

FP Quantification of Thermal Barrier Ceramics by Micro-EDXRF

Introduction

Ceramic coatings are used to protect the underlying component material from damaging environmental conditions. Typical applications include corrosion-resistance (e.g. bio-implants), wear-resistance (e.g. cutting tools) and high temperature-resistance. Thermal Barrier Ceramics (TBC), an example of high temperature-resistant ceramic coatings, is used in high temperature environments to insulate the underlying substrate during temperature spikes. For example, transient elevated temperatures occur inside a jet engine during take-off. Manufactured products using thermal barrier ceramics include jet engine and land-based turbines, rocket engine and combustion chamber components, and automotive engines.

The TBC can be applied via plasma spraying, flame spraying or a variety of vapor deposition processes. The performance of a TBC derives from its chemical composition and microstructure which is influenced by deposition methodology and control parameters. Hence, it is of critical importance to characterize the deposition methodology and parameters with respect to the composition and microstructure of the resulting thermal barrier ceramic material.

In this application note, the EDAX Orbis Micro X-ray Fluorescence (Micro-XRF) Elemental Analyzer was used to determine the composition of a doped zirconia thermal barrier coating as deposited by a physical vapor deposition (PVD) reactor. Test substrate panels were placed in several positions throughout the PVD reactor in order to characterize the compositional homogeneity of the deposition as a function of deposition parameters and reactor design configuration.

Orbis Micro-XRF Elemental Analyzer

The Orbis uses a low-power X-ray tube and collimating or focusing optics to generate an X-ray beam. Multiple samples can be placed directly on the XYZ stage and positioned under the excitation/detection system for automated measurements. The X-ray detector is sealed with a Be window which allows for an elemental detection range from Na to U. The Orbis is an ideal tool for measuring the composition of ceramic materials including thermal barrier ceramics because:

- XRF is non-destructive and non-contact
- Little or no sample preparation is required
- Quantification can be accomplished using no standards or one standard depending on accuracy requirements
- Compositional variation on a single component can be measured automatically
- Compositional variation between individual components can be measured automatically

Experimental

For this study, the Orbis configuration was as follows:

- Rh tube (50 kV, 50 W)
- Polycapillary lens (< 30 μm spot size FWHM @ Mo(K α))
- 30 mm² Si(Li) detector

Test panels, reactor feedstock briquettes and briquette chips were placed directly on the sample stage. The TBC evaluated was a zirconium oxide doped with three oxides (A-oxide, B-oxide and C-oxide). We named the oxides A, B, and C to maintain the anonymity of our customer's sample. The main goal was to monitor compositional variation of the A-oxide in the TBC. The third oxide (C-oxide) is present only as an impurity. Feedstock briquettes are made by mixing the oxide powders in defined ratios, pressing the powder mixture and sintering. Compositional characterization of the briquettes via Scanning Electron Microscope-Energy Dispersive Spectroscopy (SEM-EDS) is subject to substantial variations due to the analytical beam size and the length scale of inhomogeneity of the sintered powder briquettes.

Sets of test panel substrates were positioned in the PVD reactor. Each set of panels was subjected to a TBC deposition conducted while varying one or more of the following reactor variables: feedstock, operating conditions, design configuration. Typical deposition conditions deposit 5 to 10 mils (125 μm to 250 μm) of TBC on the substrate. This deposition thickness is sufficient for XRF compositional analysis to be treated as a bulk analysis.

Compositional analysis was made under the following conditions:

- Tube power = 40 kV, 2.8 W
- Chamber atmosphere: Vacuum
- Detector resolution: < 145 eV for MnK α
- Analysis time per point: < 3 minutes
(Note: Analysis time could be reduced by further optimization of acquisition conditions.)
- FP Quantification
- Samples were analyzed “as is”, without preparation or treatment

Fundamental Parameter (FP) quantification was done using EDAX’s patented FP-XRF software which is the first software of its kind to account for the influences of capillary optics on the exciting spectrum for improved accuracy without standards. Fundamental Parameter quantification methods utilize atomic parameters and physics modeling to convert XRF intensities into composition. The advantage of FP quantification methods is that quantification can be achieved without type calibration standards or with a very limited set of type standards depending on the required accuracy. Even a single type standard can be sufficient. (A “type” standard is a standard which has the same base matrix and oxidative state as the unknown samples to be analyzed.)

Results and Discussion

Feedstock briquette ZrO-1 was selected to demonstrate accuracy of the standardless FP quantification, measurement repeatability and sample homogeneity. The briquette was measured 20 times in the same position and also one time at 20 different positions with the following quantification results.

