

# **ADVANCED CHARACTERIZATION OF SLAGS AND REFRACTORY BRICKS USING ELECTRON BACKSCATTER DIFFRACTION**

Final Report

*(for the period of March 1, 2006, through September 30, 2007)*

*Prepared for:*

AAD Document Control  
National Energy Technology Laboratory  
U.S. Department of Energy  
3610 Collins Ferry Road, MS 921-107  
PO Box 880  
Morgantown, WV 26507-0880

DOE Contract No. DE-FC26-98FT40320  
Performance Monitor: Rick Dunst

*Prepared by:*

John P. Kay  
Kurt E. Eylands

Energy & Environmental Research Center  
University of North Dakota  
15 North 23rd Street, Stop 9018  
Grand Forks, ND 58202-9018

## **DISCLAIMER**

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government, nor any agency thereof, nor any of their employees makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report is available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161; phone orders accepted at (703) 487-4650.

## **EERC DISCLAIMER**

**LEGAL NOTICE** This research report was prepared by the Energy & Environmental Research Center (EERC), an agency of the University of North Dakota, as an account of work sponsored by the U.S. Department of Energy (DOE). Because of the research nature of the work performed, neither the EERC nor any of its employees makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement or recommendation by the EERC.

## **SUBTASK 3. 14 – ADVANCED CHARACTERIZATION OF SLAGS AND REFRACTORY BRICKS USING ELECTRON BACKSCATTER DIFFRACTION**

### **ABSTRACT**

Numerous studies have been conducted to determine changes that occur in slag that cause a rapid change in viscosity, but these studies have been limited by the inability to characterize/identify the phases present in the slag. Rapid freezing of slag in entrained gasifiers and slagging combustion systems can cause a shutdown of the system. The reactions occurring in slag that result in rapid freezing of slags are not well understood. It is believed that electron backscatter diffraction (EBSD) can be used to analyze slags and aid in their characterization although its use has not been found in literature. The EBSD technique allows particle-by-particle mineralogy based on diffraction patterns generated by the electron beam when the sample is tilted to a high angle. The diffraction pattern (Kikuchi bands) can only come from crystalline phases, which makes this technique ideally suited to study crystal formation in slags where oftentimes the crystals are very small and a reasonable chemical analysis cannot be made by conventional energy-dispersive spectrometry (EDS) methods in the scanning electron microscope. The ability to have mineralogical data based on the crystalline structure of a phase rather than a chemical analysis by EDS allows much better interpretation of the temperature regimes in which specific phases tend to form. Knowing the type and relative amounts of a phase crystallizing in a slag is critical in predicting the viscosity of a slag at a given temperature.

Six slag samples were selected based on the parent coal. Unfortunately, none of the slags appeared to have any crystalline material associated with them. The funding for this project was not adequate for generating more slags from the various coal types. For this reason, sample archives were searched for those containing slags that were not rapidly quenched. A slag from a bituminous coal was found to contain several dendritic crystals (10  $\mu\text{m}$  to 50  $\mu\text{m}$  in size) that formed near the edges of the slag. Analysis of these crystals identified the crystalline phase epidote –  $\text{Ca}_2\text{Al}_2\text{O}(\text{Al}, \text{Fe}^{3+})\text{OH}(\text{Si}_2\text{O}_7)(\text{SiO}_4)$ . The identification could not have been performed from EDS alone because of Ca deficiency. However, looking at the crystal structure combined with EDS shows that the phase present is a Ca-deficient epidote. From this information, a temperature range of formation was determined. This gives a good example of the additional clarity that can be derived from utilizing EBSD.

Evaluation of corrosion products by EBSD at the refractory brick and slag interface did reveal penetration and corrosion of slag into the brick through examination of crystalline phases alone. The degree of corrosion was dependent on the type of refractory and chemical makeup of the slag.

This technique has not been used before to analyze slags and slag/refractory interactions. More work needs to be performed to better utilize EBSD for this type of analysis. This project demonstrates that the method is a valid technique that can be used to characterize slags and their interactions with refractory materials.

## TABLE OF CONTENTS

LIST OF FIGURES .....	ii
LIST OF TABLES .....	ii
EXECUTIVE SUMMARY .....	iii
INTRODUCTION .....	1
EXPERIMENTAL .....	3
RESULTS .....	4
Slag Samples .....	4
Crystalline and Amorphous Phases .....	9
Refractory Samples .....	11
CONCLUSIONS .....	13
REFERENCES .....	14

## LIST OF FIGURES

1	Schematic of the EBSD system.....	2
2	Slag polished with diamond paste.....	5
3	Slag polished on the vibratory polisher for several hours.....	5
4	A slag derived from an acidic coal with no crystallization near the edges.....	6
5	A slag derived from a basic coal with no crystallization near the edges.....	6
6	Dendrites formed in a slag.....	7
7	The diffraction pattern from the dendritic phase that crystallized during the quenching of the slag.....	8
8	The solution or match by the software for the dendritic crystals.....	8
9	Amorphous and crystalline material in the matrix with large white hematite crystals.....	9
10	The backscatter diffraction patterns generated at each of the points from Figure 9.....	10
11	The interface between a chrome oxide aggregate (lower half of image) and slag (upper half of image).....	11
12	An aggregate grain of alumina surrounded by crystals of pyroxenes.....	12

## LIST OF TABLES

1	Chemistry by EDS Results for Dendrites in Figure 6.....	9
2	Chemical Compositions of the Points in Figure 9.....	9

## **SUBTASK 3. 14 – ADVANCED CHARACTERIZATION OF SLAGS AND REFRACTORY BRICKS USING ELECTRON BACKSCATTER DIFFRACTION**

### **EXECUTIVE SUMMARY**

Numerous studies have been conducted to determine changes that occur in slag that cause a rapid change in viscosity, but these studies have been limited by the inability to characterize/identify the phases present in the slag. The reactions occurring in slag that result in rapid freezing of slags are not well understood. Electron backscatter diffraction (EBSD) provides the opportunity to better understand the crystallization, phase immiscibility, nucleation, and transformations that occur in high-temperature slag.

Analyzing the corrosion products on and within a refractory specimen once it has been exposed to molten slag is an important step in understanding what needs to be done to improve the quality of the refractory. The actual chemical phases present and their effect on the refractory, the depth of penetration into the refractory, and the location, whether it is localized or distributed equally throughout the refractory, need to be thoroughly understood. In order to determine the reactions taking place between the slag and refractory, the crystalline and amorphous phases, and their locations, a method such as EBSD must be utilized.

