

High-Temperature Strength Evolution in Cokes

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Abstract

The strength and behaviour of coke at high temperatures has a huge impact on its performance in the ironmaking process. Prior studies reporting the effect of temperature on the failure stresses of cokes have not always shown consistent trends owing to differences in sample sizes, properties, and testing methods. In the present work, a high-CSR Australian coke was subjected to high-temperature mechanical tests using a unique high-temperature test facility at ANSTO to determine its compression strengths and the associated microstructural and mineralogical modifications. X-ray diffraction analysis and micro-CT analysis were used to determine the mineralogical and microstructural changes in the cokes after testing. The work showed that there were three regimes of deformation in the coke with increasing temperature. Furthermore, the work showed that compression strengths of the coke were higher at elevated temperatures in comparison to the observed values at room temperature. Microstructural analysis showed an increase in the extent of porosity after high-temperature testing owing to the in situ reduction of ash species in the coke. With increase in temperature, it is expected that glassy phases formed by ash fusion as well as increased graphitisation assist in enhancing plastic flow, which contributes to an increase in strength of the coke samples at these temperatures. However, with increasing graphitisation extents, the load-bearing capacity would decrease, leading to a lowering of the maximal strengths at the top temperatures. The findings provide an improved understanding of the mechanisms affecting high-temperature strength development in cokes and can further assist in correlations the strengths with variations in coke and parent coal characteristics.

Keywords: Coke, CSR, high-temperature strength, ironmaking

1. INTRODUCTION

Blast furnace ironmaking is the predominant process for producing metallic iron from iron ore. Due to the increasing use of supplementary fuel injection in a blast furnace, coke added with the burden is required to possess higher strength in order to avoid deterioration, especially at high temperatures. Therefore, under such conditions, the thermal properties of coke are one of the most important factors with regard to efficient blast furnace operation. Past studies on blast furnaces have confirmed that the change in coke quality begins to occur in the lower part of the shaft or near the bosh; in these regions, the coke serves its most important role in providing a porous bed which controls the gas permeability through the layer (**Bertling 1999; Geerds et al 2004**). Various interrelated factors can cause coke degradation in the blast furnace and these include mechanical stresses owing to shattering and abrasion, solution loss reaction, alkali attack, high temperature attack, and impact shock by hot blast

(**Babich et al 2006; Gupta et al 2008**). A realistic assessment of coke performance should include those properties of coke that reflect its resistance to degradation under the chemical and thermal environment within the blast furnace (**Diez et al 2002**). Coke strength and reactivity at high temperatures is commonly estimated through the NSC CRI/CSR test (**ASTM 1999, ISO 188894, 2006**). Empirically, high CSR coke is preferred for low coke-rate and high productivity operations even though there are concerns about this test method and its ambiguous association with the actual performance (**Best 2002**). Therefore, tests that can determine the mechanical properties and structure of coke at high temperatures would provide information that may assist in enhancing the efficiency of blast furnace operation.

The compression test has been also shown to be a good indicator of the inherent strength of coke. The relationship between CSR and compressive strength of cokes after reactivity tests appears to display a trend similar to those exhibited in the common drum indices based on bulk samples. Moreover, compression tests have been shown to provide a better differentiation for the higher strength coke samples (**Bennett et al 2008**). Xing et al. showed that the graphitisation degree of the reactive maceral-derived component (RMDC) was slightly lower than that of the inert maceral-derived component (IMDC) component in tested cokes before annealing. However, graphitisation of the RMDC progressed faster than that of the IMDC during annealing at 1400°C and became significantly higher after annealing at 2000°C. Moreover, the microstrength of cokes significantly degraded during heat treatment (**Xing et al 2014**). Further work by Xing et al. on subjecting metallurgical coke samples to treatment with blast furnace-like gas composition-temperature profile to 1400°C followed by annealing to 2000°C and gasification and subsequent annealing at 1600° and 2000°C showed that both gasification and annealing decreased the mechanical strength of coke, with gasification having expectedly the more significant effect for the high reactivity cokes (CRI~47%) while annealing at 2000°C had the dominant effect for the less reactive cokes (CRI ~21-25%) . The work was able to show that the degradation of low reactivity cokes was focussed on the periphery with minimal effects on the core (**Xing et al 2016**). However, these strengths were measured at room temperature.

