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Microstrength, strength and microstructure of carbonaceous materials

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Abstract

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Keywords

carbonaceous, strength, materials, microstructure, microstrength

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**STRENGTH, MICRO-STRENGTH AND MICROSTRUCTURE
OF CARBONACEOUS MATERIALS**

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ABSTRACT

The effect of heat treatment at 700-1500°C on the mechanical strength, micro strength and pore structure of carbonaceous materials, including coke, char and coals, were studied using tensile test, ultra micro indentation and image analysis. Strength of chars and pyrolysed coals was strongly enhanced by heat treatment at temperature below 1100°C; strength of cokes was slightly degraded after heat treatment at 1500°C. Mechanical strength of carbonaceous materials was demonstrated to be significantly affected by micro strength and porosity. Micro strength of chars and coals was significantly enhanced by heat treatment, whereas micro strength of cokes was only marginally increased by heat treatment. The major growth in the micro strength of chars and coals took place at annealing temperature below 1100°C. Porosity of chars and coals significantly increased during annealing at temperatures below 1100°C. Further increasing annealing temperature from 1100-1500°C caused marginal porosity evolution in pyrolysed coals and chars. Porosity of cokes increased slightly in the temperature range of 1300-1500°C.

KEYWORDS: *Strength, micro-strength, pore structure, carbonaceous materials, annealing.*

1. INTRODUCTION

Carbonaceous materials used in submerged electric arc furnace for the production of manganese alloys include cokes, chars and coals. Coke is a major material for blast furnace ironmaking, while chars and coals are widely used in direct ferroalloy making processes and iron smelting. Replacing coke with coal and char will however lead to significant economic and environmental benefits. As carbonaceous materials are the only solid materials in the lower region of the submerged electric arc furnace (coke bed zone); they are required to have good mechanical strength to ensure good permeability of liquid and gas phases through the burden. Carbonaceous materials are highly porous, with strength strongly depending on both matrix strength and pore structure [1-3]. Matrix strength and pore structure of carbonaceous materials are significantly changed by the heating in a furnace; however the choice of carbonaceous materials used for ferroalloy production is usually determined empirically, rather than being based on examination of their properties under a range of conditions in ferroalloy furnaces.

Upon heating in furnace, pore structure of coal is changed significantly as a result of pyrolysis. Development of pore structure of coal is influenced by the properties of parent coal, pyrolysis temperature and pressure [4, 5]. Pore structure of chars and cokes is also changed by

heating. Gomez-Serrano et al. [6] found that total porosity and microporosity enlarged with increasing heat treatment temperature in the range 350-750 °C, and reduced with further increase of temperature.

Matrix strength of carbonaceous materials is also influenced by heating in the furnace. Tomoki et al. [7] found that the Young's modulus in the matrix of metallurgical coke increased with rising pyrolysis temperature.

Pore structure of carbonaceous materials has been intensively studied [5, 8, 9], with a focus on the pore structure evolution during carbonization of coals. Micro strength of carbonaceous materials has been investigated by ultra-micro indentation [7, 10], with concentration on the hardness and Young's modulus. Andriopoulos et al. [10] suggested that the macro strength of carbonaceous materials is not directly related to the hardness or Young's modulus but to the fracture toughness.

However, few papers have reported the effect of heat treatment on the pore structure and micro strength of carbonaceous materials, especially in the temperature range of submerged electric arc furnaces, although the variations of pore structure and micro strength determine the mechanical strength of carbonaceous materials.

The aim of this paper is to study the effect of heat treatment on mechanical strength, pore structure and micro strength of carbonaceous materials (cokes, chars and coals) under conditions of submerged electric arc furnaces and to develop a better understanding of the factors affecting mechanical strength of carbonaceous materials.