EBSD has been used predominantly in metallurgy, texture measurements, and grain orientation measurements. This technique has never been utilized in the characterization of slag; however, it is believed that EBSD provides one of the best opportunities to better understand the crystallization, phase immiscibility, nucleation, and transformation that occur in high-temperature slag. The EBSD technique allows particle-by-particle mineralogy based on diffraction patterns generated by the electron beam when the sample is tilted to a high angle. The diffraction pattern (Kikuchi bands) can only come from crystalline phases, which makes this technique ideally suited to study crystal formation in slags, where oftentimes the crystals are very small and a reasonable chemical analysis cannot be made by conventional energy-dispersive spectrometry (EDS) methods in the scanning electron microscope (SEM). Chemical analysis by EDS collects an x-ray spectrum that is generated from the surface of the sample to a depth of 3 to 4  $\mu\text{m}$ . Very small crystals, such as dendritic crystals formed during rapid quenching of a slag, are often masked by the x-rays generated from the matrix in which they crystallized. Because EBSD uses the diffraction pattern to determine the mineralogy, there is no signal from the amorphous matrix and only the crystalline material is represented in the analysis. When a specific mineral phase is identified, the temperature regime in which it formed can often be inferred.

Six slag samples were selected based on the parent coal. The slags were prepared by melting ash derived from various coals and then quenched on a large brass plate. Unfortunately, none of the slags appeared to have any crystalline material associated with them. The funding for this project was not adequate for generating more slags from the various coal types. For this reason, sample archives were searched for those containing slags that were not rapidly quenched.

A slag from a bituminous coal was found to contain several dendritic crystals that formed near the edges of the slag. These dendrites form from large temperature differentials between the molten slag and the quenching medium. Because of the small size of the dendritic crystals, chemical analyses by SEM always include the matrix in which the dendrites occur, and the contribution to the x-ray signal is unknown. The crystalline phase was identified by EBSD as the mineral epidote –  $\text{Ca}_2\text{Al}_2\text{O}(\text{Al}, \text{Fe}^{3+})\text{OH}(\text{Si}_2\text{O}_7)(\text{SiO}_4)$ . Examination by EDS chemical analysis alone would not have yielded this result because of the deficiency of Ca. However, looking at the crystal structure combined with EDS shows that the phase present is a Ca-deficient epidote. From this information, a temperature range of formation was determined to be between 630° and 650°C. This gives a good example of the additional clarity that can be derived from utilizing EBSD.

Evaluation of corrosion products by EBSD at the refractory brick and slag interface showed that there were penetrations of both Si and Al into the refractory brick matrix as well as metal oxide migration from the brick into the slag. The degree of corrosion was dependent on the type of refractory and chemical makeup of the slag. Refractory brick high in Al appeared to be corroded readily by slags with a high Fe content. A Cr-rich brick tended to have less corrosion, with less of the Fe and Si phases penetrating into the brick as compared to the Al-rich refractory brick.

The ability to have mineralogical data based on the crystalline structure of a phase rather than a chemical analysis by EDS alone allows much better interpretation of the temperature regimes in which specific phases tend to form. Knowing the type and relative amounts of a phase crystallizing in a slag is critical in predicting the viscosity of a slag at a given temperature.

This technique has not been used before to analyze slags and slag/refractory interactions. More work needs to be performed to better utilize EBSD for this type of analysis. This project demonstrates that the method is a valid technique that can be used to characterize slags and their interactions with refractory materials.

## **SUBTASK 3.14 – ADVANCED CHARACTERIZATION OF SLAGS AND REFRACTORY BRICKS USING ELECTRON BACKSCATTER DIFFRACTION**

### **INTRODUCTION**

Numerous studies have been conducted to determine changes that occur in slag that cause a rapid change in viscosity, but these studies have been limited by the inability to characterize/identify the phases present in the slag. Rapid freezing of slag in entrained gasifiers and slagging combustion systems can cause a shutdown of the system. The reactions occurring in slag that result in rapid freezing of slags are not well understood. This phenomenon of slag freezing is typically determined by a physical measurement using a slag viscometer. In the viscosity vs. temperature curves generated from measurements, the rapid increase in viscosity is known as the temperature of critical viscosity ( $T_{cv}$ ). At temperatures below this, the slag is thought to rapidly crystallize and cause rapid slag buildup in slagging gasification as well as combustion systems. Electron backscatter diffraction (EBSD) provides the opportunity to better understand the crystallization, phase immiscibility, nucleation, and transformations that occur in high-temperature slag. This will lead to 1) a better understanding of slag properties; 2) better identification of unreacted, partially reacted, reacted, and immiscible phases; 3) direct evidence of liquid phase responsible for slag flow behavior; 4) direct verification of crystalline and amorphous phases; and 5) a valuable forensic tool to aid in the determination of fuel quality and performance impacts.

Analyzing the corrosion products on and within a refractory specimen once it has been exposed to molten slag is an important step in understanding what needs to be done to improve the quality of the refractory. Current capabilities for understanding the basic chemistry of the resulting corrosion products are not adequate. The actual chemical phases present and their effect on the refractory, the depth of penetration into the refractory, and the location, whether it's localized or distributed equally throughout the refractory, need to be thoroughly understood. In order to determine the reactions taking place between the slag and refractory, the crystalline and amorphous phases, and their locations, a method such as EBSD must be utilized.

EBSD, also known as Kikuchi diffraction, is a technique developed in the 1980s at Bristol University and improved in the 1990s at Yale University. The system is composed of a detector, essentially a digital camera charged coupled device (CCD) chip, placed behind a phosphor screen and interfaced with a scanning electron microscope (SEM). The EERC operates a JEOL 5800 SEM that was used for the initial EBSD designs. The technique is performed in the SEM by tilting the flat, highly polished sample surface to a shallow angle, usually approximately 20 degrees to the incident electron beam. The electron beam is then diffracted by the crystal lattice of the sample. The diffracted beam is intercepted by the phosphor screen, which converts the diffracted electrons into a light pattern composed of Kikuchi bands that is recorded by the CCD (1). A schematic of the system is shown in Figure 1. Just as in powder x-ray diffraction (XRD), these patterns are unique for every crystalline phase. Computer software then compares this pattern to a known database and thus identifies,