Thus limited data and limited understanding about the mechanism of coke in compression at high temperatures is available. The deformation mechanism of porous coke has been shown to be similar to that of brittle foam, such that it shows a distinct region of linear elasticity, followed by brittle fracture under compressive loads (**Amanat et al 2009**). Ultra-micro-indentation studies showed the microstructural properties have been related to compact tensile measurements of coke strength. The microstructures of the strongest cokes showed a relatively thick coke wall and a small mean pore size distribution as well as high pore density. Inert maceral derived coke micro-textures displayed the highest hardness values, while the hardness of reactive maceral derived coke was lower, and decreased with increasing mosaic size (**Andriopoulos et al 2003**). The majority of these studies have focussed on the association of coke strength at room temperatures and microstructural parameters. There have been attempts, with limited success (**Haapkangas et al 2000**), to measure in situ high temperature high strength.

However, no studies have been successful in measuring expansion behaviour, creep-compression and compressive strengths on coke samples at high-temperatures, and this is the focus of the present work..

2. EXPERIMENTAL

2.1 Sample Selection and Preparation

20 kg of high CSR coke lumps (~40 mm size) were obtained from the industry partners. The lumps were cored using a stainless steel core drill to produce cylindrical samples (~21 mm height, ~19 mm diameter). The end-polished samples were then heat treated at 1100°C for 5 h in a tube furnace under flowing argon to remove any volatiles. Grinding of the end faces of each specimen normal to the specimen axis and parallel to each other using 320 grit SiC paper. Samples with consistent bulk

densities and defect-free surfaces were selected for conducting the high-temperature tests at ANSTO. This was done to minimise sample variability and to ensure consistency.

2.2 Room Temperature Compression Testing:

Three of the cored samples were subjected to compression testing in a 100 kN Instron universal testing machine. The samples were placed on a flat platen and then the top platen was moved slowly to bring it in close proximity to the sample surface. Then the load was applied at a rate of 1 N/min until the material fractured completely.

2.3 In Situ High-Temperature Strength Measurements

Specimens were loaded in compression in an Elatec high temperature graphite element furnace equipped with a hydraulic ram and a 100 kN load cell. The load to the specimen was transmitted by a graphite push rod and each specimen had a Grafoil pad at the top and bottom. The 20 mm diameter specimens were contained within a 25 mm internal diameter graphite die, the sides of which were lined with Grafoil. The furnace temperature was logged by a thermocouple up to 1200°C and then by an optical pyrometer above 1200°C. The ram displacement was monitored by a long travel LVDT outside the furnace for the complete run. The operation of the Elatec furnace was controlled by two Eurotherm controllers, one for temperature and the other for hydraulic force. A computer running a Labview program was used to load the test sequence onto the Eurotherm controllers and to also log the operating parameters at an interval of 12 s.

Two methods were followed for the testing process and these are outlined below:

Expansion Test Method: The specimen was preloaded lightly and the furnace was evacuated to vacuum of 10^{-3} Torr. The hydraulic ram pressure such that the specimen compressive stress increased at 1 MPa/min to a hold stress of 5 MPa. The specimen were heated to 1800°C (7°C/min) and held for 30 min at a stress of 5 MPa. Then the specimen was unloaded after that and the sample was cooled to room temperature.

Strength Test Method: The specimen was preloaded lightly and the furnace was evacuated to vacuum of 10^{-3} Torr. The hydraulic ram pressure such that the specimen compressive stress increased at 1 MPa/min to a hold stress of 2.5 MPa. The specimen were heated to 1800°C (7°C/min) and held for 30 min the same stress. Then the load was increased till the sample fractured. Then the sample was cooled to room temperature.

2.4 Structural and Microstructural Analysis

Micro-CT facilities located in the Tyree X-Ray Facility UNSW were used to analyse the changes in the microstructural characteristics of the coke samples prior to and after mechanical testing at high temperatures. The coke samples were analysed to determine the microstructural features at different cross-sections along the length of the sample. The images were further analysed using proprietary image-processing software to obtain important information on the changes in total porosity, grain sizes and shapes, and ash phase distribution with distance from the edges (vertically and horizontally). These facilities were also used to obtain the microstructural images of the different coke samples.

The mineralogical characteristics of the coke samples prior to and after testing were analysed using powder diffraction capabilities at UNSW. PANalytical X'Pert Multipurpose Diffractometer (45 kV, 40 mA) was used to visualise the changes in the coke mineralogy, particularly ash phases and coke graphitisation after testing at different temperatures.

