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Oxides reactions with a High-chrome sesquioxide refractory

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In slagging coal-gasifier systems, the combination of oxides present as impurities in coal and combustion temperatures that can exceed 1650°C restrict the use of liner materials in the coal combustion chambers to refractories. In this study, the slag-refractory interactions of a new high chrome sesquioxide refractory was characterized. High-temperature cup tests showed that the molten oxides infused into the refractory and that the sesquioxide refractory reacts with the oxides in a manner similar to spinel phase refractories. Studies of the coal slag's individual oxide components showed CaO reacts with the chrome refractory to form a low melting $Ca(CrO_2)_2$. FeO reacts with the sesquioxide to form a interface layer of $(Cr,Fe)_3O_4$ spinel phase. Results of this study now make it possible to design studies for improving corrosion resistance to increase refractory life.

1. Introduction

Slagging coal-gasifiers operate at temperatures that can exceed 1650°C in a reducing environment. Under these conditions the impurities in coal are molten when they come into contact with the combustion chamber walls. The materials of choice for chamber wall liners are high chrome refractories. Recently, a new series of high chrome refractories have been designed for use in gasifiers. In this study, one of these new high chrome refractories was allowed to react with coal slags and combinations of oxides present in coal slag to characterize slag-refractory corrosion. Once the slag-refractory interaction is understood, it becomes possible to develop means of reducing the corrosion rate and extend refractory life.

Early in the design of coal-gasifiers, studies were begun to determine the best refractory material for use in the coal combustion chamber [1–5]. Accelerated rotating refractory cylinder tests were conducted in a molten artificial slag using chrome-alumina and chrome-magnesia spinel refractories. The artificial slag was a combination of oxide powders designed to simulate impurities in coal. These studies indicated that material of choice was chrome and the higher the refractory chrome concentration the lower the corrosion rate. Although distinctive oxide-refractory interactions were observed, no attempt was made to study the effects of individual impurities or of combinations.

In this study, a high chrome-alumina sesquioxide refractory was subjected to corrosion using a coal gasifier slag, a coal slag, an artificial coal slag made from a blend of oxide powders, and several combinations of oxides designed to evaluate the effect of the different impurities present in coal [6]. Results of these laboratory tests were compared to previous studies of spinel refractories and to analysis of spent refractories removed from a commercial gasifier after two years of operation.

2. Experimentation

Oxide reactions with a high chrome refractory were accomplished by means of modified cup tests [7–9]. A high chrome/alumina sesquioxide refractory (75 $wt\%Cr_2O_3$ - $25wt\%Al_2O_3$) brick was sectioned to form slabs 40 mm wide × 30 mm thick × 200 mm long. Nine 10 mm diameter holes were drilled to a depth of 10 mm into the 40 × 200 mm face. Spacing between holes was approximately 20 mm. These holes were filled with blends of oxides or with coal slag powders (Table I). Oxide powders were sieved so that the powder particle diameters were between 0.044 and 0.074 mm. Identical sample sets were made and two separate tests were conducted.

The oxide-refractory slab was placed in an environmentally controlled tube furnace and heated to 1550°C for 24 hours (heating and cooling rates 100°/hour). To ensure a reducing atmosphere, a gas mixture of 50 : 50 Argon : CO, that had been bubbled through H_2O, was passed through the tube.

After furnace heat treatment, the samples were examined using light microscopy and photographed (Fig. 1). The loss of oxides/slag in the cup due to infusion into the refractory was characterized. The oxide/slag - refractory interface (i.e., the bottom of the cup) was examined to determine if there was any slag-refractory interaction that changed the surface morphology.

The cup test slabs were then sliced to produce a cross-section of each of the cups. One of each of these sections was metallographically polished and examined using a scanning electron microscope (SEM) to determine the

TABLE I Slag - refractory interactions: cup like test, A-70 refractory, 1550°C, 24 hours, environment: Ar-CO/H_2O