2. EXPERIMENTAL

2.1. Materials and Preparation

Carbonaceous materials were supplied by the Tasmanian Electro Metallurgical Company (Australia) and METALLOYS (South Africa), and included three coke samples, three char samples and three coal samples. The proximate and petrographic analyses were completed by Sinosteel Anshan Research Institute of Thermo-energy Co., Ltd. compliance with Chinese National Standards. The coal samples were processed at the CSIRO Energy Centre in an 8-kg-retort furnace at 700°C to remove volatile matter and obtain laboratory chars (pyrolysed coals). Approximately 200 g of coke and char samples with particle size of 19-21 mm were heat treated in a graphite furnace under argon atmosphere for 2 hours at temperatures of 700, 900, 1100, 1300 and 1500°C.

2.2. Tensile strength

Cylindrical cores with 8 mm in diameter were drilled from coke and char, and then pellets with 7-8 mm thickness were cut from these cylindrical cores to make samples for tensile tests. Test samples (50) were examined for the tensile strength determination. The samples were tested on an Instron 1185 Screw universal testing machine with a 30 kN load cell. The rate of load application was standardized at a machine crosshead speed of 0.5 mm/min. The tensile strength, σ was calculated using Equation (1) below:

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

where P is load and σ is tensile strength, d and l are diameter and thickness, respectively.

2.3. Ultra micro indentation

Micro strength of carbonaceous materials was determined using a UMIS2000 ultra micro indentation system (UMIS). Earlier indentation studies showed that using Berkovich indenter with a face angle of 65.27°, there was very little plastic deformation with no residual indenter impress after full load, and no crack formation [10]. Therefore, a sharper cube corner indenter with a face angle of 35.26° was used when a residual impression and measurable radial cracks were needed. Indentation was placed on the resin-mounted, polished samples with an appropriate indenter. Measurements were carried out on different types of micro texture.

A three sided Berkovich indenter was applied to determine the hardness and Young modulus. Loads of 100 mN were used, and at least 35 measurements (for each type of microtexture of carbonaceous material) were made across several samples. Hardness and Young's modulus were determined according to the loading-unloading curve generated by increasing applied load, and measuring the depth of penetration of a diamond indenter. The hardness, H and Young's modulus, E were calculated according to the multiply point method developed by Oliver and Pharr [11]:

$$h_c = h_{max} - 0.72 \frac{P_{max}}{dP/dh} \quad (2)$$

where P_{max} is the maximum load applied, dP/dh is the slope of a tangent at initial unloading, h_c is the plastic penetration depth, and h_{max} is the maximum penetration. Once h_c is known, the area of contact A was calculated as [12]

$$A = 3\sqrt{3}h_c^2 \tan^2 \theta \quad (3)$$

where θ is the face angle of applied indenter. The area of contact for Berkovich indenter with $\theta = 65.27^\circ$ was:

$$A = 24.5h_c^2 \quad (4)$$

The hardness and Young modulus were calculated using Equations (5) and (6):

$$H = \frac{P_{max}}{A} \quad (5)$$

$$E = \frac{1}{2} \frac{dP}{dh} \frac{\sqrt{\pi}}{\sqrt{A}} \quad (6)$$

The measurement of fracture toughness relies upon the optical measurement of crack length of the residual impression formed by indentation. The fracture toughness K_{Ic} was calculated as [12]

$$K_{Ic} = k \left(\frac{E}{H} \right)^n \frac{P_{max}}{c^{3/2}} \quad (7)$$

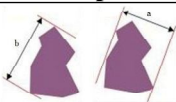
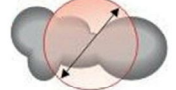

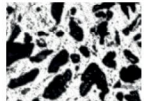
where c is crack length; constants k and n depend on the geometry of applied indenter. For the cube corner indenter, $k = 0.036$ and $n = 1/2$.

Fracture toughness of carbonaceous materials was determined using 50 mN and 100 mN loads with the cube corner indenter. Measurements were carried out on both inert maceral derived component, IMDC, and reactive maceral derived component, RMDC, microtexture. Each microtexture was indented at 15 locations and crack lengths of residual impression after full unload were measured from images obtained by a digital camera linked to the UMIS microscope.