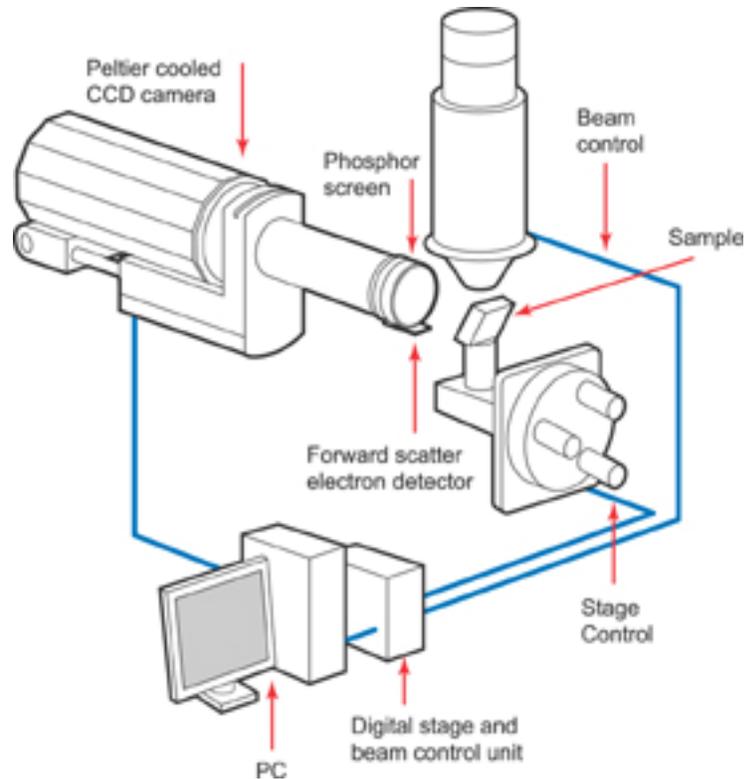


Figure 1. Schematic of the EBSD system.

or indexes, the crystalline phase. Over the past 5 years, the speed of identification has increased from a few patterns per second to over 100 patterns per second. This allows the indexing of multiple points quickly over an area producing maps that can include information such as grain orientation and residual stress.

This technique has a huge advantage over powder XRD in that the sample can be analyzed for morphology and chemical composition in conjunction with crystalline phase identification without removing the sample from the SEM. Also, powder XRD requires a fairly large powdered sample, whereas EBSD can be performed over large areas with possible resolutions equal to the SEM, with a JEOL 5800 down to 0.8  $\mu\text{m}$ , without destroying the sample. The EBSD technique has grown into an essential SEM tool for material scientists over the last 8 years and is becoming an expected form for data gathering and presentation among peers.

Previous work conducted to determine the changes that occur in slag that cause the rapid change in viscosity have been limited by the ability to characterize/identify the phases present in the slag. Rapid freezing of slag in entrained gasifiers and slagging combustion systems can cause a shutdown of the system. The reactions occurring in slag that result in rapid freezing of slags are not well understood. This phenomenon of slag freezing is typically determined by a physical measurement using a slag viscometer. Crystallization of slag due to a decrease in temperature alters the linear relationship expected when a slag behaves as a

glass. On a viscosity vs. temperature curve, the point at which the straight-line slope (linear glasslike behavior) displays a sharp change is the point at which the viscosity rapidly increases and is known as the temperature of critical viscosity ( $T_{cv}$ ) (2). At temperatures below this, the slag is thought to rapidly crystallize and cause rapid slag buildup in gasification as well as combustion systems. Successful analysis requires that the crystallization of the slag be better understood and the phases formed be more easily identifiable.

Analyzing the corrosion products on and within a refractory specimen once it has been exposed to molten slag is an important step in understanding what needs to be done to improve the quality of the refractory. Current capabilities for understanding the basic chemistry of the resulting corrosion products are not adequate. The actual chemical phases present and their effect on the refractory, the depth of penetration into the refractory, and the location, whether it is localized or distributed equally throughout the refractory, need to be thoroughly understood. In order to determine the reactions taking place between the slag and refractory, the crystalline and amorphous phases, and their locations, a new method must be utilized.

EBSD has been used predominantly in metallurgy (3), texture measurements, and grain orientation measurements (4). This technique has never been utilized in the characterization of slag; however, it is believed that EBSD provides one of the best opportunities to better understand the crystallization, phase immiscibility, nucleation, and transformation that occur in high-temperature slag. Successful implementation would lead to 1) a better understanding of slag properties, 2) better identification of unreacted, partially reacted, reacted, and immiscible phases, 3) direct evidence of liquid phase responsible for slag flow behavior, 4) direct verification of crystalline and amorphous phases, and 5) a valuable forensic tool to aid in the determination of fuel quality and performance impacts.

## **EXPERIMENTAL**

Slag and ceramic samples were selected, prepared, and examined using EBSD. The slags consist of material derived from bituminous, subbituminous, and lignite coals. The bituminous slags were defined as either basic or acidic slag based on the weight percent ratio of basic oxides  $Fe_2O_3 + CaO + MgO + K_2O + Na_2O$  and acidic oxides  $SiO_2 + Al_2O_3 + TiO_2$ . A base-to-acid ratio of 0.4 is considered acidic, and above that is considered basic. Slag samples associated with ceramics were also examined to determine if phase changes occur near the slag/ceramic boundary that incorporates elements from both the slag and ceramic material. Samples were prepared by mounting them in epoxy, cutting them with a diamond saw to expose a cross section and then polishing the sample surface, with the final grit being a 0.5  $\mu m$  diamond polish. Duplicate samples were made with conductive epoxy and polished for several hours on an automated vibratory polisher.

Traditionally, samples to be examined by SEM methods need to be carbon coated to dissipate the static charge that develops on the sample surface by the electron beam. Carbon coating completely obliterates the diffraction pattern so no coatings can be used. A small

amount of air must be allowed to enter the sample chamber of the SEM in order to dissipate the surface charging. Environmental or low-vacuum SEMs are ideally suited for EBSD.

Sample preparation is an extremely important step in obtaining reliable data by EBSD. Little difference was noted for the various epoxies, which include Buehler Epo-Kwick, Buehler Epo-Thin, Buehler Epo-Color, Allied EpoxySet, and Allied EpoxyMount. Conductive filler can be added to any of the epoxy mounting resins. Little difference was noted when the conductive filler was used with any of the resins.

The final polish was found to be a critical step in obtaining EBSD patterns. Samples that were prepared with the diamond polish rarely produced usable diffraction patterns. Those patterns tended to be very faint with few visible lines. The same samples put on the automated vibratory polisher for several hours produced excellent diffraction patterns in the crystalline material with several clearly visible lines and nodes. Figure 2 shows a sample polished with diamond paste and a poor diffraction pattern, and Figure 3 shows a slag sample polished on the vibratory polisher for several hours where the diffraction pattern is much clearer for a more reliable analysis.