Artificial composition, wt%				**X-ray data**	
SiO_2	CaO	FeO	X	**major**, minor	**Refractory microstructure**
100				**$(Cr,Al)_2O_3$**	Slag infusion: limited slag infusion however, Surface Interaction: limited surface reaction
50	50			**$(Cr,Al)_2O_3$**, $Ca(CrO_2)_2$	Slag infusion: Complete slag infusion into refractory Surface Interaction: sag-refractory interaction, at temperature had regions that were liquid
50		50		$FeO \cdot Cr_2O_3$, tr Fe_2SiO_4	Slag infusion: limited infusion Surface Interaction: Fe eating into Cr(Al) particles, at temperature had melt surface
33	33	33		**$(Cr_2\text{-}CrAl)O_3$**[a] $(FeCr)_3O_4$	Slag infusion: complete slag infusion into refractory Surface Interaction: significant reaction at surface layer, at temperature had melt surface
25	25	25	C	**$(Cr_2\text{-}CrAl)O_3$**[a] $(FeCr)_3O_4$	Slag infusion: complete slag infusion into refractory Surface Interaction: significant reaction at surface layer, at temperature had melt surface
33	33		FeS	**$(Cr_2\text{-}CrAl)O_3$**[a] $(FeCr)_3O_4$	Slag infusion: complete slag infusion into refractory Surface Interaction: at temperature had regions that were liquid
Slags, wt%					
Artificial (Blend of oxide powders) $52SiO_2$, $20Fe_2O_3$, $20Al_2O_3$, 7CaO, 1MgO -0C				**$(Cr,Al)_2O_3$**, $(FeCr)_3O_4$ amorphous matrix	Slag infusion: complete slag infusion into refractory Surface Interaction: significant reaction at surface layer, at temperature had melt surface
Ill. no. 6 (Oxidating atmosphere) $53SiO_2$, $18Fe_2O_3$, $19Al_2O_3$, 7CaO, 1MgO -0C				**$(Cr,Al)_2O_3$**, $(FeCr)_3O_4$ $Ca_2Al_2SiO_7$, Fe_2O_3	Slag infusion: complete slag infusion into refractory Surface Interaction: significant reaction at surface layer, at temperature had melt surface
Gasisifer (Reduducing atmosphere) $38SiO_2$, $23Fe_2O_3$, $13Al_2O_3$, 4CaO, 1MgO - (23C)				**$(Cr,Al)_2O_3$**, Al_2O_3, Fe(metal)	Slag infusion: complete slag infusion into refractory Surface Interaction: significant reaction at surface layer, at temperature had melt surface
Spent gasifier refractory [ref. 7, 8, 9]				**$(Cr,Al)_2O_3$**, $(FeCr)_3O_4$	

[a] The spinel phase had split into two peaks: one characteristic of pure Cr_2O_3, the other of solid solution $(Cr,Al_2)O_3$.

