Federal Institute for Materials Research and Testing

in co-operation with the Committee of Chemists of the GDMB
Gesellschaft für Bergbau, Metallurgie, Rohstoff- und Umwelttechnik

Certified Reference Material

BAM-S003
Silicon Carbide Powder (green micro F 800)

Please notice the safety guidelines (see page 7)

ausverkauft / out of stock

Element/ Constituent	Certified Values		
	Symbols	Mass fraction [1] in mg/kg	Uncertainty [2] in mg/kg
Aluminium	Al	372	20
Boron	B	63	7
Calcium	Ca	29.4	1.8
Chromium	Cr	3.5	0.4
Copper	Cu	1.5	0.4
Iron	Fe	149	10
Magnesium	Mg	6.3	0.6
Manganese	Mn	1.44	0.17
Sodium	Na	17.7	0.8
Nickel	Ni	32.9	2.7
Titanium	Ti	79	4
Vanadium	V	41.4	2.8
Zirconium	Zr	25.2	2.0
Free Carbon [3]	C_{free}	493	79
Oxygen [5]	O	910	35
		Mass fraction [1] in %	Uncertainty [2] in %
Total Carbon [4]	C_{total}	29.89	0.07

1) The certified values are the means of 4-22 series of results (depending on the parameter) obtained by different laboratories. 2 up to 8 different analytical methods were used for the measurement of one parameter. The calibration of the methods applied for determination of element mass fractions were carried out by using pure substances of definite stoichiometry or by using solutions prepared from them, thus achieving traceability to SI unit.
2) The certified uncertainty is the expanded uncertainty estimated in accordance with the Guide to the Expression of Uncertainty in Measurements (GUM) with a coverage factor $k = 2$. It includes contributions from sample inhomogeneity.
3) The mass fraction of carbon free is a method–depending value. It was determined by two different methods and is only related to the application of these methods, which are described as “Method M1” and “Method M2” respectively, attached to this certificate.
4) The recommended “Method M3” described in attachment can be used for the determination of mass fraction of carbon total.
5) The recommended “Method M4” described in attachment can be used for the determination of mass fraction of oxygen.

Date of certification: 2004

Sample description

The certified reference material BAM-S003 is a silicon carbide powder (type green micro F800). The material is supplied in glass bottles containing 50 g each.

Indicative values

Not certified indicative values were determined in the interlaboratory comparison by participating laboratories.

Parameter	Indicative Values	
	Mass fraction [1] in mg/kg	Uncertainty [2] in mg/kg
Nitrogen	93	22
Silicon dioxide free	600	148
Silicon free	481	223

1) The indicative values are the means of 6-11 series of results (depending on the parameter) obtained by different laboratories. 1 up to 4 different analytical methods were used for the measurement of one parameter. The methods applied for determination of mass fractions were not always calibrated by using pure substances of definite stoichiometry or by using solutions prepared from them, thus was not achieved traceability to SI units.
2) The uncertainty is the expanded uncertainty estimated in accordance with the Guide to the Expression of Uncertainty in Measurements (GUM) with a coverage factor $k = 2$.

Additional Material Data

Additional material properties were determined by using one method, and can be used as informative values only.

Parameter		Additional Material Data	
		Mass fraction in %	Uncertainty in mass %
Phases:	SiC-6H	89.2 [1]	0.2 [2]
	SiC-15R	6.1 [1]	0.2 [2]
	SiC-4H	4.7 [1]	0.2 [2]
Parameters of particle size		Particle size in µm	
	D_{10}	5.55 [3]	
	D_{50}	10.18 [3]	
	D_{90}	16.69 [3]	

1) The measurements were carried out by X-ray powder diffraction using Rietveld method for evaluation.
2) The calculation of the standard uncertainty is based on a raw estimation from the evaluation of the Rietveld method.
3) The particle size distribution was determined by laser light diffraction method.

Berlin, 2004-09-01

BAM Berlin
Department I
Analytical Chemistry;
Reference Materials

Prof. Dr. U. Panne
(Head of Department)

BAM Berlin
Division I.1
Inorganic Chemical Analysis;
Reference Materials

Dr. R. Matschat
(Head of Division)

Supply of the reference material by
Bundesanstalt für Materialforschung und –prüfung
Richard-Willstätter-Straße 11, D-12489 Berlin, Germany
Phone: +49 (0)30 8104 2061 Fax: +49 (0)30 8104 1117 E-Mail: sales.crm@bam.de

Means of the series of measurements for the analytical procedure of one laboratory (Laboratory means)

mass fractions in mg/kg (C_{total} in mass%)

