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# Influence of Wettability and Reactivity on Refractory Degradation – Interactions of Molten Iron and Slags with Steelmaking Refractories at 1550°C

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Additional information is available at the end of the chapter

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## Abstract

Refractories, materials that can withstand high temperatures, play an important role in the iron and steel sector which alone accounts for ~70% of total refractories produced. In this chapter, detailed wettability and interfacial phenomena investigations on alumina-carbon and zirconia-carbon refractories at steelmaking temperatures. The wettability between refractory substrates and molten iron/slugs was investigated at 1550°C using the sessile drop approach in a horizontal tube furnace equipped with a CCD camera. Detailed experimental results were obtained on alumina-carbon/molten iron system at high temperatures. Alumina is known to be non-wetting to molten iron while carbon can be easily wetted. Observed contact angles were found to depend strongly on the substrate composition and contact time. While the refractory substrates containing 50 and 60% carbon were found to be non-wetting to molten iron, the substrates containing higher amounts of C ( $\geq 70\%$ ) were found to become increasingly wetting. Molten iron droplets were seen to spread on these substrates.

The wettability of zirconia-carbon and alumina-carbon (C: 10-20 wt %) with two steelmaking slugs (Slag 1: MnO: 50%, SiO<sub>2</sub>: 25%, Al<sub>2</sub>O<sub>3</sub>:25%, and Slag 2: MnO: 40%, SiO<sub>2</sub>:60%) was investigated at 1550°C. The wettability with Slag 1 was found to become poorer with increasing carbon content in the refractory; however a complete wetting was observed after 20 minutes of contact. Slag 2 showed a better wettability with higher carbon refractories. The extent of gasification of ZrO<sub>2</sub> – C system was found to be 9 times higher than the Al<sub>2</sub>O<sub>3</sub> – C system. At ~5 minutes of contact, the slag appeared to get lifted away from the substrate leading to a slowing down of slag penetration. The maximum height of the gaseous gap decreased with increasing carbon in the substrate [880µm, 630µm & 440µm respectively for 20%, 15% & 10% carbon in the substrate]. The formation of the gaseous gap between slag 1 and the substrate was attributed to poor wetting and gas pressure. Slag 2 did not exhibit the formation of a gaseous gap due to lower contact angles between the slag and refractory. Alumina – carbon showed higher contact values but no gas gap forma-

tion was detected. The absence of gaseous gap was attributed to insufficient gas generation in this case.

**Keywords:** Carbon based refractories, alumina, zirconia, steelmaking

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## 1. Introduction

Refractories—ceramics which can withstand very high temperatures—are used extensively by the steel industry in the internal linings of furnaces, in vessels for holding and transporting steel and slag, slide gate plates, shrouds and tundish rods [1,2]. Iron and steel producers are the largest consumers of refractories, accounting for the consumption of nearly 70% of all refractories. One of the greatest challenges lies in finding refractories that can withstand harsh environments for extended periods of time without degradation and associated product contamination. Carbon is added to a range of oxides such as alumina, magnesia, zirconia, silica, calcia etc. to enhance refractory resistance to slag corrosion, thermal shock and wear. However the degradation of carbon based refractories through interactions with molten iron and/or steelmaking slags is an important issue, as their failure/wear can lead to a loss of production time, equipment and even the steel product itself.

Globally, the industry generates several million tonnes of spent refractories annually. Refractories may last from just hours to several years, depending on service conditions and material performance [3]. When refractories reach the end of their service life, these are generally landfilled and replaced with new refractories. Carbon-bearing refractories are used extensively in steelmaking because of their excellent thermal shock, wear resistance, and strength at high temperatures. While the addition of even small amounts of carbon (<5%) to oxide refractories has resulted in significant improvements in refractory performance, these refractories can undergo rapid carbon depletion on contact with molten steel [2, 4]. Refractory selection plays a critical role in optimizing productivity, enhancing energy efficiency and minimising labour costs.

High temperature wettability of carbon based refractories with molten iron and steelmaking slags is an important rate controlling factor influencing refractory degradation. The corrosion of alumina-graphite immersion nozzles at the slag/metal interface is caused by the oxide phase in the refractory dissolving preferentially in the slag, thereby producing a graphite rich layer [5]. Alumina itself has very poor wettability with molten iron; but the addition of even small amounts of carbon can affect its contact angle (a quantitative measure of wettability) with molten iron [6]. Atomistic computer simulations to investigate the wettability behaviour of alumina-carbon substrates with molten iron showed the presence of alumina inhibited the metal penetration in the refractory strongly depressing carbon dissolution [7].

The wettability of alumina by liquid iron has been investigated extensively; the contact angles have been reported to range from 100° to 141° in the temperature range 1530 -1600°C in inert atmosphere. However in an oxidising atmosphere, the contact angle was found to reduce, with

liquid metal wetting the alumina substrate [8]. Kapilashrami et al [9] observed that in the static mode, the contact angles were found to decrease with increasing oxygen content of the metal phase. In the dynamic mode, the change of contact angle with time showed three stages at specific oxygen partial pressures; this phenomena was influenced by the diffusion of oxygen through the metal phase. A product layer consisting of  $\text{FeAl}_2\text{O}_4$  was identified over the contact area between the metal drop and substrate.

Adsorption and chemical reaction are two types of chemical interactions during the wetting process: these occur when liquid is in mechanical and thermal equilibrium but not in chemical equilibrium with the solid and gaseous phases [10]. Adsorption involves the attraction of surface-active species to the two-phase interface; the time to reach equilibrium will depend on the diffusion rates of the active species to the surface. At high temperatures, the rate of diffusion would generally be quite high and the contact angle is expected to vary with time due to associated changes in surface tensions, energies and chemical composition.

Three types of chemical reactions can occur in a solid-liquid-vapour system: the formation of a new phase at the solid-liquid interface, the dissolution of some of the substrate constituents into the liquid or the dissolution of the liquid into the substrate [11]. The wetting behaviour can be characterised easily for the system in chemical equilibrium; the change in system behaviour is controlled by the system attaining mechanical and thermal equilibrium. When surface-active elements are present at the interface, these can alter the interfacial energy at that interface [12].

Understanding the wetting behaviour for non-reactive systems is relatively simple as compared to reactive systems. In non-reactive systems, characterized by the rapid kinetics of wetting and by weak temperature dependent variations of the contact angle ( $\theta$ ), the nature of the solid surface is not significantly changed by the contact with liquid phases. Solid and liquid contact phases under conditions of thermodynamic equilibrium with the chemical potential of each component; temperature and pressure in each of the contacting phases are the same. In a non-reactive wetting system, the process of adsorption could be observed at the interface, the interfacial energy in a non-reactive system depends on the nature and structure of the contacting phases [13].

The wettability and associated interfacial reactions in the metal/refractory system are influenced by the chemical compositions of species involved, the nature and concentration of impurities and additives, experimental conditions and the physical properties of the refractory [14]. In this chapter, we present detailed wettability and interfacial phenomena investigations on alumina-carbon and zirconia-carbon refractories at steelmaking temperatures during interactions with molten iron and a casting slag at 1550°C. The focus in this chapter is on the influence of reactions taking place in the interfacial region, production of gases through in-situ chemical reactions and subsequently the contact between the refractory and the molten steel or slag.

The chapter is organised as follows. Basic experimental details and contact angle measurement methodology is presented in section 2. Recent developments in the wetting behaviour of alumina-carbon refractories due to extended contact with molten iron are presented in section

3. Chemical interactions in the  $\text{Al}_2\text{O}_3\text{-C/Fe}$  system have recently been observed at  $1550^\circ\text{C}$  [5, 15-16] leading to low temperature carbothermic reduction of alumina in the presence of molten solvent. Implications of these reactions on the wetting behaviour are discussed. In section 4, the interactions of casting slags with carbon based refractories are presented as a function of refractory composition. The role of in-situ gas generation on interfacial contact and refractory corrosion is discussed. Section 5 summarises key findings and recent developments with implications for future developments in the field towards minimising refractory degradation and extending the operating life of steelmaking refractories.

## 2. Experimental

High purity (99.8%) fused alumina was mixed thoroughly with synthetic graphite with 5 wt % phenolic resin as a binder. The concentration of carbon in the substrate ranged between 50 and 90 wt%. Refractory substrates were prepared by compacting the mixture in a steel die using a hydraulic press and pressing to a pressure up to 10MPa. The compacted cylindrical substrates (25 mm diameter, 3-4 mm thick) were baked at  $150^\circ\text{C}$  for 48 hours for enhancing their structural integrity. The weight of the metallic iron (0.03 %C) used was 1.0 gm. Sessile drop wettability investigations on the system were carried out at  $1550^\circ\text{C}$  in a laboratory scale, horizontal tube resistance furnace (Figure 1) [15]. Initially, the sample was held on a specimen holder, which could be pushed to the centre of the hot zone of the furnace with the help of a graphite rod.

The melting of iron marked the beginning of contact time. A high resolution charge-coupled device (CCD) camera fitted with an IRIS lens was used to capture the live in-situ phenomena in the furnace. The output from the CCD camera was channelled to a digital video recorder (DVD) and a television monitor to record the entire experimental process as a function of time. This feature allows specific images, displaying the contact between the metal and carbonaceous material to be captured as a function of time from the DVD, which were subsequently processed by a computer. A time-date generator was used in the system to display the duration of the experimental process. Specially designed software was used to measure contact angles on the basis of a curve fitting exercise. Details of this software have been given elsewhere [17].

Wettability investigations were also carried out on alumina-carbon (C: 10-20 wt %) refractories with a steelmaking slags (Slag 1: MnO: 50%,  $\text{SiO}_2$ : 25%,  $\text{Al}_2\text{O}_3$ :25%; Slag 2: MnO:40%,  $\text{SiO}_2$ :60%) at  $1550^\circ\text{C}$ . These studies were focussed on the role played by in-situ reduction reactions, gas generation and interfacial phenomena on the wettability between carbon-based refractories and molten slags.