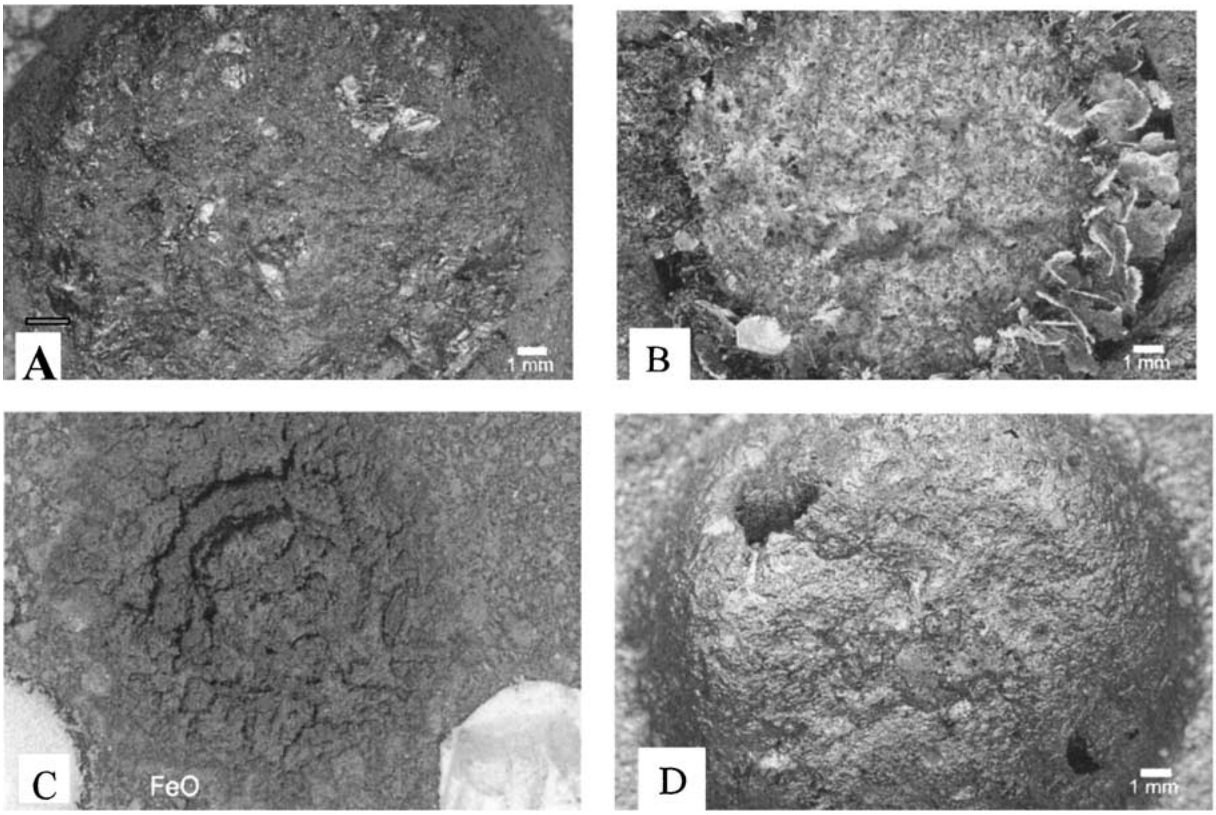

Figure 1 Cup-test oxide-slag/refractory interface before and after 24 hour furnace treatment in Ar/CO atmosphere, 1550°C, (A) Aurex-75 refractory as-drilled, (B) SiO_2 - CaO powder blend fomation of low melting $Ca(CrO_2)_2$, (C) SiO_2 - FeO powder blend formation of spinel $(Cr,Fe)_3O_4$, (D) Coal-gasifier slag.