Serial N°	Al	B	Ca	Cr	Cu	Fe	Mg	Mn	Na	Ni	Ti	V	Zr	C_{total} (%)	C_{free}	O	*N*	*$SiO_{2\ free}$*	*Si_{free}*
1	-	55	21.2	2.5	1.0	-	3.8	1.00	-	24.1	-	-	19.1	-	415	825	*47*	*488*	*117*
2	305	55	25.4	2.6	1.1	-	5.5	1.10	15.0	24.2	-	28.83	21.2	-	500	845	*59*	*552*	*398*
3	327	61	-	2.6	1.2	131	5.8	1.30	15.3	26.2	68	30.83	22.0	29.57	515	862	*64*	*583*	*400*
4	334	62	27.4	3.2	1.2	135	5.9	1.32	15.7	28.7	70	36.29	22.4	29.75	540	865	*80*	*608*	*468*
5	345	63	29.1	3.3	1.3	135	5.9	1.33	16.7	29.8	72	37.00	22.8	29.82		873	*89*	*632*	*550*
6	354	63	29.1	3.4	1.3	137	6.0	1.36	17.0	30.5	73	38.00	23.2	29.85		902	*89*	*733*	*950*
7	367	63	29.1	3.4	1.4	137	6.0	1.37	17.3	30.9	74	39.27	23.7	29.86		915	*94*		
8	371	65	29.5	3.5	1.4	140	6.1	1.38	17.7	31.0	77	39.67	23.7	29.87		948	*99*		
9	371	66	29.5	3.5	1.4	142	6.3	1.41	17.8	31.1	77	41.25	24.3	29.89		951	*115*		
10	373	66	29.8	3.6	1.8	143	6.3	1.42	18.0	31.3	77	41.35	25.4	29.90		988	*128*		
11	377	67	29.8	3.6	2.3	143	6.4	1.47	18.7	31.7	77	42.38	25.6	29.91		1032	*151*		
12	378	-	30.5	3.9	2.5	146	6.5	1.48	18.8	32.2	79	42.53	25.8	29.91		-			
13	381	-	32.0	4.0	-	149	6.5	1.49	19.1	32.6	79	44.38	26.0	29.92					
14	385		32.7	4.1		149	6.8	1.53	19.3	33.1	81	45.48	26.6	29.94					
15	392		35.7	4.2		149	6.9	1.72	19.4	35.2	83	45.87	27.0	29.94					
16	399		-	4.4		152	8.2	1.79	19.5	35.5	83	46.07	28.7	29.96					
17	402		-	-		154	9.0	2.03	-	36.5	84	47.49	29.1	29.96					
18	403					155	-	-	-	39.2	84	48.27	30.4	30.03					
19	415					158	-			39.4	85	49.92	31.0	30.13					
20						162				39.4	85		-						
21						164				40.5	87								
22						164				41.1									
23						173													
24						-													
M:	372	63	29.4	3.5	1.5	149	6.3	1.44	17.7	32.9	79	41.38	25.2	29.89	493	910	*93*	*600*	*481*
s_M:	30	5	3.4	0.6	0.5	12	1.1	0.24	1.5	5.0	6	5.74	3.2	0.12	55	65	*31*	*83*	*273*

The „ - “ indicates that an outlying value has been detected by a statistical test which was withdrawn or omitted after discussion in GDMB meetings.
Values given in *italic type* are indicative values only.
Note: The serial number should not be mistaken for the laboratory code number.
M: Arithmetic mean of the laboratory means
s_M: Standard deviation of the laboratory means

Analytical methods used for final determination

List of abbreviations

CGHE/comb.-IR	Carrier gas hot extraction/combustion method with infrared detection
Comb./coul.	Combustion of free carbon followed by coulometric determination
Comb.-IR	Combustion method with infrared detection
DCarc-OES	Direct current arc optical emission spectrometry
ET AAS	Atomic absorption spectrometry with electrothermal atomization
ETV-ICP OES	Inductively coupled plasma optical emission spectrometry with electrothermal vaporisation
F AAS	Flame atomic absorption spectrometry
F AES	Flame atomic emission spectrometry
GRAV	Gravimetry
ICP OES	Inductively coupled plasma optical emission spectrometry
ICP-MS	Inductively coupled plasma mass spectrometry
INAA	Instrumental neutron activation analysis
K_0-INAA	K_0- Instrumental neutron activation analysis
MAS	Molecular absorption spectrometry
Method M1	Coulometric determination after wet chemical oxidation with hot chromic sulfuric acid, (described in appendix)
Method M2	Combustion of free carbon followed by coulometric determination comprising weighing back the sample boat, (described in appendix)
SS ET AAS	Solid sampling electrothermal atomic absorption spectrometry
TITR	Titrimetry
Vol.	Gas volumetric determination

Element	Serial Nº.	Analytical method used
Al	4, 12	DCarc-OES
	8	ET AAS
	2	ETV-ICP OES
	(1)	F AAS
	16	ICP-MS
	3, 5, 6, 7, 9, 10, 11, 13, 14, 15, 17, 18, 19	ICP OES
B	3	DCarc-OES
	1, 2, 4, 5, 7, 8, 9, 10, 11, (12), (13)	ICP OES
	6	MAS
Ca	1	ETV-ICP OES
	5, (17)	F AAS
	13	ICP-MS
	2, 3, 4, 6, 7, 8, 9, 10, 11, 12, 14, 15,(16)	ICP OES
Cr	2	DCarc-OES
	9, 16	ET AAS
	3	ETV-ICP OES
	8	ICP-MS
	1, 4, 6, 11, 12, 13, 14, 15, (17)	ICP OES
	7, 10	INAA
	5	K_0-INAA
Cu	11	DCarc-OES
	4	ET AAS
	3	ETV-ICP OES
	9	ICP-MS
	1, 2, 5, 6, 7, 8, 10, 12, (13)	ICP OES

