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# COKE MICROSTRUCTURE AND STRENGTH UNDER BLAST FURNACE CONDITIONS

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## ABSTRACT

The effects of gasification reaction and annealing under blast furnace conditions on the mechanical strength, micro-strength and graphitisation of two Australian cokes were studied using tensile test, ultra micro indentation, XRD and Raman spectroscopy. Mechanical strength of coke was decreased by both annealing and gasification. Gasification had a stronger effect on coke's mechanical strength than annealing at 1400 °C; however, annealing in the high temperature range 1400-2000 °C caused a more significant decrease in mechanical strength. Annealing also decreased the cokes micro-strength, particularly above 1400 °C. The reactive maceral derived components (RMDC) of feed (original) cokes had lower micro-strength than inert maceral derived components (IMDC), and increasing annealing temperature had a more significant effect on the degradation of micro-strength of RMDC. Both annealing and gasification increased the graphitisation degree of cokes; significant increase in the graphitization degree was caused by annealing at temperatures above 1400 °C. Graphitisation of RMDC was higher than that of IMDC after annealing, and annealing had a stronger effect on the graphitisation of RMDC compared to IMDC.

**Keywords**: Blast furnace ironmaking; coke degradation; annealing; gasification; mechanical strength; micro-strength; microstructure; coke microtextures

## INTRODUCTION

Coke and coke quality remain critical to all blast furnace ironmaking operations. Charged cold to the top of the furnace, it remains solid, but subject to mass loss through reaction, on its passage through the furnace until ultimately being combusted in the raceway, or dissolved into the descending hot metal. Peak coke temperatures are up to 2000-2200 °C (typical raceway flame temperatures). The coke is required to maintain adequate hot strength to support the furnace burden column and resist abrasion, minimising fine coke generation with consequent diminution of burden permeability.

Metallurgical cokes are highly porous materials. Coke strength is dependent on both pore structure and the microstrength of pore wall components [1-3]. Gas-solid reactions and mineral matter reactions impact the pore structure while graphitisation (annealing) reduces the microstrength of the pore walls. Overwhelmingly, previous studies of the mechanical strength and micro-strength of cokes have focused on the effect of coking conditions [4-8].

This work has focussed on the effects of gasification under blast furnace-aligned conditions (of the thermal reserve and cohesive zones) and annealing under an inert atmosphere to temperatures approaching those of the raceway, on the tensile strength, microstrength and microstructure of two Australian cokes.

## COKE SAMPLES

Two cokes have been studied to date. Coke A is a production coke of a medium volatile base blend of moderate inertinite content with 11% semi-soft addition. Coke C is a pilot oven coke prepared from a low volatile, low-moderate inertinite content, coal. Summary coke analyses are presented in **Table 1**.

**Table 1: Summary proximate, CSR and CRI analyses for the cokes tested**

| | Coke A | Coke C |
|---|---|---|
| Volatile Matter %(db) | 1.40 | 1.54 |
| Ash %(db) | 12.0 | 12.1 |
| CSR [9] | 70.2 | 62.7 |
| CRI [9] | 20.7 | 24.6 |

The coke samples for investigation were prepared from as-received bulk samples by jaw crushing and sieving to a final lump sample size or -21 +19 mm.

## REACTION AND THERMAL PROCESSING

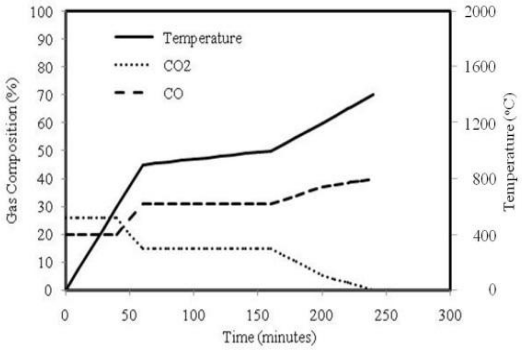
### Heat treatment (annealing)

Approximately 200 g of coke, contained in a graphite cassette, was heated under nitrogen in a graphite furnace for 2 hours at temperatures of 1400, 1600, 1800, and 2000 °C. The heating rate, from ambient to the required annealing temperature, was controlled at 25 °C/min.

### Gasification under blast furnace-like conditions

200 g samples of coke, contained in a silicon carbide reaction vessel, were reacted under a blast furnace-like gas composition-temperature profile from 900 to 1400 °C. The gas composition–temperature profile (detailed in **Figure 1**) was based on vertical probing of the blast furnace as described by van der Velden et al. [10]. In the current experiments, water and hydrogen were excluded, and $CO_2$ content decreased from 5% at 1200 °C to 0% at 1400 °C instead of 1310 °C. The rationale advanced by van der Velden et al. was that the temperature increment between 900 and 1000 °C corresponds to coke passage through the furnace thermal reserve zone and from 1100 to 1310 °C (1400 °C in this work) represented passage through the furnace cohesive zone. The gasification was stopped once the temperature reached the desired temperature, then the sample was quenched in a nitrogen atmosphere.