The liquidus temperature of both meniscus slags was estimated using the thermodynamic package *Fact Sage* [18]. High purity reagent grade oxides MnO and  $\text{SiO}_2$  powders supplied by Sigma Aldrich Chem., UK (Purity >99%) and, reactive  $\text{Al}_2\text{O}_3$  powder supplied by Alcoa, Australia (Purity >99%) were mixed uniformly in appropriate weight proportions and the melting of oxide mixture was carried out in a platinum crucible in an induction furnace

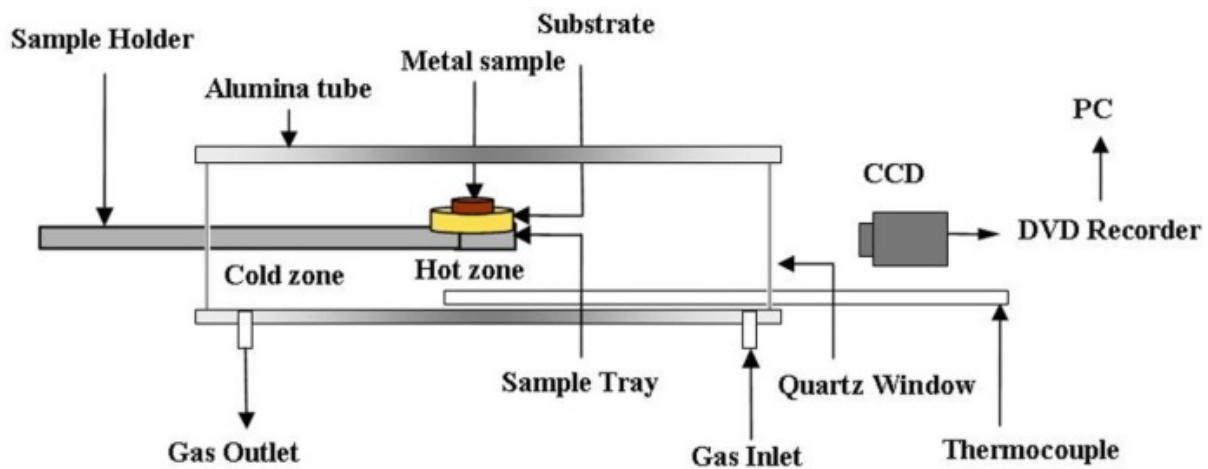


Figure 1. A schematic representation of the experimental arrangement

maintained at the melting temperature. The molten slag was water quenched, dried, grounded and remelted several times to ensure compositional homogeneity. The interfacial region between the slag and the refractory was analysed by optical and scanning electron microscopy (SEM) on Model S-3400X. Energy dispersive spectroscopy (EDS) was used to identify the elemental distribution in selected regions.

### 3. Interactions of $\text{Al}_2\text{O}_3$ -C refractories with molten iron

#### 3.1. Wettability of $\text{Al}_2\text{O}_3$ with molten iron

The wettability of alumina by liquid iron has been investigated extensively. The contact angles were found to be in the range  $100^\circ$  to  $141^\circ$  at  $1530$  -  $1600^\circ\text{C}$  in the presence of inert gases such as helium, argon, hydrogen gases and under vacuum. Under oxidising atmosphere, the contact angle was found to reduce significantly and molten iron was found to wet alumina substrate [8]. Kapilashrami et al [19] also made a similar observation that in the static mode, the contact angles of liquid iron on alumina substrate were found to decrease with increasing oxygen content of the metal phase. Pitak and P'yanykh [20] investigated the wetting of refractories with molten steel; a change in wetting from  $112^\circ$  to  $90^\circ$  was observed starting from 7 min to 15 min at  $1560^\circ\text{C}$ .

Alumina may therefore be expected to act in an inert manner, creating a physical barrier to chemical reactions and/or mass transfer and influence wettability when interacting with iron [19, 21-22]. Key experimental results on the wettability of alumina with molten iron have been summarised in Table 1.

The composition of molten iron used in these studies is given below:

*ARMCO (M15) iron (ppm):* 180[C]; 100[Si]; 1600[Mn]; 60[P]; 250[S]; 550[O]; 36[N]

*St20K steel (%):* 0.19C, 0.3Si, 0.65Mn, 0.03S, 0.016P, 0.02Ti, 0.025Al, 0.0075O



*St35 steel (%)*: 0.35C, 0.29Si, 0.7Mn, 0.025S, 0.026P, 0.09Cr, 0.29Ni, 0.22Cu

Argon+%O: slightly oxidized Argon

*St35L steel (%)*: 0.38C, 0.42Si, 0.56Mn, 0.03S, 0.04P

*St60 steel (%)*: 0.61C; 0.67Mn; 0.27Si; 0.016P; 0.25S; 0.12Cu; 0.03Cr; 0.04Ni

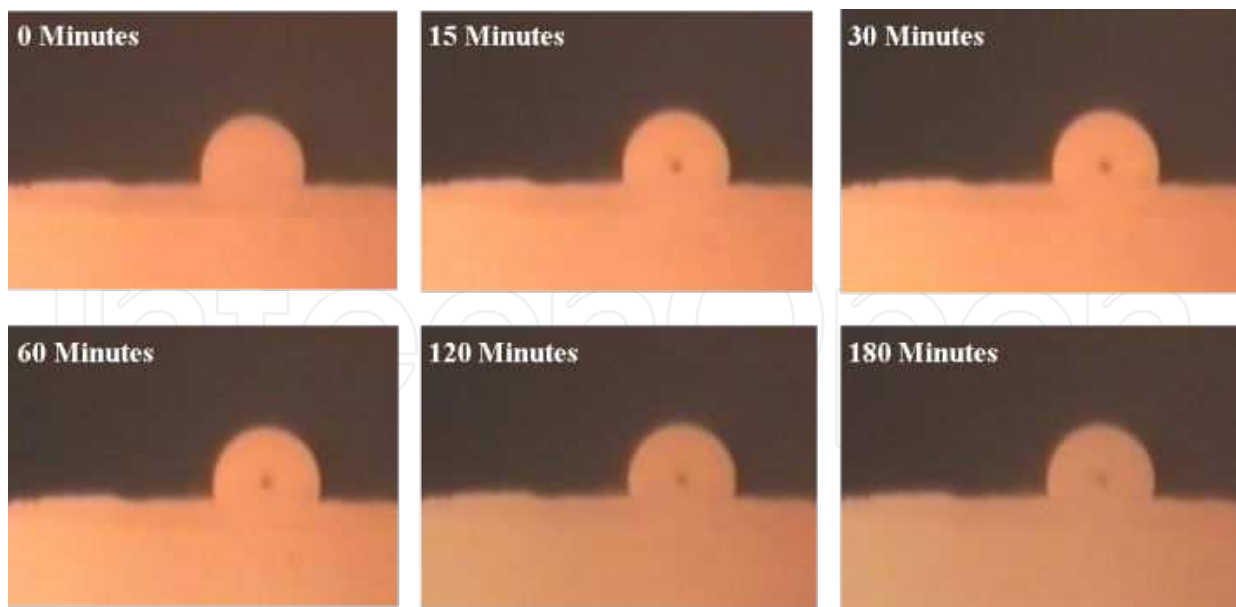
Metal	Atmosphere	T (°C)	$\theta$ (°)
ARMCO (M15)	Vacuum	1550	141
Electrolytic iron	H <sub>2</sub>	1550	121
Electrolytic iron	Helium	1550	129
Fe+3.9%C	Helium	1570	105
St50steel	Helium	1560	120
St60steel	Helium	1560	117
08Yu steel	Helium	1560	125
Fe+0.2%C	Argon	1550	123
St20K steel	Argon	1560	115
St35 steel	Argon	1500	112
St35 steel	Argon	1550	105
St35L steel	Argon	1560	130
Fe+0.45%C		1535	105
St60 steel	Helium	1530	109-100
St60 steel		1550	136

**Table 1.** The wettability of alumina with molten iron [23]

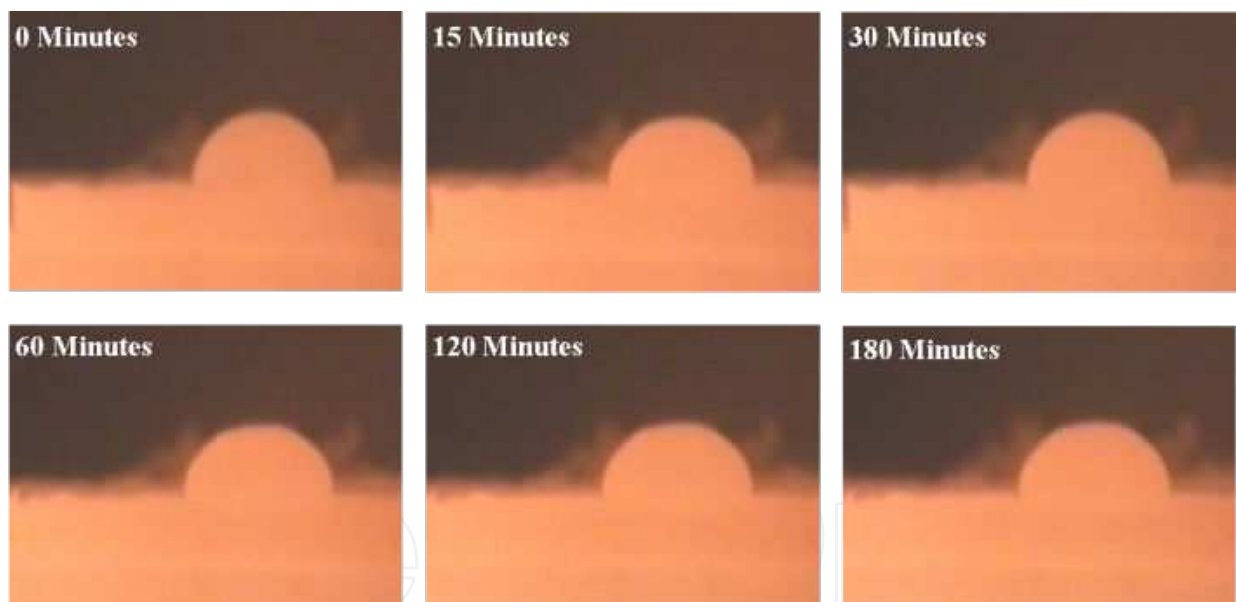
### 3.2. Effect of carbon concentration in the substrate

Experimental results in the form of video images of alumina-carbon (50-90%) substrates in contact with molten iron are shown in Figures 2 to 6. With 50% C in the substrate, molten iron is clearly non-wetting at  $T=0$ . There was not much change in the video images even after three hours of contact (Figure 2). The system continued to remain non-wetting; not much change was observed in contact angles.