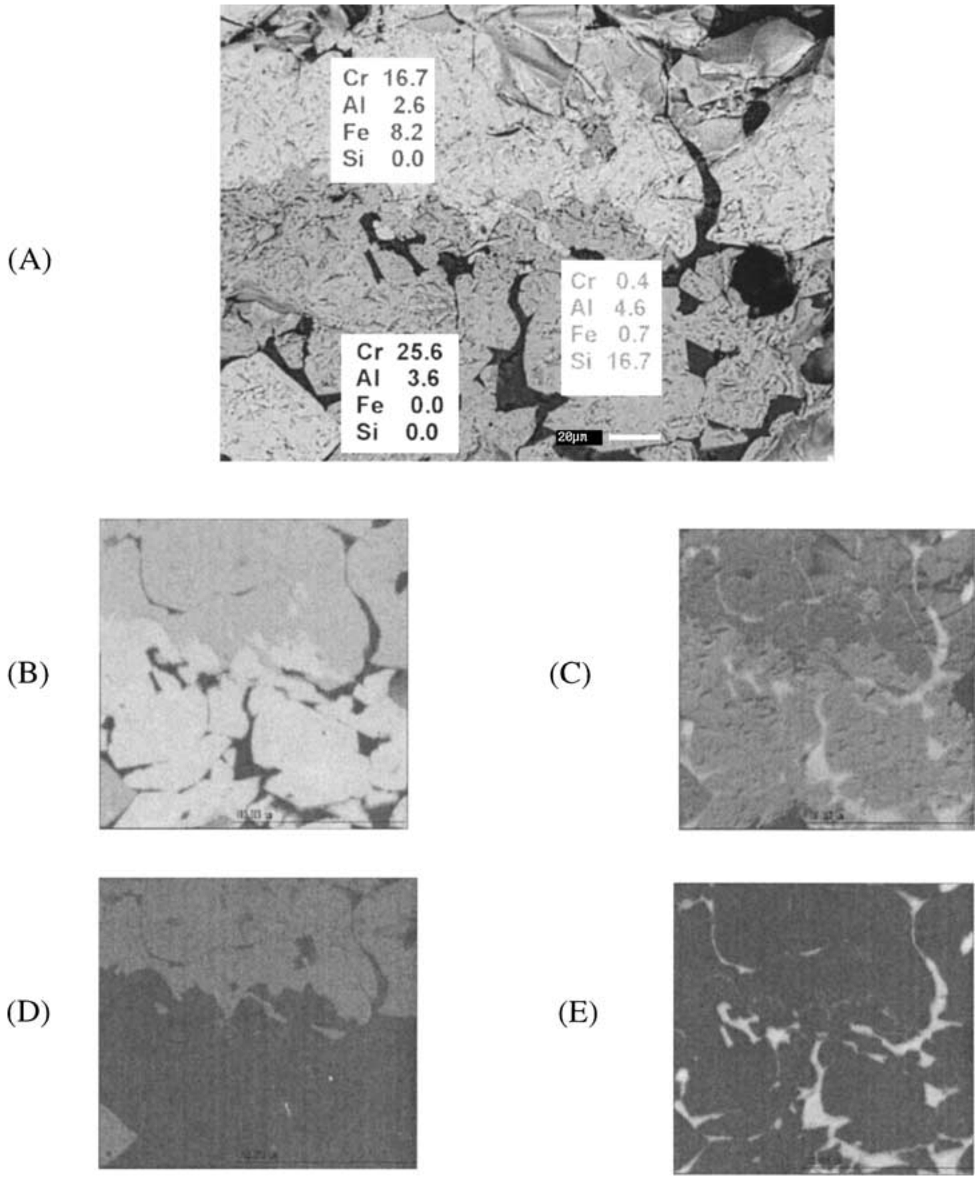

Figure 2 Scanning electron micrographs of the cross section of the gasifier slag refractory cup-test, (a) back scatter and wavelength chemical analysis of spinel phase (upper left), infused slag (lower right), and refractory (lower left), (b) secondary Cr map: reduced chromium concentration in semi-continuous spinel interface surface region, (c) secondary Al map: loss of aluminium in spinel phase, infused slag enriched in aluminium, (d) secondary Fe map: limited to the spinel phase present at the interface region, (e) secondary Si map: indepth infusion penetration of slag.

depth of oxide/slag penetration and changes in refractory microstructure. The chemistry of the infused slag was measured using SEM-wavelength dispersion analysis (Table I, Fig. 2).

The reaction product of the oxides with the refractory was determined by machining a couple of millimeters off the oxide-refractory interface at the bottom of the cup of the remaining cup section. The removed powder was subjected to X-ray diffraction analysis (Table II).

3. Data and analysis

Table I lists the oxide powder blend compositions (weight percent), the phases present at the oxide-refractory interface, and visual analysis of the oxide infusion into the refractory, i.e., the morphology of the oxide-refractory interface. Fig. 1 shows the refractory interface before and after the cup test of oxide-refractory interactions.

Table II lists the oxide elemental components (atomic percent/mole percent), the chemistry of the infused oxide at the slag-refractory surface and approximately 5 mm into the refractory, and a description of the refractory interior microstructure. Fig. 2 shows a SEM backscatter image of the oxide-refractory microstructure and the elemental mapping of the same region.

The high chrome refractory selected for this study is a commercial refractory, AUREX - 75 (Harbinson-Walker, Pittsburgh, PA, USA), currently being tried in several demonstration commercial coal-gasifiers. The refractory chemistry is a solid solution chrome (75 wt%) -alumina (25 wt%) in a sesquioxide phase. The refractory bricks are composed of sinter bonded particles producing an approximately 85% dense brick. In a separate study of the oxide-refractory infiltration region, the chrome refractory was dissolved leaving behind the infused slag which showed that the 15% porosity was interconnected (Fig. 3, ref. 10).