## **RESULTS**

### **Slag Samples**

Six slag samples were selected based on the parent coal. The slags chosen were used in a previous project and were well characterized as to their chemical composition. The slags were prepared by melting ash derived from various coals and then quenched on a large brass plate. Unfortunately, none of the slags appeared to have any crystalline material associated with them. Figures 4 and 5 show an acidic and basic slag but are completely amorphous. Slags allowed to cool on their own tend to get crystallization near the edges where there is a large temperature differential and cooling is just slow enough to allow the migration of some elements such as Fe. In both Figures 4 and 5, the large, featureless grains are the slag, and the darker material with the white crystals is the conductive mounting epoxy. The small white particles are copper filings added to the epoxy as filler material. The funding for this project was not adequate for generating more slags from the various coal types. For this reason, sample archives were searched for those containing slags that were not rapidly quenched.

A slag from a bituminous coal was found to contain several dendritic crystals that formed near the edges of the slag. These dendrites form from large temperature differentials between the molten slag and the quenching medium. Because of the small size of the dendritic crystals, chemical analyses by SEM always include the matrix in which the dendrites occur and the contribution to the x-ray signal is unknown. Using EBSD, the dendritic crystals form a diffraction pattern and the amorphous matrix in which they occur forms no pattern, meaning that the analysis is for the crystals only.

Figure 6 is a backscattered SEM image showing dendrites forming in the glass near the edges of the sample. The small black cross on the dendrites just down and left of the center

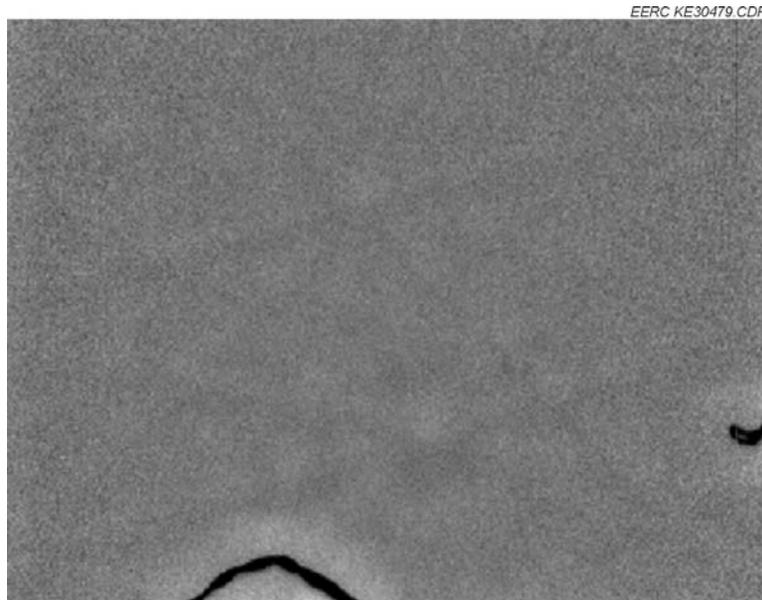


Figure 2. Slag polished with diamond paste.

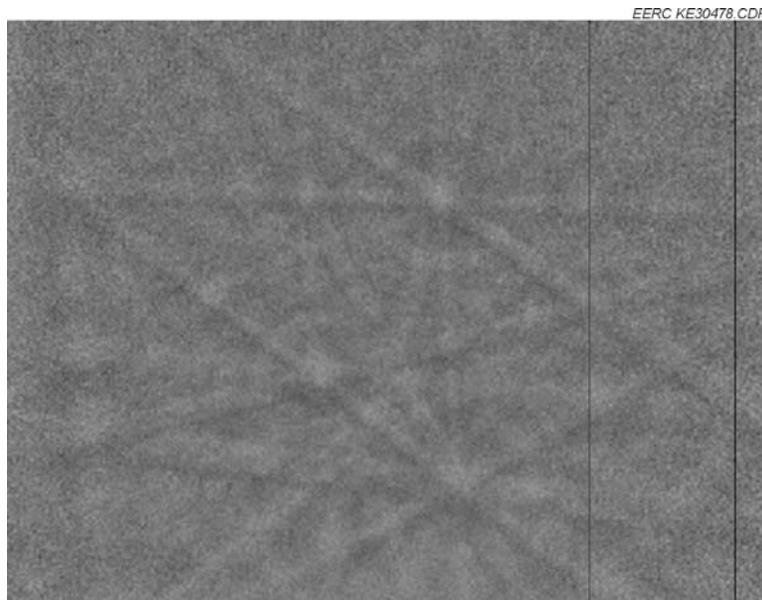


Figure 3. Slag polished on the vibratory polisher for several hours.

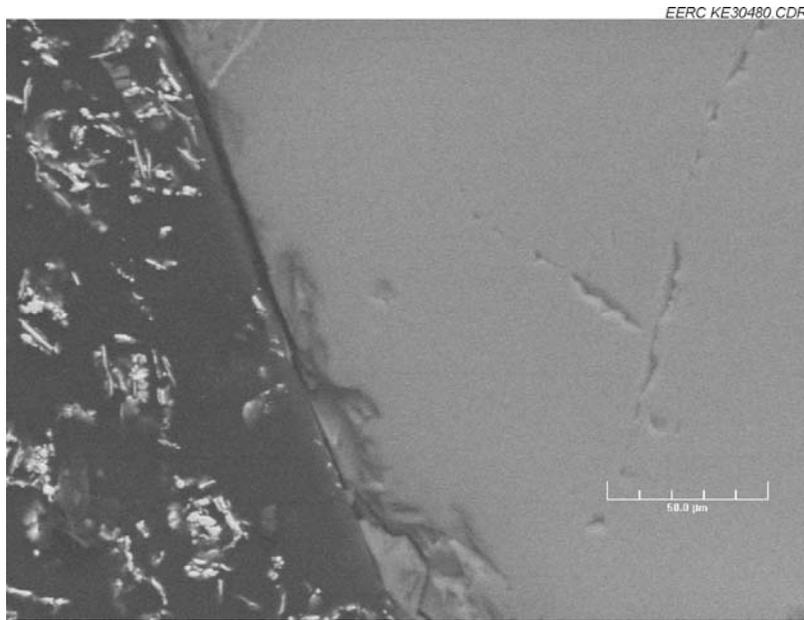


Figure 4. A slag derived from an acidic coal with no crystallization near the edges.