With C increasing to 60% in the substrate (Figure 3), although the system was still non-wetting, the overall contact angles appear to have decreased. Once again, time did not have much influence on wettability. However, the system appeared to be reacting slightly as indicated by the gaseous whitish clouds rising from the substrate and tending to surround the melted iron droplet.



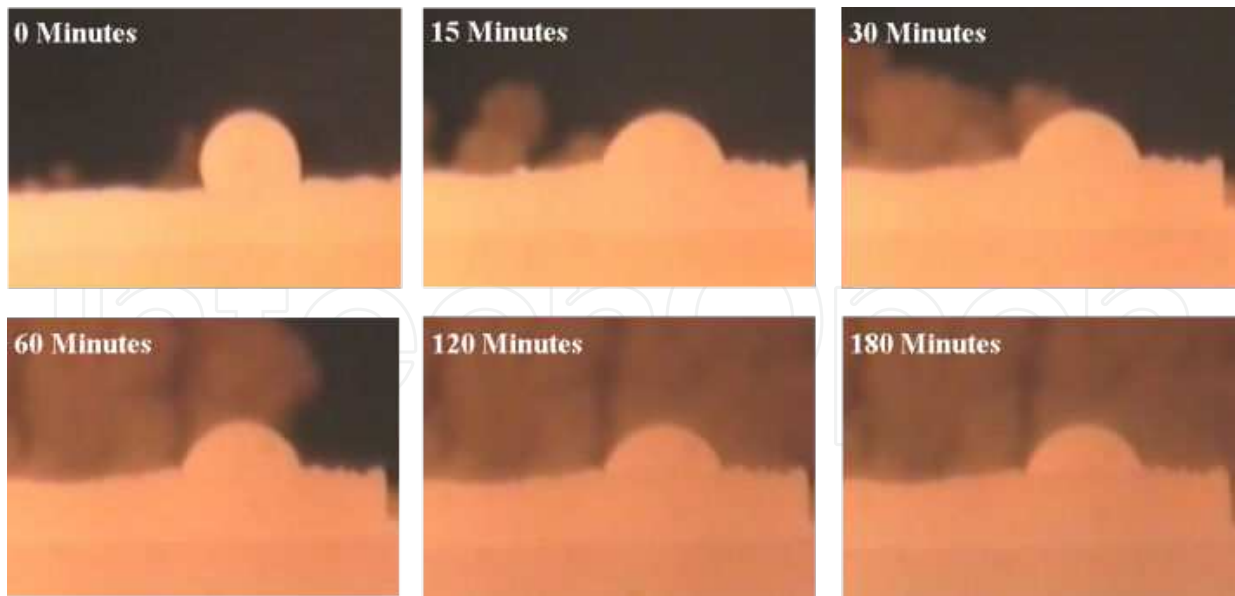
**Figure 2.** High temperature (1550°C) images of Alumina-50 wt% synthetic graphite substrate in contact with molten iron droplet after extended period of contact.



**Figure 3.** High temperature images of Alumina-60 wt% synthetic graphite substrate in contact with molten iron droplet after extended period of contact. A small amount of gaseous cloud can clearly be observed in the background.

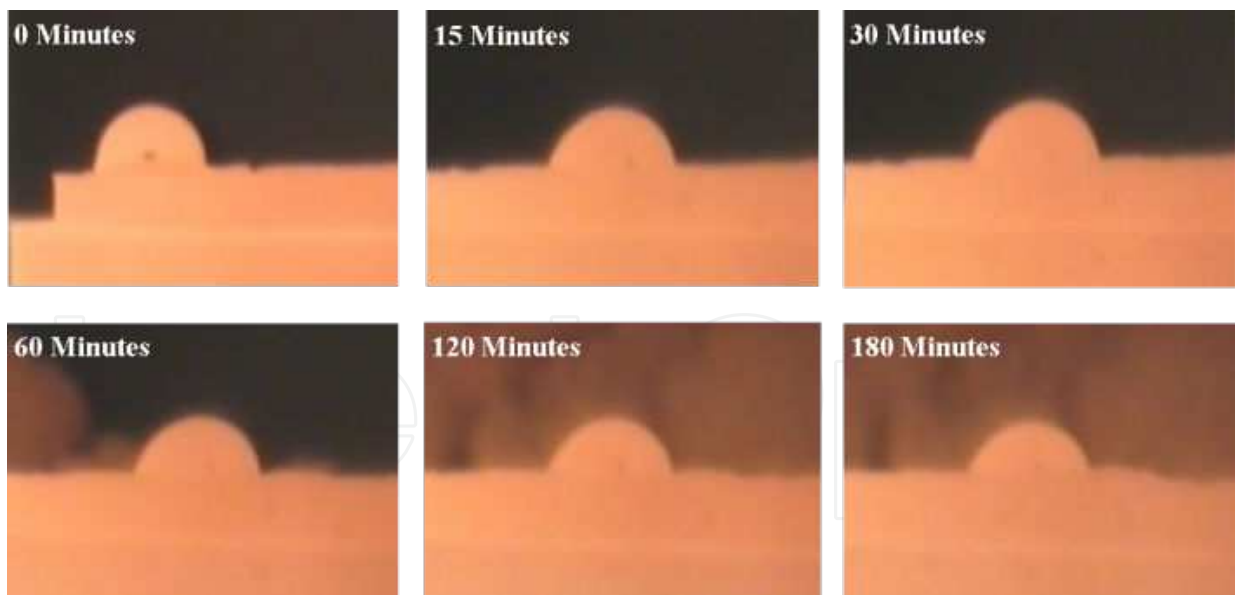
With carbon concentration increasing to 70% in the substrate (Figure 4), although it was still non-wetting ( $\theta > 90^\circ$ ) initially, the contact angle decreased rapidly within 15 minutes of contact. The droplet was seen to flatten out on the substrate. This increased level of contact was seen to persist even after three hours. The system also started to show high level of gaseous activity. Some gaseous clouds could be seen even at  $T=0$ ; these spread right across the iron droplet after 2 and 3 hours. These gaseous products indicate chemical/reduction reactions occurring in the





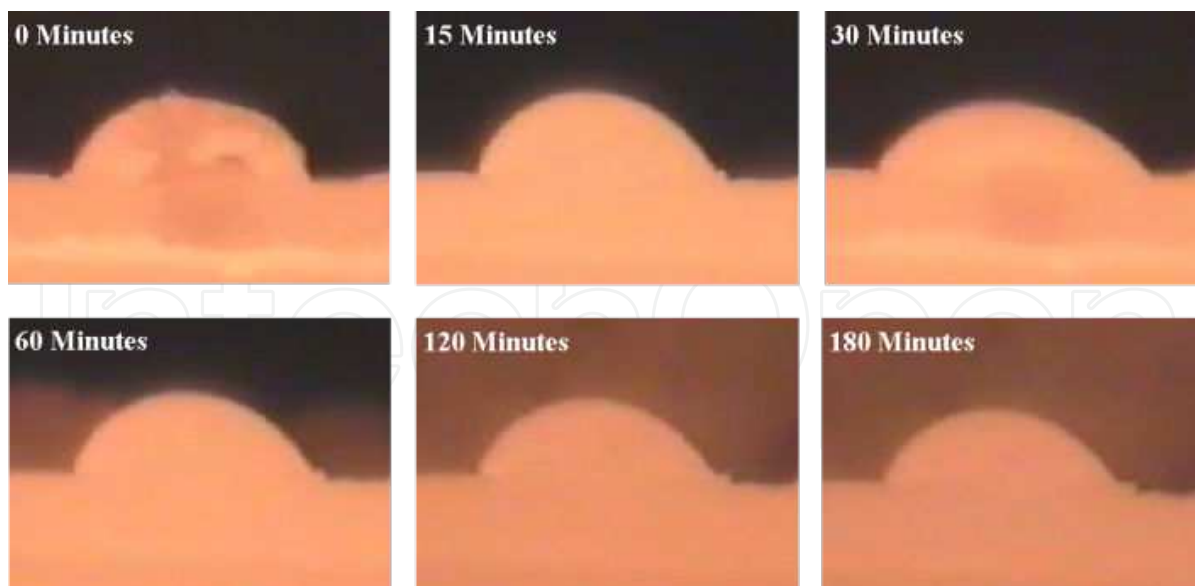
**Figure 4.** High temperature images of Alumina-70 wt% synthetic graphite substrate in contact with molten iron droplet after extended period of contact. A large amount of gaseous cloud can clearly be observed in the background.

system. Similar results were obtained for carbon contents of 80 and 90% in the substrate (Figures 5 and 6).



**Figure 5.** High temperature images of Alumina-80 wt% synthetic graphite substrate in contact with molten iron droplet after extended period of contact. A large amount of gaseous cloud can clearly be observed in the background.

Numerical values of contact angles as determined by especially designed software [17] have been plotted in Figure 7. For 50 wt% C in the substrate, the contact angles started at  $96^\circ$  initially and rose to  $100^\circ$  over extended contact. On the other hand, initial contact angles were higher

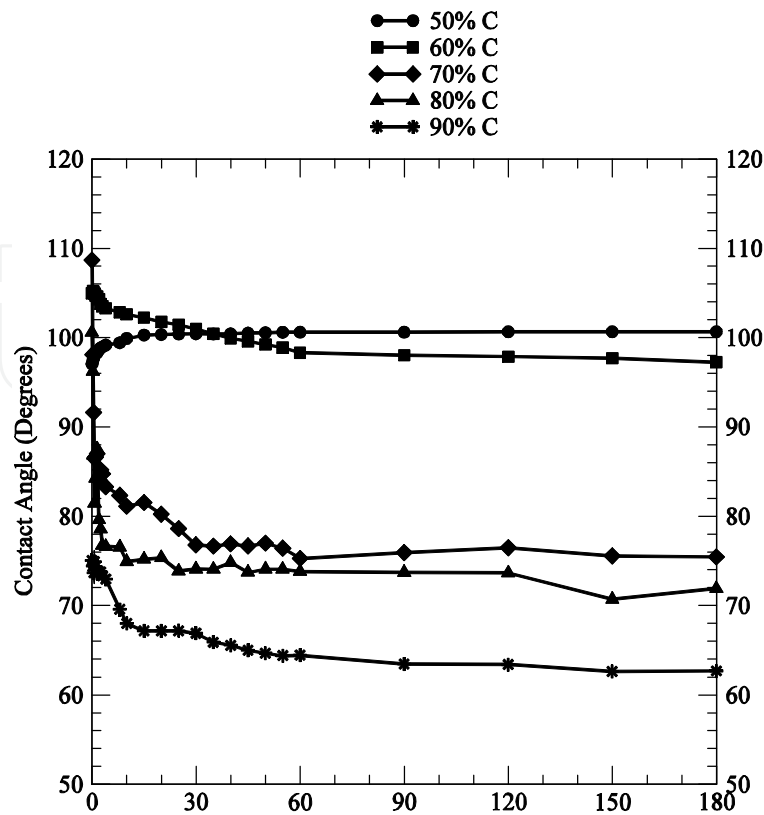


**Figure 6.** High temperature images of Alumina-90 wt% synthetic graphite substrate in contact with molten iron droplet after extended period of contact. A large amount of gaseous cloud and the flattening of metal droplet on the substrate surface can clearly be observed.