2.4. Pore structure

Sixty samples were mounted in epoxy resin blocks and polished for image analysis. Care was taken to achieve a well-polished surface and avoid damage, for example, to coke walls during polishing. At least 60 images were captured on 60 samples of each type of carbonaceous materials by a Nikon Model EPIPHOT 200 microscope with Nikon digital camera. Since the large pores were of most interest, a low power objective lens, magnification $\times 5$, was used under which small pores ($< 12 \mu\text{m}$) were invisible. The captured images were binarized using image analysis software ImageJ developed by NIH. After binarization, the black area represents the pores and white area represents walls of cokes and chars. The porosity of carbonaceous materials was calculated using ImageJ from the proportion of black area. Pore geometry parameters were determined by LAS Image Analysis software developed by Leica. Table 1 lists the pore geometry parameters determined in this study.

Table 1: Pore geometry parameters of carbonaceous material

Parameters	Schematic Representation	Description
Feret Ratio = $\frac{b}{a}$		The shape of pore described by the ratio of Feret breadth to Feret length
Equivalent Circle Diameter		The diameter of the circle that has the same area as the feature
Cross Section Area		Size of the pore quantified using the average area
Pore Density		The number of pores per mm^2

3. RESULTS AND DISCUSSION

3.1. Effect of heat treatment on tensile strength of carbonaceous materials

Tensile strength of original carbonaceous materials and these materials annealed at different temperatures is presented in table 2.

Table 2: Tensile strength of original carbonaceous materials and carbonaceous materials after annealing at different temperatures, Mpa

	Original	700 °C	1100 °C	1300 °C	1500 °C
Coke 1	8.47	-	-	8.26	7.25
Coke 2	6.94	-	-	6.85	6.43
Coke 3	7.14	-	-	7.09	6.86
Char 1	4.02	-	5.16	-	5.29
Char 2	2.54	-	2.88	-	2.94
Char 3	6.17	-	5.80	-	5.92
Coal 1	3.28	2.00	3.85	-	4.12
Coal 2	2.91	3.44	3.92	-	4.08
Coal 3	3.20	2.36	3.67	-	3.84

Tensile strength of carbonaceous materials varied widely in the range of 2.0-8.5 MPa, depending on the type of material. Cokes had the highest tensile strength in comparison with other carbonaceous materials.

Tensile strength of all tested cokes decreased as the heat treatment temperature rose. Annealing at temperatures 1300°C and below caused only marginal decrease in tensile strength; while decrease in the coke strength after annealing at 1500 °C was more evident. Over 14 % decrease in tensile strength was observed for Coke 1 after heat treatment at 1500 °C. This coke had the highest tensile strength before and after annealing.

Tensile strength of original chars varied from 2.54 MPa to 6.17 MPa depending on the type of the char. After annealing at 1500°C, tensile strength of Char 1 and Char 2 increased by 32% and 14 % to 5.3 MPa and 2.9 MPa, respectively. In contrast, heat treatment slightly decreased the tensile strength of Char 3 from 6.2 MPa to 5.9 MPa. This degradation could be attributed to the changes in porosity and micro strength during annealing.

Tensile strength of original coals was approximately 3 MPa. In the process of pyrolysis, coals softened progressively, and reached maximum fluidity between 350 °C and 450 °C. With increase of temperature to 450-550 °C, coals started losing fluidity and hardening into char. Micro strength and pore structure of coals changed dramatically during this process, thereby influencing the macro strength of char derived from coal (pyrolysed coal). Tensile strength of pyrolysed coal produced at 700 °C had the tensile strength in the range of 2.0-3.4 MPa. Further annealing from 700 to 1500 °C increased the tensile strength of all pyrolysed coals to approximately 4 MPa, and the rate of this increase was higher in the temperature range 700 °C to 1100 °C.

3.2. Effect of heat treatment on fracture toughness of carbonaceous materials

Fracture of carbonaceous materials was calculated using experimental data on hardness, Young's modulus and crack length of residual impression after indentation. Table 3 lists the fracture toughness of original carbonaceous materials and after annealing at different temperatures. The overall micro strength of cokes was calculated from volume fractions of IMDC and RMDC in each coke, and their fracture toughness. It represented the weighted average fracture toughness of a carbonaceous material and was used to correlate with tensile strength of the carbonaceous material.

