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Characterization of Ancient and Modern Ceramics using EDS with Silicon Drift Detectors on SEM and TEM

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Introduction: The element analysis of small structures in ceramic material is relevant for both cultural heritage and advanced technology. The composition of thin electron transparent samples can be analysed in the nm-range using transmission electron microscopes (TEM) or, specific sample holders provided, in the field emission scanning electron microscope (FE-SEM). Nevertheless both methods often require complex sample preparation. An alternative method is to analyse bulk samples with a FE-SEM. In order to decrease the excitation volume for generated X-rays, low accelerating voltages (HV<10) are required. Consequently, only low to intermediate energy X-ray lines can be evaluated and many peak overlaps have to be deconvoluted since the high energy range is not available. Specific examples of both approaches will be discussed for SiAlON ceramic, dental metal-ceramic alloy, titanium based hard coatings on steel and medieval ottoman pottery.

Methods: A BRUKER Quantax EDS system with an XFlash® Silicon Drift Detector was used on a FE-SEM ZEISS Supra 55 VP, a HITACHI SU 6600 and on a JEOL JEM 2200FS STEM. EDS spectra were saved as individual point spectra and in spectrum images. To separate overlapping peaks, an extended atomic database [1] was used. For bulk samples, quantification was carried out using a truly standardless quantification routine without internal references.

Results: (A) Secondary triple junctions at SiAlON ceramic reveal that ytterbium was always found together with aluminium (Figure 1). It documents that EDS can be used to separate the overlapping Yb-M and Al-K lines in addition to other analytical TEM techniques, e.g. EFTEM-3 window and STEM-SI-EELS mapping [2]. The composition of the aluminium-rich triple junction phases effect the high temperature properties of SiAlON materials to be used as cutting tools.

(B) In a dental metal ceramic complex [3], the following elements were detected: O, Zn, Na, Al, Si, W, Y, Zr, Mo, K, Ca, Ba, Ti, Ce, Cr, Fe, Co, Ni. The depletion of chromium in the Cr-Co-alloy toward the opaque layer is associated with the formation of a chromium oxide layer ~0.15-1.5 µm in size (Figure 2). The opaque layer contains different minerals e.g. cerium oxide (Ce_2O_3), zirconium oxide (ZrO_2) and titanite ($CaTiSiO_5$). The controlled crystallisation of alumosilicates has relevance on the mechanical stability.

(C) Five titanium based hard coating samples (see Figure 3 as an example) reveal different compositions (Table 1). It indicates the presence of Ti_2C at sample 1, TiC at sample 5 and three different titanium carbonitride compositions at samples 2-4. The characterisation provides information on the tribological properties e.g. corrosion and diffusion barriers on steels.

(D) Lead glazed Anatolian pottery of the 14th to 15th century contains an interaction zone (Figure 4) between the body and the glaze. The formation of uniaxial potassium lead feldspar $Mg_{0.03}Ca_{0.04}Fe_{0.12}K_{0.35}Na_{0.17}Pb_{0.43}Al_{1.30}Si_{2.56}O_8$ and equiaxial copper ferrites $Cu_{0.46}Al_{0.26}Mg_{0.58}Fe_{1.71}O_4$ is indicated.

The results demonstrate that SDD-based EDS analysis in SEM and TEM contributes essential information on the microstructure of the investigated ceramics which helps to understand their macroscopic behaviour.

1. A. Aßmann and M. Wendt, Spectrochimica Acta Part B 58, p. 711-716.
2. H. Yurdakul and S. Turan, Anadolu University Journal of Science and Technology10-1, p. 67-78.
3. D. Pritzel, PhD thesis. Freie Universität Berlin, p. 118.

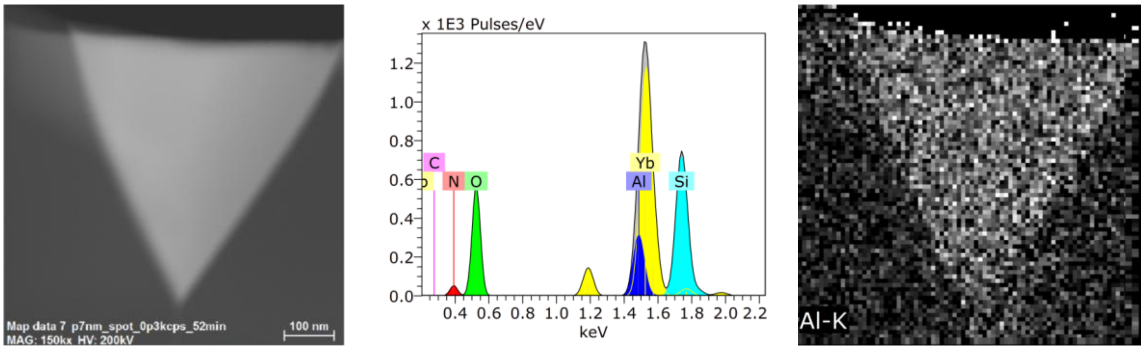

Figure 1. HAADF micrograph (left) showing a secondary triple junction in SiAlON ceramic. It contains aluminium and ytterbium as indicated by the deconvolution result (middle) and the net intensity map (right). 200 kV, 3 kcps.