(109°) for the substrate containing 60 wt% C; these slowly reduced to 96° over extended period of contact. For substrates containing 70 wt% C, even though the contact angles showed poor wetting (92°) during initial contact, these showed a rapid decline and later settled down after 1 hour of contact. A similar behaviour was observed by substrates containing 80 and 90 wt% C, which showed a further improvement in wettability as represented by a reduction in contact angles.

These results indicate that the relative proportion of carbon in the refractory substrate had a very strong influence on their wettability with molten iron at 1550°C. Observed results can clearly be separated in to two groups: first group (C: 50%, 60%) which is non-wetting to molten iron and the second group (C ≥ 70%) which shows good wettability with molten iron. A clear transitional behaviour can be observed between the two groups. One of the key differences between the two groups was the high level of gaseous activity for the second group. The occurrence of chemical/reduction reactions between alumina-carbon substrates and molten iron can result in the generation of gaseous products (CO, CO<sub>2</sub>, AlO, Al<sub>2</sub>O etc.). These reactions appear to have a strong influence on wettability. While time had a strong influence for all substrates during initial stages of contact (up to 30 minutes), generally stable values of contact angles were observed over longer times up to 3 hours.

These studies have shown that the wettability of alumina-carbon refractories with molten iron is a strong function of substrate composition and carbon content. This study is expected to play a crucially important role in understanding degradation of carbon based refractories and the contamination of steel with reaction products. Extensive generation of gaseous products was observed after the system undergoing transition from poor wetting to good wetting; this study is therefore expected to help define limiting values of carbon that could help minimise refractory degradation.



**Figure 7.** Contact angles as a function of substrate composition and time. The level of carbon in the refractory substrate has clearly been marked.

### 3.3. Effect of impurities

The effect of impurities present in carbons can have a significant influence on wettability. In this section, results on the use of synthetic as well as natural graphite are presented. The failure of the refractories depends on the interfacial behavior of the metal/refractory system and the ability of the liquid metal to 'wet' the refractory. The wettability investigations of liquid iron on alumina-synthetic graphite substrates were conducted at 1550°C using the sessile drop approach. From the video images captured by the CCD camera, contact angles at various times were measured in different alumina-graphite substrates containing 10, 20 and 30% synthetic graphite labelled as AS1, AS2 and AS3 respectively. Figure 8 shows high temperature sessile drop images for AS1, AS2 and AS3 refractory substrates containing 12.9 wt %C, 22.8 wt% C and 32.7 wt %C respectively at 1, 5 and 30 minutes time intervals.

From Figure 9, it can be seen that for all the substrates, there was a sharp drop in contact angles in the first five minutes followed by an increase in the next ten minutes with contact angles finally stabilizing after 15 min from the time of initial contact. With increasing carbon level from 10 to 30% affects wettability, but it does not have a strong influence and is not able to change the wetting behaviour from non-wetting to wetting. As with increased carbon content, the contact angle gets reduced, but still after 30 minutes of experimental time, where contact angle becomes stable, the final contact angle was more than 90°.

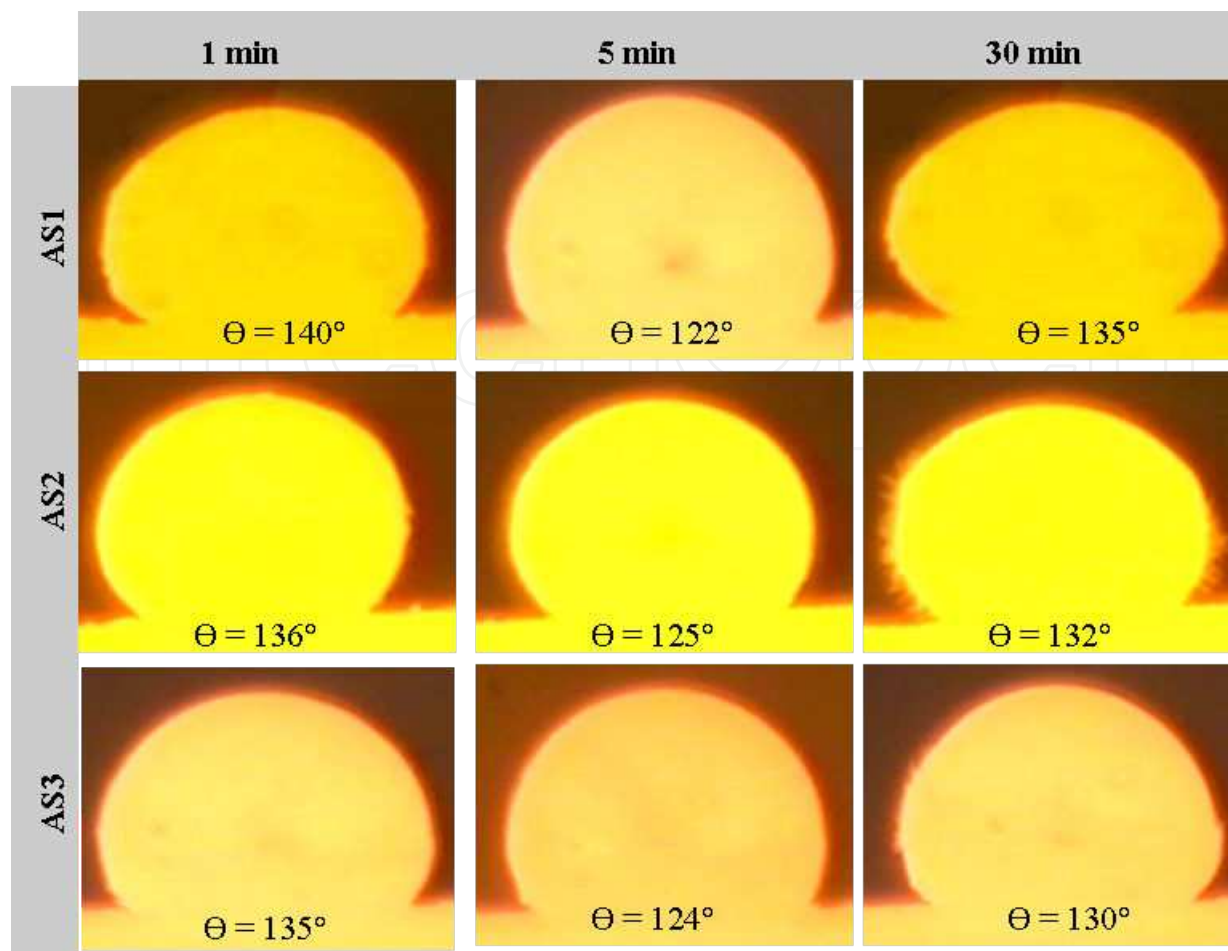


Figure 8. Molten iron droplet images at 1550 °C for different time intervals for alumina-synthetic graphite substrates

The wettability and contact angle measurements of liquid iron with natural graphite/alumina substrates were carried out at 1550°C under argon atmosphere to determine contact angles as a function of time. From the video images captured by CCD camera, the contact angles at various times were measured in different alumina-graphite substrates containing 10, 20 and 30% natural graphite labelled as AN1, AN2 and AN3 respectively.

Figure 10 represents high temperature images of molten iron droplets during reaction with alumina-natural graphite for AN1, AN2 and AN3 substrates containing 12.7wt%C, 22.4 wt% C and 32.1 wt% C respectively at 1, 5 and 30 minutes time interval. The measured data has been plotted in Figure 11 outlining the trend of the wetting behavior of all three alumina-natural graphite substrates during 30 minutes experimental time. It is seen that, there was first a drop in contact angles for all the substrates in the first five minutes which was followed by an increase over the next 10 minutes, after which the contact angles stabilized to around 130° for all the substrates within 15 min from the start of the experiments.

From the wettability data, it was concluded that the system was in chemical non-equilibrium till 15 minutes of reaction time and after that system achieved a state of chemical equilibrium from 15 to 30 minutes of reaction time. In alumina-natural graphite/iron refractory system, all

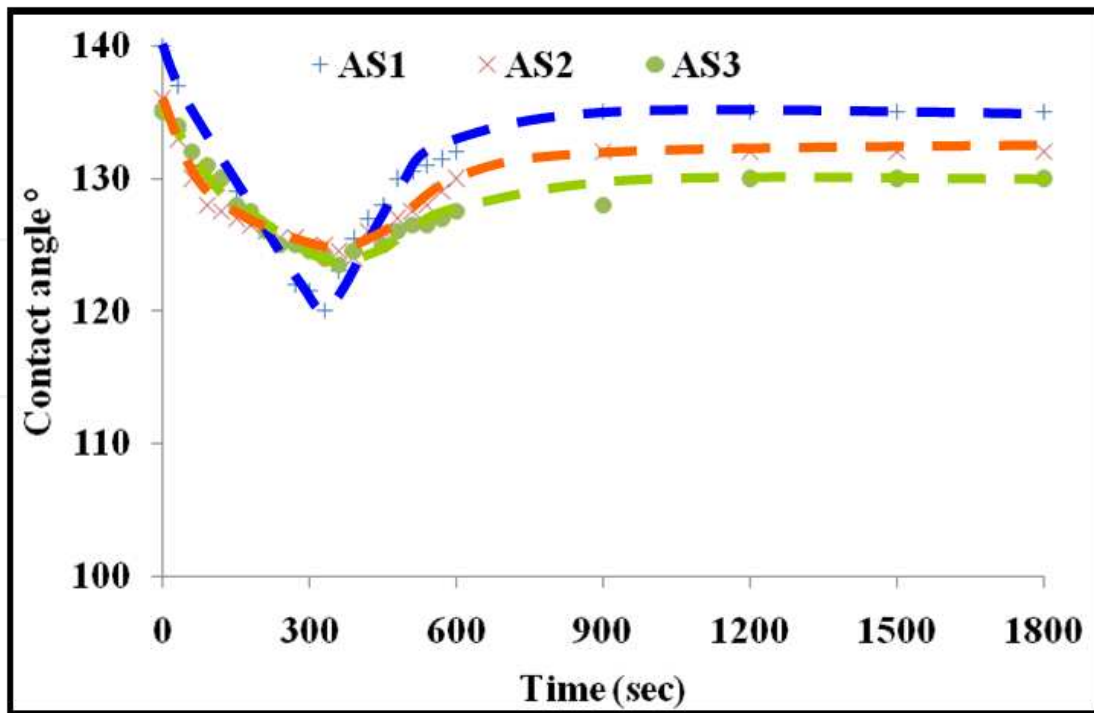


Figure 9. Variation of contact angles of molten iron with time for alumina-synthetic graphite substrates at 1550 °C.

three refractory substrates had stabilized at contact angles of 130°, while alumina-synthetic graphite substrates/iron refractory system, final angles were stabilized at 135°, 132° and 130° respectively for AS1, AS2 and AS3 substrates during 15 to 30 minutes of reaction time.

