AXT Application Note

Correlative XRD and XRF Analysis of an Alumina Wear Tile

by

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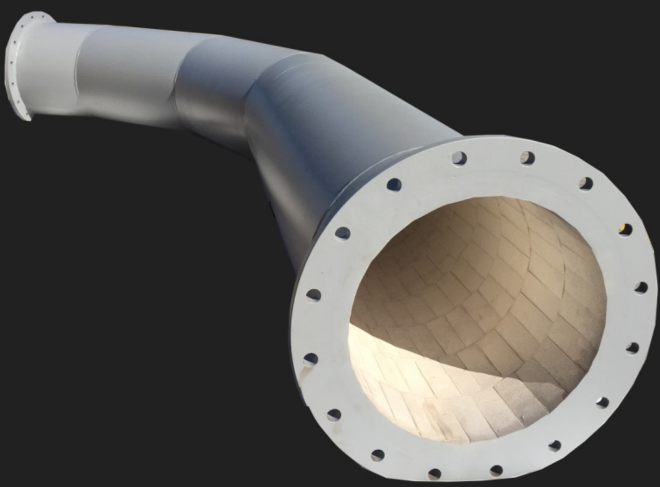

Rigaku

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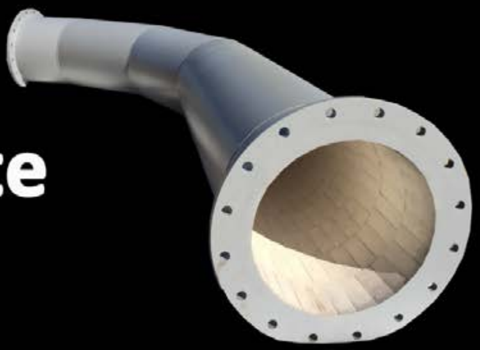

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Introduction

There are many applications where wear is a major problem such as in mineral processing, mining, coal and materials handling. In many of these applications hard metals and alloys including tool steels and tungsten carbides have been traditionally used but are not up to the task. As more advanced materials have come to the fore, engineering ceramics such as alumina (Al_2O_3) have demonstrated their ability to extend the life of wear surfaces, improve component life, reduce downtime and increase productivity.

Alumina is a very hard and wear resistant ceramic material as well as being chemically inert, electrically insulating and able to work at high temperatures. High purity, fully dense components with a uniform fine-grained microstructure take full advantage of alumina's beneficial properties. However, high purity raw materials can be expensive and require higher sintering temperatures. Hence, lower purity options are available. While they can offer a more economical alternative, there will be a compromise in performance.

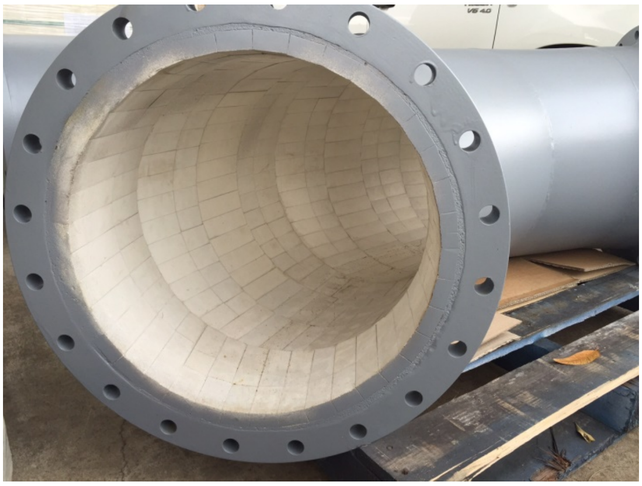

Figure 1. Alumina lined pipe.

Ceramic manufacturers are now able to produce tiles, components and even monolithic parts that are designed to operate in highly abrasive environments. Using processes such as isostatic pressing, they are able to achieve high density components that will provide excellent wear resistance.

In this application note, we examine a 92% alumina wear tile using X-ray diffraction (XRD) and X-ray fluorescence (XRF). We compare and contrast the results and show how these two analytical techniques can complement each other.