Table 3: Fracture toughness of original carbonaceous materials and carbonaceous materials after annealing at different temperatures, $\text{MPa}\cdot\text{m}^{1/2}$

	IMDC, $\text{MPa}\cdot\text{m}^{1/2}$	RMDC, $\text{MPa}\cdot\text{m}^{1/2}$	Overall, $\text{MPa}\cdot\text{m}^{1/2}$		IMDC, $\text{MPa}\cdot\text{m}^{1/2}$	RMDC, $\text{MPa}\cdot\text{m}^{1/2}$	Overall, $\text{MPa}\cdot\text{m}^{1/2}$
Coke 1 Original	1.39	1.18	1.26	Char 3 1500 °C	0.55	-	0.55
Coke 1 1500 °C	1.40	1.22	1.30	Coal 1 Original	0.22	-	0.22
Coke 2 Original	1.35	0.97	1.11	Coal 1 700 °C	0.34	-	0.34
Coke 2 1500 °C	1.34	1.06	1.15	Coal 1 1100 °C	0.77	-	0.77
Coke 3 Original	1.51	1.16	1.25	Coal 1 1500 °C	0.84	-	0.84
Coke 3 1500 °C	1.51	1.21	1.31	Coal 2 Original	0.18	-	0.18
Char 1 Original	0.51	-	0.51	Coal 2 700 °C	0.40	-	0.40
Char 1 1100 °C	0.88	-	0.88	Coal 2 1100 °C	0.81	-	0.81
Char 1 1500 °C	0.95	-	0.95	Coal 2 1500 °C	0.85	-	0.85
Char 2 Original	0.50	-	0.50	Coal 3 Original	0.22	-	0.22
Char 2 1100 °C	0.68	-	0.68	Coal 3 700 °C	0.39	-	0.39
Char 2 1500 °C	0.72	-	0.72	Coal 3 1100 °C	0.85	-	0.85
Char 3 Original	0.42	-	0.42	Coal 3 1500 °C	0.95	-	0.95

Fracture toughness of IMDC of original cokes was 1.4-1.5 MPa·m^{1/2}, slightly higher than RMDC which was in the range of 1.0-1.2 MPa·m^{1/2}. Heat treatment had no effect on the fracture toughness of IMDC but slightly increased that of RMDC. RMDC of cokes was derived from reactive macerals in the parent coals; condensation reactions continued during heat treatment and as a result the micro strength of RMDC slightly increased after heat treatment at 1500°C. Inert components had more condensed aromatic rings than reactive components; condensation reaction of IMDC was completed during coke making process at approximately 1000 °C which lasted 16-18 hours. Thus, change in fracture toughness of IMDC was not expected. Overall fracture toughness of original Coke 1 and Coke 3 was approximately 1.3 MPa·m^{1/2}, which was higher than that of Coke 2 (1.1 MPa·m^{1/2}). Fracture toughness of all cokes was slightly enhanced by heat treatment at 1500°C for 2 hours as a result of increase of fracture toughness in RMDC.

Fracture toughness of chars and pyrolysed coals was represented by the fracture toughness of IMDC. Fracture toughness of original chars was about 0.49 MPa·m^{1/2}. Heat treatment resulted in a significant enhancement of micro strength of all chars. After annealing at 1500 °C for 2 hours, over 80 % increase of fracture toughness was observed for Char 1 which was the largest enhancement among three chars. Increase in fracture toughness for Char 2 was 48% and for Char 3 was 30%. The major enhancement of micro strength took place during annealing at temperatures below 1100 °C; further increase in heat treatment temperature only caused a marginal increase in fracture toughness.

The fracture toughness of original coals was approximately 0.20 MPa·m^{1/2}. Pyrolysis of coals enhanced their micro strength. Fracture toughness of pyrolysed Coal 2 and Coal 3 at 700°C was about 0.40 MPa·m^{1/2}, while pyrolysed Coal 1 had lower fracture toughness at 0.34 MPa·m^{1/2}. Heat treatment increased the micro strength of all pyrolysed coals in the same manner as that of supplied chars. Significant increase in micro strength of pyrolysed coals took place in the temperature range 700-1100°C, in which heat treatment doubled the fracture toughness. Further increase of annealing temperature from 1100 to 1500°C caused less than 10 % increase in micro strength. After heat treatment at 1500°C for 2 hours, pyrolysed coals were four times as strong as the original coals.