It can also be seen that increasing the carbon level from 10 to 30% had some influence on wettability, but it was not sufficient to change the wetting characteristics from non-wetting to wetting. With increased carbon content, the contact angles showed an increase; however throughout the course of the experiments, the angles were higher than 90°.

During extended contact of refractories with molten iron, some iron is known to penetrate the refractory substrates as carbon is being depleted. To study the influence of metal within the refractory substrate itself, the used refractory of AS1-Fe sample with 10, 20 and 30 % was mixed with virgin refractory composition of AS-1; the mixture termed as recycled refractory was labelled as AS1-10R, AS1-20R and AS1-30R. The wt% ratio of alumina and carbon content in these recycled refractories are given in Table 2.

Sample label	Used Refractory	Virgin Refractory	Wt. % Al <sub>2</sub> O <sub>3</sub>	Wt. % C
AS1-10R	10%	90%	87.3	12.7
AS1-20R	20%	80%	87.6	12.4
AS1-30R	30%	70%	87.9	12.1

Table 2. Composition of recycled refractory substrates



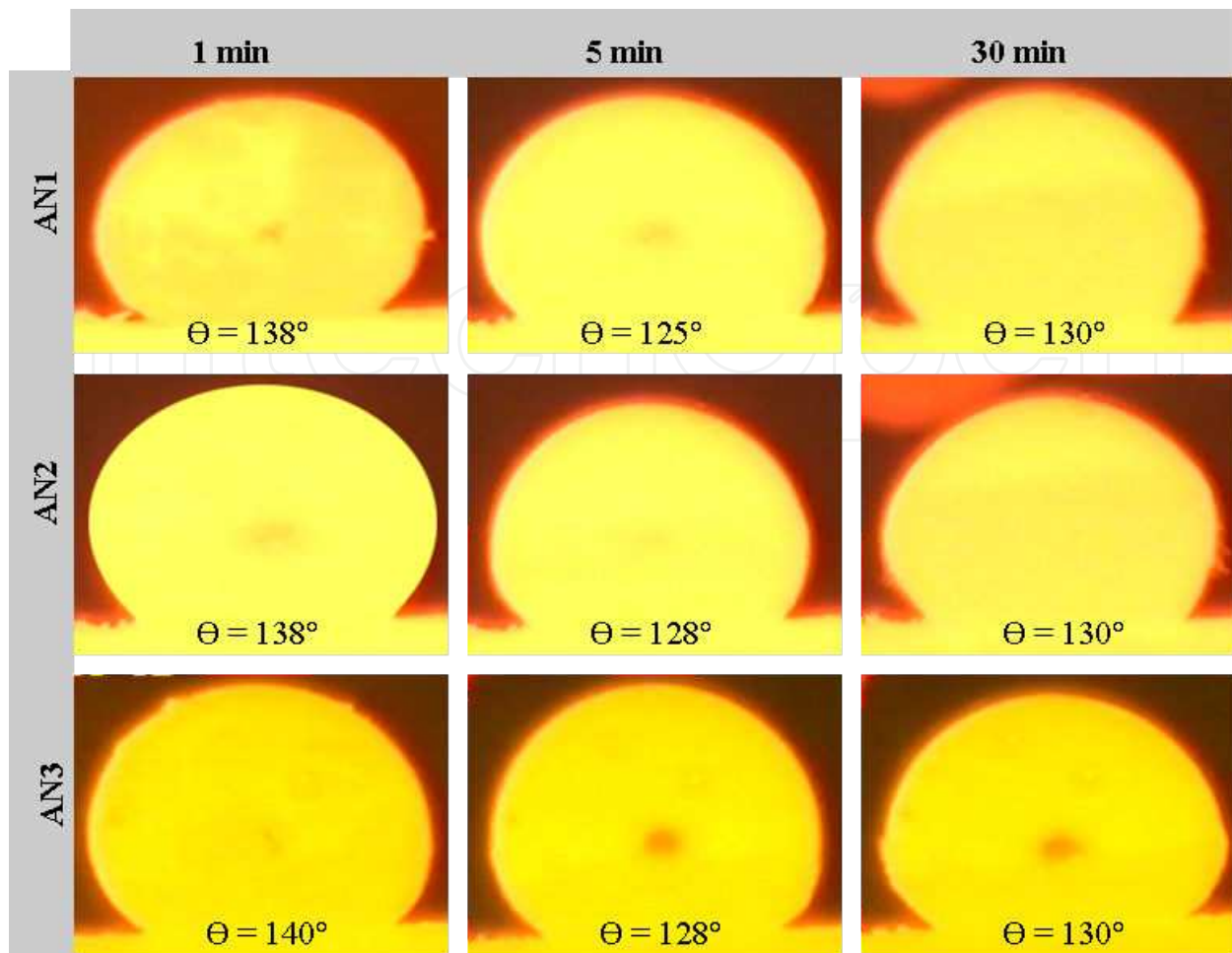


Figure 10. Molten iron droplet images at 1550 °C for different time intervals for alumina-natural graphite substrates

The wettability investigations of liquid iron droplet with recycled refractory substrates were conducted at 1550 °C under argon atmosphere and contact angles were measured as a function of time from the video images captured by a CCD camera. Figure 12 shows high temperatures sessile drop images for AS1-10R, AS1-20R and AS1-30R refractory substrates respectively containing 12.7 wt %C, 12.4 wt% C and 12.1 wt %C at 1, 5 and 30 minutes time intervals.

From Figure 12, the contact angles were determined as 118°, 119° and 130° during the first minute of the reaction for substrates AS1-10R, AS1-20R and AS1-30R respectively. After that contact angles dropped to 115°, 116° and 127° respectively for these substrates in the next 5 min. These then increased to 122°, 124° and 132° over the next ten minutes respectively and then these angles remained fairly unchanged during the reaction time (30 min).

It is seen from Figure 13 that for all the substrates, there was a sharp drop in contact angles in the first five minutes followed by an increase in the next ten minutes with the angles finally stabilizing within 15 min from the time of initial contact. This trend was quite similar to the one observed for virgin refractories as detailed above.



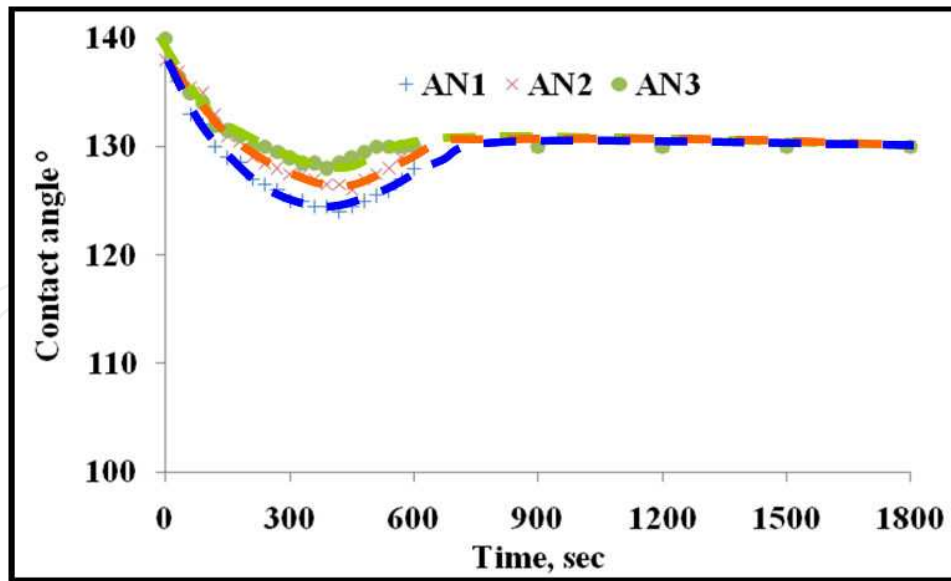


Figure 11. Variation of contact angles of molten iron with time for alumina-natural graphite substrates at 1550 °C.