X-Ray Fluorescence (XRF)

XRF is a commonly employed analytical technique for the determination of chemical composition of solids, liquids, powders and coatings. As such, it is often used in the analysis of cement, oil, plastics, food, geological samples etc.

It is suitable for the detection of elements heavier than beryllium in most cases and has a detection limit of the order of parts per million. However, this is influenced by the particular element being measured and the quality of sample preparation.

X-Ray Diffraction (XRD)

XRD is a staple tool for phase identification in geology and materials science. It is commonly used to determine the modal composition of crystalline materials. In conjunction with databases such as the ICDD (International Centre for Diffraction Data) XRD can be a powerful tool for determining the composition of unknown materials.

For XRD analysis the sample is analysed in air with no complex and time-consuming sample preparation procedures. Modern advances in XRD instrumentation and software require only a few keystrokes and few minutes of measurement to generate a complete analysis.

To this end, the benchtop Rigaku Miniflex XRD instrument is an ideal solution offering good throughput, a comprehensive hardware/software package, compact size at an affordable price and ease of use making it ideal for operators of any experience level.

Experimental Methodology

Wear Tile

We acquired a commercially available 92% alumina wear tile, nominal dimensions 150 x 100 x 12mm. As the tile was very flat, it was simply cut into suitable sized pieces to fit into the XRD and XRF spectrometer.

X-Ray Fluorescence

The Supermini200 is the only sequential benchtop wavelength dispersive (WD) XRF spectrometer on the market. WDXRF instruments provide superior resolving power and hence more accurate results compared to energy dispersive (ED) XRF spectrometers. Its compact and thoughtful design eliminates the need for cooling water, while at the same time minimising space and power requirements.

It is also equipped with an air-cooled 200W X-ray tube and up to three analysing crystals (LiF200, PE and a synthetic multi-layer crystal for light elements) and two detectors (flow and scintillation detector). The instrument can analyse elements from oxygen to uranium.

Its compact size and 12 position sample carousel make it the ideal candidate for scenarios that require low to moderate throughput or as a backup for larger high throughput XRF's such as those used in critical production environments or testing/commercial labs.

Figure 2. The Rigaku Supermini200 WDXRF spectrometer with a 12 sample carousel (right)

The ZSX software provides users with high flexibility to set up calibrations for any type of material. The standard-less analysis program "SQX" is user friendly and can be used to quickly perform a qualitative and quantitative analysis of unknown samples without any selection and preparation of reference materials.

X-Ray Diffraction

The MiniFlex 600 is the most powerful benchtop XRD on the market and is capable of producing publication quality data. The instrument was used in the configuration as per Figure 3, except the single sample holder was used as the sample was too large for the ASC-6 sample holders.

Figure 3. Rigaku MiniFlex 600 benchtop XRD (left) with ASC-6 (6 sample multi-changer) and D/tex Ultra 250 high speed silicon strip detector (right).

