BRUKER

Ceramics sample

Peak deconvolution

EDS map

Quantitative analysis

Phase analysis

Application Note # EDS-10

Advanced light element and low energy X-ray analysis of a TiB$_2$–TiC–SiC ceramic material using EDS spectrum imaging

Silicon drift detector (SDD) systems have become state of the art technology in the field of EDS (X-ray microanalysis). One of the main advantages of XFlash® SDDs is the extremely high pulse load capacity of up to 750,000 counts per second combined with good energy resolution (<123 eV Mn-Kα, 47 eV C-K at 100,000 cps). These two factors and modern data processing allow spectrum imaging where an entire EDS spectrum at each pixel of the SEM image is collected in a database termed "HyperMap". This approach allows data evaluation with advanced analysis options, such as the Maximum Pixel Spectrum (Bright & Newbury 2004, Application Note # EDS-04) for improved element identification and spectroscopic phase analysis called "Autophase" (Application Note # EDS-03) for evaluating the composition and area fraction of major and minor components.

A challenging analytical problem is the standardless quantification of light elements and low energy X-ray lines. It is complex due to (1) large variations in absorption effects in the low energy range and (2) variations in background calculation caused by high absorption edges and high statistical error. Bruker has developed an improved quantification algorithm which is particularly useful for the low energy region. It is called "TQuant" and based on the combination

of results from net count intensity ratio determination and results from the quantification method using the peak to background ratio with ZAF correction (P/B-ZAF).
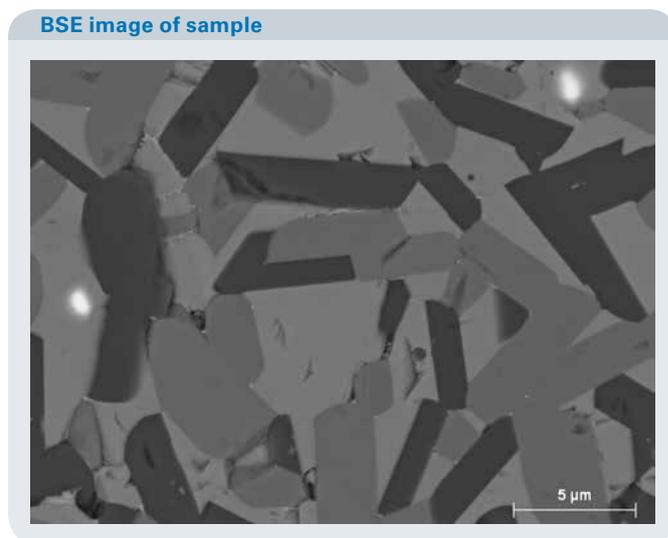
BSE image of sample

Fig. 1 BSE image of the analyzed area of the polished sample showing three major phases (dark, medium and light grey) and a minor, bright phase ~500 x 750 nm in size.

The accurate microanalysis of light elements such as boron and carbon by spectrum imaging will be demonstrated using a sintered hard ceramic material composed of the three major phases titanium boride (TiB_2), titanium carbide (TiC), silicon carbide (SiC) and minor phases, sub-µm in size. The combination of these three materials leads to improved mechanical and tribological properties. Silicon carbide is a material used for mechanical seals. It has the disadvantage of reduced failsafe running functions, causing increased wear when running dry. The added titanium components (TiC and TiB_2) improve the failsafe running functions. This technology has already been transferred to industrial applications.

Methods

The polished, uncoated sample (Fig. 1) was analyzed with the drift correction option using the following conditions:

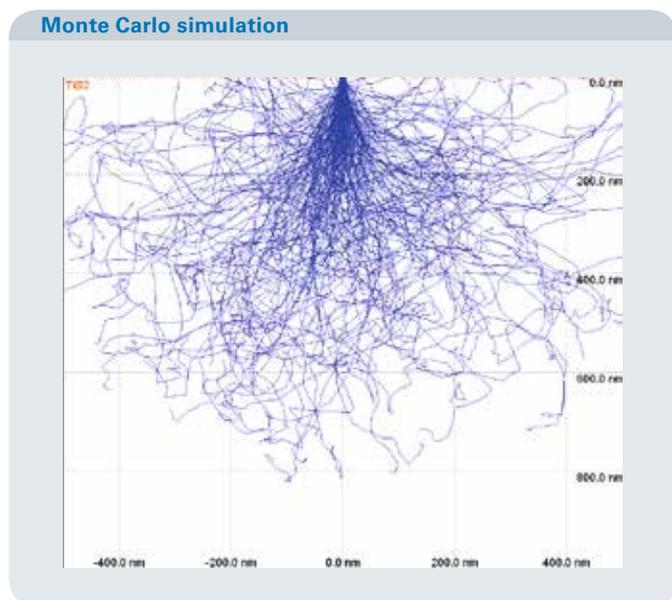|	
EDS detector:	XFlash® 5010
	(Res. <123 eV Mn-Kα, 47 eV C-K)
SEM:	ZEISS Supra 55 VP
Accelerating voltage:	10 kV
Probe current:	2.2 nA
	(60 µm aperture,
	high current mode)
Input count rate:	16.4 kcps
Output count rate:	14.4 kcps (dead time 12 %)
Resolution:	320 x 240 pixels,
	76,800 spectra HyperMap
Pixel size:	80 nm
Measurement time:	37 min