TABLE II Slag - refractory interactions: cup like test, A-70 refractory, 1550°C, 24 hours, environment: Ar-CO/H_2O

Artificial composition, mole% *atomic %*				**Slag chemistry, atomic % (SEM-EDX)**							
SiO_2	CaO	FeO	X	Cr	Al	O	Si	Ca	Fe	**-X- -**	**Refractory microstructure**
100				0.3	0.06	66.9	32.7				Top: no notable reaction
Si = 33				1.6	0.27	64.3	32.7				Interior: nominally 5mm from interface
48	52			0.4	4.4	69.7	12.5	12.9			Top: Ca + Si eating into refractory particles,
Si = 16	Ca = 26			1.9	0.8	68.3	31.3	10.0			Interior: dissolving small refractory particles
55		45		0.4	1.2	69.1	25.0		2.9		Top: Fe eating into Cr(Al) refractory particles,
Si = 18		Fe = 22		0.5	4.7	65.8	26.1		0.3		solid $(FeCr)_3O_4$ layer
											Interior: no noticeable reaction
34	37	29		0.5	8.2	59.9	15.4	15.5	0.6		Top: dissolved small refractory particles,
Si = 11	Ca = 18	Fe = 15		2.1	9.3	63.1	15.9	8.9	0.1		solid $(FeCr)_3O_4$ layer
											Interior: no noticeable reaction
13	14	11	**C = 61**	0.3	3.5	67.7	12.7	13.7	1.0	$C \approx 11$	Top: dissolved refractory particles, solid
Si = 4	Ca = 7	Fe = 5		1.6	5.3	67.8	11.9	14.2	0.1	$C \approx 11$	$(FeCr)_3O_4$ layer, metal Fe ppt.
											Interior: no noticeable reaction
36	39		FeS	12.1	5.3	67.9	12.1	14.3	0.1	S = 0.2	Top: Two distinct slag regions, solid
Si = 12	Ca = 20		Fe = 12	16.8	-.-	-.-	0.2	0.1	28.2	S = 54.2	$(FeCr)_3O_4$ layer
			S = 12	3.5	3.2	59.8	6.3	10.5	7.8	S = 0.7	Interior: Two distinct slag regions
				6.9	1.5	8.3	3.1	4.2	33.7	S = 41.3	FeS inside refractor
Slags, mole%/atomic %				Cr	Al	O	Si	Ca	Fe	Mg	
Artificial oxide powers				0.6	4.9	69.7	13.9	9.4	0.3	0.5	Top: Na = 0.9, K = 0.8 Ca + Si slag, eating into particles
$58SiO_2$, $19Fe_2O_3$, $13Al_2O_3$, 8CaO,				1.4	5.2	69.3	13.7	9.2	0.0	0.6	Interior: Na = 0.3
2MgO -0C				0.0	8.7	63.	21.4	5.0	5.6	0.0	starting slag composition, at%
Coal: Ill. no. 6				0.3	4.9	68.0	19.7	4.1	0.6	0.2	Top: Na = 1.4, K = 0.8 Fe-Cr solid interface
$59SiO_2$, $18Fe_2O_3$, $13Al_2O_3$, 7CaO,				1.6	5.5	67.0	14.5	10.0	0.2	0.8	Interior: Na = 0.1, K = 0.0
1MgO -0C				0.0	8.4	63.	22.7	5.0	4.8	0.0	starting slag composition, at%
Coal: Gasifier[a]				0.4	4.7	68.9	19.4	3.2	0.5	1.3	Top Na = 1.2, K = 0.8 No interaction noticed:
$33/54SiO_2$, $10/27Fe_2O_3$, $4/11Al_2O_3$,				1.6	4.5	68.8	18.7	2.3	0.0	1.3	Interior: Na = 0.3, K = 0.3
2/6CaO, 1/2MgO - (23/0C)				0.0	2.6	21.5	7.2	1.3	2.0	-.-	starting slag composition, at% [C] = 65.5
				0.0	7.9	63 .	20.7	3.8	5.7	0.0	carbon free starting slag composition, at%
Spent gasifier refractory [ref. 7, 8, 9]				0.1	4.5	67.3	23.2	2.4	0.6	0.5	Top: 10 mm from inerface
				1.8	5.4	68.5	16.3	4.9	0.1	2.1	

[a] Mole fraction of slag oxides for carbon free salg.