Element	Line No.	Analytical method used
Fe	(1), 5	DCarc-OES
	22	ETV-ICP OES
	9	F AAS
	12	ICP-MS
	(2), 3, 4, 7, 8, 10, 11, 13, 14, 15, 16, 17, 18, 19, 20, 21	ICP OES
	23	INAA
	6	K_0-INAA
	(24)	Titrimetry
Mg	5	DCarc-OES
	9	ET AAS
	12	ETV-ICP OES
	17	F AAS
	15	ICP-MS
	1, 2, 3, 4, 6, 7, 8, 10, 11, 13, 14, 16, (18), (19)	ICP OES
Mn	15	DCarc-OES
	6, 11	ET AAS
	17	ETV-ICP OES
	9	ICP-MS
	1, 2, 4, 8, 10, 12, 13, 14, 16, (18)	ICP OES
	3, 7	INAA
	5	K_0-INAA
Na	(1)	ETV-ICP OES
	5, 7, 11, 16	F AAS
	15	F AES
	8	ICP-MS
	2, 3, 6, 10, 14, (17), (18)	ICP OES
	4, 9	INAA
	12	K_0-INAA
	13	SS ET AAS
Ni	2, 5	DCarc-OES
	7	ET AAS
	1	ETV-ICP OES
	18	F AAS
	10	ICP-MS
	3, 4, 6, 8, 9, 11, 12, 13, 14, 16, 17, 19, 20, 21, 22	ICP OES
	15	K_0-INAA
Ti	(1), 21	DCarc-OES
	4	ETV-ICP OES
	13	ICP-MS
	(2), 3, 5, 6, 7, 8, 9, 10, 11, 12, 14, 15, 16, 17, 18, 20	ICP OES
	19	K_0-INAA
V	2, 16	DCarc-OES
	(1)	ETV-ICP OES
	11	ICP-MS
	3, 4, 5, 6, 7, 8, 9, 10, 12, 13, 14, 15, 18, 19	ICP OES
	17	K_0-INAA
Zr	15	DCarc-OES
	17	ETV-ICP OES
	10, 16	ICP-MS
	1, 2, 3, 4, 5, 6, 7, 8, 9, 12, 13, 14, 19, (20)	ICP OES
	18	INAA
	11	K_0-INAA
C_{total}	(1), 3, 4, 5, 7, 8, 9, 10, 11, 13, 14, 15, 16, 17, 18	CGHE/comb.-IR
	(2)	CGHE/titr.
	6	CGHE/grav.
	12, 19	Coul.

Element	Line No.	Analytical method used
C_{free}	(1), (2), (3), (4), (13), (14)	CGHE/comb.-IR
	(9), (10), (11), (12)	Coul.
	6, 7	Comb./coul. (Method M1)
	5, 8	wet chem. oxidation/coul. (Method M2)
O	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, (12)	CGHE
	11	CGHE/coul.
N	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11	CGHE
SiO_{2free}	1	Vol.
	2, 3	MAS
	4, 5	ICP OES
	6	Grav.
Si_{free}	1	Coul.
	2, 4, 5, 6	Vol.
	3	Comb.

Line numbers in parenthesis refer to values not used in the calculation of the certified value.

Participating laboratories (arranged alphabetically)

BAM, Bundesanstalt für Materialforschung und -prüfung Berlin (Germany)
- Laboratory: Activation Analysis; Gas Analysis
- Project group: Quality Assurance and Metrological Aspects in Production of High Tech Reference materials

Chinese Academy of Sciences, Shanghai Institute of Ceramics, Analysis and Testing Center for Inorganic Materials, Shanghai (PR China)

CRB GmbH, Hardegsen (Germany)

DIFK Deutsches Institut für Feuerfest und Keramik GmbH, Bonn (Germany)

Elektroschmelzwerk Delfzijl B.V., TE Farmsum (Netherlands)

ESK-SiC GmbH, Frechen (Germany)

Forschungszentrum Jülich GmbH, Jülich (Germany)

H.C. Starck Ceramics GmbH & Co. KG; Selb (Germany)

H.C. Starck GmbH & Co. KG; Goslar (Germany)

H.C. Starck GmbH & Co. KG; Laufenburg (Germany)

Institut für Festkörper und Werkstoffforschung, Dresden (Germany)

Japan Fine Ceramics Center, Atsuta-ku Nagoya (Japan)

Johannes Gutenberg Universität, Institut für Kernchemie, Mainz (Germany)

Jožef Stefan Institute, Ljubljana (Slovenia)

Max-Plank-Institut für Metallforschung, Stuttgart (Germany)