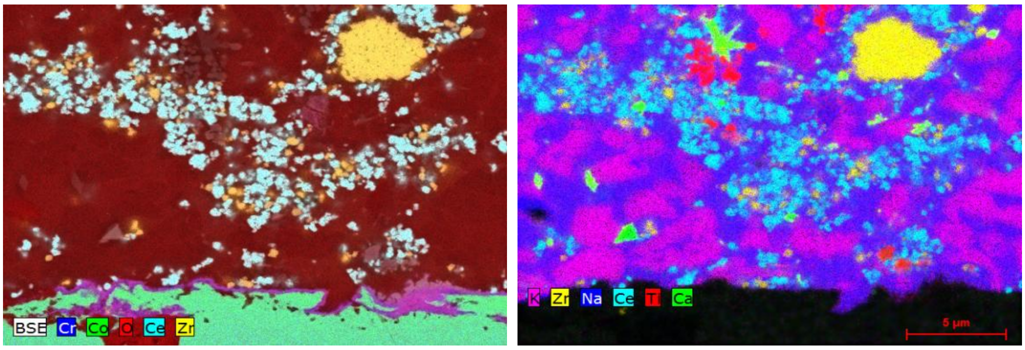

Figure 2. Composite intensity element map of a dental metal ceramic complex overlaid with a BSE micrograph (left) and without (right). 10 kV, ~25 kcps, 60 min, 42 nm pixel size.

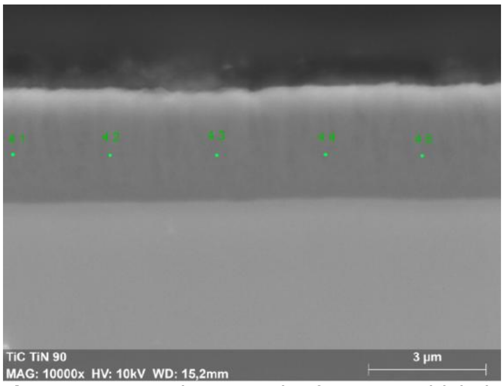

Figure 3. BSE micropgraph of a ~3 µm thick titanium carbonitride hardcoating with the locations where the point spectra were acquired.

Sample	C	N	Ti
1	32.9 ± 0.44	n.d.	67.1 ± 0.44
2	30.4 ± 0.83	13.0 ± 0.51	56.6 ± 0.41
3	17.1 ± 0.78	27.3 ± 0.52	55.6 ± 1.07
4	9.9 ± 0.19	37.3 ± 0.53	52.8 ± 0.44
5	(0.46 ± 0.52)	48.4 ± 0.44	51.2 ± 0.50

Table 1. Mean results (at.%, n=5) of titanium nitride, titanium carbide and titanium carbonitride. A carbon coating calibration function was applied in order to compensate the carbon intensity by coating and contamination. 10 kV, ~4.6 kcps, 20 s. n.d.: not detected.

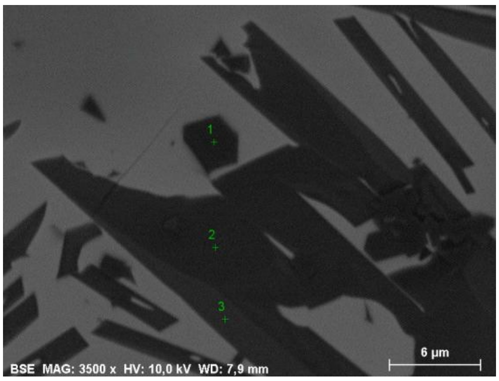

Figure 4. BSE micrograph of lead glazed pottery (10 kV, ~13 kcps, 700-900 s) with the locations where the point spectra were acquired.

Element	Series	Point 1	Point 2+3
SiO_2	K	44.0	n.d.
Al_2O_3	K	18.9	6.3
Fe_2O_3	K	2.7	64.9
MgO	K	0.4	11.2
CaO	K	0.6	n.d.
PbO	M	27.2	n.d.
CuO	L	n.d.	17.6
Na_2O	K	1.5	n.d.
K_2O	K	4.8	n.d.
Total		100.0	100.0

Table 2. Quantification results (mass.%) of the uniaxial potassium lead feldspar (point 1) and equiaxial copper ferrites (mean of point 2 and3) in lead glazed pottery. 10 kV, ~13 kcps, 700-900 s)