

# IRON CATALYSED GRAPHITISATION IN THE BLAST FURNACE

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## INTRODUCTION

The present paper presents results of Raman microprobe spectroscopy and X-ray diffraction studies on a set of blast furnace coke samples. The main aim of the study was to investigate the distribution of the catalytically formed graphite in the blast furnace using the Raman microprobe technique and to compare and contrast these results with the Raman spectral features of the coke unaffected by catalytic graphitisation.

## EXPERIMENTAL

The study used five drill core coke samples from the various regions of a blast furnace. The polished coke samples were examined employing optical microscopy, XRD and Raman microprobe spectroscopy. A detailed description of the experimental procedure has been presented previously<sup>1</sup>.

## RESULTS AND DISCUSSION

### Optical microscopy

Microscopic examination of the samples revealed the presence of large graphite flakes inside iron globules and around the edge of the iron particles. Carbon material associated with finer iron particles also has a better ordered structure than the corresponding iron free coke present in the samples.

### X-ray diffraction results

XRD study of the coke samples showed that the (002) peak is a combination of three peaks. Peak 1 which occurs at the lowest angle represents the disordered carbon in the original coke. Peak 2, the dominant peak corresponding to heat treatment and peak 3, at the highest angle, is due to the graphitic carbon formed by iron catalysed graphitisation. Table 1 shows that the crystallite height of the catalytically formed carbon range from over 60 nm in B to 40 nm in D whereas in sample E the  $l_c$  value is only 20 nm. The  $d_{002}$  values increase from 0.3366 nm to 0.3371 nm from B to E. Previous study<sup>2</sup> indicated that the maximum heat treatment temperature decreases in the

order B, C, A, D and E. The changes in  $d_{002}$  and  $l_c$  for both the coke and the graphitic carbon reflect the thermal history of the individual sample.

Table 1 XRD results for the blast furnace cokes

sample	$d_{002}/\text{nm}$ peak			$l_c/\text{nm}$ peak		
	1	2	3	1	2	3
A	0.3505	0.3420	0.3366	3.3	14.6	56.0
B	0.3500	0.3410	0.3366	4.2	17.6	63.0
C	0.3503	0.3411	0.3365	4.2	16.3	59.5
D	0.3508	0.3422	0.3367	3.3	12.2	39.8
E	0.3520	0.3436	0.3371	2.4	7.6	21.4

### Raman spectral results

The first order Raman spectral data for the various samples are presented in Table 2. For each sample, Spectrum 1 is for the carbon associated with iron particles and 2 is for the coke particle. For samples A, B and C there is no significant difference in the  $\Delta\nu_D$  values between the coke and the carbons associated with iron whereas for samples D and E,  $\Delta\nu_D$  values are significantly higher for the coke particles than for the carbons associated with iron.  $\Delta\nu_G$  are higher for the coke than for the iron associated carbons. In the case of samples D and E,  $\Delta\nu_G$  for the cokes are more than twice as high as that of the carbon associated with iron. For the coke particle in sample E, the G band was so broad that it was not possible to separate the disorder induced D' band from the G band and the position of the composite band has shifted to 1588  $\text{cm}^{-1}$ .

Figure 1 shows some of the typical second order Raman spectra observed and the corresponding data are presented in Table 3. The most noticeable difference in the second order Raman spectra between the carbon associated with the iron and the coke is the resolution of the former into an overlapping doublet at  $\sim 2705$  and  $2735 \text{ cm}^{-1}$  whereas that of the coke is a symmetric single peak centred at

~2710-2720 cm<sup>-1</sup>. The resolution of the second order Raman G' band into a doublet is a typical feature of the well ordered graphitic carbon<sup>3</sup>. The asymmetric second G' bands were observed for sample A, B, C and D. In contrast to other samples, the second order G' band for E1 is only a narrow and intense single band. The failure to observe the typical second order Raman spectra from sample E is consistent with the XRD results which show that only a very small amount of the graphitic material has been formed in E. This is probably due to the lower temperature experienced by the coke and the relatively lower iron content in the sample. The Raman spectral results of these catalytically formed carbons show less well resolved doublet G<sub>1</sub>' and G<sub>2</sub>' and a higher intensity of G<sub>1</sub>' band compared with the natural graphite. This suggests that the graphitisation process is not complete possibly due to the short contact time between the coke and the iron.

**Table 2 First order Raman spectral data**

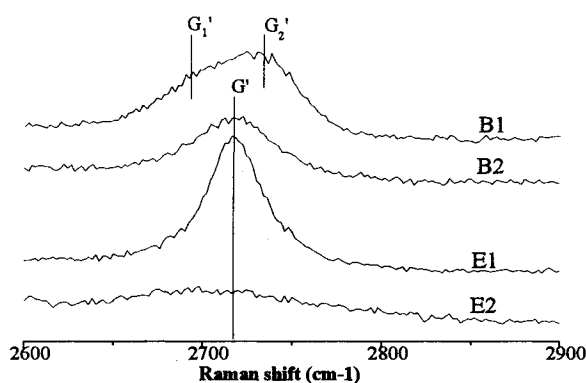
sample	$\nu_D$	$\Delta\nu_D$	$\nu_G$	$\Delta\nu_G$	$\nu_{D'}$	$\Delta\nu_{D'}$
A1	1361	37	1582	21	1622	13
A2	1357	32	1582	27	1618	48
B1	1357	38	1578	20	1618	9
B2	1359	31	1583	26	1621	23
C1	1363	40	1583	19	1624	12
C2	1359	36	1582	23	1621	15
D1	1357	36	1578	20	1618	10
D2	1356	48	1583	46	1615	21
E1	1357	39	1580	26	1619	27
E2	1356	71	1588	64	--	--

**Table 3 Second order Raman spectral data**

sample	G'		G <sub>1</sub> '		G <sub>2</sub> '	
	$\nu_{G'}$	$\Delta_{G'}$	$\nu_{G_1'}$	$\Delta_{G_1'}$	$\nu_{G_2'}$	$\Delta_{G_2'}$
	cm <sup>-1</sup>	cm <sup>-1</sup>	cm <sup>-1</sup>	cm <sup>-1</sup>	cm <sup>-1</sup>	cm <sup>-1</sup>
A1			2706	49	2738	38
A2	2721	48				
B1			2701	50	2734	36
B2	2716	53				
C1			2709	54	2741	33
C2	2719	44				
D1			2703	53	2736	31
D2	2708	71				
E1	2718	36				
E2	2705	137				

## CONCLUSION

The direct link obtained between optical microscopy and Raman spectroscopy in the Raman microprobe instrument has proved useful in linking morphology to molecular structure. XRD results show that the iron catalysed graphitisation is a multiphase process. With increasing heat treatment temperature,  $l_c$  increases and  $d_{002}$  decreases for both the graphite and the coke. The most noticeable Raman spectral difference between the graphite and the coke is the resolution of the second order Raman G' band of the former into an overlapping doublet, whereas the latter only has a single symmetric peak. The results suggest that sample thermal history and the amount of iron in contact with the coke are important factors in the catalytic graphitisation process occurring in the blast furnace.



**Figure 1 The typical second order Raman spectra observed from some of the samples**

## REFERENCES

- 1 W. X. Wang, K. M. Thomas, R. M. Poultney, R. R. Willmers, accepted for publication in *Carbon*.
- 2 R. R. Willmers, R. M. Poultney, D. E. Clark and J. W. Patrick, ECSC final report agreement No. 7220 EB/832 (British Steel), 1991.
- 3 P. Lespade, A. Marchand, M. Couzi, and F. Cruege, *Carbon*, **22**, 375, (1984).

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