The critical component in the TBC is A-oxide. The RSD of A-oxide due to measurement repeatability is approximately 1% from Table 1, while inhomogeneity in the raw briquette accounts for approximately 3% RSD out of the total 3.2% RSD

	A-oxide	B-oxide	C-oxide	HfO ₂	ZrO ₂
Average Wt%	26.10	11.76	0.34	1.78	60.03
Std. Dev.	0.23	0.14	0.03	0.07	0.14
RSD%	0.9	1.21	8.61	3.88	0.23

Table 1. FP standardless quantitative results for 20 repeat measurements at the same position on ZrO-1 briquette chip. Note that Hafnia is a natural impurity in Zirconia.

shown in Table 2. Thus, with a measurement beam size of nominally 40 μ m, it is possible to measure compositional variations in the feed briquettes due to material inhomogeneity. However, these small measurement variations were minor and acceptable for this study.

Table 3 shows the best possible quantification accuracy since the ZrO-1 standard calibration is being applied to quantify all the ZrO-1 measurements. Several spectral measurements from ZrO-1 were used to supply the FP quantification model with average intensities and known concentrations to account for sample inhomogeneity. But, only a single type standard, ZrO-1, was used for the calibration. Several other raw briquettes were measured using this ZrO-1 calibration (see Table 4).

	A-oxide	B-oxide	C-oxide	HfO ₂	ZrO ₂
Average Wt%	26.00	11.72	0.29	1.73	60.26
Std. Dev.	0.82	0.19	0.04	0.14	0.54
RSD%	3.16	1.59	12.45	7.96	0.89
Reported Wt%	24.54	10.95	0.14	1.45	62.82
Relative Accuracy %	5.93	7.04	110.48	19.5	-4.08

Table 2. FP standardless quantitative results for single measurements at 20 different positions on ZrO-1 briquette chip.

	A-oxide	B-oxide	C-oxide	HfO ₂	ZrO ₂
Average Wt%	24.64	11.15	0.14	1.52	62.55
Std. Dev.	0.79	0.18	0.02	0.12	0.54
RSD%	3.21	1.61	12.57	7.95	0.86
Reported Wt%	24.54	10.95	0.14	1.45	62.82
Relative Accuracy %	0.41	1.81	1.43	5.17	-0.42

Table 3. Reprocessed FP quantitative results from Table 2 using 6 of the spectral measurements in Table 2 as a standard reference for the quantitative routine.

Briquette		A-oxide	B-oxide	C-oxide	HfO ₂	ZrO ₂	Number of Measurements
ZrO-2	Average Wt%	32.67	9.46	0.18	1.34	56.35	1
	Reported Wt%	32.15	9.43	0.15	1.31	56.80	
	Relative Accuracy %	1.62	0.31	13.33	2.17	-0.79	
ZrO-3	Average Wt%	30.12	13.16	0.12	1.54	55.06	2
	Reported Wt%	29.14	13.35	0.14	1.47	55.79	
	Relative Accuracy %	3.37	-1.46	-14.82	4.86	-1.32	
ZrO-3 Repeat	Average Wt%	30.06	13.23	0.12	1.40	55.18	3
	Reported Wt%	29.14	13.35	0.14	1.47	55.79	
	Relative Accuracy %	3.17	-0.88	-16.56	-4.63	-1.10	
ZrO-4	Average Wt%	28.02	15.63	0.18	3.29	52.88	1
	Reported Wt%	27.53	15.63	0.16	2.92	53.68	
	Relative Accuracy %	1.78	0.00	9.52	12.48	-1.50	
ZrO-5	Average Wt%	24.97	11.27	0.09	2.24	61.43	2
	Reported Wt%	25.18	11.15	0.08	2.16	61.29	
	Relative Accuracy %	-0.82	1.05	2.17	3.85	0.23	
ZrO-5 Chip	Average Wt%	25.19	10.75	0.09	2.21	61.76	1
	Reported Wt%	25.18	11.15	0.08	2.16	61.29	
	Relative Accuracy %	0.06	-3.58	8.70	2.34	0.76	

Table 4. FP quantification measurements of several ceramic briquettes using the ZrO-1 calibration from Table 3 data. A repeat measurement of ZrO-3 was made on a different day. Measurements were made on the ZrO-5 briquette and a chip off the ZrO-5 briquette.

Relative accuracy of better than 3.5% was achieved for the A-oxide dopant, which was suitable for characterization of the deposition reactor. Sample inhomogeneity contributes to this value of relative accuracy since only three or fewer measurements were made on these briquettes. It should be noted again that samples were measured “as is” to allow for a rapid, non-destructive measurement.

The test panels used to characterize the deposition homogeneity within the reactor were approximately 15 mm wide and 100 mm long. To characterize the reactor at certain operating conditions, a set of 7 test panels were distributed at fixed positions throughout the deposition chamber. Each panel was held at one end. The panels within a set were numbered L1 through L7 depending on the location within the reactor.