Monte Carlo simulation

Fig. 2 The Monte Carlo simulation shows the electron trajectories for TiB_2 at an accelerating voltage of 10 kV. The interaction volume has a size of ~ 800 nm in all directions.

In order to improve the spatial resolution, analyzing this bulk sample, it is necessary to work with low excitation voltages. This decreases the interaction volume for electron trajectories (Fig. 2) and the emitted X-rays (Fig. 3).

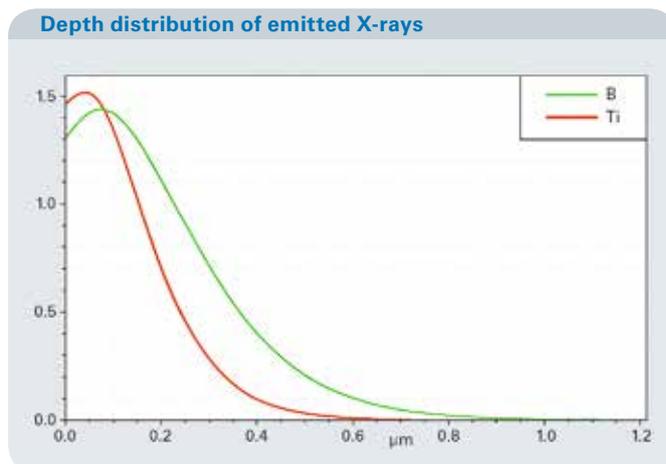**Depth distribution of emitted X-rays**

Fig. 3 The X-ray depth functions of boron-K and titanium-K radiation display the intensity of emitted X-rays depending on their depth in the sample. The graphic shows that the B-K and Ti-K intensities are emitted mainly from a depth <200 nm and <300 nm, respectively.

Major and minor elements were identified using the EDS database. The Maximum Pixel Spectrum function synthesizes a spectrum which contains the highest count level found in each spectrum energy channel. Thereby, elements which are present in only one pixel of the map can be easily identified.

The distribution of elements without peak overlaps e.g. boron-K, carbon-K and oxygen-K can be displayed by integrating the peak intensity (usually 87 % of the peak area) from the EDS database. Element lines with overlapping peaks, such as silicon-K and tungsten-L, were separated by peak deconvolution algorithms. The distribution of these elements was determined by quantitative mapping "QMap" with binning of 16 spectra from 4 x 4 pixels. In addition, area spectra of major phases were extracted out of the database for standardless quantification.

Finally, spectroscopic phase analysis was carried out using the "Autophase" function. Here, similar chemically composed spectra/pixel were detected automatically and grouped into one component. Each component is displayed by one individual color in a phase map.

Results

Identification

Major elements such as boron, carbon, silicon and titanium can be easily detected in the sum spectrum of the complete analyzed area (Fig. 4a). The Maximum Pixel Spectrum reveals the presence of additional minor elements such as aluminum and oxygen. The deconvolution result of the Maximum Pixel Spectrum clearly indicates the presence of yttrium and tungsten (Figs. 4b–d).