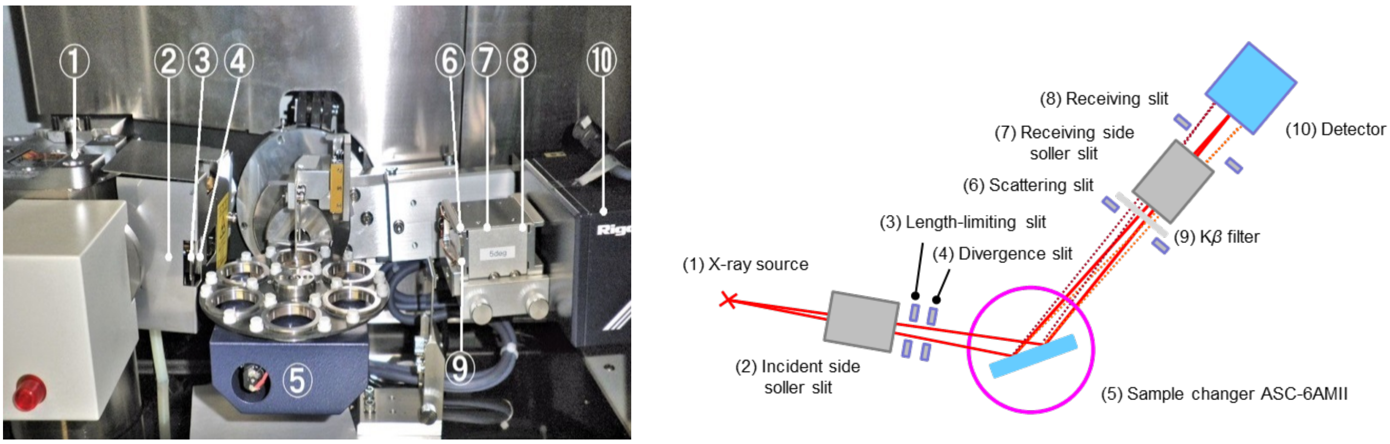

Figure 4. MiniFlex optical configuration.

The system comes with the Rigaku Guidance software that controls all operations and the configuration of the instrument. The PDXL software in conjunction with the ICDD *(International Centre for Diffraction Data)* PDF-4+ database of diffraction data was used to identify the phases present in the samples. Apparatus configuration and measurement conditions are provided in tables 1 and 2 respectively.

Table 1. Miniflex configuration.

Apparatus Configuration	
X-Ray source	Cu Kα (1.54186 Å)
Goniometer radius	150mm
Incident optics	
Divergent Slit	1.25°
Incident soller slit	Soller slit 2.5°
Length-limiting slit	10mm
Attachment	Single sample holder
Receiving optics	
Scattering slit	8mm
Receiving soller slit	Soller slit 2.5°
Receiving slit	13mm
Detector	
Detector	D/tex Ultra 250
Monochromator	Kβ filter

Table 2. Experimental measurement conditions.

Measurement Conditions	
Voltage-Current	40kV – 15mA
Scan axis	2θ / θ
Scan mode	Continuous
Scan range	10 – 80°
Scan Speed	2°/min
Step size	0.02°
Scan time	~37min

Note: This sample could be scanned much faster.

Results and Discussion

The XRF results are presented in Table 3. This shows that the alumina content of the tile was slightly above the specified 92%. The provided datasheet for the wear tile did not specify any other components apart from alumina.

Table 3. Quantitative XRF analysis of the alumina wear tile (mass %).

Component	Result
Na_2O	0.79
MgO	0.57
Al_2O_3	93.2
SiO_2	3.23
K_2O	0.15
CaO	1.46
TiO_2	0.10
Fe_2O_3	0.10
BaO	0.13
Other	0.27

XRD data is presented in Figure 5. XRD results indicated the presence of a number of phases, of which corundum (Al_2O_3) was the dominant phase as expected from the XRF results.

Identification of secondary phases was facilitated by access to the ICDD database. By importing this data from the Supermini200, the number of possible matches is vastly reduced, as any candidate that did not contain elements identified by XRF were immediately excluded.

To quantify the amount of each phase present in the tile, we performed a WPPF (Whole Powder Pattern Fitting) analysis. This yielded the data in table 4.