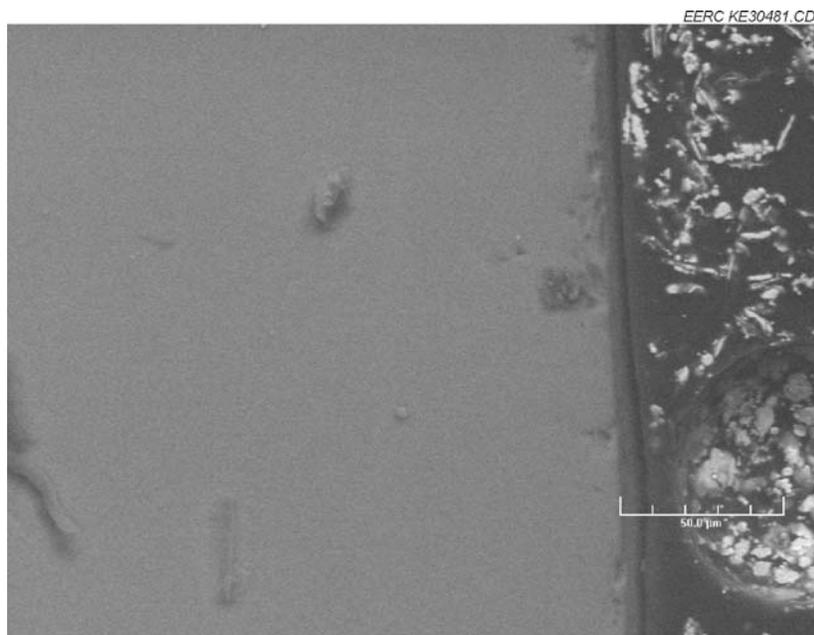


Figure 5. A slag derived from a basic coal with no crystallization near the edges.

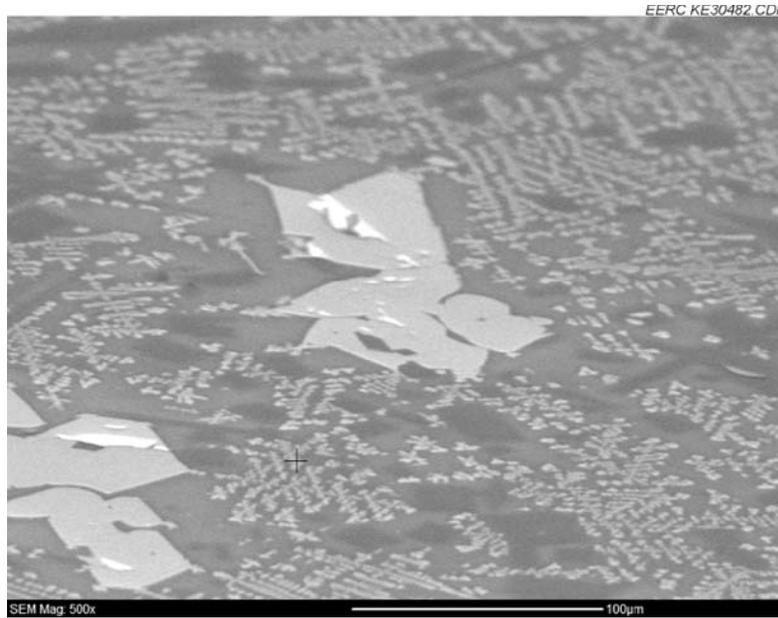


Figure 6. Dendrites formed in a slag.

of the image marks the point where the diffraction pattern in Figure 7 comes from. The pattern in Figure 7 is made of Kikuchi bands, which are the diffraction bands analogous to the peaks generated in an XRD diffractogram. Intensities are calculated by the software for a particular reflecting plane ( $h k l$ ) and compared to databases for diffraction supplied by American Mineralogist, National Institute for Standards and Testing (NIST), and the Inorganic Crystal Structure Database, which are the industry standards for diffraction data. The search takes into account the chemical composition either manually supplied by the user or a chemical analysis can be done by energy-dispersive spectrometry (EDS) as part of the EBSD analysis. Figure 8 shows the solution as determined by the software for the point on the dendritic crystals shown in Figure 6. The crystalline phase was identified as the mineral epidote –  $\text{Ca}_2\text{Al}_2\text{O}(\text{Al}, \text{Fe}^{3+})\text{OH}(\text{Si}_2\text{O}_7)(\text{SiO}_4)$ .

Table 1 shows the chemical results in wt% taken by EDS for the dendritic crystals in the glassy matrix. While the chemical analysis is very useful in the interpretation of the temperature regimes during formation of the dendrites, the positive identification of epidote indicates the temperature of formation between 630°C and 650°C. The chemical analysis does not contain enough Ca to identify the dendrites as epidote, which should be approximately 9.5 wt% according to the Inorganic Crystal Structure Database. The Ca is contained in the epidote, and the glassy matrix from which the crystals formed is deficient in Ca. This can be further verified in other analyses by EBSD of the darkest spots visible in the backscattered image of Figure 4 which were identified as vesuvianite –  $\text{Ca}_{19}(\text{Al}, \text{Fe})_{10}(\text{Mg}, \text{Fe})_3(\text{SiO}_7)_4(\text{SiO}_4)_{10}(\text{O}, \text{OH}, \text{F})_{10}$ . Vesuvianite forms at intermediate temperatures (450°C to 720°C) and low pressure. At higher temperatures, either diopside, wollastonite, or anorthite are the primary phases to crystallize depending on the availability of Ca.

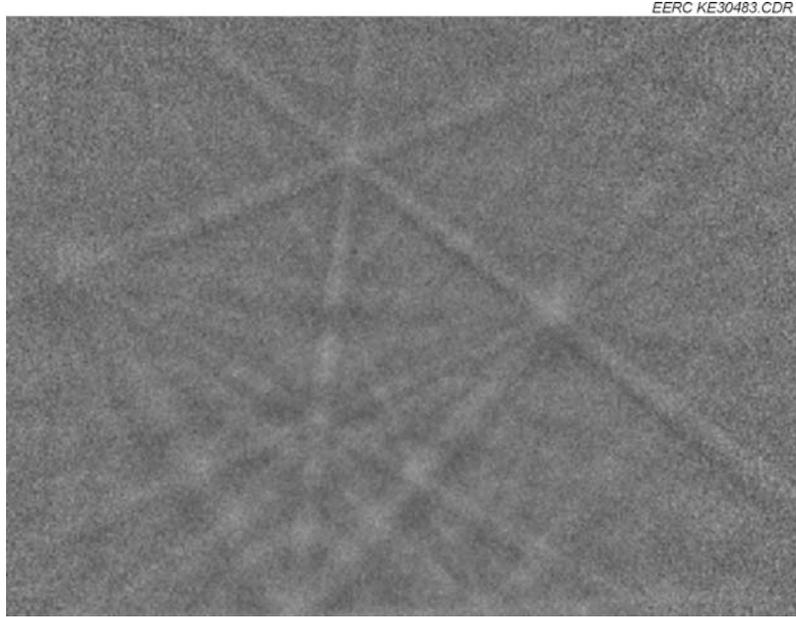


Figure 7. The diffraction pattern from the dendritic phase that crystallized during the quenching of the slag.