3. RESULTS AND DISCUSSION

The stress vs. strain curves for room temperature testing of cylindrical coke samples are shown in **Figure 1**. The curves showed quite similar trends across the samples; there was a linear elastic portion to the curve after which there was a sudden drop in the stress possibly arising from crack formation; after this point there was a further increase in the stress experienced by the material, possibly arising from self-compression of the cracked body. Ultimately the material suffered further fracture leading to a gradual drop in the stresses. The average compressive strength of the samples was determined to be ~13.4 MPa which is similar to values observed typically for coke samples.

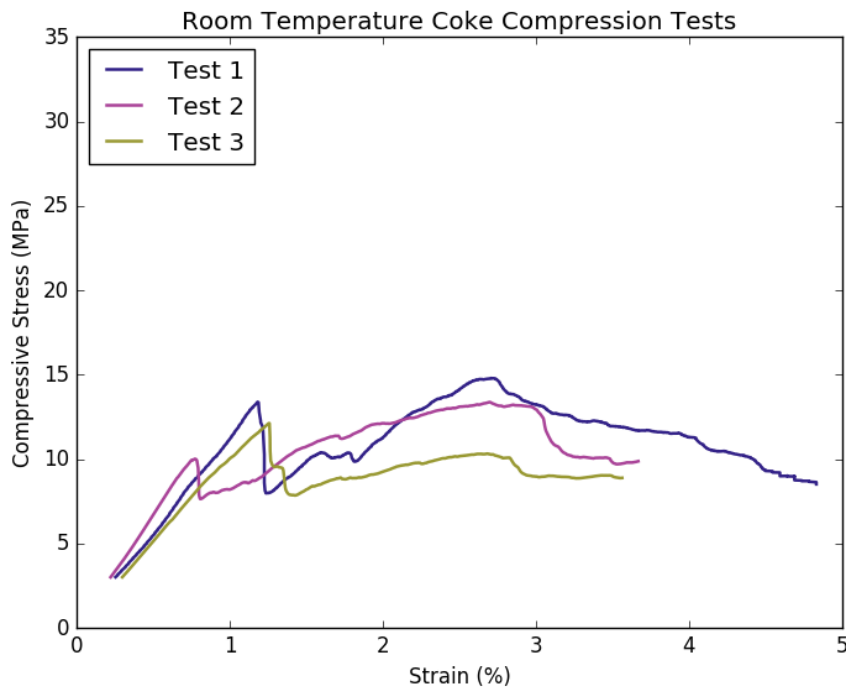


Figure 1: Room temperature compression strength tests on the coke samples

From the data from the expansion test to 1800°C (**Figure 2**), the rate of thermal expansion was almost constant up to about 1050°C, decreased and changed to a lower almost constant rate of expansion between about 1225 and 1515°C. The expansion rate then again decreased during further heating to 1550°C. The higher resolution of these measurements indicates that the rates of thermal expansion vary with temperature, particularly above 1200°C.