Determination of all elements in the sample via Maximum Pixel Spectrum and deconvolution
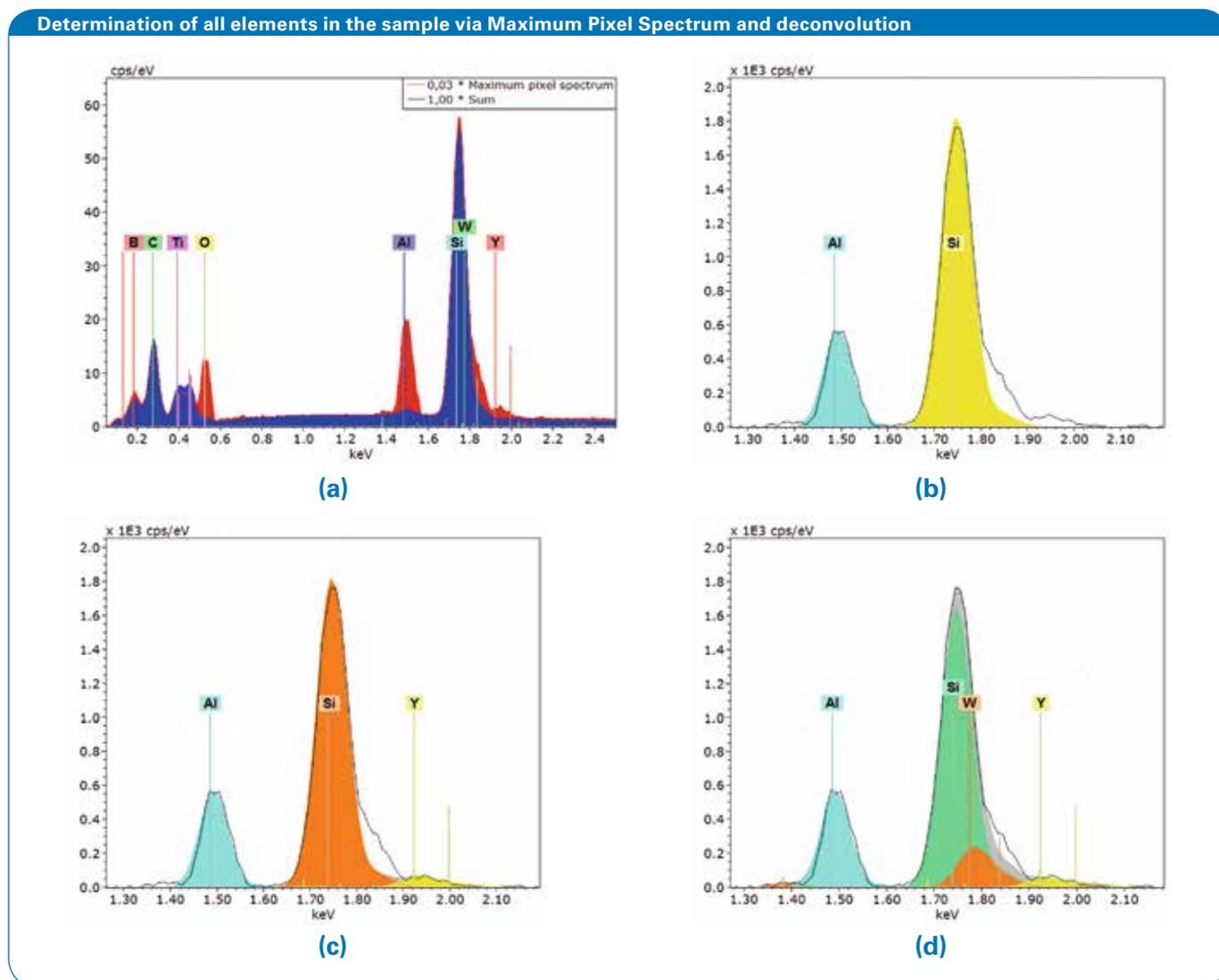
(a)

(b)

(c)

(d)

Fig. 4 (a): Comparison of the sum spectrum (blue) of the analyzed area and the Maximum Pixel Spectrum (red). Elements which are present only in a few pixels of the map cannot be displayed in the sum spectrum due to the low overall concentration but are clearly identifiable in the Maximum Pixel Spectrum. (b–d): Deconvolution result of the Maximum Pixel Spectrum with considerations of different elements (colored peaks). Deconvolution with aluminum and silicon only (b) shows a mismatch in the range of 1.8–2.0 keV and at 1.35 keV when compared to the background corrected Maximum Pixel Spectrum (black line). This indicates that not all element X-ray lines were correctly identified. The result with consideration of additional yttrium (c) fills the gap in the range of 1.9–2.0 keV. With consideration of additional tungsten (d), the grey area which is the sum of each deconvolved element matches the Maximum Pixel Spectrum in the range of 1.8–1.9 keV and also at 1.35 keV. The remaining small deviation at ~1.85 keV of the deconvolution result when compared to the Maximum Pixel Spectrum can be explained due to the fact that the Maximum Pixel Spectrum is not a normal area spectrum but synthesized from channel intensities of different pixels. Here, the intensity is not a true combination of both elements Si and W as these are not really present in the same pixel. Thus, the amount of W is underestimated in the deconvolution result producing the described deviation.