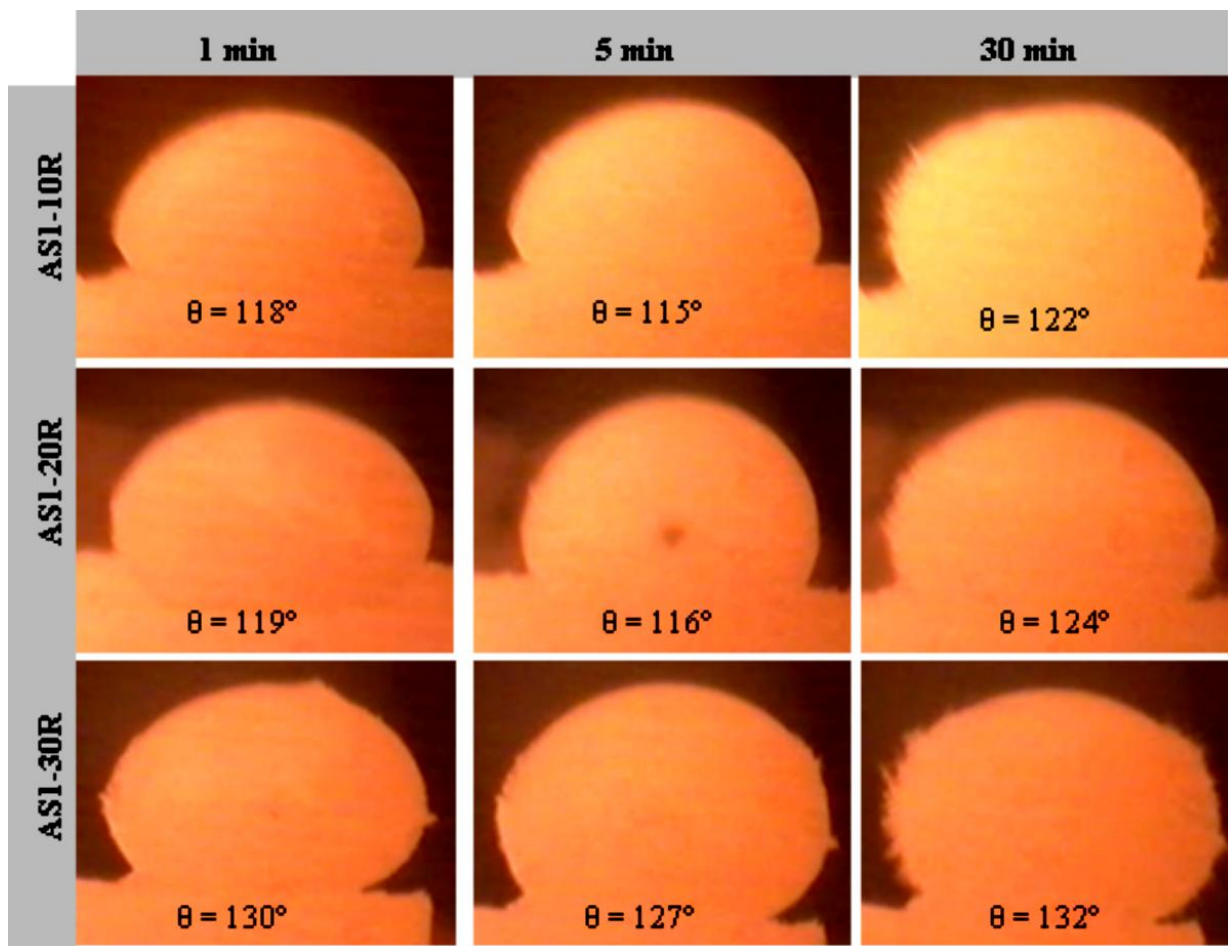


Figure 12. Molten iron droplet images at different times for recycled refractory substrates

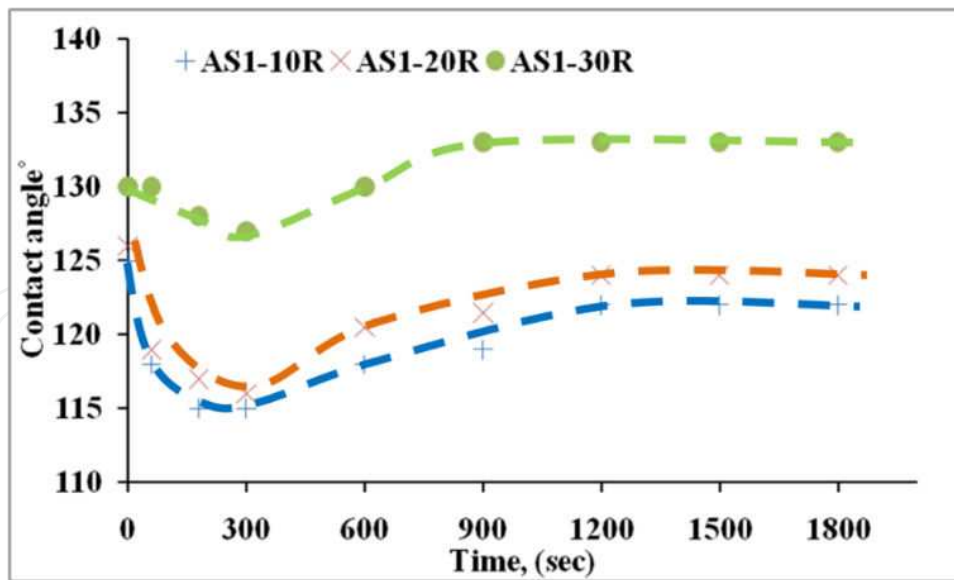


Figure 13. Dynamic contact angles of AS1-10R, AS1-20R and AS1-30R substrates at 1550 °C

#### 4. Interactions of ZrO<sub>2</sub>-C and Al<sub>2</sub>O<sub>3</sub>-C industrial refractories with molten slags

Detailed results presented in section 3 represent experimental results under controlled laboratory conditions. In this section, we present results from some industrial carbon based refractories with molten slags, typically encountered during casting. The composition of some of substrates investigated is given in Table 3. The chemical composition of slag 1 is given in Table 4.

Composition	Slag	Duration (min)	Shape	Surface
85%ZrO <sub>2</sub> +15%C	1	60	Flat	Non-Oxidized
85%ZrO <sub>2</sub> +15%C	1	60	Flat	Oxidized
85%Al <sub>2</sub> O <sub>3</sub> +15%C	1	60	Flat	Non-Oxidized

Table 3. Industrial flat ZrO<sub>2</sub>-C & Al<sub>2</sub>O<sub>3</sub> samples

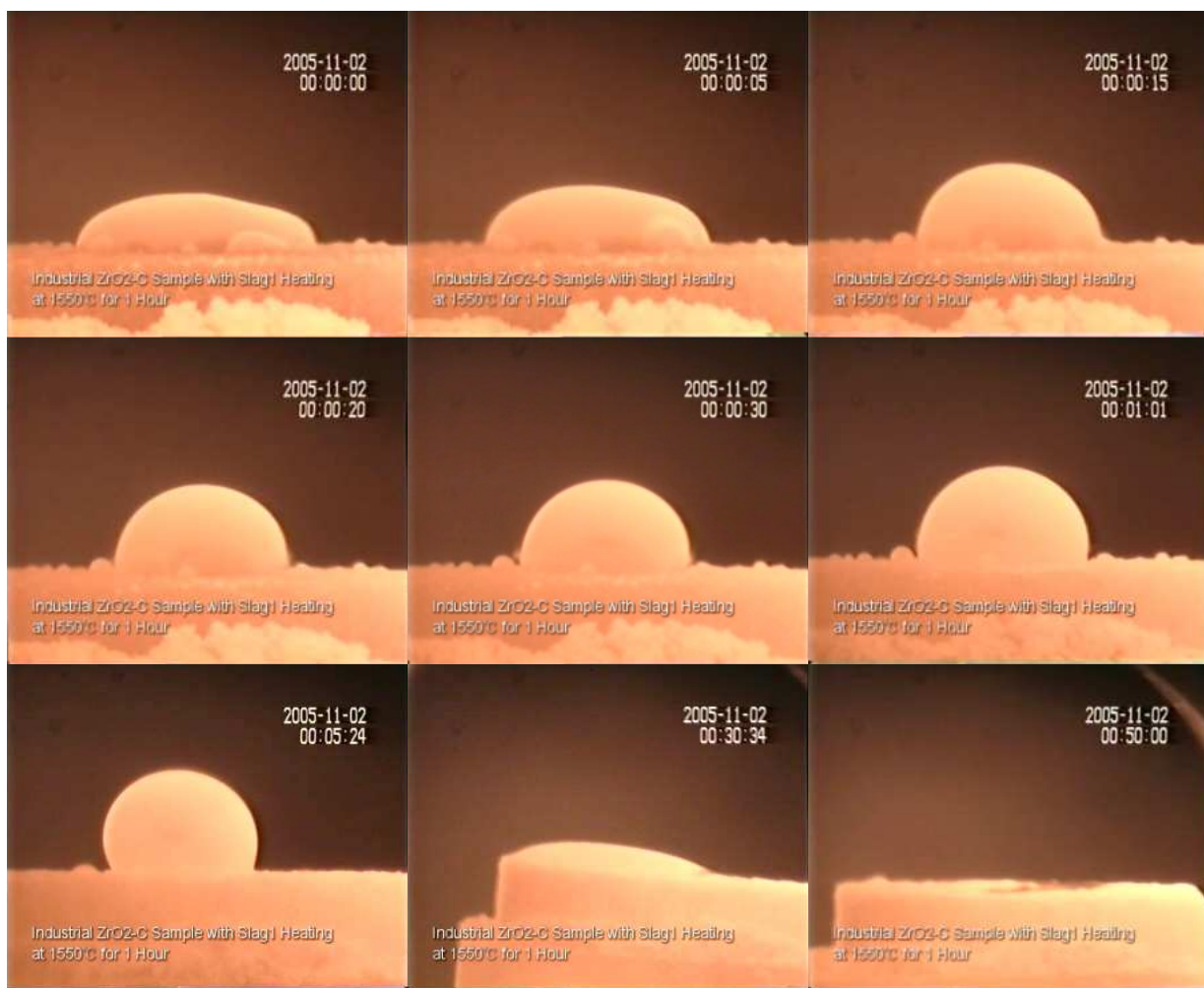
		Slag 1
Slag composition, wt %	MnO	50
	SiO <sub>2</sub>	25
	Al <sub>2</sub> O <sub>3</sub>	25
Estimated liquidus temperature, °C		1420
Melting temperature, °C		1600

Table 4. Chemical compositions of laboratory prepared slags

#### 4.1. Industrial Flat ZrO<sub>2</sub>-C Samples with Slag 1

In the sessile drop investigation, the contact angle between slag and refractory substrate can be used to investigate the slag wettability to the substrate samples. Video images of the reaction assembly during interactions at 1550 °C are given in Figure. 14. The time of interaction is indicated on the top right corner of these sessile drop images.

The contact angle measurement results of the non-oxidized ZrO<sub>2</sub>-C sample (Figure. 14) shows that the contact angle between the substrate and slag 1 reached the highest value of 120° at 5 minute, then decreases dramatically to 60° and stable at around 60° for 15 minutes, after that the contact angle dropped quickly until the slag 1 entirely spreads onto the ZrO<sub>2</sub>-C substrate. These results have been summarised in Figure. 15.