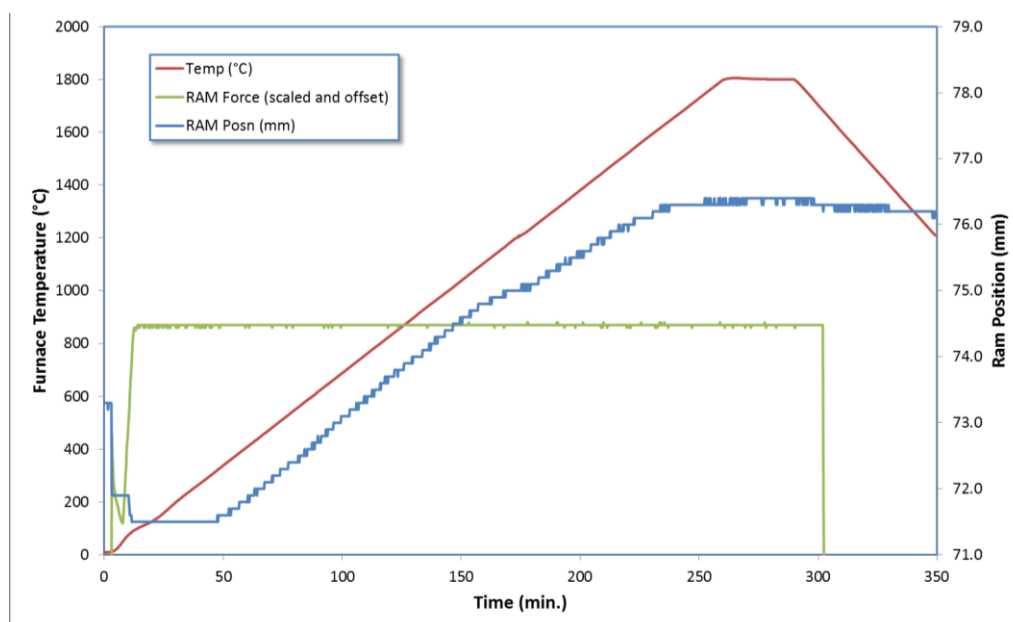


Figure 2. Deformation profile during expansion test of the coke to 1800 °C

Based on these observations, the three temperatures for compression tests were selected to be 1400°, 1550°, and 1700°C and the data are shown in **Table 2**. Compression tests conducted at the aforementioned temperatures showed that the strength of the coke was significantly greater at higher temperatures as compared to the values observed at lower temperatures. The ultimate failure stresses of coke specimens were higher at elevated temperatures than at room temperature. The highest ultimate failure stresses were at 1400°C. The elastic moduli were lower at room temperature than at elevated temperature. Overall, the elastic limit stresses were similar at room temperature and at high temperature.

Table 2: Summary of strength and strain variations with testing temperature

Test Temperature (°C)	Elastic Limit Stress (MPa)	Ultimate Failure Stress (MPa)	Maximum Strain (%)
25	10 – 13	10 – 15	3.6 – 4.8
1400	11 – 15	30 – 30	3.8 – 4.3
1550	10 – 11	23 – 24	3.7 – 4.2
1700	8 – 11	22 – 23	3.8 – 4.9

XRD analysis (not shown here) showed that the coke sample was amorphous at room temperature and quartz was the major ash component. Data showed that with increase in the test temperature, the coke starts to graphitize and there is a significant increase in the graphite peak intensity. Furthermore, ash melting is expected at 1400°C and this could explain the absence of the quartz peak at this temperature. Micro-CT results indicate an increase in porosity and decrease in ash content with increase in the test temperatures. This validates the previous hypothesis that ash-carbon reactions are contributing to the removal of the ash species from the coke at high temperatures, leading to an increase in the porosity of the coke samples. The increased apparent densification could be attributed to the increased graphitization with increase in the test temperatures.

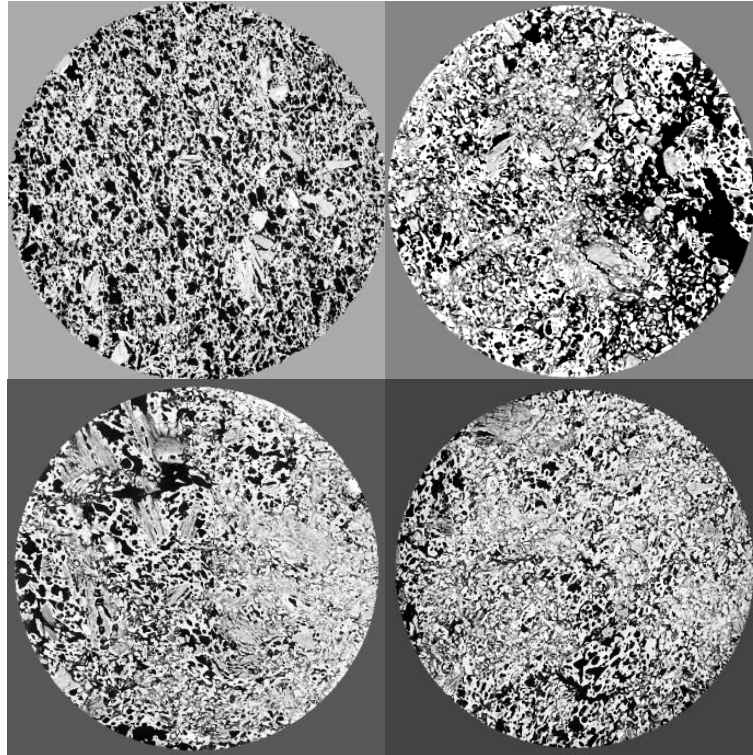


Figure 2. *Micro-CT images of the coke samples (in clockwise direction) – Room temperature, 1400°C, 1550°C, 1700°C*

4. CONCLUSIONS

Expansion tests to 1800°C showed that the cokes showed three temperature regimes at which deformation of the cokes deviated from the natural thermal expansion. Further, the test results showed that the high-temperature strengths of the cokes were higher than those that measured at room temperatures. The increased strengths are attributed to potentially ash melting at 1400°C, as well as the increased graphitization and plastic deformation of these cokes at the higher temperatures. The work was successful in the development of a reliable and repeatable testing methodology for cokes at high-temperature using the unique facilities at ANSTO.

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