**Figure 1: Gasification gas composition-temperature profile**




## CHARACTERISING MEASUREMENTS

### Tensile strength

The tensile strength of cokes was tested on an **Instron 1185** screw universal testing machine. For the 8mm diameter by 8 mm long prepared coke pellets, the tensile strength, σ, was calculated using equation (1) below:

$$\sigma = \frac{2P}{\pi d l} \quad (1)$$

where $P$ is load at sample failure and $d$ and $l$ are diameter and length, respectively.

### Micro-strength

The micro-strength of cokes was tested using a **UMIS2000** ultra micro indentation system (UMIS). Hardness and Young's modulus of coke matrix were determined using a Berkovich indenter, and the fracture toughness of coke matrix was determined using a sharper cube corner indenter. Fracture toughness, $K_{1c}$, was calculated as [11]

$$K_{1c} = k\left(\frac{E}{H}\right)^{n} \frac{P_{max}}{c^{3/2}} \quad (2)$$

where E and H are Young's modulus and hardness, respectively; $c$ is crack length; constants $k$ and $n$ depend on the geometry of applied indenter. For the cube corner indenter, k = 0.036 and n = 0.5. Measurements were carried out with a 200 mN load on both inert maceral derived component (IMDC) and reactive maceral derived component (RMDC) microtextures. The crack lengths of the residual impressions were measured from images obtained by a digital camera linked to the UMIS microscope.

### Graphitisation from X-ray diffraction

The crystallite size, $L_c$, and interlayer spacing between aromatic planes of carbon crystallites, $d_{002}$, were determined using X-ray diffraction (XRD) and calculated as:

$$L_c = \frac{K \cdot \lambda}{B \cdot \cos\theta} \quad (3)$$

$$d_{002} = \frac{\lambda}{2 \cdot \sin\theta} \quad (4)$$

where $B$ and $\theta$ are the width at half maximum intensity of (002) peak and peak position, respectively. For (002) peak, the factor $K$ is equal to 0.89 and Cu $K_\alpha$ radiation wavelength $\lambda$ is 1.54Å.

### Graphitisation from Raman Spectroscopy

Raman spectrum of cokes was determined using a **Renishaw inVia Raman** microscope with a 514-nm excitation wavelength. The Raman spectrum of cokes was deconvoluted into five peaks with Lorentzian band fitting: G, D, D', $R_1$ and $R_2$. The G fraction which characterises coke graphitisation was defined as:

$$G\ Fraction\ (\%) = 100 \times \left(\frac{A_G}{A_T}\right) \quad (5)$$

where $A_G$ is the area(s) under the G peak, $A_T$ is the total area.

## RESULTS AND DISCUSSION

### Effect of annealing and gasification on tensile strength of cokes

The effects of annealing and gasification on tensile strength of cokes are presented in **Table 2.**

**Table 2: Tensile strength (MPa) of cokes after annealing and gasification**

| | Coke A | | Coke C | |
|---|---|---|---|---|
| Temperature (°C) | Gasified | Annealed | Gasified | Annealed |
| Feed | 7.71 | | 4.62 | |
| 1000 | 7.07 | | 4.28 | |
| 1200 | 6.91 | | 4.06 | |
| 1400 | 6.92 | 7.10 | 3.81 | 4.30 |
| 1600 | | 6.38 | | 3.82 |
| 1800 | | 5.51 | | 3.35 |
| 2000 | | 4.95 | | 2.86 |

For both cokes, the tensile strength decreases with increasing processing temperature under both gasification and annealing conditions. At 1400 °C, gasified samples showed lower tensile strengths than the annealed samples.

### Effect of annealing on the micro-strength of cokes

Fracture toughness of original cokes and cokes after annealing, measured using ultra micro indentation, is shown in **Table 3**. For Coke A it was possible to undertake fracture toughness determinations on both the fused (RMDC) and unfused/partially fused inert maceral derived (IMDC) microtextures. For Coke C, where the RMDC component was dominated by coarse mosaic and foliate microtextures, it was impossible to reliably measure crack length and no

reliable determination of fracture toughness could be provided on RMDC. In coke A, fine and medium grained mosaic dominated the RMDC component.

**Table 3: Fracture toughness (MPa·m$^{1/2}$) of cokes after annealing**

| | Coke A | | Coke C |
|---|---|---|---|
| Temperature (°C) | RMDC | IMDC | IMDC |
| Feed | 1.43 | 1.55 | 1.49 |
| 1400 | 1.38 | 1.49 | 1.36 |
| 1600 | 1.09 | 1.29 | 1.28 |
| 1800 | 0.90 | 1.20 | 1.08 |
| 2000 | 0.68 | 1.04 | 0.90 |

Fracture toughness of IMDC in original cokes was 1.5-1.6 MPa·m$^{1/2}$. Annealing decreased the fracture toughness of both cokes, and significantly, the decrease was more pronounced in the RMDC component of Coke A.

**Effect of annealing and gasification on graphitisation degree of cokes**

Graphitisation degree of cokes measured using XRD and Raman spectroscopy is presented in **Tables 4** and **5**.

