A Comprehensive Study of Modern Gasification Slags and Refractories Used in Gasifiers to Guide the Development of Novel/Improved Lining Materials

J. Nakano

To understand how gasification slags formed from mixtures of coal and petcoke feedstock impact the erosion and corrosion behaviors of refractory materials in gasifiers, research was divided into three areas. First, interactions of synthetic coal and petcoke slag with high-Cr_2O_3 refractory were investigated using a controlled atmosphere heating chamber attached to a confocal scanning laser microscope. Dynamic slag/refractory interactions were studied through in situ observations under gasification conditions. Second, thermodynamic equilibria of crystals formed in slag mixtures were examined using a series of long-term equilibration experiments. V_2O_3 crystals were found to be in equilibrium with molten slag if there was a sufficient amount of vanadium content in the bulk slag. Finally, the formation kinetics of crystals, including V_2O_3, in coal-petcoke slag mixtures was studied. It was found the V_2O_3 crystal could form as quickly as 35 s if more than 80 mass-% petcoke was added to coal feedstock.

Fig. 1 A schematic of an entrained slagging gasifier

1 Introduction

World's economic growth depends in part on reliable and affordable electricity, which has driven the need for reliable, renewable,

Jinichiro Nakano
US Department of Energy National Energy
Technology Laboratory
97321 Albany/OR
USA and URS Corp
97321 Albany/OR
USA
Corresponding author: J. Nakano
E-mail: jinichiro@gmail.com

and sustainable energy technologies. Fossil-fuel gasification processes are one way of achieving these goals. An example of one type of gasifier is shown in Fig. 1. Modern gasification systems, such as the integrated gasification combined cycle (IGCC), utilize carbon feedstock (mainly coal and/or petcoke), H_2O, and O_2, producing heat and a synthesis gas composed primarily of H_2 and CO. CO_2 is generated during gasification as a minority process by-product, and can be easily captured for sequestration or use in other processes because the gasification process is a closed system. There are currently 412 gasifiers in operation worldwide, with 76 additional units scheduled to start by 2016. Coal resources are available in many countries, with the largest reserves in the USA, Russia (plus former USSR countries), China, and India. At current consumption rates, coal reserves are estimated to last approximately 119 years compared to oil re-
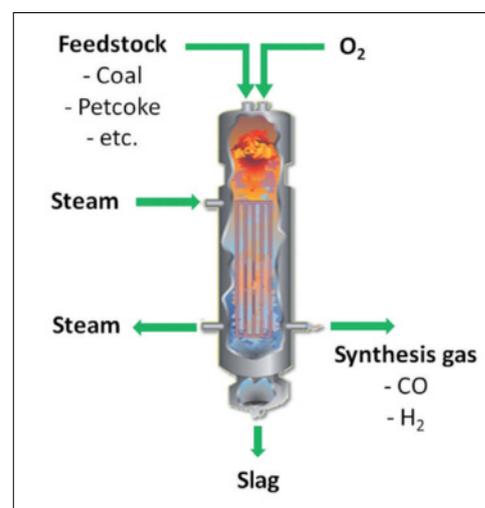
serves, which are projected to last approximately 46 years. By-products of petroleum processing, petroleum coke (petcoke), are increasingly used as a carbon source in gasification. Currently, 100 % petcoke or mixtures of coal and petcoke are used in the gasification industry as a carbon feedstock.