Peak intensity and quantitative element mapping

Integrated peak intensity maps display the distribution of the major constituents boron and carbon (Fig. 5a) as well as the enrichment of aluminum and yttrium as oxides at grain boundaries (Figs. 5b–d). The quantitative map (Fig. 6) shows the concentration of each element in false colors: Boron (Fig. 6a) is displayed by an orange color corresponding to 66.7 at.% (TiB_2), carbon (Fig. 6b) as well as silicon (Fig. 6c) appear in green color (50.0 at.%; TiC, SiC). The different stoichiometry for titanium (33.3 at.% in TiB_2 and 50.0 at.% in TiC) can be distinguished by their blue and green color (Fig. 6d). Tungsten-enriched inclusions (Fig. 6e) can be observed within titanium carbide. The accurate distinction of tungsten and silicon demonstrates the accuracy of the peak deconvolution model.

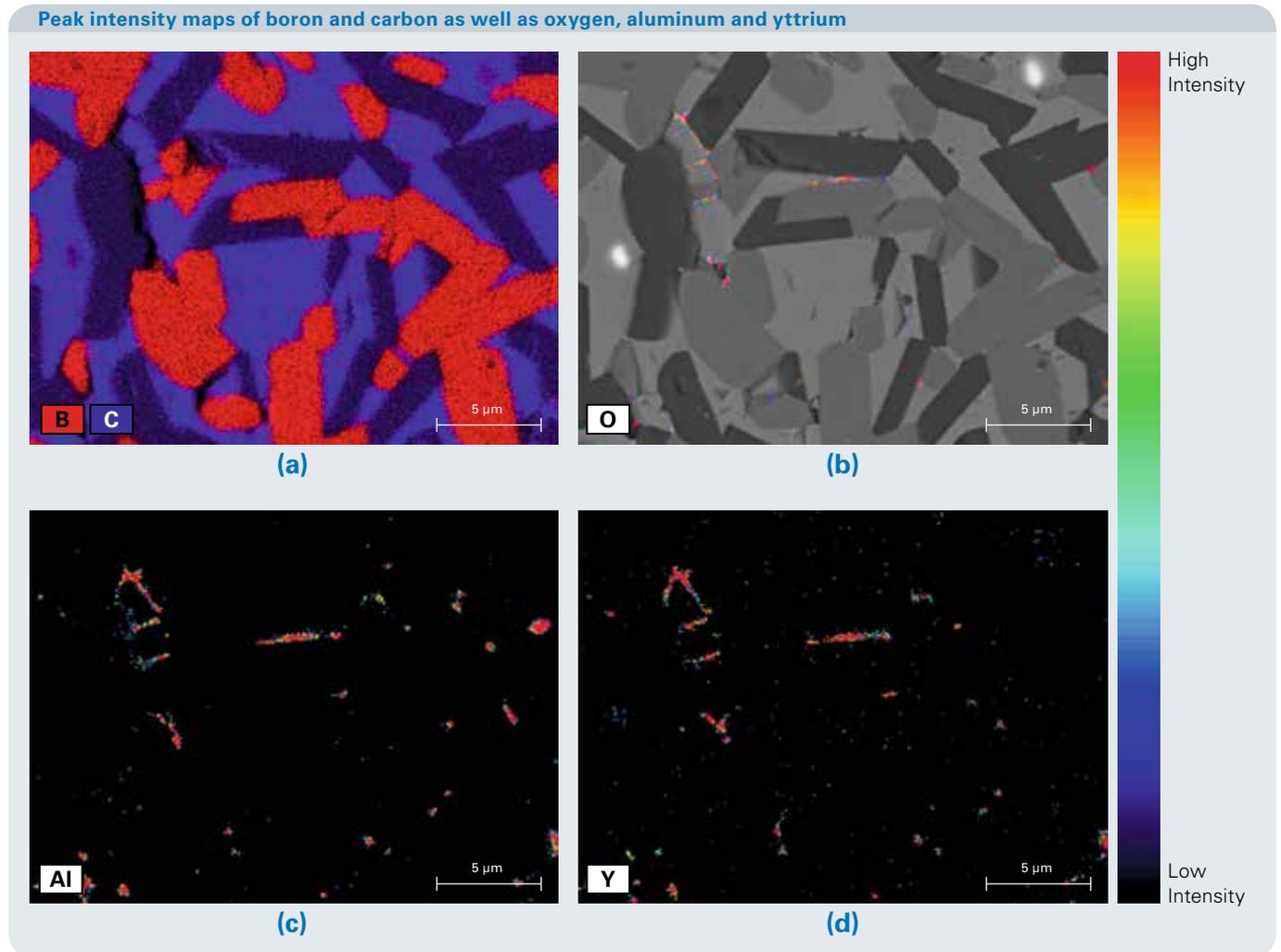**Peak intensity maps of boron and carbon as well as oxygen, aluminum and yttrium**