Molab AS, Mo I Rana (Norway)

NGK Insulators, LTD., Chemical analysis materials research lab., Nagayo (Japan)

OSRAM GmbH, München (Germany)

Plansee AG, Reutte (Austria)

Saint Gobain Ceramic Materials AS, Lillesand (Norway)

Saint Gobain Industrial Ceramics and Plastics, Northboro (USA)

Saint Gobain Industriekeramik, Geschäftsbereich Feuerfesttechnik, Rödental (Germany)

Schunk Kohlenstofftechnik GmbH, Heuchelheim (Germany)

SGL Carbon GmbH, Bonn (Germany)

SGL Carbon GmbH, Meitlingen (Germany)

W.C. Heraeus GmbH, Hanau (Germany)

Wacker Ceramics, Kempten (Germany)

Zhuzhou Cemented Carbide Group Corp., LTD., Zhuzhou, Hunan (PR China)

Recommendations for Correct Sampling and Sample Preparation

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. Each sub-sample has to be taken separately. According to the different sub-sample masses for the homogeneity testing different minimum sub-sample masses are specified for different analytes (in paranthesis /mg): Al, Ca, Fe, Mg, Ni, Ti, Zr(8); Cr, Cu, V(14); B(500); C_{total}(25); C_{free}(500); O(80). 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. Sample preparation for the determination of the analyte boron has to be carried out by using fusion technique with sodium peroxide followed by an extraction to avoid losses. For subsequent elemental analysis the sample has to be treated thermally at (135 ± 5) °C for 12 hours to achieve defined starting conditions. For the determination of metallic analytes the required pressure digestion has to be verified concerning absence of analyte losses.

Recommendations for Correct Storage

The sample should be stored in a dust-free and dry environment.

Expiration of Certification

The date of expiry of certification is ten years after the date of certification. Before this date a new certificate will be prepared with a new date of expiry.

Safety Guidelines

1. First aid measures

   In the event of contact with the skin, rinse off with water and soap. Contamination of the eyes must be treated by thorough irrigation with water, with the eyelids held open.
   If product is swallowed, induce vomiting and consult a physician. The product is not known to be toxic.

2. Accidental release measures

   Precautionary measures regarding persons: Avoid formation and deposition of dust. Ensure effective ventilation.
   Methods for cleaning up / taking up: Take up mechanically; avoid dust formation. Fill into labelled, sealable containers.

3. Handling

   Avoid formation and deposition of dust. Ensure adequate ventilation and if necessary, exhaust ventilation when handling or transferring the product.

4. Exposure restriction and personal protection

   Respiratory protection: If necessary use a respirator mask with filter type P according to DIN EN 143.
   Hand protection: protective gloves
   Eye protection: protective goggles

5. Limit values of dust concentration in air to be monitored

   Regulatory instructions concerning limit values of concentration of different particle size are to be maintained.

6. Disposal considerations

   Unused material: reuse if possible. Address manufacturer of the starting material.
   Or: May be disposed of in approved special landfills provided local regulations are observed.

Regulatory Information

- ANSI American National Standards Institute, Methods of chemical analysis of silicon carbide abrasive grain and abrasive crude, ANSI B74.15-1992, ANSI American National Standards Institute, 1992, pp. 20
- DIN, ISO 51079-1, Prüfung keramischer Roh- und Werkstoffe, Chemische Analyse von Siliciumcarbid als Rohstoff und als Bestandteil von Werkstoffen, Teil 1 Soda-Borsäure-Aufschluss
- DIN, ISO 51079-2, Prüfung keramischer Roh- und Werkstoffe, Chemische Analyse von Siliciumcarbid als Rohstoff und als Bestandteil von Werkstoffen, Teil 2 Säure-Druck-Aufschluss

- DIN, ISO 51079-3, Prüfung keramischer Roh- und Werkstoffe, Chemische Analyse von Siliciumcarbid als Rohstoff und als Bestandteil von Werkstoffen, Teil 3 Aufschluß des freien Kohlenstoffs durch naßchemische Oxidation
- DIN, ISO, 51075 - 1-5, Prüfung keramischer Roh- und Werkstoffe, Chemische Analyse von Siliciumcarbid, Teil 1-5
- FEPA (Féderation Européenne des Fabricants de Produits Abrasifs), Chemische Analyse von Siliciumcarbid, FEPA-Standard 45-D-1986, Fachverband Elektrokorund- und Siliziumkarbid-Hersteller e.V., Verein Deutscher Schleifmittelwerke e.V., 1986, 1-25