Gasifiers suffer a number of serious material problems limiting their wide spread use, the most serious of which is degradation/loss of the protective lining refractory along the inner walls of a gasifier. Lining loss is due to the severe gasification environment involving high temperature, high pressure, low oxygen partial pressure (reducing environment), and physical and chemical attack by ash impurities in the carbon feedstock. The ashes liquefy at the high gasification temperatures, and the corrosive/erosive interactions between molten ashes (i.e., slags) and refractory liners limit gasifier's service life to a few months up to 3 years; depending on operation conditions, feedstock chemistry, and the amount of gasifier cycling (from room to operating temperatures). A high-Cr_2O_3 refractory brick after commercial
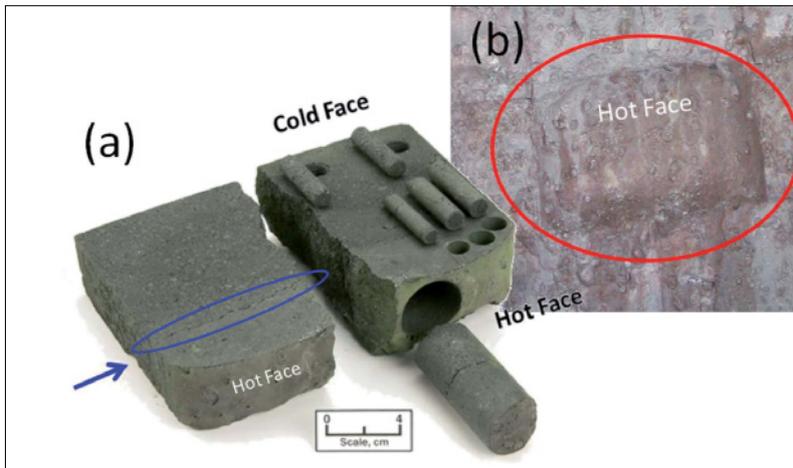
Fig. 2 A refractory brick after commercial use in gasifier showing: (a) cross-section indicating slag penetration/interaction, and (b) hot face bricks as installed in a gasifier

use in a gasifier shows extensive interaction with slag (Fig. 2). An arrow in Fig. 2a indicates a crack where structural spalling occurred due to slag penetration into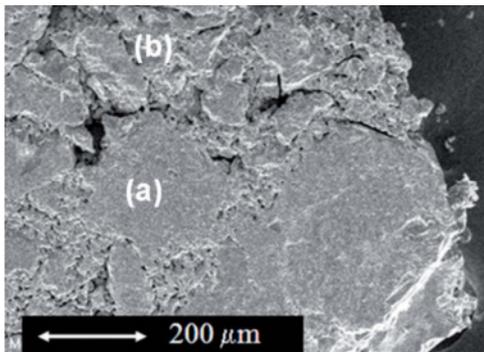 the brick during the gasification operation. A large-scale gasifier is installed with 1000–2000 refractory pre-fired bricks, the replacement or repair of which requires about 5 days to several weeks of gasifier shutdown, and can cost up to USD 1 million per gasifier, depending on the extent of repairs necessary. Operation temperature of the gasifier (typically between 1325–1575 °C) is determined so slag remains fluid enough to flow down the gasifier sidewall and exits the unit, with the temperature as low as possible to minimize refractory deterioration by the harsh slag attack. The type of carbon feedstock is in part selected based on performance, cost, and availability. In the open literature, studies describing the degradation mechanisms caused by "gasifier" slags share the difficulty to simulate real time interactions between slag and refractory due to limitations in experimental methodology. No thermodynamic data exists for slag systems utilizing petcoke as a carbon feedstock, limiting the ability to predict slag behavior or refractory slag interactions. Without a fundamental understanding of refractory liner/slag interactions and thermodynamics, it is laborious and time consuming to pursue the development of novel gasifier liner refractories. The current research was systematically performed to study slag/refractory interactions and to build a thermodynamic database that would allow researchers to predict and model slag and refractory behavior. In addition, the kinetics of crystal formations in molten slags was examined over various temperatures and compositions. How fast crystals form in molten slags during gasification is critical information that would aid re-

Fig. 3 A micrograph showing a microstructure of a 90 mass-% Cr_2O_3 – 10 mass-% Al_2O_3 refractory: (a) grain aggregate, and (b) fine matrix region
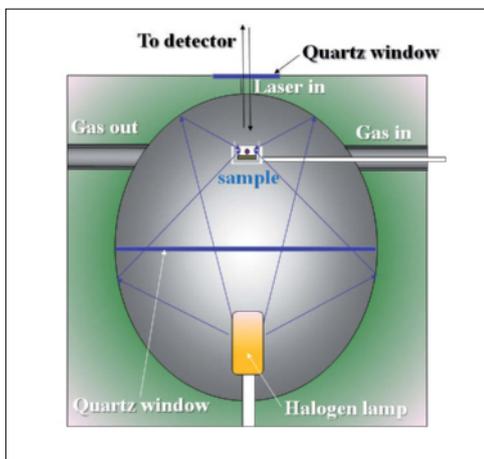