3.3. Effect of heat treatment on pore structure of carbonaceous materials

3.3.1. Effect of heat treatment on porosity of carbonaceous materials

Porosity of original carbonaceous materials and after annealing at different temperatures is presented in table 4. Relative standard deviation (RSD) of the porosity measurement is in brackets.

Table 4: Porosity and relative standard deviation (in brackets) of carbonaceous materials before and after 2-hour annealing at different temperatures, % (RSD)

	Original	700°C	1100°C	1300°C	1500°C
Coke 1	46.8 (0.115)	-	-	48.6 (0.110)	52.2 (0.094)
Coke 2	51.4 (0.133)	-	-	51.1 (0.114)	53.2 (0.139)
Coke 3	51.0 (0.148)	-	-	51.7 (0.145)	53.4 (0.119)
Char 1	43.7 (0.333)	-	53.6 (0.289)	-	55.6 (0.264)
Char 2	69.0 (0.184)	-	79.5 (0.157)	-	82.6 (0.102)
Char 3	18.8 (0.483)	-	23.8 (0.454)	-	24.9 (0.440)
Coal 1	21.3 (0.363)	59.4 (0.106)	63.6 (0.114)	-	64.6 (0.096)
Coal 2	19.0 (0.365)	46.0 (0.309)	59.7 (0.217)	-	62.1 (0.195)
Coal 3	22.7 (0.392)	60.5 (0.220)	69.0 (0.156)	-	71.7 (0.116)

Porosity of original cokes was in the range of 47-51 %. Heat treatment at 1300°C caused a slight increase of porosity. After 2-h annealing at 1500°C, the porosity of cokes increased more noticeably, to approximately 53 %.

Porosity of original chars was very different, from 19% for Char 3 to 69% for Char 1. Heat treatment of chars at 1100 °C caused a 15-20% increase of porosity. Porosity increased further with increasing temperature to 1500 °C; its change in temperature range 1100-1500°C was insignificant.

The porosity of original coals was 19-23%; the porosity increased greatly during the char production at 700 °C (pyrolysed coal). A 38% porosity increase was found for Coal 1 and Coal 3 while porosity of Coal 2 increased by 28%. Further annealing of the pyrolysed coals increased porosity with decreasing increment. Effect of increasing annealing temperature on porosity was more prominent in the temperature range 700-1100°C than of 1100-1500°C.

Heat treatment promoted the porosity evolution of all carbonaceous materials. The relative standard deviation of the porosity measurement decreased with increasing annealing temperature, which indicates that increasing annealing temperature made a more homogeneous pore structure for the carbonaceous materials.

3.3.2. Effect of heat treatment on pore geometry of carbonaceous materials

Pore geometry parameters-Feret (aspect) ratio, cross section area, equivalent circle diameter and pore density, were determined using LAS Image Analysis. The pore geometry parameters of original cokes, chars and pyrolysed coals are presented in table 5. The pore parameters of the carbonaceous materials heat treated at 1500 °C for 2 hours are presented in table 6.

Table 5: Pore geometry parameters of original carbonaceous material

	Coke 1	Coke 2	Coke 3	Char 1	Char 2	Coal 1	Coal 2	Coal 3
Feret ratio, %	56.7	57.5	57.2	52.4	51.6	58.8	52.9	58.8
Area, μm^2	14002	18859	19231	12830	14927	21030	9700	4555
Equivalent circle diameter, μm	104.7	115.5	114.1	94.7	105.9	115.2	91.3	68.7
Pore density, pores/mm^2	31.9	25.8	26.9	41.5	43.5	26.8	51.0	86.8