Informative References

- Kato, K.; “Atomic absorption spectrophotometric determination of total silicon in silicon carbide” in: Atomic Absorption Newsletter 15 (1976) 4-6
- Schwetz, K. A., Hassler, J.; “A wet chemical method for the determination of free carbon in boron carbide, silicon carbide and mixtures thereof” in: J. of the Less-Common Metals, Elsevier Sequoia/Netherlands, 117 (1986) 7-15
- Hunold, H., Reh, H.; “Die Hochleistungskeramik. II. Die Werkstoffe: Siliciumcarbid (SiC), ein alter Bekannter“ in: Keramische Zeitschrift, (1987) 521-525
- Kriegesmann, J.; “Die Technologien der modernen Siliciumcarbidkeramiken, Teil I: Rohstoff und Formgebung“ Keramische Zeitschrift (1988) 857-863
- Kriegesmann, J.; ”Die Technologie der modernen Siliciumcarbidkeramiken Teil III: Eigenschaften“ in: Keramische Zeitschrift (1989) 17-22
- “JIS Japanese Industrial Standard, Method for chemical analysis of silicon carbide abrasives” in: JIS R 6124-1987, Japanese Standards Association, Tokyo, Japan, (1989) 1- 51
- Broekaert, J. A. C., Graule, T., Jenett, H., Tölg, G., Tschöpel P.; “Analysis of advanced ceramics and their basis products” in: Fresenius Z. Anal. Chem. 332 (1989) 825-838
- Graule, T., Tschöpe, P.; “Analyse von hochreinen Keramikpulvern und Sinterkörpern mit der optischen Emissions- (OES) und der Atomabsoprtionsspektrometrie“ in: cfi/Ber.DKG 68 No. 1/2 (1991) 5-9
- Roßberg, A., Otto, K., Matthe, P.; “Analysenmodell zur Bestimmung von freiem Kohlenstoff in feindispersen SiC-Pulvern in Gegenwart von freiem Silizium“ in: cfi/Ber. DKG 69 No. 7/8 (1992) 251-254
- Docekal, B., Broekaert, J. A. C., Graule, T., Tschöpel, P., Tölg, G.; “Determination of impurities in silicon carbide powders” in: Fresenius J. Anal. Chem., 342 (1992) 113-117
- Záray, G., Leis, F., Kántor, T., Hassler, J., Tölg, G.; “Analysis of silicon carbide powder by ETV-ICP AES” in: Fresenius J Anal Chem, 346 (1993) 1042-1046
- Csato, I., Zaray, Gy., Gal-Solymos, K., Hassler, J.; “Direct analysis of silicon carbide powder by total reflection X-ray Fluorescence Spectrometry” in: Applied Spectroscopy 51 No. 7 (1997) 1067-1072
- Schäffer, U., Krivan, V.; “Multielement analysis of graphite and silicon carbide by inductively coupled plasma atomic emission spectrometry using solid sampling and electrothermal vaporisation” in: Anal. Chem. 71 No.4 (1999) 849-854
- Hassler, J., Förster,O.; Schwetz, K. A.; “Moderne chemische Analysenverfahren von keramischen Werkstoffen“ cfi/Ber. DKG 77 No. 7 (2000) D11-17
- Schwetz, K. A.; “Silicon carbide based hard materials” in: Handbook of Ceramic Hard Materials, R. Riedel (Ed.), Vol 2 Wiley-VCH, Weinheim, N.Y., (2000) 683-748

M1 Prescribed method 1 for determination of free carbon in silicon carbide

Coulometric determination of free carbon (C_{free}) in silicon carbide after wet-chemical oxidation with hot chromic-sulfuric acid

According to Dr. Jürgen Haßler, Wacker-Chemie GmbH, Max-Schaidhauf-Str.25 D-87437 Kempten, Germany

Purpose:

C_{free}-determination in silicon carbide by wet chemical oxidation and coulometric detection

Scope:

The method is applicable preferably to very fine grain powders (grain size less than 10 µm) or low contents of free carbon (less than 0,2 % mass fraction) as well as if there are evaporable and/or components easy to oxidize in the analyzed silicon carbide.
The method releases organic carbon and carbonate carbon, too (as CO_2).
The method is applicable to free carbon mass fractions of 0,01 % to 5 %. At higher concentrations incomplete recovery is possible. The method is not applicable to samples containing compounds which could adulterate the result (e.g. B_4C).

Principle

The free carbon of the sample is oxidized to carbon dioxide by adding chromic sulfuric iodic acid at a temperature of 120 ºC ± 5 ºC. The inert gas carries the CO_2 to the coulometric detection system.
SiC does not react under these conditions, or only to a negligible amount in case of very fine powders.

Apparatus

In addition to standard laboratory equipment, the following apparatus shall be used.

Coulometric detection system for determination of carbon mass fraction (e.g. coulometric system of "Coulomat 702", Ströhlein, Germany)
Analytical balance,
precision ± 0,05 mg
Aluminium heating-block with temperature control to 130 ºC ± 5 ºC
Reaction vessel, with cooling device and drying trap (figure 1)
Aluminium capsules, e.g. diam.=6 mm, L 15 mm, prepared from aluminium foil (carbon free)
External PC and plotter/printer