Fig. 4 A schematic of the heating chamber attached to the confocal scanning laser microscope

fractory development and can be used to predict slag behavior molten slag chemistry.

2 Experimental

Slag-refractory interactions of a 90 mass-% Cr_2O_3 – 10 mass-% Al_2O_3 refractory were investigated by sessile-drop type experiments using a confocal scanning laser microscope (CSLM), with elemental analyses taken over different locations as shown in Fig. 3. A sessile drop of a premelted slag particle (0,02 to 0,04 mg) was placed on select microstructure areas (grain aggregate and matrix) of a polished refractory surface, and heated at 1500 °C for various times in a 64 % CO – 36 % CO_2 atmosphere. To minimize slag/refractory interactions measured by conventional experimental techniques using slow heating and cooling rates, a gold image heating chamber attached to the CSLM was utilized for the *in situ* observations of crystallization. This heating chamber of the CSLM allows rapid heating (77 K/s) and hequenching (99 K/s). This rapid cooling is significantly faster than the critical cooling rate for glass transition, so the slag/refractory interaction phenomena occurring at temperatures of interest were quenched to room temperature for further analysis. Details of the CSLM are available in the literature [1]. A simplified schematic of the heating chamber attached to the CSLM is shown in Fig. 4. A sample is located at one of the focal points in the chamber so that heat from the halogen lamp located at the other focal point is effectively utilized for sample heating. Synthetic slag samples were premelted in a 64 % CO – 36 % CO_2 gas environment, and their compositions analyzed by ICP-OES (optical emission spectroscopy) as shown in Tab. 1. Further details of the experiment can be found in [2].

By conducting a series of long-term equilibration experiments with various chemistries encompassing industrial mixtures of coal slag and petcoke slag, the thermodynamic stability of crystal phases formed in gasifier slags were investigated. Approximately 450 mg of each reagent grade powder mixture was placed in a platinum crucible and heated in a resistance tube furnace at 1500 °C in a 64 % CO – 36 % CO_2 atmosphere to simulate gasifier conditions. Samples were quenched in water after 3 days of soaking at 1500 °C. The sample compositions were then analyzed by ICP

(Tab. 2) after removing from the crucible. Phases present in slag were identified by X-ray diffractometry (XRD), scanning electron microscope (SEM), and X-ray wavelength dispersive spectroscopy (WDX). Crystal structures were investigated using the transmission electron microscope (TEM). More experimental details are explained elsewhere [3].

The kinetics of crystal formations in coal-petcoke slag mixtures was studied by measuring the time taken to form precipitates in the CSLM. Each mixture of reagent grade oxide powders was placed in a platinum crucible and heated to a designated temperature in air. After the test temperature was stabilized in the furnace, a 64 % CO − 36 % CO_2 atmosphere was introduced to create a reducing environment and the time required for each slag sample to crystallize recorded for different temperatures and slag compositions. The slag chemistry studied is shown in Tab. 3. Details of the experimental set-up are explained elsewhere [4].

