Mo	Ni	V	Zr
1	67.87	30.48	0.324	< 10	35.4	88.9	---	0.95	---	9.9	---	8.7	---
2	67.93	30.61	0.356	10.3	35.9	89.1	559	1.05	3.25	< 10	21.5	9.4	105
3	68.02	30.65	0.356	10.9	39.2	92.0	564	1.27	3.37	10.4	22.1	9.7	115
4	68.20	30.71	0.366	11.4	40.0	92.6	597	1.56	3.43	11.0	22.2	< 10	121
5	68.27	30.76	0.393	11.9	41.5	95.6	601	1.75	3.44	11.3	22.2	10.0	120
6	68.53	30.78		12.5	43.0	96.2	627	1.87	3.61	11.6	23.3	10.1	121
7	68.55	30.97		13.4	43.6	97.4	643	2.00	3.77	11.6	23.6	10.3	121
8	68.86	---		13.5	44.2	97.8	646	2.24	3.78	11.8	23.7	10.4	122
9				---	45.6	98.2	652	< 6	3.79	12.0	23.8	11.0	123
10				< 30	48.2	98.8	657	< 10	4.33	12.1	23.8	12.2	125
11					49.9	100.1	667		4.47	12.1	23.8	---	125
12					52.7	101.5	662		4.62	12.3	24.1		126
13					54.0	101.5	680		< 10	12.8	24.6		126
14						107.7	690			12.9	27.0		131
15						---	764						---
<i>M</i>	68.28	30.71	0.359	12.0	44.1	97.0	643	1.59	3.81	11.7	23.5	10.2	121
<i>s_M</i>	0.35	0.15	0.025	1.2	5.9	5.1	53	0.46	0.47	0.9	1.4	1.0	6

Informative Values

Line No.	Mass fraction in %				Mass fraction in mg/kg				
	C	N	O	R _{acid}	Si	Na	Nb	S	W
1	---	0.107	---	0.200	3.5	0.17	1700	2	114
2	---	0.115	---	0.202	6.3	0.42			
3	0.147	0.115	0.436	0.202	9.7	< 1			
4	0.164	0.116	0.438	0.257	< 10	2.65			
5	0.168	0.120	0.475		10.9	< 5			
6	0.171	0.123	0.482		16.2	< 6			
7	0.172	0.127	0.499		18.3	< 10			
8	0.174	0.128	0.500		< 50				
9	0.175	0.133	0.503						
10	0.180		0.508						
<i>M</i>	0.169	0.120	0.480	0.215	10.8	< 10			
<i>s_M</i>	0.010	0.008	0.029	0.028	5.7				

The laboratory mean values have been examined statistically to eliminate outlying values. Where a " --- " appears in the table it indicates that an outlying value has been omitted (Grubbs 95 %).

A data set consists of at least 5 but usually 6 single values of one laboratory.

M : Arithmetic mean of the laboratory means

s_M : Standard deviation of the laboratory means

Note: "< - values" were not included into the calculation of *M* and *s_M*.

The line number should not be mistaken for the laboratory code number.

Analytical Method used for Certification

Element	Line Number	Method
Ti	1, 6, 8 2, 3, 7 4, 5	Spectrophotometry ICP OES XRF
B	1, 2, 6 3, 4, 5, 7	Titrimetry ICP OES
B ₂ O ₃	1 2, 3, 4, 5	ICP OES Titrimetry
Al	1, 2, 3, 4, 5, 6, 7, 8, 10	ICP OES
Ca	1, 3, 4, 5, 6, 7, 8, 9, 10, 12, 13 2 11	ICP OES F AAS ICP-MS
Cr	1, 2, 3, 4, 6, 7, 8, 9, 10, 12, 13, 14 5, 11	ICP OES ICP-MS
Fe	2, 13 3, 4, 5, 6, 7, 8, 9, 10, 11, 14, 15 12	F AAS ICP OES ICP-MS
Mg	1, 2, 3, 4, 6, 7, 8, 10 5 9	ICP OES F AAS ICP-MS
Mn	2, 3, 4, 5, 8, 9, 11, 12, 13 6, 7 10	ICP OES ICP-MS F AAS
Mo	1, 2, 3, 4, 5, 6, 7, 9, 10, 11, 13, 14 8, 12	ICP OES ICP-MS
Ni	2, 3, 4, 7, 8, 9, 10, 11, 12 5 6, 13	ICP OES F AAS ICP-MS
V	1, 2, 3, 4, 5, 8, 9, 10 6	ICP OES ICP-MS
Zr	2, 3, 4, 5, 6, 7, 8, 9, 12, 13 10, 11	ICP OES ICP-MS
C	3, 4, 5, 6, 7, 8, 9, 10	Comb-IR
N	1, 2, 3, 4, 5, 6, 7, 8, 9	CGHE-TC
O	3, 4, 5, 6, 7, 8, 9, 10	CGHE-IR
R _{acid}	1, 2, 3, 4	Gravimetry
Si	1, 3, 5, 7, 8 2 4 6	ICP OES ET AAS Spectrophotometry SS-ET AAS