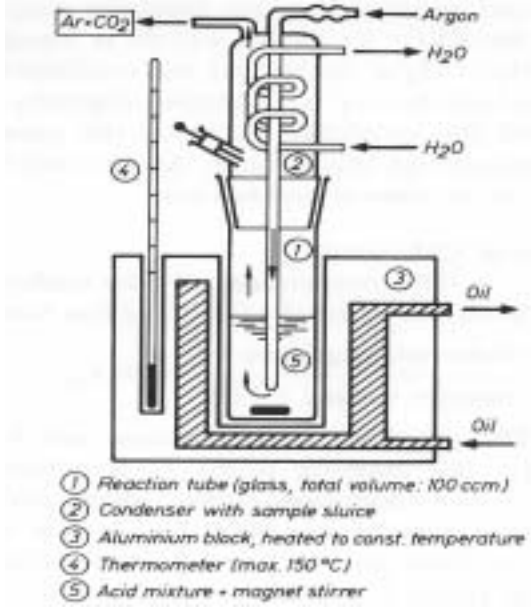

Fig.1: Aluminium heating block with reaction vessel

Reagents and auxiliary means

All reagents must be of known analytical grade. The used water shall be distilled water or water which has been fully demineralized by ion exchange (deionized water). Unless otherwise specified, solutions are aqueous solutions.

Calcium carbonate; $CaCO_3$ (dried 2h/285°C)
Barium carbonate; $BaCO_3$
Barium perchlorate; $Ba(ClO_4)_2$,
$Ba(ClO_4)_2$-solution; 20% (mass%) in H_2O
Sodium dichromate; $Na_2Cr_2O_7$ x 2 H_2O
Potassium iodate; KIO_3
Sulfuric acid H_2SO_4; ρ = 1,84 g/ml
Argon; Ar, 99,998 % pure

Chromic sulfuric acid solution: prepared by dissolving 22 g of sodium dichromate in 300 ml H_2O, and adding 700 ml sulfuric acid. The solution is heated for 30 min at 150 ºC ± 10 ºC. After cooling the solution is stored in a glass bottle.

Little porcelain boats, not glazed Aluminium capsules, made from aluminium foil, free of carbon.

Procedure

If the total dryness of sample is not assured, the sample has to be dried at 120°C ± 5 ºC for 2 hours and should be stored after cooling down in a dry surrounding (e.g. desiccator). Samples of higher grain size have to be milled to grain size ≤ 53 µm (e.g. in a steel mortar).

Use test assembly in accordance with the operating instructions.

Adjust the temperature of the heating block to 120 ºC ± 5 ºC.

Weigh ca. 0,5 g KIO_3 into the reaction vessel and pipette 30 ml of chromic sulfuric acid to it.

Insert the reaction vessel into the heating block and connect it via cooler tightly with the coulometric detection system and adjust the carrier gas with a surplus of carrier gas and a pressure compensation.

To control the tightness of the system, run an Ar-blank of about 5 min to 10 min after a heating time of 20 min.

Weigh, depending on the sample material and the expected content of free carbon, 20 mg - 150 mg to the nearest 0.01 mg into an aluminium capsule.

Close the capsule with tweezers. After the chromic sulfuric acid has reached a temperature of 120°C, put the capsule in the sample insertion device of the reaction vessel and drop it into the hot acid. When the sample drops into the acid, switch on the measuring mode of the detection unit.

The total reaction time is about 60 min. The detection time depends on the chosen detection system.

Evaluation and calculation of C_{free} content

The evaluation is made graphically, counts (ordinate) versus time (abscissa).

Usually coulometric systems record add up counts for a specific time interval. Therefore it is not possible to draw running counts versus time or its first derivative.

Using a suitable interface, a measuring curve can be recorded by PC and printed out via plotter or printer.

Graphical evaluation by hand:

The slow and constant slope in the second part of the CO_2-reaction curve (system blank and negligible amount of C_{SiC}) is to be lengthened to the ordinate.
The ordinate is to shift ca. one minute before the sharp rise of the counts (moment of destruction of capsule and the start of reaction).
The stretch between the intersections of the lengthened constant line and the measuring curve (on the lower end) with the shifted ordinate corresponds to C_{free} oxidized by the hot chromic sulphuric acid attack.

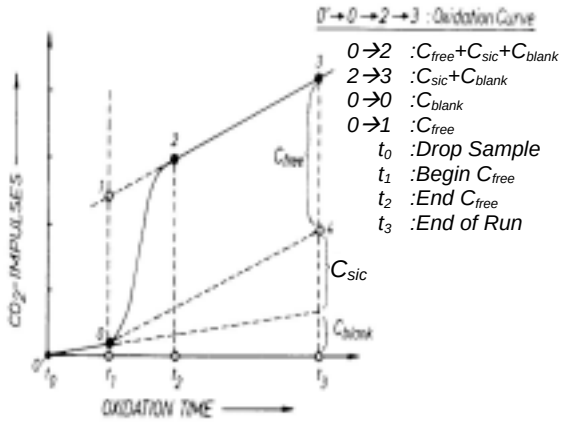

Fig. 2. Analysis of free carbon in silicon carbide: a plot of CO_2 concentration vs. time with graphical extrapolation.