3 Results and discussion
3.1 Interactions between molten slags and refractories

In order to provide fundamental information needed to understand corrosion and wear issues between refractory and slag, interactions between them were studied. Through real-time video recording of interactions of pulverized coal and petcoke slag particles with specific microstructure areas of the high-Cr_2O_3 refractory, it was found that petcoke addition initially promoted slag fluidity on refractory surface; however, the flow was quickly impeded when crystals of spinel and/or karelianite (V_2O_3) formed at the interface as vanadium pentoxide liquid from the petcoke slag was reduced to sesquioxide solid, which reacted with chromium from the refractory. Coal slag remained on coarse grains of the refractory material's surface while the majority of coal slag penetrated into refractory if placed on porous fine particle size regions. The highest refractory material loss occurred in the refractory matrix region due to its rapid chemical dissolution into the slag, which caused debonding of grains from the refractory surface. Petcoke slag, on the other hand, showed aggressive interactions with refractories. Fluid petcoke slag wetted the refractory grain aggregates, rapidly penetrating into the microstructures. During the penetration process, porous matrix regions were aggressively dissolved into petcoke slag. When vanadium in the petcoke slag reacted with chromium from the refractory, V-Cr-bearing spinel crystals formed, which subsequently
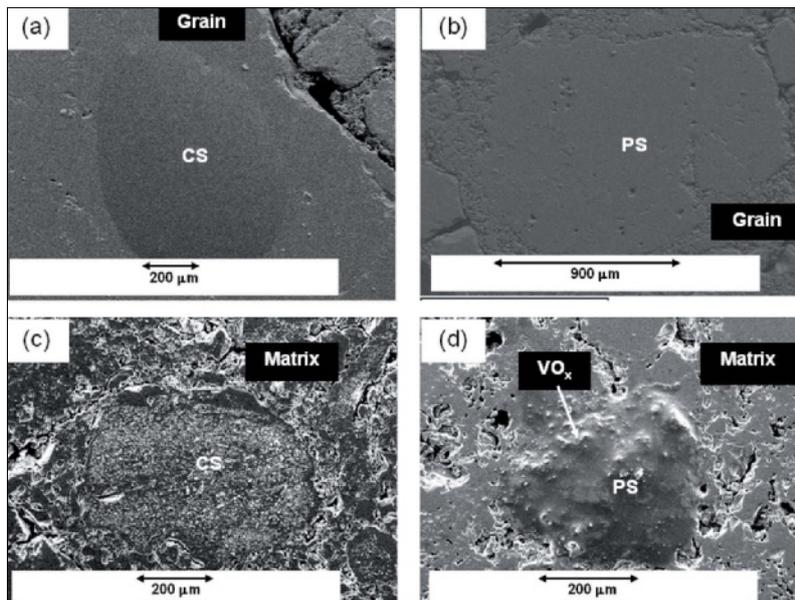
Tab. 1 Chemical composition of synthetic coal and petcoke slags (ICP-OES)

	Petcoke Slag [mass-%]	Coal Slag [mass-%]
Al_2O_3	7,8	24
CaO	10,1	6,4
Fe_2O_3	10,2	14,5
K_2O	1,2	2,9
SiO_2	25	52
V_2O_5	46	–
Total	100,3	99,8

Tab. 2 Experimental compositions of equilibrated samples (after equilibration) by ICP-OES

Sample	Bulk Composition [mass-%]					Phase Analysis
	Al_2O_3	CaO	FeO	SiO_2	V_2O_3	Method
1	14,7	6,9	12,8	65,6	0	XRD
2	18,8	6,9	12,8	61,4	0	XRD
3	23,3	7,2	13,4	56	0	XRD
4	14,7	6,7	12,8	64,2	1,7	XRD
5	25,1	6,6	12,7	55,7	0	XRD, TEM
6	36,5	6,6	15,8	41	0	XRD
7	38,9	7	13,5	39	1,6	XRD
8	35,4	7	14,3	39,8	3,5	XRD
9	33,6	7,5	14	38,9	6	XRD
10	32,8	6,9	13,7	44,4	2,1	XRD
11	26,9	6,7	14,3	49	3,1	XRD
12	14,2	6,8	14	62	3	WDX
13	15	7	12,1	60,9	4,9	XRD
14	11,7	6,4	12,3	60,9	8,7	XRD
15	20,8	6,6	15,9	49,6	7	XRD
16	18,7	6,9	13,2	55,8	5,5	WDX, TEM
17	25,1	6,9	14,2	46,4	7,4	XRD, TEM
18	28,7	7,6	13,1	42,8	7,7	XRD
19	33,9	7,7	13,8	36,6	8	XRD
20	24	7	12,4	51,4	5,2	XRD