Table 6: Pore geometry parameters of carbonaceous material annealed at 1500 °C

	Coke 1	Coke 2	Coke 3	Char 1	Char 2	Coal 1	Coal 2	Coal 3
Feret ratio, %	57.1	58.1	57.4	55.2	52.4	57.4	50.2	57.4
Area, μm^2	15018	19590	19946	16128	22736	26939	15753	9029
Equivalent circle diameter, μm	106.3	119.4	119.8	104.3	128.6	128.9	107.2	93.8
Pore density, pores/mm^2	32.8	25.5	26.3	36.2	31.8	23.3	37.1	68.1

Only pores with size above 1000 μm^2 were considered (tables 5 and 6) since smaller pores were expected to have insignificant effect on the mechanical strength of carbonaceous materials [10].

Feret ratio, the shape factor, of all carbonaceous materials varied between 52-59 %. After annealing at 1500°C for 2 hours, no significant variation in the pore shape was observed.

Mean pore cross section area of original cokes, chars and pyrolysed coals was in the range of 4555- 21030 μm^2 depending on the type of carbonaceous materials. The mean pore diameter varied from 68.7-115.5 μm . The pyrolysed Coal 3 had the smallest pore size which was 68.7 μm in pore

diameter and $4555 \mu\text{m}^2$ in mean pore cross section area, while Coke 2, Coke 3 and pyrolysed Coal 1 had significantly larger pore size. Pore size of original cokes increased slightly after heat treatment at 1500°C ; however, more significant enlargement of pores caused by annealing was observed in chars and pyrolysed coals. Over $22 \mu\text{m}$ increase in diameter was found in Char 2 and pyrolysed Coal 3. The smallest pore enlargement of $9.6 \mu\text{m}$ occurred in Char 1.

Pore density of original cokes was varied in the range of 25.8-31.9 pores/ mm^2 ; annealing at 1500°C had a slight effect on the pore density of cokes. Pore density of chars and pyrolysed coals significantly decreased after annealing as a result of enlargement of pores.

Consistent with porosity development of carbonaceous materials, the change in the pore geometry parameters upon heat treatment of cokes was marginal. However, annealing caused significant changes in pore geometry parameters of chars and pyrolysed coals.

3.4. Factors affecting tensile strength of carbonaceous materials

Tensile strength of carbonaceous materials can be related to the micro strength, porosity and pore geometry. A Correlation between pore structure, micro strength and tensile strength was presented by empirical equation (8):

$$\sigma = 27.74 \times K_{1c}^{0.365} \times \exp(-1.35 \times F_{ratio}^{-0.95} \times p - 2.32 \times D) \quad (8)$$

where σ is tensile strength; K_{1c} is fracture toughness; D and F_{ratio} represent equivalent circle diameter of pores and Feret ratio, and p is porosity. Figure 1 shows a good correlation ($R^2=0.9664$) described by equation (8). Tensile strength increases with increasing fracture toughness and Feret ratio, and decreasing equivalent circle diameter of pores and porosity.

If pore geometry on tensile strength is not considered, then only porosity and micro strength are taken into consideration. In this case, relationship between the tensile strength and porosity and micro strength can be described by the empirical equation (9):

$$\sigma = 17.567 \times K_{1c}^{0.798} \times \exp(-2.075 \times p) \quad (9)$$

Figure 2 shows that this relationship also has good correlation, which shows the effect of pore geometry on macro strength of the carbonaceous materials involved in this study was marginal.

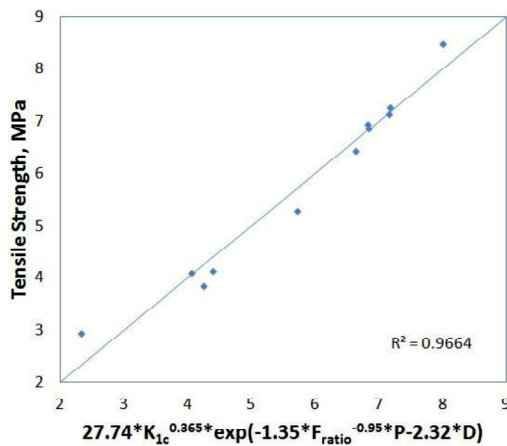


Figure 1: Correlation between pore structure, fracture toughness and tensile strength