**Table 4: Crystallinity parameters (Å) from X-ray diffraction for Cokes A and C**

| Temperature °C/ Process | **Coke A** | | **Coke C** | |
|---|---|---|---|---|
| | **$L_c$** | **$d_{002}$** | **$L_c$** | **$d_{002}$** |
| Feed | 22.31 | 3.516 | 19.26 | 3.502 |
| 1000 / gasified | 23.49 | 3.507 | 20.01 | 3.505 |
| 1200 / gasified | 24.23 | 3.503 | 24.05 | 3.491 |
| 1400 / gasified | 31.99 | 3.477 | 34.48 | 3.465 |
| 1400 / annealed | 37.38 | 3.470 | 38.79 | 3.465 |
| 1600 / annealed | 55.43 | 3.448 | 58.57 | 3.448 |
| 1800 / annealed | 94.08 | 3.433 | 119.40 | 3.438 |
| 2000 / annealed | 142.12 | 3.434 | 172.49 | 3.431 |

**Table 5: G fraction (%) from Raman spectroscopy for Cokes A and C**

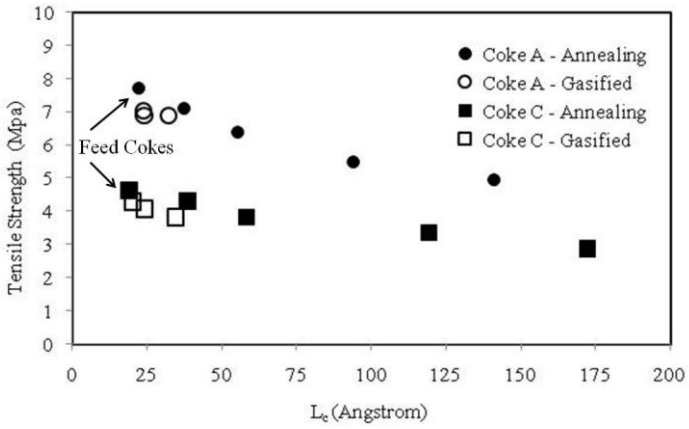
| Temperature °C/ Process | **Coke A** | | **Coke C** | |
|---|---|---|---|---|
| | **RMDC** | **IMDC** | **RMDC** | **IMDC** |
| Feed | 14.68 | 16.22 | 13.28 | 14.81 |
| 1000 / gasified | 16.54 | 18.37 | 14.47 | 14.87 |
| 1200 / gasified | 15.87 | 17.40 | 15.70 | 16.23 |
| 1400 / gasified | 18.64 | 17.74 | 18.44 | 17.93 |
| 1400 / annealed | 20.67 | 20.43 | 18.77 | 18.79 |
| 1600 / annealed | 27.76 | 22.90 | 26.81 | 21.32 |
| 1800 / annealed | 31.34 | 26.04 | 31.62 | 25.76 |
| 2000 / annealed | 40.53 | 31.34 | 41.65 | 29.15 |

Both sets of measurements indicate substantial progression in graphitisation under thermal (annealing) conditions, with little perturbation being suggested for the reaction component. Graphite stacking height increased, with a concomitant increase in the indicated G-fraction,

and the interlayer spacing reduces, approaching the value found for pure graphite (3.3555 Å [12]). The extent of graphitisation, relative to the feed coke values, was consistently greater in the case of Coke C. Also, Raman spectroscopy allowed differentiation between the RMDC and IMDC components, and the extent of graphitisation is indicated to be more pronounced in the case of the RMDC component in both cokes.

Tensile strength (bulk) is plotted against graphitisation, measured by Lc, in **Figure 2**. A significant relationship, paralleling temperature/annealing temperature, is indicated.

**Figure 2: Tensile Strength (MPa) versus Lc for gasified and annealed Cokes A and C**




The starting strength of the feed coke was strongly affected by the microtexture/microstructure of the cokes. In both cases, gasification reduced the tensile strength more than projected for straight annealing. Optical (reflected light) microscopic examination of polished lump samples indicates the loci of reaction, appearing as domains of "reacted material" [13], is substantially confined to the peripheral regions of the gasified lumps and within the pore walls. Pore surfaces in the peripheral zones, and across the full section of the lumps, remained substantially smooth and in an original condition.

## CONCLUSIONS

The effect of reaction and annealing under blast furnace conditions on the properties of two Australian cokes was studied. The major findings are summarised below.

1. Both gasification and annealing decreased the mechanical strength of the cokes. Compared with annealing at 1400 °C, gasification at the same temperature caused larger degradation for both types of coke, and the effect on Coke C was more apparent.
2. Annealing decreased the micro-strength of cokes. This degradation effect was more significant above 1400 °C. RMDC had lower micro-strength than IMDC, and increasing annealing temperature had a greater effect on the degradation of micro-strength of RMDC.
3. Graphitisation degree of cokes was increased by both annealing and gasification, with the increase more significant in the temperature range above 1400 °C. The graphitisation degree of RMDC was lower than that of IMDC in the feed cokes. Graphitisation degree of RMDC became higher than that of IMDC for annealing above 1400 °C and the differences became larger with increasing annealing temperature.

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