**Figure 14.** Industrial non-oxidized flat ZrO<sub>2</sub>-C samples with slag 1 (MnO 50%wt, SiO<sub>2</sub> 25%wt, Al<sub>2</sub>O<sub>3</sub> 25%wt) heating at 1550°C for 1 hour

The condition of the refractory surface appeared to have a significant influence on the wettability behaviour of refractories. Figure 16 shows corresponding results when the refractory surface had been pre-oxidised. In contrast, the CCD images indicate good wetting

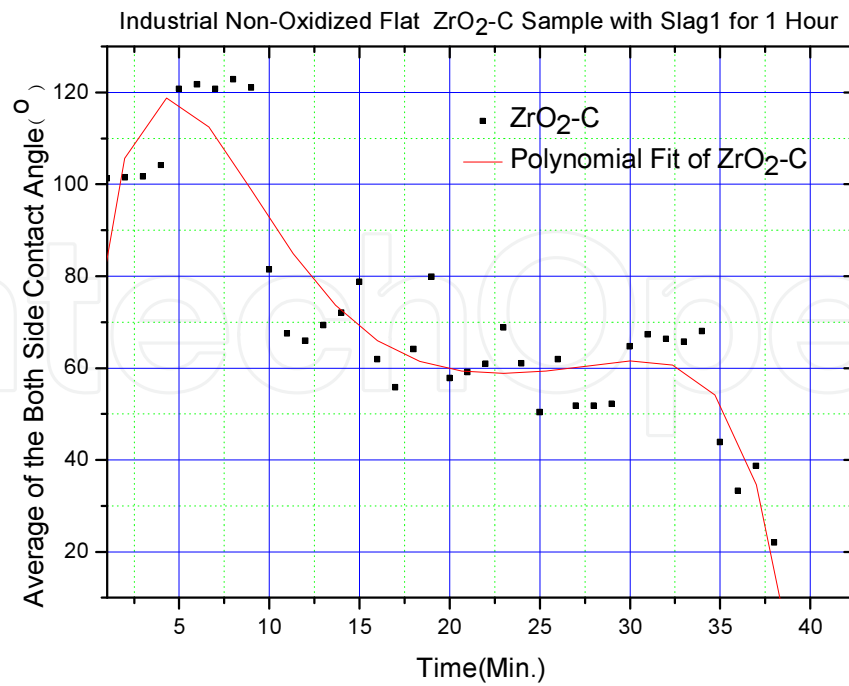


Figure 15. Industrial non oxidized flat  $ZrO_2-C$  sample with slag1 heating at  $1550^{\circ}C$  for 1 hour

between the oxidized  $ZrO_2-C$  substrate and slag 1. The slag 1 drop had spread on the top of the substrate, after the slag powder had fully melted in only 1 minute. Due to the limitation of the contact angle software, the quantitative contact angle trend is not available.

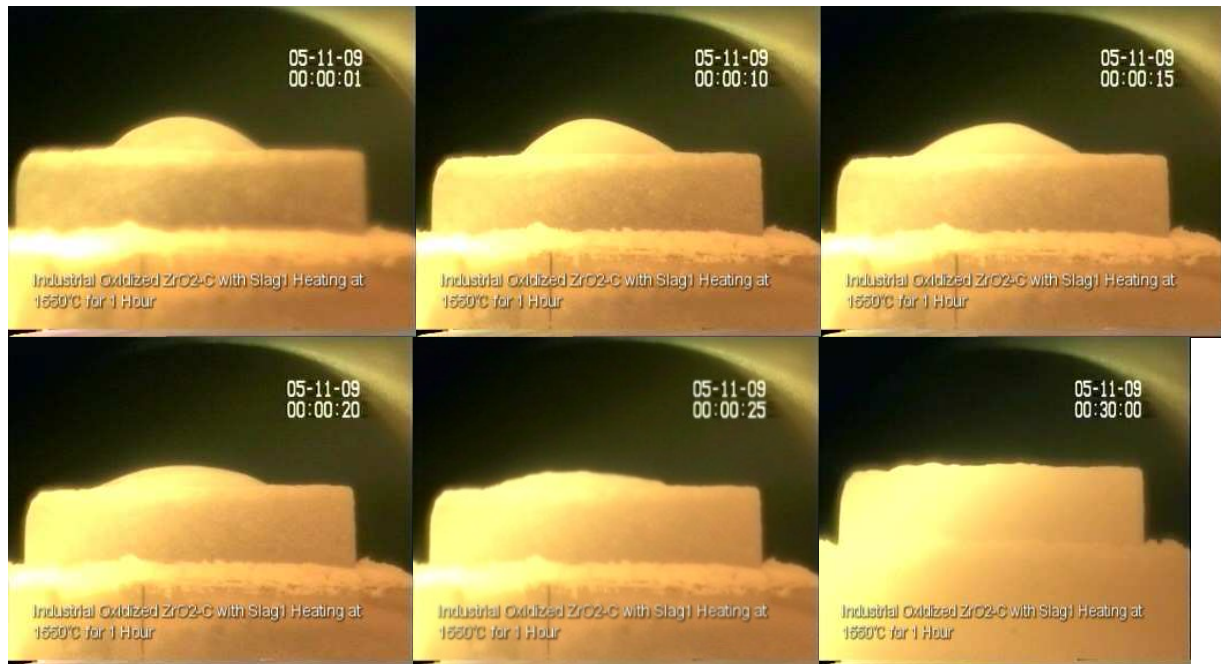


Figure 16. Industrial flat oxidized  $ZrO_2-C$  samples with slag 1 heating at  $1550^{\circ}C$  for 1 hour



#### 4.2. Industrial Flat Al<sub>2</sub>O<sub>3</sub>-C Samples with Slag 1

Figure 17 and 18 show contact angles and video images for alumina-carbon refractories in contact with slag 1.

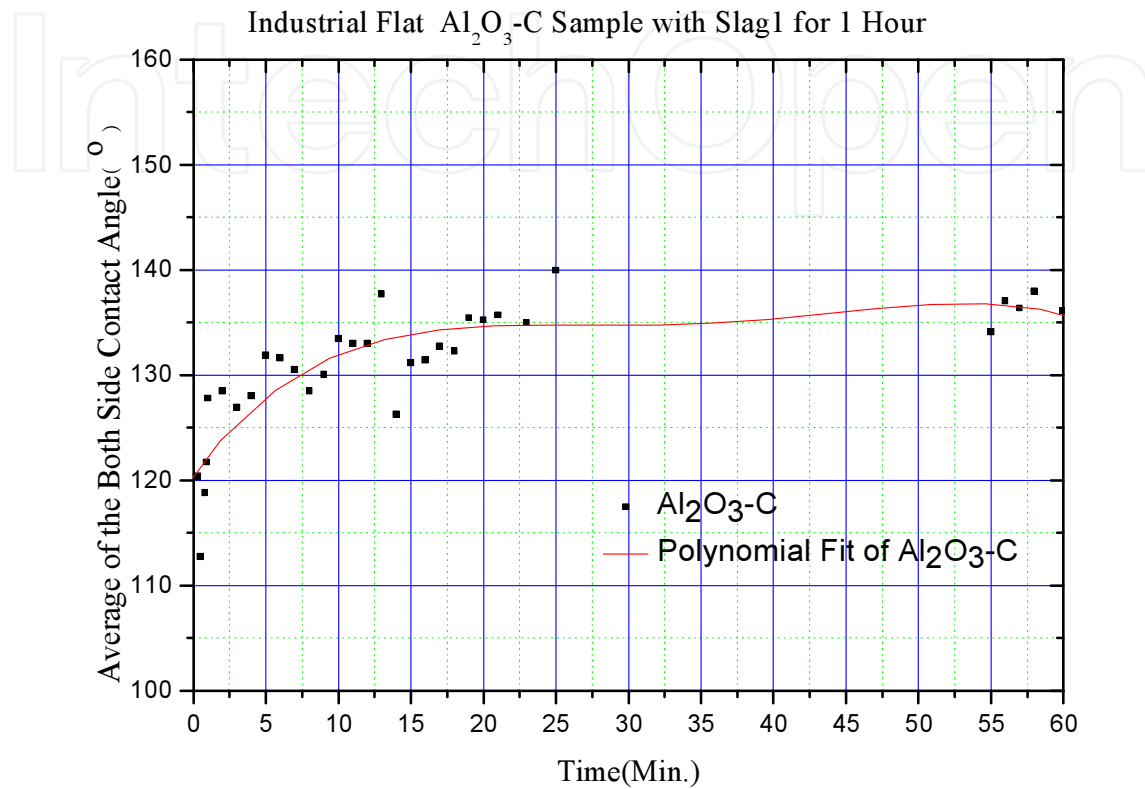


Figure 17. Industrial flat Al<sub>2</sub>O<sub>3</sub>-C sample with slag1 heating at 1550°C for 1 hour

These images show the contact angle between the Al<sub>2</sub>O<sub>3</sub>-C substrate and slag 1 was constantly more than 120° during 1 hour heating at 1550°C. Both industrial oxidized and non-oxidized flat ZrO<sub>2</sub>-C samples had better wettability with slag 1 than the industrial flat Al<sub>2</sub>O<sub>3</sub>-C samples. Especially the oxidized ZrO<sub>2</sub>-C sample was fully wetted by slag 1 in one minute.

Results for the gas data from the blank substrates is presented. Infrared analyser was used to analyse the outlet gas from the furnace. The IR results showed the outlet gases content of the CO and CO<sub>2</sub>, and this can be converted to the removal amount of carbon. For the industrial non-oxide zirconia refractory, the cumulative volume of CO reached 1.8 litres after 60 minutes; similar volumes were recorded for the oxidised refractory (Figure 19). The corresponding volumes of CO<sub>2</sub> were negligibly small. Alumina-carbon refractories showed much lower levels of gas generation. Gases generated were generally higher in the presence of slag (Figure 20).

The generation of gases at the interface led to the production of gas bubbles in the slag, which in-turn had a significant influence on the contact between the slag and the refractory (Figure 21).



**Figure 18.** Industrial flat oxidized  $\text{Al}_2\text{O}_3\text{-C}$  samples with slag 1 heating at  $1550^\circ\text{C}$  for 1 hour

Detailed studies reported in this section have shown that reactions taking place in the interfacial region and associated gas generation can have a significant influence on the wettability of refractory substrates with strong implications for refractory degradation and corrosion.

## 5. Concluding remarks

These studies have shown that the wettability of alumina-carbon refractories with molten iron is a strong function of substrate composition and carbon content. Alumina and carbon are commonly used constituents of steelmaking refractories. Gases generated during the interaction make it easier for metal to penetrate in the substrate enhancing refractory degradation. As more and more gaseous products were generated after the system underwent transition from poor wetting to good wetting, this study will help define limiting values of carbon that could help minimise refractory degradation.