Tab. 3 Chemistry of coal-petcoke mixed samples analyzed by ICP [mass-%]

Petcoke Addition to Coal		Constituents in Mixtures					
Slag Basis	Feedstock Basis	Al_2O_3	CaO	Fe_2O_3	K_2O	SiO_2	V_2O_5
0	0	24,0	6,4	14,5	2,9	52,0	0
10	53	22,4	6,8	14,1	2,7	49,3	4,7
30	81	19,2	7,5	13,2	2,4	43,9	13,7
50	91	15,9	8,3	12,3	2,0	38,4	23,1
70	96	12,6	9,0	11,5	1,7	32,9	32,5
100	100	7,8	10,1	10,2	1,2	25,0	46,0

Fig. 5 SEM images of coal and petcoke slags on 90 mass-% Cr_2O_3–10 mass-% Al_2O_3 refractory (after 10 min at 1500 °C): (a) coal slag on grain aggregate; (b) petcoke slag on grain aggregate; (c) coal slag on matrix; and (d) petcoke slag on matrix
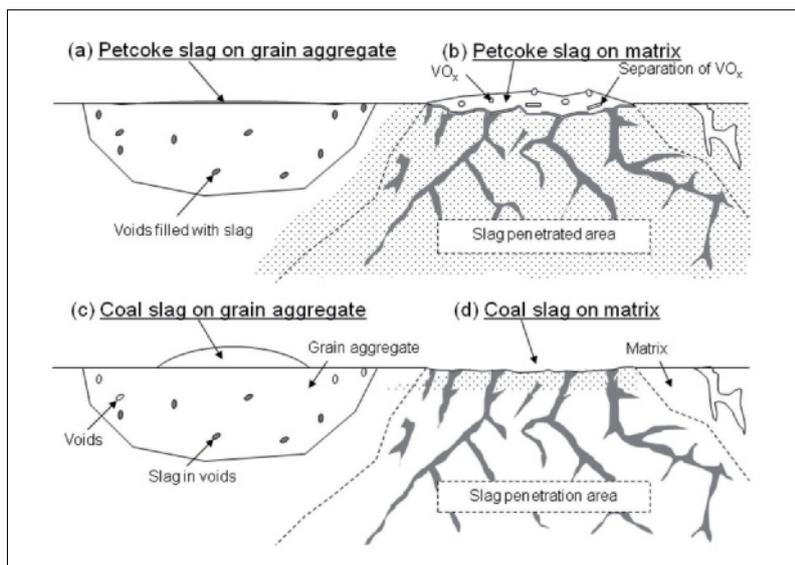

Fig. 6 General models of interactions of coal and petcoke slags with high-Cr_2O_3 refractory after 10 min at 1500 °C in P_{O_2} = 10^{-8} atm

impeded slag penetration within the studied time. Volume changes and interfacial misfit of the new V-Cr phase caused a thin layer to separate from the refractory surface, leading to chemical spalling. This work revealed in situ the extensive vulnerability of the porous matrix areas of refractory materials against slag attack in a gasifier environment. Chemical reactions and slag penetration occurred rapidly in the matrix due to a large surface energy and porosity which promoted chemical and structural spalling (loss of materials). SEM micrographs of interacted samples after quenching by He gas are shown in Fig. 5. Based on these results, general models to describe degradation mechanisms depending on slag types and microstructures were proposed as shown in Fig. 6 [2].