Fig. 5 Peak intensity maps of elements without peak overlaps. (a) Boron-K (red) and carbon-K (blue) are displayed as composite element maps. (b) Oxygen-K distribution shown in false color display overlaid with the BSE image, (c) aluminum-K and (d) yttrium-L. To avoid that the yttrium distribution is falsified by the overlap with the tungsten peak, a smaller peak area was used to display the yttrium intensity. The intensity scale on the right applies to the false color maps (b–d).

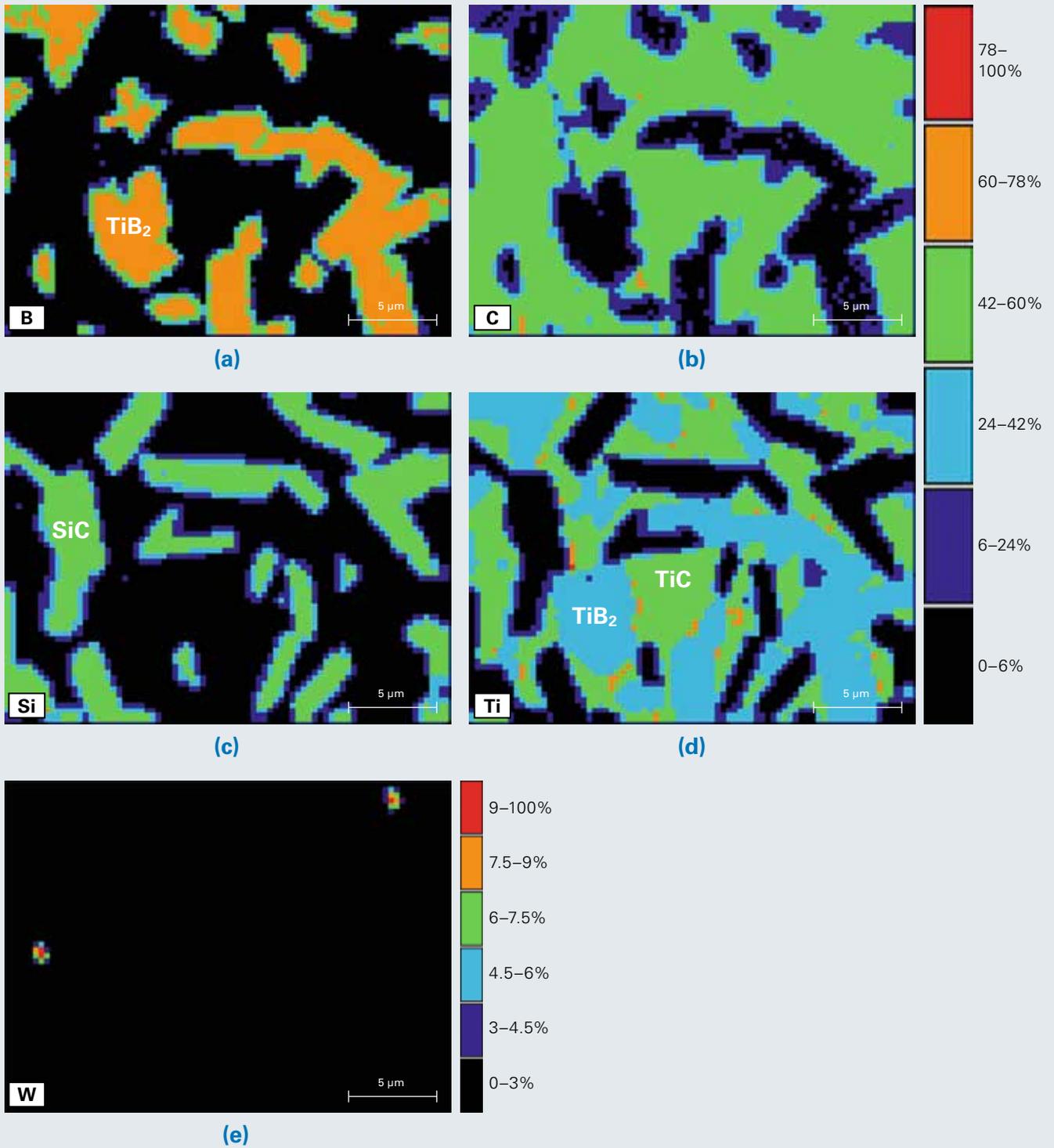**Quantitative maps of major constituents**