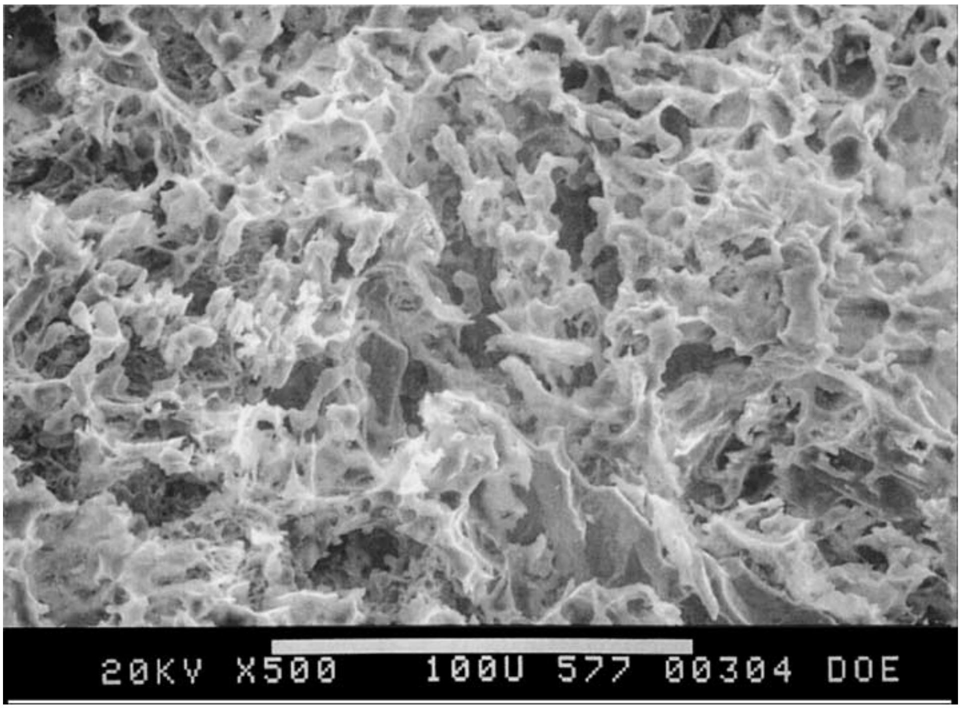

Figure 3 Infused gasifier slag. SiO_2 penetrated along the porosity openings in the refractory and formed a continuous layer. Interface surface just to left of micrograph. Refractory removed using perchloric acid solution [ref. 11].

At the laboratory cup test temperature of 1550°C, the oxide powder blends reacted to form a molten solution that wetted and infused into the 85% dense refractory, over 5 mm in 24 hours. Examination of the cup surfaces after the furnace treatment showed complete oxide/slag infusion into the refractory (except for the 100% SiO_2 test cup). All the cup bottom surfaces had undergone noticeable morphological changes. Most often the cup bottom showed that an oxide-refractory reaction had taken place at the interface and had produced new phases that were molten at the cup test temperature.

In the cup test, the oxide powder blends or slag containing iron (either FeO or FeS) formed a uniform and continuous surface layer of high melting ($>$1700°C) spinel phase $(Cr, Fe)_3O_4$ at the oxide/slag-refractory interface [11]. This spinel phase limited the extent of iron oxide penetration into the refractory to a thin surface layer. No significant iron penetration was measured or observed below the surface of the spinel phase in the infused oxide/slag except for the cup test that contained FeS. The FeS low melting point is $<$1200°C and readily infused into the refractory, probably before any of the oxides had melted. No mixture of the oxide and sulfide phases was observed, however, there appears to be a synergism between the two with respect to enhancing the dissolution of the chrome refractory (Tables I and II).

The presence of carbon mixed with the oxide blends had no measurable effect on the oxide-refractory interactions except that there were trace amounts of metallic iron present at the oxide-refractory interface. The presence of these metallic particles indicates the reducing gas atmosphere allowed some of the FeO particles to react with C to produce Fe and CO_x.

The SiO_2-CaO cup test showed that CaO reacted with the chrome refractory and dissolved the smaller refractory grains forming a lower melting $Ca(Cr,AlO_2)_2$ phase [12, 13].

Analysis showed no significant difference in either (i) the slag/oxide infusion into the refractory bricks or (ii) the reaction between the refractory with either the artificial slag blend of oxide powders or between the refractory and the gasifier coal slags.

The interaction between the artificial slags and the coal slags with the refractory was also compared to the analysis of a similar high chrome spinel refractories that had been removed from service after two years of operation in a commercial slagging gasifier (refs., Tables I and II).