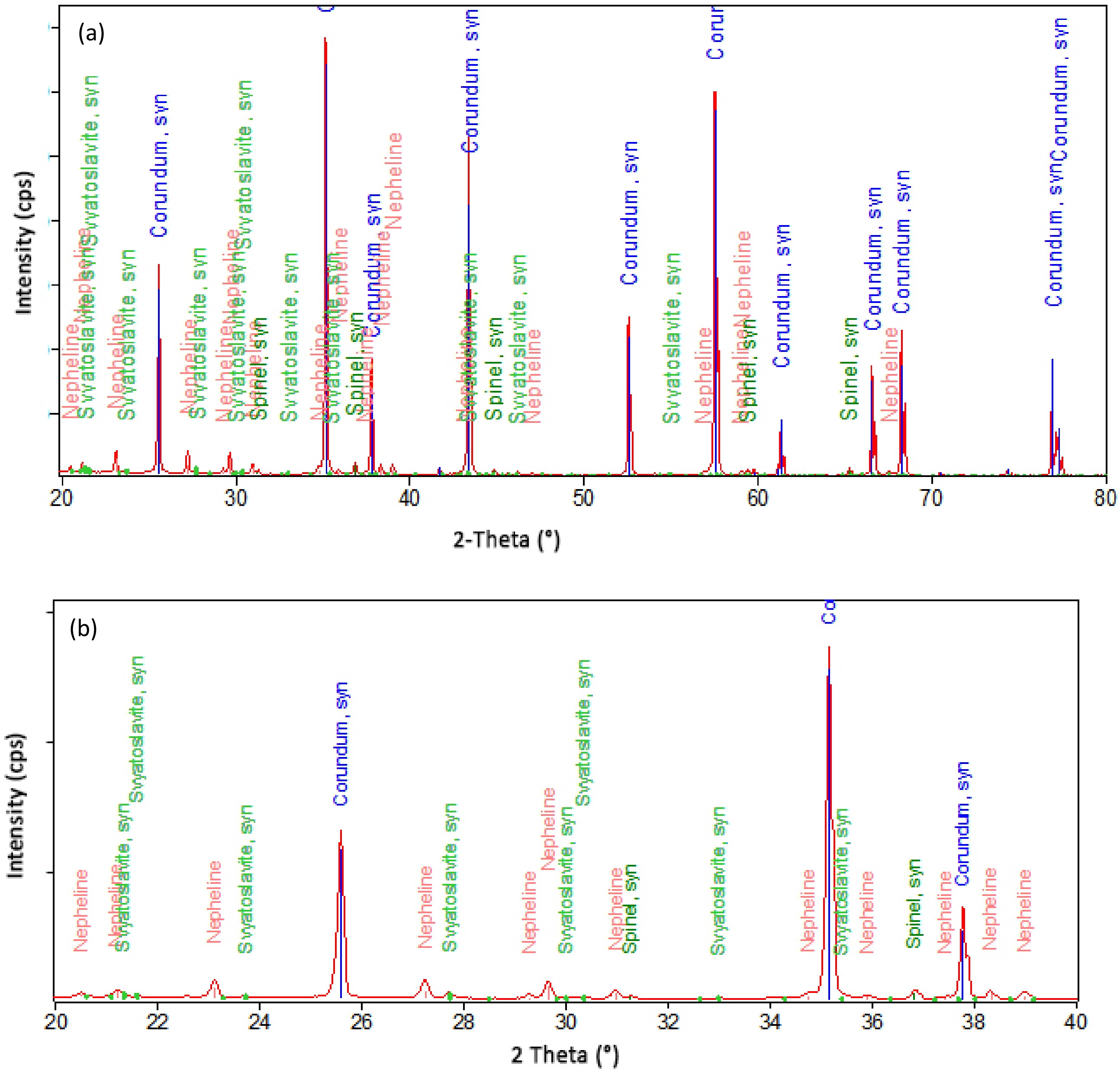

Figure 5. XRD patterns generated by the alumina wear tile (a) 20-80° 2θ and (b) the 20-40° 2θ regions.

Table 4. Quantitative analysis of the alumina wear tile using WPPF analysis of XRD data.

Phase	Formula	WPPF (%)	ESD
Corundum	Al_2O_3	91.5	0.22
Nepheline	$(Na,K)AlSiO_4$	5.54	0.16
Spinel	$MgAl_2O_4$	1.44	0.07
Svyatoslavite	$CaAl_2Si2O_8$	1.03	0.13

Based on the composition of each phase, the elemental composition was then calculated and results compared to XRF results (table 5).

Table 5. Comparison of XRF and oxides calculated from the XRD data (in mass %).