Fig. 6 Quantitative maps (at.%) of (a) boron, (b) carbon, (c) silicon, (d) titanium and (e) tungsten. Major phases are easily identifiable by comparing concentrations in the same regions in different quantitative maps – TiB_2, SiC and TiC have been labeled accordingly for easy reference.

Standardless quantification of area spectra

The mean values (Table 1) of representative areas consisting of 16 pixels (Fig. 7) for major phases are in good agreement with the expected stoichiometry. When compared to expected values, the deviation of the quantification result is <5 %. It has to be noted that 16 pixels of the map correspond to an integration time of only <0.5 sec and an impulse statistics of 5000–9000 counts in the complete spectrum.

Table 1 Expected, stoichiometric values (at.%) of major phases are compared to quantification results. Mean values and standard deviations were obtained by results of five different locations per phase, as shown in Fig. 7. The relative deviation is the difference between the quantification result and the expected, stoichiometric value. N.a. – not analyzed, n.d. – not detected.

Quantification results of major phases

	TiB_2 Expected	TiB_2 Measured	s /±at.%	Deviation /%	TiC Expected	TiC Measured	s /±at.%	Deviation /%	SiC Expected	SiC Measured	s /±at.%	Deviation /%
B	66.7	68.1	0.7	2.1	–	n.d.	–	–	–	n.d.	–	–
C	–	n.a.	–	–	50	49.8	1.2	-0.4	50	50.9	1.1	1.8
Ti	33.3	31.9	0.7	-4.2	50	50.2	1.2	0.4	–	n.d.	–	–
Si	–	n.d	–	–	–	n.d.	–	–	50	49.1	1.1	-1.8

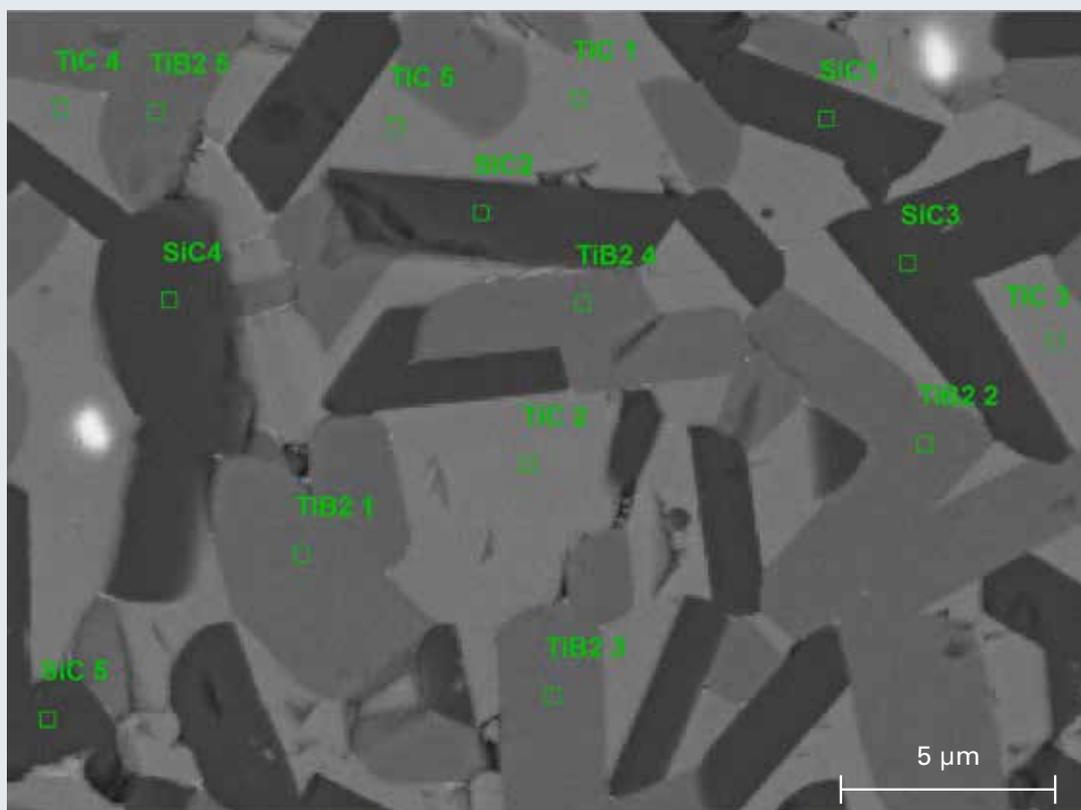### Measurement locations for quantitative analysis of major phases

Fig. 7 Areas of major phases (4x4 pixels) where spectra were extracted and quantified (Table 1).