4. Results and discussion

Slagging coal-gasifiers present new challenges to material science. These gasifiers are designed to operate most efficiently at coal combustion temperatures that can exceed 1650°C in a reducing environment. These elevated temperatures restrict the selection of materials that can be used to line the combustion chamber walls to refractories. In addition, at these operating temperatures, the impurities in coal become molten and can readily react with many of the commonly produced refractories. Previous laboratory studies [1–5] have shown that the higher the chrome concentration used in the refractory the better the refractory's corrosion resistance. These studies concentrated on magnesia addition to form a high Cr_2O_3-MgO and on alumina additions to form solid solution Cr_2O_3-Al_2O_3 spinel phase materials. However, because of the large quantity of refractory required and the high cost of chrome, there have been efforts to find additives to the chrome that will optimize refractory corrosion resistance and reduce cost. In the manufacture of gasifier refractories, corrosion resistance is improved by using a fully dense material. However, due to the thermal gradient and the differential thermal expansion encountered during heat-up and cool-down and the occasional local thermal excursion that may occur during operation, it is necessary to have a small amount of porosity present in the refractory bricks. Thus, the refractory bricks are produced by sintering chrome particles resulting in an 85% dense material.

Previous studies with artificial coal slags on high chrome-magnesia (chrome concentrations approaching 90%) and chrome alumina (chrome concentrations approaching 50%) refractories have shown that coal slags are extremely corrosive [1–5]. It was suggested that the principal slag reacting components were calcia (CaO) and iron oxide (FeO).

One part of this study was designed to determine the effect of the various coal impurity components by themselves and in combination. By examining the reactions of individual oxide and blends of oxide with the refractory, it maybe possible to determine if the reaction of refractories taken from commercial gasifiers is the effect of the individual components, or combinations of several components, or results from synergetic effects. Individually, the coal impurities, generally oxides, had melting temperatures above the test temperature. However, when combined with SiO_2 these oxides formed lower melting complexes that were molten at the test temperature, 1550°C. Once the slag-refractory interactions are understood it becomes possible to (a) alter the refractory material, (b) alter the processing environment, or (c) add to/eliminate from the coal chemistry to reduce the refractory interaction.

In many of the previous slag-refractory studies [1–5], refractory cylinders were immersed in molten slag and, to expedite the testing, rotated at high rpm to provide a kinetic enhanced reaction at the slag-refractory interface. The loss of refractory was measured and used to evaluate or rank the refractories. However, at the wall of an operating coal-gasifier the slag velocity running down the refractory wall is 1–5 mm/s ($<$10 m/hr., [3] suggesting an almost static slag layer at the refractory wall. This study was designed to determine the static effects that occur at the oxide-refractory interface and the change in oxide composition as it infuses into the refractory. By determining the change in oxide chemistry as it infuses into the refractory it is possible to determine if, during the prolonged slag-refractory contact time, the oxide solution is reacting with and dissolving the refractory. If there is an increase in the chromium and/or aluminium concentration in the oxide with infusion depth, than the refractory material is reacting with the oxides/slag and dissolving the bonds between refractory particles to weaken the refractory.

The results of this study are consistent with the results of previous studies of reactions of artificial blends of coal slag oxides with high chrome spinel refractories [1–5]. Slags and oxide blends readily infused into the refractory. FeO in the oxide powder blends/slag reacted with the chrome-alumina sesquioxide refractory to produce an iron-chrome/aluminium spinel phase that was limited to the slag-refractory interface. The spinel phase formed a uniform surface at the interface. The spinel lattice is greater than the sesquioxide lattice which increased the refractory surface density and, once formed, may have limited or restricted further oxide infusion into the refractory. The formation of a solid surface would limit further slag-refractory interaction to the dissolution of this iron-chromium/aluminium spinel phase [1].

When carbon was present in the oxide powder mixture or in the slag, there was little or no difference in the oxide/slag-refractory interaction, either in the phases formed or in the refractory dissolution. For the oxide-carbon powder blend cup test, a drop or two of metallic iron was observed on the oxide-refractory interface. It is probable that these metallic drops formed while the furnace was heating up and the classical reduction of iron oxide by carbon occurred. The metallic iron was stable in the reducing atmosphere. The molten iron did not wet the refractory and thus remained on the surface as the oxide infused into the refractory. Note, in examination of commercial gasifier slag powder, flakes of iron were occasionally observed.