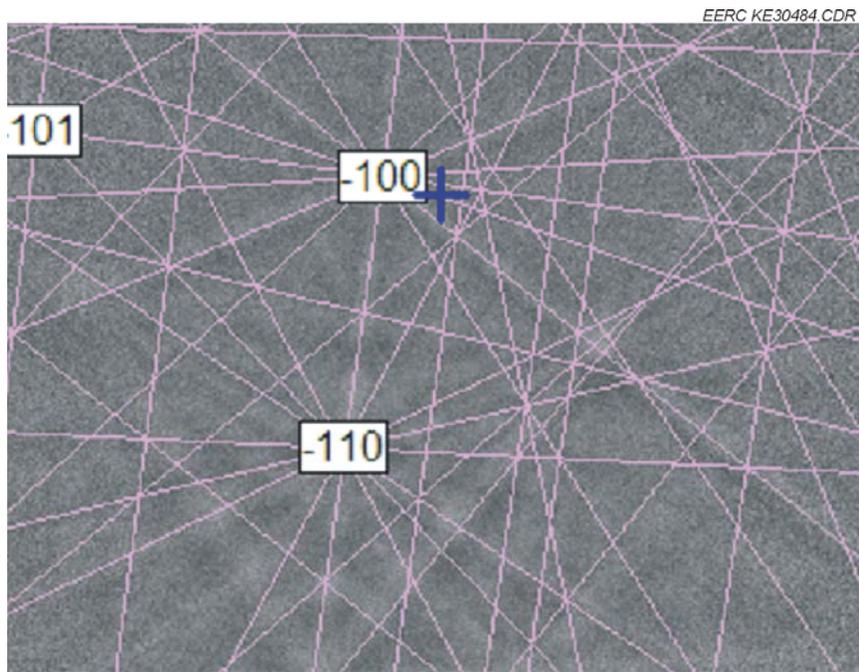


Figure 8. The solution or match by the software for the dendritic crystals.

**Table 1. Chemistry by EDS Results for Dendrites in Figure 6**

Mg	Al	Si	K	Ca	Ti	Fe
0.17%	19.61%	45.00%	3.82%	2.41%	0.71%	28.29%
0.35%	19.22%	42.38%	3.73%	1.94%	0.74%	31.64%

### Crystalline and Amorphous Phases

The formation of crystalline material in a slag changes the slag properties both chemically and physically. As mineral phases form, the melt in which they form can be depleted in the availability of some component even though the bulk chemical composition may indicate that a component may be there. Figure 9 shows a slag with large, Fe-rich, hematite crystals in a glassy matrix. Table 2 shows the chemistry associated with each of the points labeled in the micrograph. Figure 10 shows the eight diffraction patterns associated with each point.

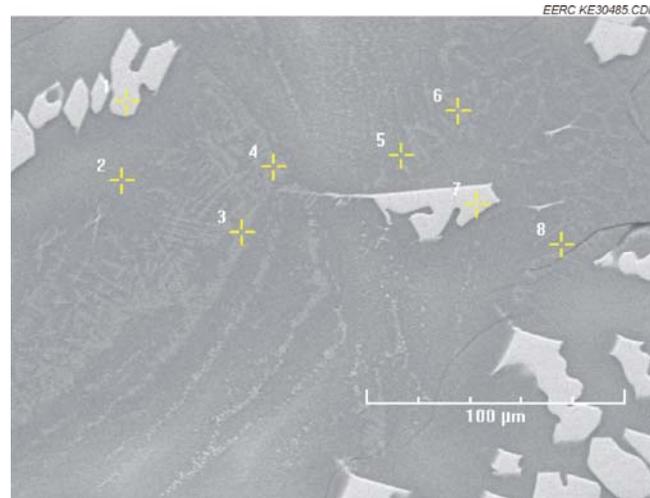
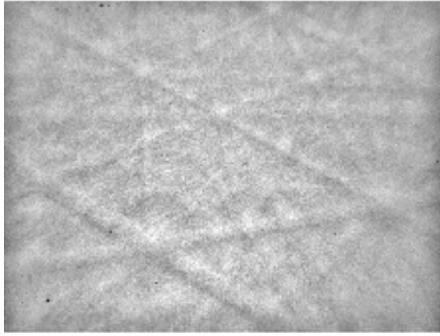


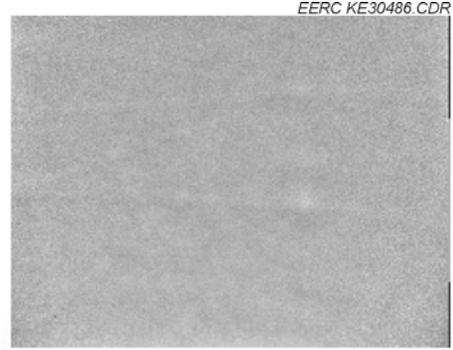
Figure 9. Amorphous and crystalline material in the matrix with large white hematite crystals.

**Table 2. Chemical Compositions of the Points in Figure 9**

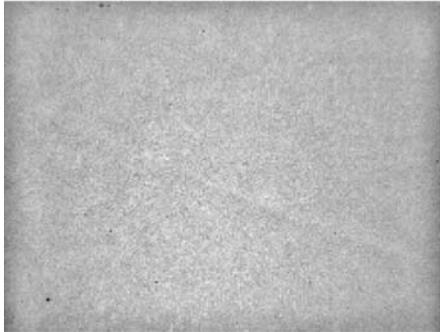
Point	Mg	Al	Si	K	Ca	Ti	Fe
1	0.00%	9.63%	8.96%	0.37%	1.20%	2.79%	77.06%
2	0.30%	16.94%	52.97%	3.36%	12.68%	0.77%	12.94%
3	0.81%	15.51%	50.16%	4.79%	4.99%	0.47%	23.26%
4	1.72%	15.92%	50.15%	5.38%	3.44%	0.50%	22.88%
5	0.00%	17.32%	56.00%	3.59%	12.55%	0.21%	10.33%
6	0.80%	16.86%	51.48%	3.97%	8.43%	0.30%	16.99%
7	0.00%	9.07%	8.05%	0.43%	1.02%	2.65%	77.87%
8	0.10%	17.36%	53.46%	3.20%	12.88%	0.41%	11.23%