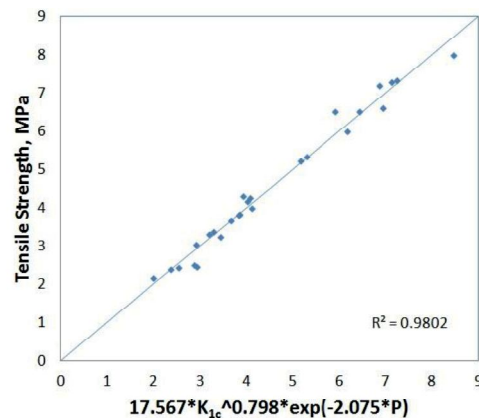


Figure 2: Correlation between porosity, fracture toughness and tensile strength

The results indicate that macro strength of carbonaceous materials can be improved by reducing porosity and/or increasing micro strength. The comparative effect of these parameters on the macro strength can be illustrated as follows.

If one parameter is fixed, and the other parameter is varied by fraction “x” (increase for fracture toughness; decrease for porosity), the relative change of tensile strength, I , as defined in equation (10), can be obtained from equation (9).

$$I = \frac{\sigma' - \sigma}{\sigma} \quad (10)$$

The change of tensile strength caused by fracture toughness increase by “x”, $I_{K_{1c}}$, will be

$$I_{K_{1c}} = (1 + x)^{0.798} - 1 \quad (11)$$

The change of tensile strength caused by porosity reduction by “x”, I_p , will be

$$I_p = \exp(2.075 \times x \times p) - 1 \quad (12)$$

where p is the original porosity of material before porosity reduction. According to equations (11) and (12), when the original porosity of material is larger than 38.5 %, the improvement of tensile strength caused by porosity reduction, I_p , is greater than that caused by the increase of fracture toughness, $I_{K_{1c}}$. In this case, porosity has more significant effect than micro strength on the tensile strength. Only two coke/char samples involved in this study had the porosity lower than 38.5 %; therefore decreasing porosity is a more effective method compared with increasing micro strength to improve the macro strength of carbonaceous materials.

4. CONCLUSIONS

The effect of annealing on the mechanical strength of carbonaceous materials and the factors influencing mechanical strength was studied by tensile test, microscopic image analysis and ultra micro indentation. The major findings are summarized below.

1. Tensile strength of chars and pyrolysed coals was strongly enhanced by heat treatment (except Char 3 which tensile strength slightly decreased); cokes were slightly degraded by annealing.

2. Major enhancement of tensile strength of chars and pyrolysed coals took place in annealing at temperatures below 1100°C; no further increase was observed with increasing temperature from 1100-1500°C. Annealing at temperatures 1300°C and below caused only marginal decrease in tensile strength of cokes, while decrease in the coke strength after annealing at 1500 °C was more evident.

3. Fracture toughness of chars and pyrolysed coals was significantly enhanced by heat treatment and the major increase occurred below 1100°C. The fracture toughness of cokes increased only marginally. Fracture toughness of IMDC was higher than RMDC. Heat treatment had no effect on the fracture toughness of IMDC but slightly increased fracture toughness of RMDC. Cokes had the highest micro strength in comparison with other carbonaceous materials.

4. Heat treatment increased the porosity of all carbonaceous materials. Effect of heat treatment on chars and coals was higher than on cokes. Porosity of chars and coals was significantly increased at temperatures below 1100°C. Porosity of cokes was not affected by heat treatment at temperatures below 1300°C, but slightly was increased by annealing in the temperature range of

1300-1500°C. Annealing had a marginal influence on the pore shape of carbonaceous materials but enlarged pore size of chars and coals and decreased their pore density.

5. The tensile strength of carbonaceous materials was strongly affected by the porosity and micro strength. The effect of pore geometry on tensile strength was marginal. Decreasing porosity was a more effective method compared with increasing micro strength to improve the macro strength of carbonaceous materials.

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