Because iron in the coal feed stock is most likely present as FeS, in one cup test the FeO was replaced with FeS. This environment would be present during the initial phase of plant operation. After the cup tests, pockets of FeS were observed deep in the interior of the refractory as well as at the surface. Both the SiO_2-CaO mixture and the FeS phases reacted with the chrome refractory and both had higher dissolved chrome concentrations than were present in the infused oxides in the other cup tests. In operation of a commercial coal gasifier facility, it is fortunate that iron-sulphur compounds readily dissociate at gasifier operating temperatures, and that once the gasifier is operating there exists a layer of oxide slag on the refractory surface walls to protect the refractory from reacting with the FeS.

In this study and in the cited studies, CaO reacted with and dissolved the high chrome refractory forming a lower melting $Ca(CrO_2)_2$ [11]. The morphology of the CaO cup test interface layer shows that CaO readily reacted with and dissolved the chrome refractory. The presence of CaO in coal slag would play an important role in shortening the refractory service life by dissolution of the refractory hot face. When gasifiers are in operation, the slag at the refractory hot-face would continuously be renewed, providing a fresh supply of CaO at the interface resulting in a gradual corrosive loss of refractory. This study was not able to determine if the high chrome-alumina sesquioxide or the chrome-iron oxide spinel had the greater corrosion resistance.

Also, the dissolution of the refractory by CaO is important as shown by the chemistry of the oxide/slag in the interior of the refractory that had a significantly higher chromium and aluminium concentration than in the oxide/slag just below the interface. This change in chromium concentration in the infused oxide/slag and a significant reduction or loss in the number of smaller particles in the refractory just below the spinel phase shows that CaO in the slag, even at concentrations as low as 4 to 7 wt%, can affect the integrity of the refractory surface layer.

Results from previous studies that characterized a similar high-chrome-alumina sesquioxide refractory bricks that had been removed from a commercial coal gasifier after two years operation are incorporated in Tables I and II [7–9]. Little difference was noted between the results from the spent refractory and the laboratory cup tests using gasifier slag, coal slag, or an artificial blend of oxides. The depth of slag/oxide infusion penetration, surface sesquioxide - to - spinel reactions, and chromium concentrations in the infused slag were nearly identical.

Results from this study: (a) show that high-chrome sesquioxides and spinel have similar interactions with respect to slag-refractory interactions, (b) indicate the principal components of the slag in reducing the high chrome refractory service life are CaO and FeO, [CaO dissolves Cr_2O_3 forming a lower melting $Ca(CrO_2)_2$ phase. FeO reacts with the Cr_2O_3 sesqioxide phase to form a $(Cr,Fe)_3O_4$ spinel layer at the slag-refractory interface], (c) show the C concentration does not affect slag-refractory life, [Although it is possible to reduce FeO to Fe, this reaction was very limited and did not affect the slag-refractory interaction in any noticeable manner.], and (d) were reassuring in showing (i) that the laboratory test can be used to simulate conditions in the coal gasifier with respect to slag-refractory interaction, (ii) that blends of oxide powders (artificial slags) react with the refractories in a manner similar to the slag from commercial coal gasifiers, and (iii) that it is now possible to design studies to improve refractory corrosion resistance and increase refractory service life.

5. Conclusions

High-chrome sesquioxide refractories react with coal slags in a manner similar to those observed of high chrome-magnesia and chrome-alumina spinel refractories. Laboratory static cup tests using oxide powder blends and coal slags produced reactions with high chrome refractory similar to those produced in commercial coal gasifiers. The oxides/slags readily wet and infused into the 85% dense refractory. Studies of blends of different coal impurity oxides showed that (a) CaO reacted with and dissolved the chrome refractory to form $Ca(CrO_2)_2$ at the interface and CaO infused into the refractory reacting with the bonds between chrome particles and dissolving the smaller chrome particles reducing the integrity of the refractory matrix, and (b) FeO reacts with the sesquioxide to form a spinel $(Cr,Fe)_3O_4$ layer at the slag-refractory interface. Laboratory cup tests were successful in duplicating the service environment and slag-refractory interactions observed in commercial coal gasifiers.

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