3.2 Phase equilibria in coal-petcoke slag mixtures

In order to determine equilibrium phases present in gasification slags, the slag/ refractory microstructure study was extended to the development of a thermodynamic phase diagram of the slag system containing Al_2O_3, CaO, FeO, SiO_2 and V_2O_3; key components in coal-petcoke gasifier slag. Besides refractory corrosion by the slag, crystalline phases formed have the potential to impact system viscosity. Based on the phase analysis across the composition matrix, an equilibrium phase diagram at 1500 °C was constructed by drawing phase boundaries between distinct homogeneity regions (Fig. 7). Four distinct phase regions with two types of crystals ($Al_6Si_2O_{13}$-mullite and V_2O_3-karelianite) were proposed in a range of industrial coal-petcoke slag mixtures [3]. Crystal structures of mullite and karelianite were confirmed by TEM diffraction analysis on samples prepared by a focused ion beam technique (Fig. 8). These phases were found to be orthorhombic and rhombohedral, respectively. From the TEM X-ray chemical analysis, atomic substitution of Al by V was noted in mullite, while doping of Al in place of V was noticed in karelianite. The proposed phase diagram can predict the types and stability of crystals which may form in gasifiers without the need for conducting expensive/laborious experiments. These equilibrium insights may be used by the gasification industry to predict slag chemistry and properties, and to guide the development of improved refractory liners. Using this and other data, a thermodynamic model is under construction for coal and petcoke containing gasification slag systems to support the lack of a database in commercial thermodynamic software packages. The phase equilibria study has been extended to lower and higher temperatures to examine the thermal effect on the phase stability in the slags. Phase boundaries drawn for 1500 °C in the present work are to be refined when data from different temperatures are obtained.

Fig. 9 presents normalzied compositions of industrial coal slag as averaged from a report by *Selvig* and *Gibson* [5] and mixtures (at a 45/55 feedstock ratio) of coal slag from *Selvig* and *Gibson* and petcoke slags from *Bryers* [6] and *Swanson* [7] that are superimposed on the proposed isothermal section at 1500 °C and P_{O_2} = 10^{-8} atm. The content of Al_2O_3 in Fig. 9 varies from 19,7 mass-% to 49,7 mass-%, corresponding to [5], for the 100 % coal slag. In this region, the mul-

lite phase is not thermodynamically favored to precipitate if the composition is slightly richer in SiO_2 than the average coal slag composition (i.e., <30 mass-% Al_2O_3 in Fig. 9). The diagram indicated that mullite may form in coal slags with certain compositions (e.g., the Al_2O_3-rich region) during gasification operations if it is kinetically allowed (e.g., if residence time is long enough to achieve equilibrium). It should be remembered that Fig. 9 is not a liquidus projection, but is an isothermal phase diagram at 1500 °C. More detailed discussion can be found elsewhere [3].

3.3 The formation kinetics of crystal formation in slags

The kinetics of crystal formations in molten slags was examined over various temperature and composition ranges. How fast these mullite and karelianite crystals would form during gasification is another critical factor to aid in refractory development and to predict slag behavior at the slag/refractory interface, which can be modified depending on slag chemistry. In order to overcome the slow heating/cooling problems, the CSLM with the rapid heating chamber was again utilized. The onset of crystal precipitation was optically measured when switching from air to a gasification reducing atmosphere at a specific temperature. This atmosphere change would cause air stable V_2O_5, a low temperature melting phase, to transform to V_2O_3, a high temperature melting phase. Recorded videos from a series of CSLM experiments were used to measure the timing of the first crystal formation in various slag chemistries and at various temperatures in the simulated gasification environment. A time-temperature-transformation diagram encompassing the entire range of coal-petcoke industrial mixtures was proposed [4]. The timing of each crystal phase formation in the slags at various gasification temperatures can be predicted using this diagram. The karelianite crystal may form within 35 s in coal-petcoke mixtures if more than 80 mass-% of petcoke is added to a coal feedstock (i.e., approximately 10 mass-% petcoke slag in Fig. 10), highlighting the potential for clogging issues due to a viscosity increase, which may be caused through slag chemistry modification. The residence time of slags before they exit a gasifier needs to be controlled if petcoke additions to carbon
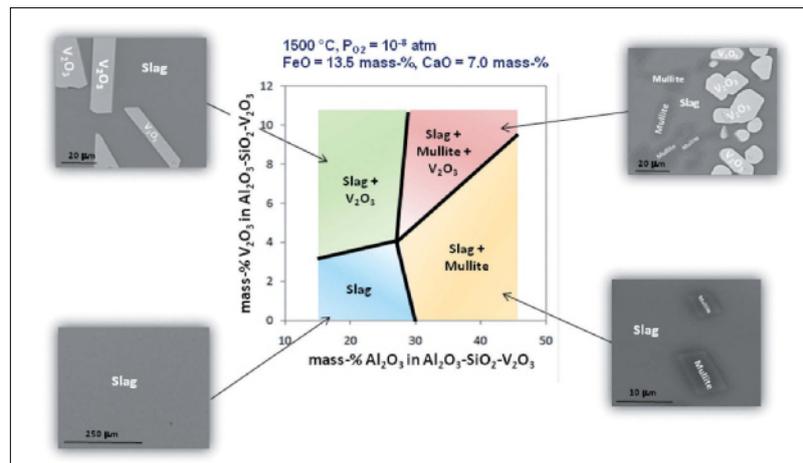