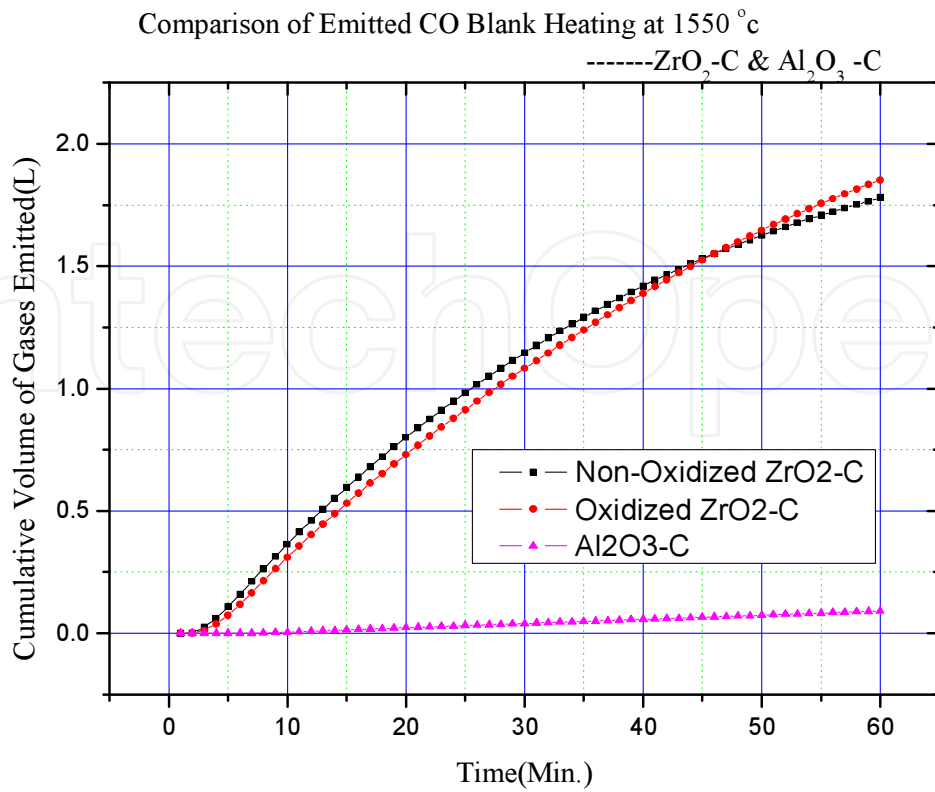


Figure 19. Comparison of emitted CO gas from blank ZrO<sub>2</sub>-C & Al<sub>2</sub>O<sub>3</sub>-C refractories

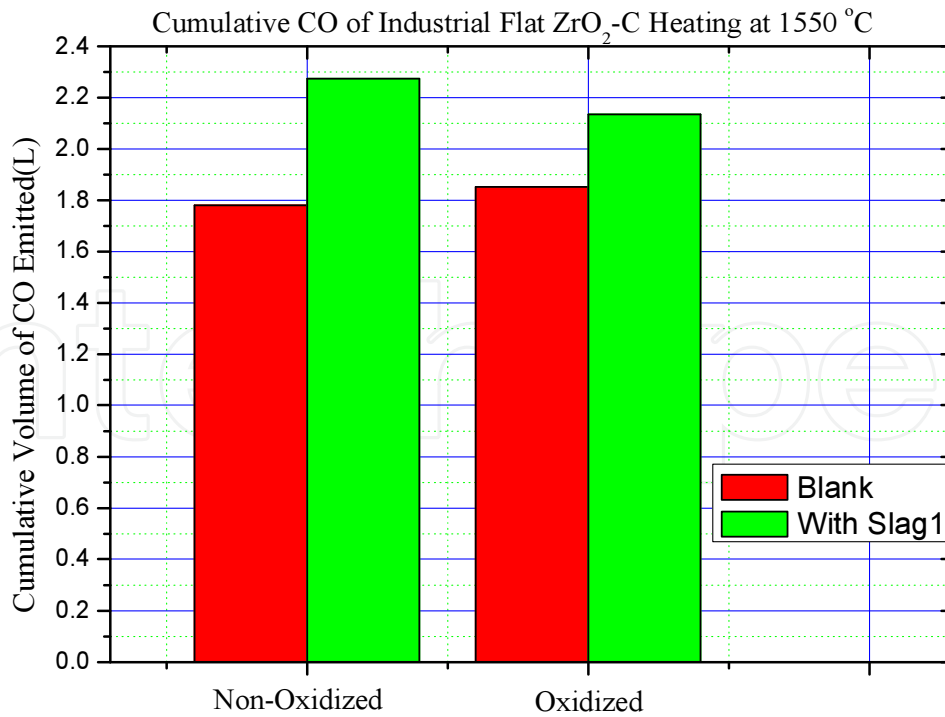
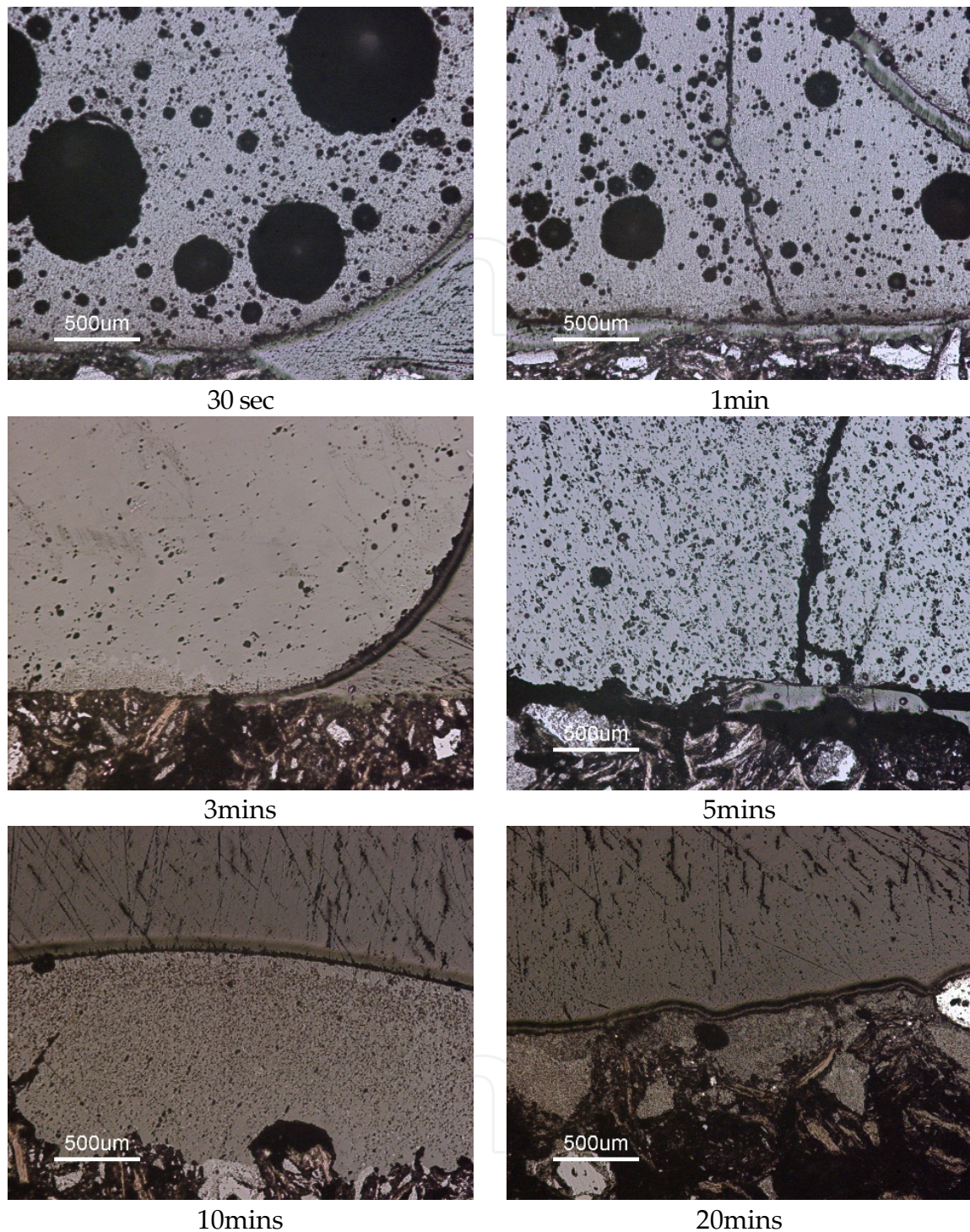


Figure 20. Cumulative CO of industrial flat ZrO<sub>2</sub>-C sample blank & with slag



**Figure 21.** Interfacial phenomena between zirconia-carbon refractories and slag 1.

Alumina-synthetic graphite substrates showed a non-wetting behavior with liquid iron at 1550 °C. The initial contact angles were 140°, 136° and 135° respectively for substrates containing 12.9 wt% C, 22.8 wt% C and 32.7 wt% C, after which these experienced a 10-18° drop during first five minutes of the experiment, which was followed by a further increase

in the angles to final values in the range of 130-135° for all the substrates. Alumina-natural graphite substrates also showed a non-wetting behavior with liquid iron at 1550 °C. The contact angles were initially at 138°, 138° and 140° respectively for substrates containing 12.7 wt% C, 22.4 wt% C and 32.1 wt% C, after which these experienced a drop of 10-15° during the first 5 minutes of reaction before stabilizing to the final contact angle value of approximately 130° for all the substrates for the rest of the experimental duration.

Recycled refractory substrates showed a non-wetting behavior with liquid iron at 1550 °C. The initial contact angles were 118°, 119° and 130° respectively for AS1-10R, AS1-20R and AS1-30R substrates, after which they experienced a 3° drop during first five minutes of the experiment, which was followed by a further increase in the angles to final values in the range of 122-132° for all the substrates. These values are much lower in comparison to virgin refractory system indicating the role played by the contamination in used refractory.

A number of experiments were reported on industrialized refractory substrates with casting slags. While zirconia based refractories generally showed good wettability, these were also associated with extensive in-situ gas generation and refractory degradation. Alumina based refractories however showed little gas generation and poor wettability. These studies have shown that a number of factors, including wettability, could play a significant role in the degradation of carbon based refractories and need to be taken into consideration.

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