Element	Line Number	Method
<i>Na</i>	<i>1, 3, 4, 6, 7</i>	<i>ICP OES</i>
	<i>5</i>	<i>F AAS</i>
	<i>2</i>	<i>SS-ET AAS</i>
<i>Nb</i>	<i>1</i>	<i>ICP OES</i>
<i>S</i>	<i>1</i>	<i>ICP OES</i>
<i>W</i>	<i>1</i>	<i>ICP OES</i>

Entries emphasized in *italics* refer to values that have been assigned “for information” only.

Abbreviations:

CGHE-IR	Carrier gas hot extraction method with infrared detection
CGHE-TC	Carrier gas hot extraction method with thermal conductivity detection
Comb-IR	Combustion method with infrared detection
ET AAS	Electrothermal atomic absorption spectrometry
F AAS	Flame atomic absorption spectrometry
ICP OES	Inductively coupled plasma optical emission spectrometry
ICP-MS	Inductively coupled plasma mass spectrometry
SS-ET AAS	Solid sampling electrothermal atomic absorption spectrometry
XRF	X-ray fluorescence spectrometry

Participating Laboratories

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 revierlabor Chemische Laboratorien für Industrie und Umwelt GmbH, Essen (Germany)
 Shanghai Institute of Ceramics, CAS, Shanghai (China)
 ThyssenKrupp Steel Europe AG, Duisburg (Germany)
 Treibacher Industrie AG, Althofen (Austria)
 Wolfram Bergbau- und Hütten AG, St. Martin im Sulmtal (Austria)

Handling

To ensure a representative sub-sampling for the analysis the bottle containing the CRM should be shaken in different directions for about two minutes before taking the sub-sample. According to the different sub-sample masses for the homogeneity testing different minimum sub-sample masses are specified for different parameters: Ti (100 mg); B (150 mg); Al, Ca, Cr, Fe, Mg, Mn, Mo, Ni, V, Zr (500 mg); C (200 mg); N, O (50 mg); B₂O₃ (5 g); R_{acid} (2.5 g). The opening duration of the bottle should be as short as possible. The lid of the bottle containing a special sealing gasket should be locked tightly immediately after usage. The sample must be dried at (110 ± 5) °C for one hour to achieve defined starting conditions for subsequent analysis. Storage in a desiccator with appropriate absorbing reagents is strongly recommended after drying until the beginning of the analytical procedure.

Transport and Storage

The material should be stored in a dry and clean environment at room temperature. Transport under normal ambient conditions.

Metrological Traceability

The ensure traceability of the certified mass fractions to the SI (Système International d'Unités) calibration was performed using certified standard solutions or pure metals or substances of known stoichiometry.

Safety Guidelines

The usual laboratory safety precautions must be applied. This material is not classified as hazardous according to Regulation (EC) No. 1272/2008. No hazardous effect is to be expected if the material is used under conditions usually adopted in analytical laboratories when handling finely dispersed powder materials. For detailed information on the safe handling of the material, please see the Material Safety Data Sheet distributed by the producer of the material (available on request).

Technical Report

A detailed technical report describing the analysis procedures and the treatment of the analytical data used to certify BAM-S012 is available on request or can be downloaded from BAM website (www.bam.de).

Accepted as BAM-CRM on 08 May 2019

Bundesanstalt für Materialforschung und -prüfung (BAM)

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Annex 1: Method M1

Extraction Method for Measurement of B₂O₃ content of TiB₂

Summary

Soluble boron compounds are extracted from a TiB₂ sub-sample with boiling water. The concentration of dissolved boron in the extract is measured using an appropriate analysis method and calculated as mass fraction of boron oxide $w(\text{B}_2\text{O}_3)$ in the TiB₂ sub-sample.