Fig. 7 The experimental phase diagram of the coal-petcoke slag system at 1500 °C and $P_{O_2} = 10^{-8}$ atm, containing SiO_2, Al_2O_3, CaO, FeO and V_2O_3
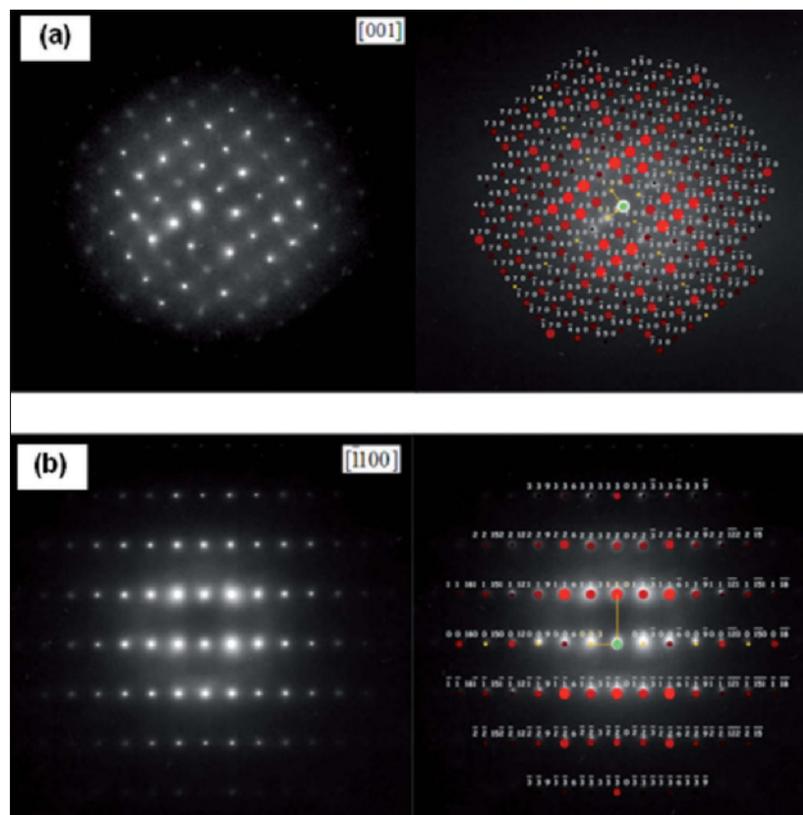

Fig. 8 TEM diffraction patterns of (a) mullite in sample 5 and (b) karelianite in sample 16, confirming orthorhombic and rhombohedral crystal structures, respectively

feedstock are large enough to cause slag supersaturation and subsequent crystallization. Metastable equilibrium must also be considered based on kinetics and residence/incubation time.