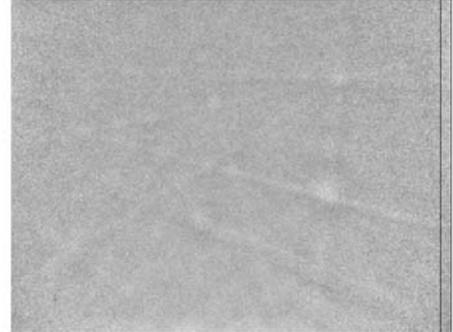
Point 1 Hematite



Point 5 Epidote



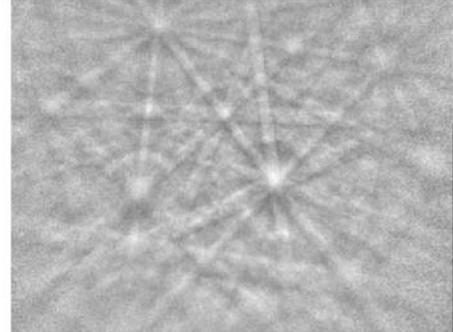
Point 2 Faint Pattern, Unable to Identify



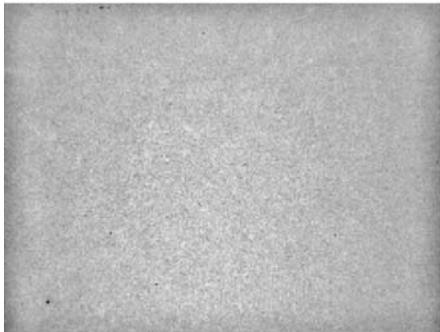
Point 6 Epidote



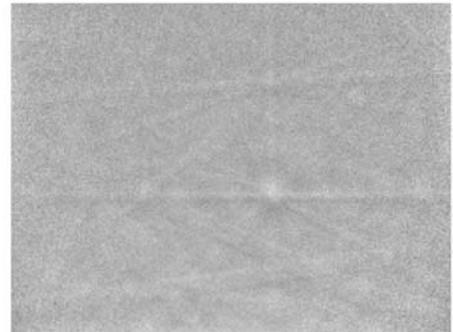
Point 3 No Pattern – Amorphous



Point 7 Hematite



Point 4 No Pattern – Amorphous



Point 8 Epidote

Figure 10. The backscatter diffraction patterns generated at each of the points from Figure 9.

The glassy matrix in which the hematite crystals form show smooth, dark areas outlined by very small, lighter-colored dendrites. The chemical composition is variable in the amount of Ca and Fe while the Al, Si, and K remain relatively constant. Ca and Fe are used in the formation of epidote. There is more Fe available than can fit into the structure of epidote, and it gets pushed away from the crystal and tends to be concentrated around the edges of the epidote crystals. Large concentrations of Fe form the large hematite crystals.

### Refractory Samples

The corrosion products of refractory bricks exposed to slags generated from a bituminous coal was also characterized using the EBSD technique. Figure 11 shows the interface between a refractory brick with a high chrome content, which is the rougher surface in the foreground, and the slag, which is the smoother material towards the top of the image. The rough surface in the foreground is a chrome oxide aggregate in the refractory brick. EBSD results show that this material is composed of  $\text{Cr}_2\text{O}_3$ .

The slag directly in contact with the refractory contained Cr and Fe phases. The large, block-shaped, light grey crystals in the top portion of Figure 11 contain components from both the refractory and the slag. Their composition is  $\text{Fe}_2\text{Cr}_2(\text{SiO}_4)_3$ . The Fe and Si are from the slag and the Cr component comes from the refractory. This phase forms at relatively high temperatures (1300°C to 1500°C), where the melt is deficient in Al. Cr substitutes for Mg in the olivine structure, which forms in nature as a solid solution series, with forsterite being the Mg-rich member and fayalite being the Fe-rich end member.

A reaction between the slag and refractory was noted several millimeters below the slag/refractory interface that resulted in the formation of a spinel mineral, chromite ( $\text{FeCr}_2\text{O}_4$ ). Slag penetration was reported well into the refractory material in a separate study

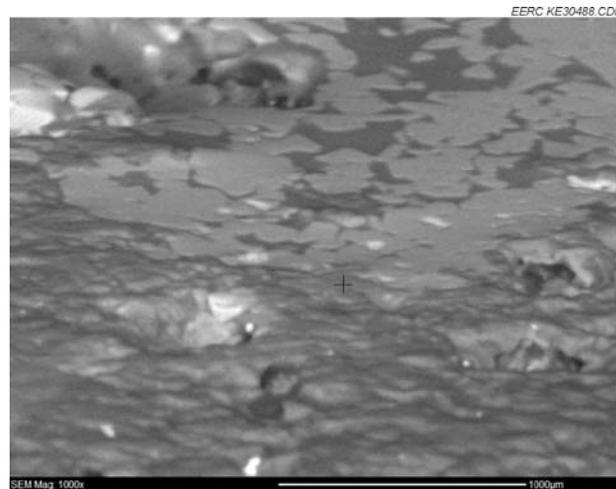


Figure 11. The interface between a chrome oxide aggregate (lower half of image) and slag (upper half of image).

based on the elemental analysis of the refractory material itself. While the chemical analysis clearly show Fe and Si mobility, no crystalline phases in the fine matrix were identified by EBSD.

An alumina refractory subjected to the basic slag showed the greatest amount of reaction between the slag and refractory brick. Figure 12 shows a reaction rim around an alumina aggregate grain in the refractory brick.

Most of the reactions between the slag and the refractory occurred close to the slag/refractory interface with the best crystal development, but Ca, Mg, and Fe were noted in the matrix throughout the brick sample. The fine material in the matrix did not produce diffraction patterns. The slag above the refractory material was found to contain several Fe-Al phases, with the most common one being  $\text{AlFeO}_3$ .

Three pyroxene minerals were identified around the rim of the aggregate grain shown in Figure 12. While none contains Al as part of the nominal composition, each has an Al component. The pyroxenes identified were aluminian enstatite ( $\text{Mg}_2\text{Si}_2\text{O}_6$ ) where the Al can substitute with the Mg, aluminian hedenbergite ( $\text{CaFe}^{2+}\text{Si}_2\text{O}_6$ ) where the Al substitutes in the  $\text{Fe}^{2+}$  site, and aluminian diopside ( $\text{CaMgSi}_2\text{O}_6$ ) where the Al fits into the Mg sites in the crystalline structure. Al can also replace some of the Si in some pyroxenes, but in the orthopyroxenes identified here, Al substitution for Si is negligible but can be up to 25% of some clinopyroxenes (not identified here) (5).