The free carbon content, C_{free} shall be calculated as a percentage by mass, to the nearest 0.01 % using the following equation:

$$\% C_{free} = \frac{I * f}{m_E} * 100$$

I number of counts found for the sample by graphical evaluation
f conversion factor count → mg C (= 0.0002 in case of Ströhlein Coulomat)
m_E sample mass, in mg

Precision:
The reproducibility of the method is: σ = ± 0.01% at a mass fraction of 0.05 –0.50% C_{free} mass fraction

Calibration:
Coulometry is an absolute method.
Use $CaCO_3$ for checking up the method and for testing assembly. The difference from theoretical value (12.00%) shall be max. ± 0.05% (absolute).
The check up is carried out daily before use.

References:

- Operating instructions, Coulomat, Fa. Ströhlein
- K.A.Schwetz, J.Haßler : A wet chemical method for the Determination of free carbon in boron carbide , silicon carbide and mixtures thereof, J. of the Less-Common Metals **117**, 7-15 (1986)
- DIN 51079-3 Chemische Analyse von Siliciumcarbid als Rohstoff und als Bestandteil von Werkstoffen
  Teil 3: Aufschluss des Freien Kohlenstoffs durch nasschemische Oxidation
  Norm-Entwurf Okt 1997

M2 Prescribed method 2 for determination of free carbon in silicon carbide

Coulometric determination of free carbon content (C_{free}) in silicon carbide comprising weighing-back the sample boat

According to Dr. Jürgen Haßler, Wacker-Chemie GmbH, Max-Schaidhauf-Str.25 D-87437 Kempten, Germany

Purpose:
Indirect C_{free}-determination by weighing-back the combustion boat after direct C_{free}-determination

Scope:
To be used for SiC-powder and grains
Remark:
This method of C_{free}-determination is usable for SiC powder or grains with high proportion of fine particles (grain size < 10µm), material containing detectable quantities of β-SiC and/or material containing more than 2 % free carbon.

Principle:
Combustion of the free carbon in oxygen gas flow at 850°C followed by coulometric determination of the released carbon dioxide. The method takes into account the oxidation of silicon carbide during the combustion of the free carbon by weighing-back the sample boat (possible side reaction: $SiC \rightarrow SiO_2 + CO_2 \uparrow$) after combustion.
Comment 1:
This method is not usable if volatile components, carbonates and/or combustible impurities, such as, Fe_{met}, Si_{met} or B_{met} are contained in the sample, which can cause a significant change in weight ("met" stands for "metallic").
Comment 2:
The method is a combination of methods described in DIN 51075 "Chemical analysis of silicon carbide", part 2, "Direct determination of free carbon" and in DIN 51075, part 5 "Indirect determination of free carbon content in silicon carbide".

Apparatus:
In addition to standard laboratory apparatus shall be used:
Apparatus for determination of carbon content consisting in a resistance heated tube furnace combined with a coulometric detection system (e.g. "Coulomat 702", Ströhlein, Germany). The resistance heated furnace is equipped with ceramic tube and adjustable at (900 ± 10)°C.
Open combustion boats of unglazed ceramic material. Before use, the boats have to be heated in a laboratory furnace at (1050 ± 25)°C for 1 hour.

Reagents:
The following reagents of high purity shall be used.
Calcium carbonate; $CaCO_3$ (dried 2h/285°C),
Barium carbonate; $BaCO_3$
Barium perchlorate; $Ba(ClO_4)_2$
Absorbing-solution, dissolve about 200 g of high purity barium perchlorate, $Ba(ClO_4)_2$ in distilled or deionized water and fill up to one litre.
Oxygen, O_2: 99.99%

Procedure:
Use test assembly in accordance with the operating instructions.
Adjust the oxygen flow rate so that there is no risk of air being sucked in from outside. The measurement is carried out without splitting of gas flows.
A few reference samples of known carbon content shall be analyzed before running the analytical sample.
Prior to series of analyses, the blank value shall be determined (with no gas volume reduction) using a pre-calcined boat.
Weigh to the nearest 0.01 mg, about (100 – 300) mg of the dried sample (dried at 120°C for 1h) into a boat from which any carbon present has previously been removed by calcination. The mass of sample boat and the mass of sample boat plus sample (difference = weighed portion SiC) are recorded in writing.
Place the boat into the heating zone of the furnace preheated to a temperature of (850 ± 10)°C and start the measurement.
At the above temperature, the determination of free carbon takes 10 minutes. During this time the combustion gases are led to the coulometric detection system, where the coulometric current is registered and displayed.
After closing the measurement and removing the sample boat from the furnace, cool down to room temperature and weigh back the sample boat including annealed sample nearest 0.01mg.
Remark:
If the free carbon content is particularly high, the volume of the combustion gas can be reduced to one-tenth (1/10 gas division) using dosing pump.