Component	XRF	XRD
Na_2O	0.79	0.52
MgO	0.57	0.57
Al_2O_3	93.2	94.2
SiO_2	3.23	3.80
K_2O	0.15	0.34
CaO	1.46	0.21
TiO_2	0.10	0.00
Fe_2O_3	0.10	0.00
BaO	0.13	0.00

In general there is good agreement between the two data sets.

XRD will only detect crystalline phases. While the recipe is proprietary, it is likely that raw materials are added to reduce the sintering temperature given that high purity alumina (99%+) sinters at around 1700°C. Reducing the sintering temperature is also important in keeping production costs down which is relevant in this case as high alumina raw materials are not cheap and these tiles sell for but a few dollars each. Furthermore, high density is important for the high wear environments where these tiles are employed. The data sheet supplied with this tile claims a water absorption rate of 0.02% and zero gas permeability indicating that close to no porosity is present.

In this case we detected the presence of nepheline $(Na,K)AlSiO_4$. Nepheline is often added as a flux to tiles, porcelains and semi-vitreous ware to reduce the melting temperature and would be useful in this case as it also contributes alumina[1]. The fact that some was present in the final composition indicates that it probably has not fully interacted with the main high alumina raw material which could be due to poor mixing, large particle size or insufficient exposure to high temperatures during sintering.

Spinel forms at high temperatures through a reaction between alumina and a magnesia bearing raw material[2]. Similarly, Svyatoslavite (a high-temperature Anorthite) is also formed at high temperatures[3].

XRF did detect the presence of very small amounts of TiO_2, Fe_2O_3 and BaO. XRD did not indicate their presence, probably because they were present in phases in concentrations too low to be detected by XRD.

Summary

XRD and XRF are excellent tools for characterising materials and minerals and are suitable for fundamental and high-end research, in both academia and industry. While XRD detects phases, XRF measures the chemical composition. Systems like the Supermin200 and MiniFlex are proven performers and despite their small size are capable of producing publication quality data.

XRD and XRF are complementary techniques. This application note illustrates how they can be used to generate complementary datasets. When the datasets are correlated, they show a high degree of consistency, reinforcing their accuracy.

In this particular application note, the analysis of the wear tile exceeded the specification of the datasheet. The datasheet did not provide much chemical information and the analyses performed in this study provide a more detailed picture of the chemical makeup of the tile.

Furthermore, using the two systems from Rigaku accelerates the analytical process. While XRD can be used to identify unknown materials, importing the results from the XRF into the XRD analytical software, the number of potential matches can be vastly reduced. This significantly reduces the time required to analyse diffraction patterns.

References

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3. Sokol E., Volkova N., and Lepezin G. 1998. Mineralogy of pyrometamorphic rocks associated with naturally burned coal-bearing spoil heaps of the Chelyabinsk coal basin, Russia. *European Journal of Mineralogy* **10**:1003–1014.

About the Authors

Dr. Cameron Chai

Cameron has a Ph.D in materials science and has hands on experience working with analytical techniques including XRD. He has an extensive list of publications including refereed journal papers and technical articles published in trade magazines and web portals. He has also presented at international conferences.

With over 25 years working in research and industry with numerous manufacturers and technologies, his broad knowledge enables him to understand the needs of a client and the solution required.

Dr. Stanislav Ulitzka

Stani is a mineralogist with more than 25 years of experience working with XRD, XRF and other complimentary technologies including sample preparation. He is well versed in these analytical technologies and has worked with instruments from all major manufacturers including Rigaku.

He regularly presents papers at AXAA conferences (Australian X-ray Analytical Association) and the Denver conference (2011). Stani is also available to conduct training on both XRD and XRF and can also help you develop analytical methodologies to suit your specific application.

About AXT

Established in 1992, AXT has grown to become the largest distributor of high end analytical instruments in Australia. They represent over 30 manufacturers from all over the world ranging from multi-nationals to small and innovative startups and primarily operate in the Australia and New Zealand territory. With complementary product lines. In the context of X-ray analysis this includes Rigaku (X-ray-based instrumentation) and the International Center for Diffraction Data, ICDD (suppliers of the JC-PDS powder diffraction database). For more details visit www.axt.com.au.