Spectroscopic phase analysis

Chemically different components are shown in individual colors in the phase map (Fig. 8). Phase spectra clearly display the elements present in the major and minor phases (Fig. 9). The area fraction of each phase is shown in (Table 2). Yttrium aluminum oxides make up to 2.3 %, the tungsten carbide phase 0.3 % of the whole area.
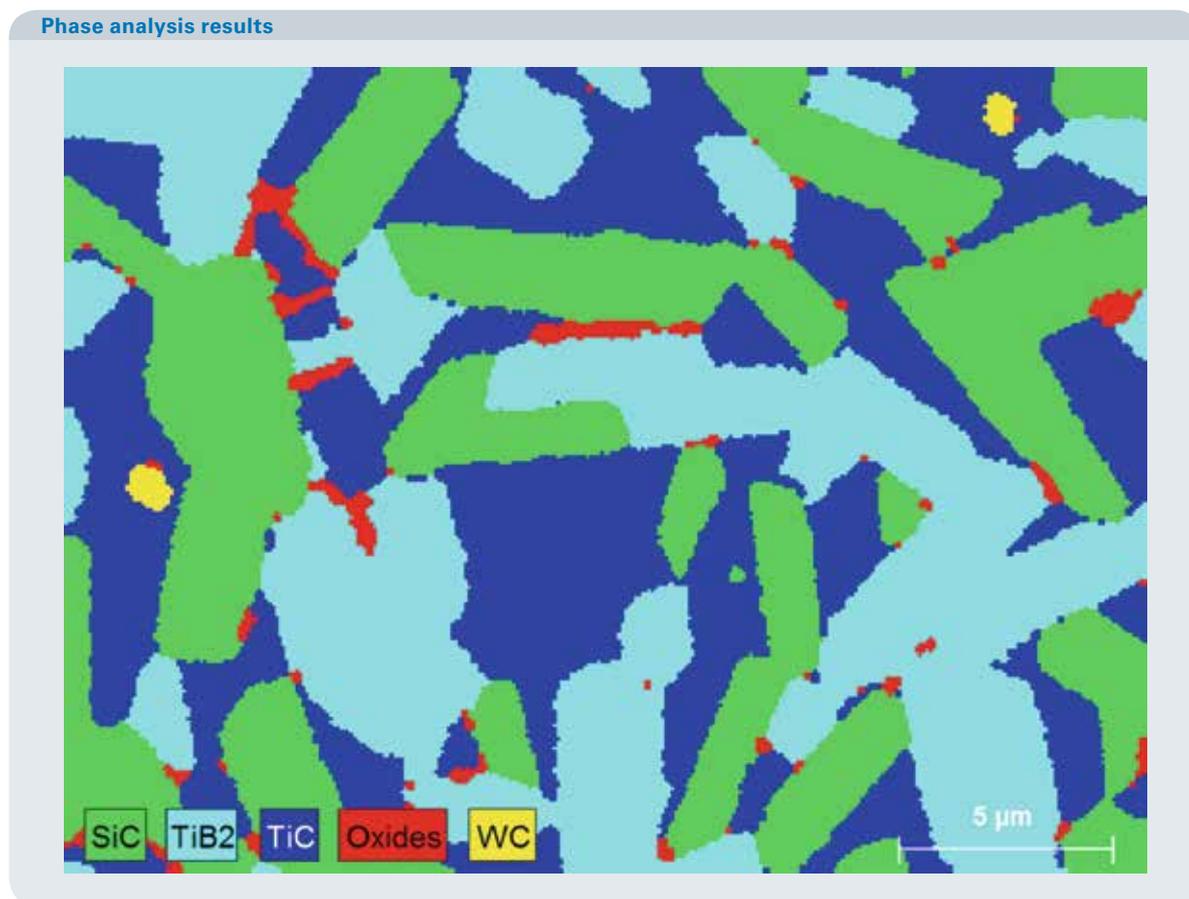
Phase analysis results