Procedure

Depending on the analysis method a sub-sample of 1 – 5 g of TiB₂ is weighed with a precision of ± 1 mg into a 250 mL Erlenmeyer flask with joint. 100 mL of deionized water is added, a condenser is connected to the joint of the Erlenmeyer flask and the TiB₂/water suspension is gently boiled under reflux for 1 h. After extraction, the condenser is thoroughly rinsed with water into the Erlenmeyer flask, the condenser is removed, and the TiB₂/water suspension is rapidly cooled down to room temperature by placing the Erlenmeyer flask into a bath with cold water.

Measurement

For measurement of boron concentration, the extract may be directly used (e.g. using titrimetric methods) or transferred into a volumetric flask (e.g. 250 mL) and filled up to volume with water. After sedimentation of the TiB₂ powder the clear supernatant shall be used for measurement of boron concentration (e.g. using photometric or spectrometric methods). The measured boron concentration is used to calculate the mass fraction of water-soluble boron $w(\text{B}_{\text{sol}})$ in the TiB₂ sub-sample which is then expressed as mass fraction of boron oxide $w(\text{B}_2\text{O}_3)$ according to $w(\text{B}_2\text{O}_3) = 3.22 \times w(\text{B}_{\text{sol}})$.

Annex 2: Method M2

Measurement of Acid Insoluble Residue of TiB₂

Summary

The acid insoluble residue is measured gravimetrically after dissolution of a TiB₂ sub-sample in a mixture of hydrofluoric acid (HF) and nitric acid (HNO₃).

NOTE: The HF/HNO₃ insoluble residue is an important parameter for process and quality control of TiB₂ production. The residue contains mainly boron carbide, boron nitride, titanium nitride, titanium dioxide and carbon.

Apparatus

Commonly used laboratory equipment and special equipment according to the following:

- 2.1 Membrane filter, cellulose nitrate, Ø 20 mm or 50 mm, pore size 0.45 µm.
- 2.2 Analytical balance, capable of reading to the nearest 0.01 mg.
- 2.3 Plastic beaker, 400 mL, resistant against HF and HNO₃.
- 2.4 Magnetic stirrer, with magnetic stir bar.
- 2.5 Cooling device, basin (2000 mL) with ice/water mixture or chiller with external cooling bath, suited to cool down the content of the plastic beaker to a temperature of 4 °C or below.
- 2.6 Filtration device, vacuum filter holder suited for membrane filters (2.1) with 2 L suction flask.

Reagents

Deionized water and reagents of known analytical grade shall be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

- 3.1 Hydrofluoric acid, HF, $c(\text{HF}) = 40\%$ (w/w), approx. 23 mol/L.
- 3.2 Nitric acid, HNO₃, $c(\text{HNO}_3) = 65\%$ (w/w), approx. 14 mol/L.
- 3.3 Acid mixture, HF (3.1) / HNO₃ (3.2), 1:3 by volume.

Procedure

The membrane filter (2.1) is dried at 105 °C ± 5 °C for 15 min. After cooling down to ambient temperature in a desiccator the mass of the membrane filter (m_1) is determined. The cooling device (2.5) is placed on the magnetic stirrer (2.4). A sub-sample of 3.0 g ± 0.1 g of TiB₂ is weighed into the beaker (2.3), a magnetic stir bar is added, and the beaker is placed into the cooling device. 30 mL HF (3.1) is added to the sub-sample and the mixture is stirred for at least 20 min to cool down to the temperature of the cooling device. Then 30 mL of the acid mixture (3.3) is slowly dosed within 20 min into the beaker.

CAUTION: The exothermal reaction of TiB₂ with the acid mixture is vigorous and releases nitrous and hydrofluoric fumes.

NOTE: A controlled addition of the acid mixture can be achieved using a peristaltic pump with HF/HNO₃ resistant tubing.

After addition of the acid mixture the mixture is stirred for 20 min. The mixture is then diluted with water to a volume of approx. 200 mL and filtered using the filtration device (2.6) through the membrane filter (2.1). The residue on the membrane filter is washed with 500 mL water. The membrane filter is removed from the filtration device and dried at 105 °C ± 5 °C for 15 min. After cooling down to ambient temperature in a desiccator the mass of the membrane filter (m_2) is determined.

Calculation

The acid insoluble residue $w(R_{\text{acid}})$ in the TiB_2 sub-sample is calculated in mass fractions in % according to:

$$w(R_{\text{acid}}) = \frac{(m_2 - m_1) \cdot 100}{m_s}$$

where:

m_1 = mass of empty membrane filter, mg

m_2 = mass of membrane filter with residue, mg

m_s = sample mass, mg