Evaluation:
The content of free carbon (C_{free}) is calculated by counting the mass of additionally oxidized part of SiC.
In case of using the “Coulomat 702” the following calculation is carried out (in analogous way for other instruments):
One count corresponds to 3.212 x 10^3 Coulomb or 2 x 10^{-4} mg C, respectively (at normal division).
The free carbon content C_{free} is calculated as a percentage by mass, to the nearest 0.01 % using the following equation:

$$C_{free} = \frac{0.6255 * C + 0.3754 * (m_1 - m_2)}{m_{SiC}} * 100$$

C_{free} = mass of free carbon [mg]; determined at a temperature of (850 ± 10)°C and measuring time of about 10 min.

C = (I – I‘) • f
I = number of counts found for the sample
I' =number of counts in the blank value determination (mean of three repeats)
f = conversion factor: count → mg C (= 0.0002 in case of Ströhlein Coulomat)

m_1 = mass of sample boat + sample mass before oxidation, (mg)
m_2 = mass of sample boat + sample mass after oxidation, (mg)
m_{SiC} = sample mass (mg)

The factors used in the equations were calculated using the relative molar masses as follows:

$$1.6009 = \frac{\frac{SiO_2 - SiC}{C} + 1}{\frac{SiO_2 - SiC}{C}} \qquad 2.6641 = \frac{SiO_2 - SiC}{C} + 1$$

$$0.6255 = \frac{1}{1.6009} \qquad 0.3764 = \frac{1}{2.6641}$$

Precision:
The reproducibility of the method is: σ = ± 0.01% at 0.05-0.50% C_{free} mass fraction.

Calibration:
Use $CaCO_3$ for check up the method and test assembly. The difference from theoretical value (12.00%) should be max. ± 0.05% (absolute).
The check up is carried out daily before use.

References:
DIN 51075 Chemical analysis of silicon carbide
Operating instructions, Coulomat 702, (Ströhlein, Germany) or other instruments.

M3 Recommended method 3 for determination of total carbon mass fraction in silicon carbide powder

Prepared by Albrecht Meyer, Max-Planck-Institut für Metallforschung, Heisenbergstraße 3, D-70569 Stuttgart, Germany
Revised by Dr. Wolfgang Gruner, Leibniz-Institut für Festkörper- u. Werkstoffforschung, Postfach 270116, D-01171 Dresden, Germany

Method

Oxidation in pure oxygen followed by IR-detection; (CO_2)-“Combustion method“

Preparation of measurement

- Use ceramic crucible with lid (11 mm hole). Anneal in muffle furnace at 1100°C for 8 hours in air; store in desiccator; anneal once more in a tube furnace at 1100°C in oxygen (or air) for a short time before use.
- Use purified Ni-capsules (purified with acetone in an ultrasonic bath) dried by a hair dryer.
- Use a weighed sub-sample of 25 mg (using semi-micro balance). The sub-sample mass depends on the size of Ni capsules used.
- Seal the capsule with a tong.
- Put the capsule into the crucible together with 0.5 g Fe (for reduction of carbon blank value in the iron material, the iron is heated at 950°C for 10 hours in an Ar stream before) and 1 g W as flux (sequence of putting into the crucible: Fe, sub-sample, W)

Measurement

- Put the crucible with the holed lid into the high frequency induction furnace and start the heating and the measurement cycle.
- Choose the duration of reaction to assure a total release of carbon. (Attention, it is a parameter strongly depending on the analytical instrument! A typical time is about 60 sec.)

Calibration

It is not allowed to use a certified matrix-reference material (such as steel). Use spectrographically pure graphite, a glassy carbon or powder of $CaCO_3$ introduced to Ni-capsules for calibration. In calibrating procedure a good signal adaptation is achieved with about 8 mg C or with an according mass of a (primary) pure substance such as $CaCO_3$.

M4 Recommended method 4 for the determination of oxygen and nitrogen mass fraction in silicon carbide powder

According to Dr. Wolfgang Gruner, Leibniz-Institut für Festkörper- u. Werkstoffforschung, Postfach 270116, D-01171 Dresden, Germany

Method

Carrier gas hot extraction in inert gas atmosphere (He) with infra-red detection (CO_2) and heat conductivity measurement (N_2)

Preparation of measurement

- use pre-cleaned Ni-capsules (acetone or trichloroethylene; ultra sonic bath; dried by hair dryer)
- use a sub-sample mass dependent on capsule geometry (e.g. ∅7 X 10 mm) of about 25-100 mg using semi-micro balance; carefully close capsule using tong; press capsule using a hand press; weigh back for control, if necessary

Measurement

Resistance heating oven; high temperature graphite crucibles; measurement modus – IMPULS; gas outlet and reaction temperature (usually equivalent to heating power POWER) are chosen in order to achieve a complete deliberation of the analytes (Attention: Instrument specific parameter (e.g. 5000 W / 70 sec when using LECO TC436 with EF 500)!)

Calibration

The detector is calibrated using (primary) pure substances (e.g. CO_2, N_2, KNO_3). Note, that this does not necessarily guarantee a complete deliberation of the analyte.

- In case of using solutions of salts (e.g. solution of KNO_3) dry the solution in the Ni-capsule slowly
- gas dose calibration for N is very critical, since the signal intensity ratio from sample and gas dose is about 1:100 (N_2) and for O still about 1:20 (CO_2)