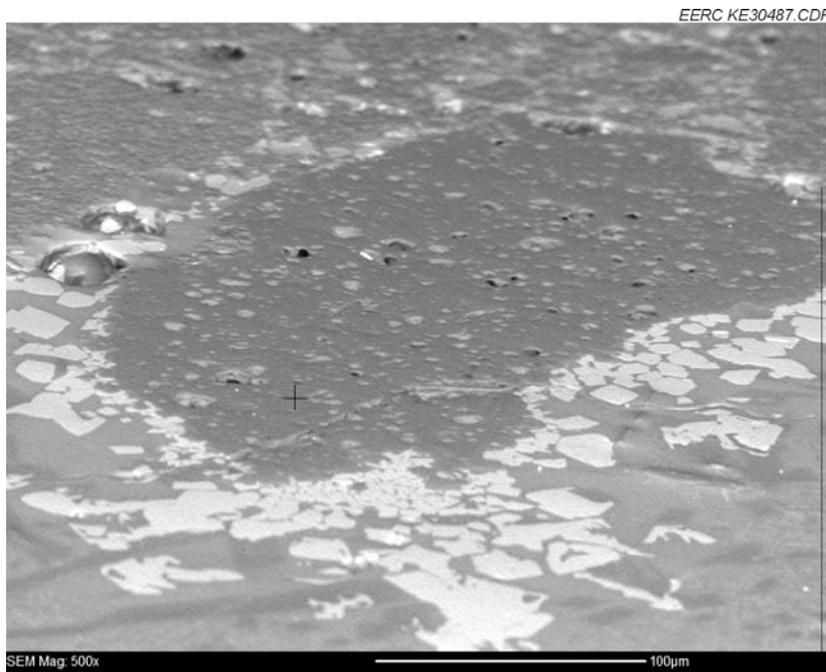


Figure 12. An aggregate grain of alumina surrounded by crystals of pyroxenes.

Refractory bricks composed of SiC and one with a high amount of Zr were also examined for slag penetration. In both of these brick types, the slags on top of the refractory material contained several crystalline phases in the form of dendrites and small crystals that produced diffraction patterns. Chemical analyses showed penetration of the slag into the brick, but no discernable diffraction patterns were produced from the brick aggregate or matrix in either of these samples.

## CONCLUSIONS

The EBSD technique allows particle-by-particle mineralogy based on diffraction patterns generated by the electron beam when the sample is tilted to a high angle. The diffraction pattern (Kikuchi bands) can only come from crystalline phases, which makes this technique ideally suited to study crystal formation in slags where oftentimes the crystals are very small and a reasonable chemical analysis cannot be made by conventional EDS methods in the SEM. Chemical analysis by EDS collects an x-ray spectrum that is generated from the surface of the sample to a depth of 3 to 4  $\mu\text{m}$ . Very small crystals, such as dendritic crystals formed during rapid quenching of a slag, are often masked by the x-rays generated from the matrix in which they crystallized. Because EBSD uses the diffraction pattern to determine the mineralogy, there is no signal from the amorphous matrix and only the crystalline material is represented in the analysis. When a specific mineral phase is identified, the temperature regime in which it formed can often be inferred.

Evaluation of corrosion products by EBSD at the refractory brick and slag interface showed that there were penetrations of both Si and Al into the refractory brick matrix as well as metal oxide migration from the brick into the slag. The degree of corrosion was dependent on the type of refractory and chemical makeup of the slag. Refractory brick high in Al appeared to be corroded readily by slags with a high Fe content. A Cr-rich brick tended to have less corrosion, with less of the Fe and Si phases penetrating into the brick as compared to the Al-rich refractory brick.

Using EBSD to evaluate the crystalline material in slags has not been reported in the literature to date. While the technique has been available for a number of years, only in the last 5 years has the technology developed to make it a reasonable analytical tool, mainly because the speed of computing now allows better search and match processes. This work shows that EBSD can be used to identify crystalline material in slags that could not be properly identified by EDS methods because the volume of the sample from which the x-rays are generated are often much larger than the crystals themselves. Since the EBSD technique relies on the crystalline structure rather than chemical signature, the background or matrix in which the crystalline material is contained does not interfere with the identification.

Since the EBSD technique is relatively new, few results can be found in recent literature. The technique will require more refinement by both users and developers. There are several factors that can alter the solution or identification of a particular mineral phase, many of which were learned by trial and error. Exact configurations must be met for proper results to be meaningful. As with all diffraction, a very specific geometry must be

maintained, in which the electron beam source, the sample, and the detector must all lie along the perimeter of a circle (Roland Circle) to satisfy a formula known as Bragg's Law:  $n(\lambda) = 2d\sin\Theta$  where  $\lambda$  is the wavelength of the electron beam,  $d$  is the interplanar distance between atomic layers, and  $\Theta$  is the angle measured in degrees. Any deviation from the geometry will reduce the quality of the analysis. The distance between the pole piece (electron beam source) and the sample surface is the most difficult to maintain and must be adjusted by raising or lowering the entire sample stage rather than refocusing the image. A small deviation in the focal distance results in poor pattern matching.

A second area for further development is in the ability to discern two distinct phases that may be represented in a single Kikuchi pattern. In several instances, very good matches can be made using some of the bands and nodes, but some of the bands and nodes did not fit the solution pattern. A complex pattern may appear to have two or more solutions and the operator must decide which is the most reasonable. Both solutions may be correct for the point being analyzed, or possibly, neither is correct and the pattern has never been indexed. Data interpretation for this technique is still subjective and will improve with more familiarity of the system.

The ability to have mineralogical data based on the crystalline structure of a phase rather than a chemical analysis by EDS allows much better interpretation of the temperature regimes in which specific phases tend to form. Knowing the type and relative amounts of a phase crystallizing in a slag is critical in predicting the viscosity of a slag at a given temperature.

## REFERENCES

1. Goehner, R.P.; Michael, J.R. Phase Identification in a Scanning Electron Microscope Using Backscattered Electron Kikuchi Patterns. *J. Res. NIST* **101**, 3, 301–308.
2. Folkedahl, B.C.; Schobert, H.H. Effects of Atmosphere on Viscosity of Selected Bituminous and Low-Rank Coal Ash Slags. *Energy Fuels* **2005**, 19, 208–215.
3. Dingley, D.J.; Randle, V. Microtexture Determination by Electron Backscatter Diffraction. *J. Mater. Sci.* **1992**, 27, 4545.
4. Wilkinson, A.J. Measurement of Elastic Strains and Small Lattice Rotations Using Electron Back Scatter Diffraction. *Ultramicroscopy* **1996**, 62, 237–247.
5. Deer, W.A.; Howie, R.A.; and Zussman, J. *Rock-Forming Minerals – Single-Chain Silicates*; Volume 2A, 2nd Edition; The Geological Society: London, 1997.