4 Conclusion

Through the present research on slags and their interactions with refractory materials used in gasifiers, thermodynamic phase equilibria and crystal formation kinetics of coal and/or petcoke mixtures were systematically studied. Rapid heating/cooling techniques using the CSLM revealed in situ microscopic interactions between slags and a gasifier lining material under gasification conditions. A general model was proposed to describe the mechanisms of refractory
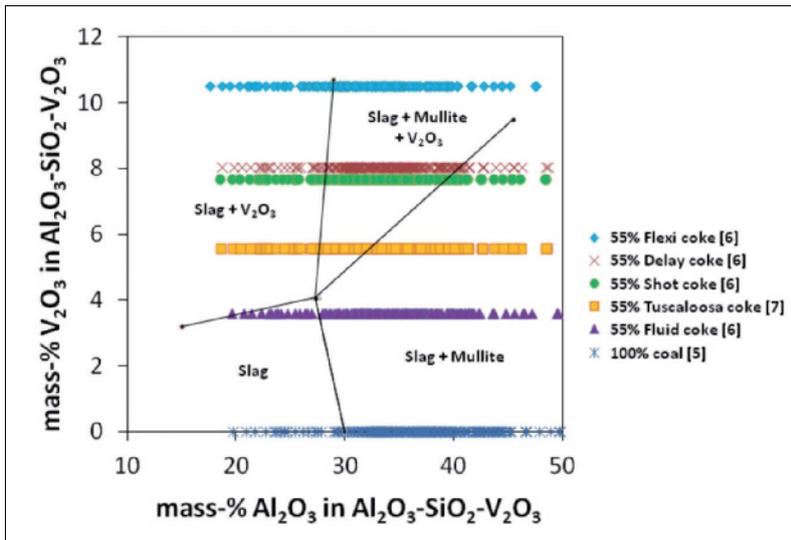
Fig. 9 Industrial mixtures of 55 mass-% petcoke, and 45 mass-% coal on the proposed phase diagram (Bryers [6], Swanson [7], and Selvig [5])
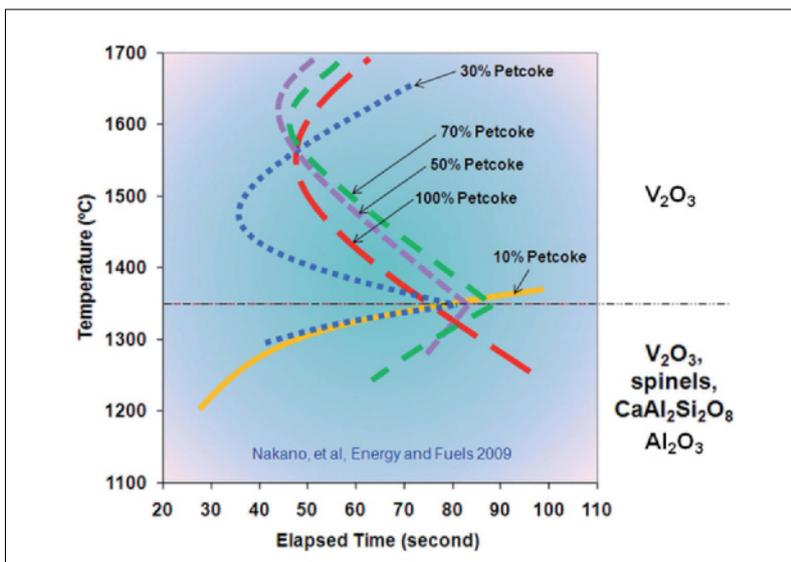

Fig. 10 The experimental time-temperature-transformation diagram for crystals formed in coal-petcoke slag mixtures under gasification conditions. Note percentage is given on a slag basis

degradation caused by molten slag interactions. A phase diagram showing the thermodynamic phase stability of crystalline phases forming in coal-petcoke mixed feedstock slags was constructed using quenched sample data. Furthermore, the onset of crystal precipitation was optically recorded in situ by the CSLM technique. The time to crystal formation in various slags was then determined on a time-temperature-transformation diagram. Coordinated information from the current research is critical to understanding and predicting gasifier slag/refractory interactions, to developing new or improved refractory materials, and to controlling the gasification process to maximize the on-line availability of gasifiers.

Acknowledgements

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