Each set of test panels, numbered T1, T2, T3 and so on, represents a separate deposition run in the reactor. XRF measurements used to make comparisons between panels were made approximately 20 mm from the free end of the panel and 7.5 mm from the side of the panel.

Figure 1 shows a comparison of the A-oxide Wt% for different test panel sets. Panel Set T1 shows reasonable homogeneity except for the panel at location 1 (L1) with an overall relative variation of approximately 12%. Panel Set T3 shows a minimum at L4 while Panel Set T8 shows a maximum around locations 5 and 6 with both panel sets having an overall range of variation of roughly 10% relative.

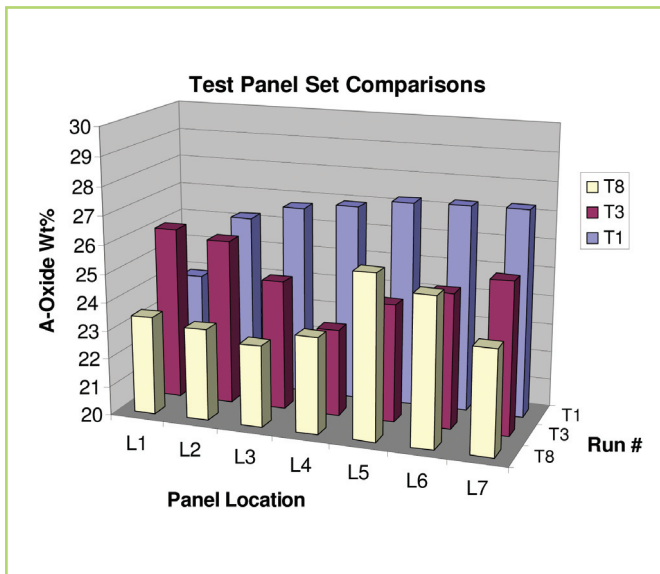


Figure 1. Comparison of A-oxide Wt% for 3 test panel sets, Trials 1, 3 and 8.

As the parts to be coated are roughly as long as the test panels, it was also decided to measure the compositional variation along the length of some of the test panels. Figure 2 shows the compositional variation of A-oxide and B-oxide along the length of 2 different panels, panel L2 of trial 3 and panel L3 of trial 1. For panel L2 of T3 shown in blue, the A-oxide wt% varies by roughly 20% relative, monotonically increasing over the length of the panel. The B-oxide wt% on the same panel decreases by roughly 15% relative over the same length. The L3 panel from trial 1, displayed in red, is more homogeneous with the A-oxide varying about 7% relative and the B-oxide varying by about 10% relative over the length of the panel.

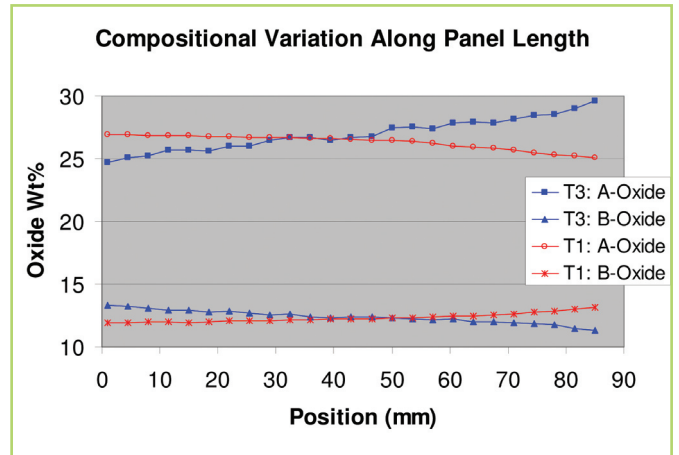


Figure 2. Compositional variation of A-oxide and B-oxide along the length of Panel 2 (L2) of Trial 3 (T3) in blue and panel L3 of Trial 1 (T1) in red. The free end of the panel starts at 0 mm. Measurements were stopped 1 mm before the end of the deposition region at the anchoring end of the panel.

Conclusions

The composition of thermal barrier ceramic material was successfully determined using EDAX's patented Fundamental Parameter quantification method. The ceramic material was measured without sample preparation or treatment to allow for a simple, rapid, non-destructive analytical procedure. Statistically significant compositional variations in the A-oxide wt% were found between the test panels and along the length of the test panels.

The Orbis micro-XRF unit is a useful tool to characterize the composition and homogeneity of protective ceramic coatings. Test panels and coated components can be mounted to the XYZ stage for automated sample positioning and analysis. EDAX patented FP quantification software can provide meaningful results without standards or with a calibration using a single type standard.