Fig. 8 Map showing the distribution of major and minor phases.
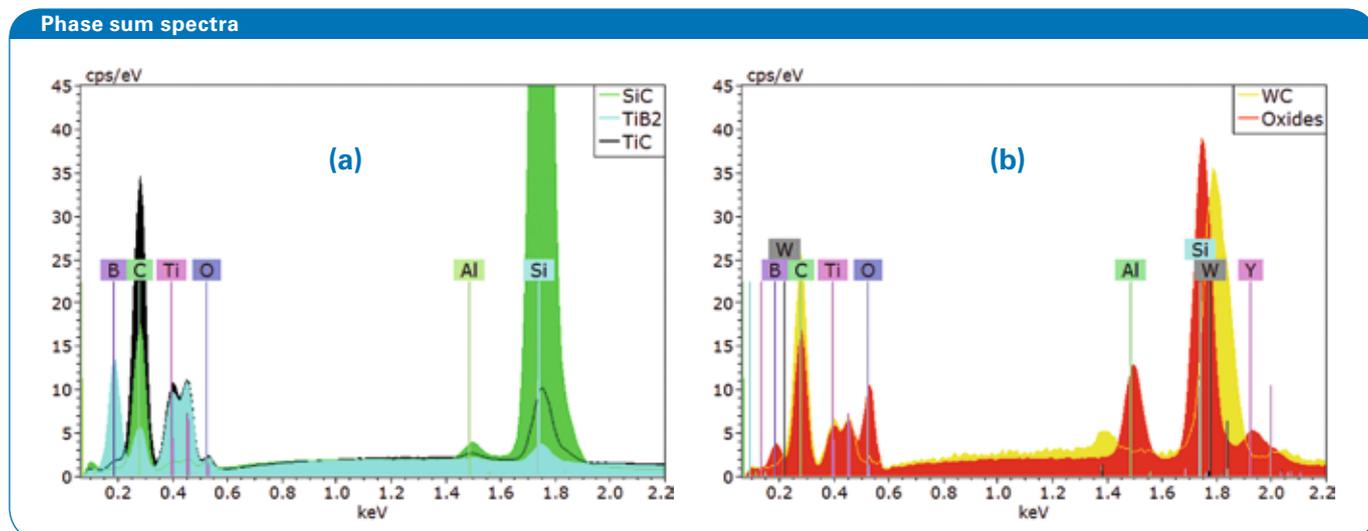
Phase sum spectra

Fig. 9 Sum spectra of (a) major boride and carbide phases and (b) minor yttrium-aluminum-oxide and tungsten carbide phases.

Conclusion

This analysis has demonstrated that state-of-the-art hardware in combination with modern data processing allows advanced spectral imaging also of light elements and low energy X-ray lines. Due to the unmatched light element performance of the XFlash® SD detector, the distribution of elements such as boron and carbon can be easily revealed by peak intensity maps.

Element identification can be significantly improved by the Maximum Pixel Spectrum. This function allows indentifying elements which are present in only a few pixels of the map. Peak deconvolution is a powerful tool for identification and discrimination of elements with overlapping lines (e.g. Si-K, W-L). The distribution of these elements can be shown in quantitative maps.

Even with low impulse statistics, area compositions of light elements can be accurately quantified. The impulse statistics of spectra can be improved by summing similarly composed areas using the "Autophase" function.

Literature

Bright, D.S. and Newbury, D.E. (2004). Maximum pixel spectrum: a new tool for detecting and recovering rare, unanticipated features from spectrum image data cubes, Journal of Microscopy, Vol. 216, Issue 2, pp. 186–193.

Author

Dr. Tobias Salge, Application Scientist EDS, Bruker Nano GmbH

Acknowledgements

The author would like to thank Dr. Rolf Wäsche and Dr. Dan Hodoroaba (BAM) for the hard material ceramics and Dr. Mathias Procop (IfG) for a stimulating discussion.

Table 2 Area fraction of major and minor phases.

Phases in sample			
Phases	**Area fraction /%**	**Area fraction /pixels**	**Area fraction /µm²**
SiC	33.1	25,404	162
TiB$_2$	32.4	24,889	159
TiC	31.9	24,490	157
Oxides	2.3	1,792	11
WC	0.3	225	1
Total	**100.0**	**76,800**	**489**

● **Bruker Nano GmbH**

Berlin · Germany
Phone +49 (30) 670990-0
Fax +49 (30) 670990-30
info.bna@bruker.com

www.bruker.com/quantax-eds-for-sem