

***In-Situ* Temperature Dependent Raman Spectra of Coal**

Ying-Fang XIE^{1,a}, Jing-Lin YOU^{1, b*}, Li-Ming LU^{2,c}

¹ State Key Laboratory of Advanced Special Steel & Shanghai Key Laboratory of advanced Ferrometallurgy & School of Materials Science and Engineering, Shanghai University, Shanghai 200072, China

² CSIRO Process Science and Engineering, Kenmore Qld 4069, Australia

^ayingfangxie@163.com, ^bjlyou@163.com, ^clu_liming@hotmail.com

*Corresponding author

Keywords: Coal, Raman Spectroscopy, Deconvolution, *In-Situ* High Temperature.

Abstract. This paper studied room temperature and *in-situ* high temperature Raman spectra of coal samples of different carbon content with 355 nm laser Raman spectrometer. The deconvoluted parameters of D band and G band were analysed. The relationship between different carbon content and the Raman spectra characteristics of different kinds of coals and the carbon content was studied. *In-situ* high temperature (from 298 to 1473 K) Raman spectra of coals was tested. The change of internal structure during pyrolysis of coals was analysed and studied. Change of G band was discussed with the increase of temperature.

Introduction

Coal is an important energy source. As irreplaceable energy sources, coal can be widely used[1]. Coal has a very complicated structure due to different forming natural conditions. Usually, study on the structure of coal is divided into chemical and physical structure research[2]. Chemical research methods of coal included hydrogenation, oxidation, functional analysis and so on. Physical research methods of coal was the use of modern new technology and advanced equipment to carry on the research of coal structure, such as X-ray diffraction analysis, Infrared spectrum analysis, and so on.

Raman spectroscopy[3] is a molecular spectroscopy in recent years as a rapid development of micro analysis techniques. As a classical experimental tool of microstructure analysis, Raman spectroscopy[4] has becoming an advanced method. Since the 1970s, Raman spectroscopy has been used to study carbon materials, such as graphite, coal and so on. Green and coworkers[5] studied the structure of coal minerals. Tuinstra and Koenig[6], Friedel and Carlson[7] published the first Raman spectra of coal and reported G peak and D peak through extensive studies. Johnson and Thomas[8] found that different grades of coal[9] as the temperature increases in the D band width decreases continuously. Benny-Bassez and Rouzaud[10] found that different levels of natural coal G+D' peak decreased with increasing coal rank, but they didn't find out such reduced regularity. Angoni[11] extracted different samples from graphite, coke, coal and anthracite to determine the difference between the Raman spectroscopy of different carbon content. He found that the width of D band was relevant to its irregular degree, but both D and G couldn't explain the irregular degree. Chunzhu Li and his collaborators_[12] analysed the pyrolysis and gasification of Australian brown coal by Raman spectroscopy, they deconvoluted Raman spectrum of coal from 800 to 1800cm⁻¹ to 10 characteristics spectrums successfully to reflect the highly disordered carbon materials and pointed out the sodium ions affect the pyrolysis of lignite in the coking reaction. Sheng[13] and his collaborators studied coal burning activity and micro structure during temperature of 1183-1773 K by Raman spectroscopy to explain the relationship between microstructure and combustion reactivity of chars[14].

The *in-situ* response experiment device can test the molecular chemical changes in the reaction conditions. It was reported that the changes of chemical bonds by *in-situ* infrared spectroscopy[15] study of coal pyrolysis. *In-situ* Raman spectroscopy has been widely used in many fields. This paper carries out an experimental research for *in-situ* temperature dependent Raman spectra of coals

and analyses the internal structure characteristics of coal combined with the peak deconvolution.

Experimental

Experimental Equipment

The experimental Raman equipment was LabRam800HR of Horiba Jobin Y'von and achieved the *in-situ* high temperature dependent Raman spectroscopy by Linkam Heating Stage 1500 heating stage. Constant temperature precision was $\pm 1\text{K}$ and temperature was determined by the thermocouple calibrated. Measurements were carried out by the 355nm line and laser light source adopted ultraviolet pulse laser. The laser power was 0.2W and scanning range was 200 - 2200 cm^{-1} . The microscope objective was 4x with long focus distance.

Experimental Samples and Method

In Tab. 1, it was showed the contents of element C, H and N of coal samples, which were tested by Elementar vario ELIII (Germany).

Tab. 1 Chemical composition of coal samples

No.	N (%)	C (%)	H (%)
C1	1.84	79.69	4.67
C2	1.92	77.84	4.72
C3	1.81	78.56	4.5
C4	1.88	78.54	4.26
C5	2.12	76.63	5.36
C6	1.84	77.02	4.62

Results and Discussion

Peak Deconvolution

All Raman spectrums were recorded in room temperature by 355 nm ultraviolet excitation light from a solid semiconductor laser. The Raman spectra of all samples in room temperature were similar, Fig.1 showed the Raman spectra of C4 in room temperature. Each Raman spectra was deconvoluted to two main peaks by Origin 8.0. One was assigned to D band and the other one G band. D band was around 1360cm^{-1} which is disorder, defect, diamond band or sp^3 hybridization carbon and G band was around 1580cm^{-1} which is the graphite, tangential band or sp^2 hybridization for carbonaceous materials[16]. Deconvolution could offer the wavenumber positions, width or FWHM (Full Width at Half Maximum) and relative intensity (peak or band area) of each peak.

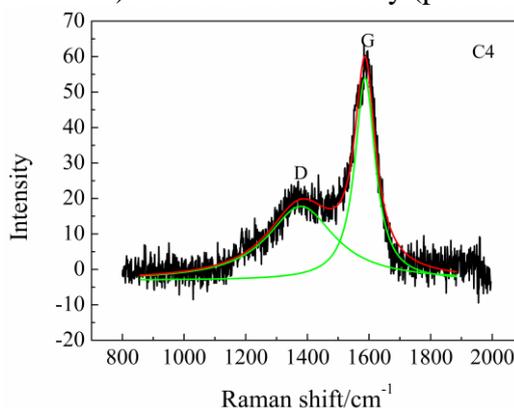


Fig. 1 Raman shift of sample C4

Compared with carbonaceous materials or organic components, inorganic materials such as

alumino-silicates, behaved more sensitive and had higher cross section in the spectral instrumentation using 355 nm excitation laser. It collects relative external and surface structure information by using shorter wavenumber laser. It was estimated that the penetration depth was about several 100 nm for the laser of 355nm. There was more graphite in the surface of coal grain. It might imply the graphitization of coal in nature would happen from outside the coal grain to its center.

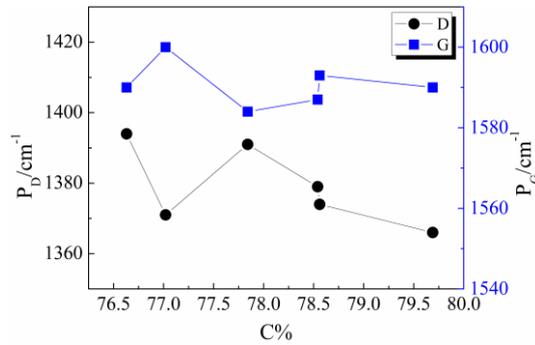


Fig. 2 Relationship of position of deconvoluted D band and G band with carbon content

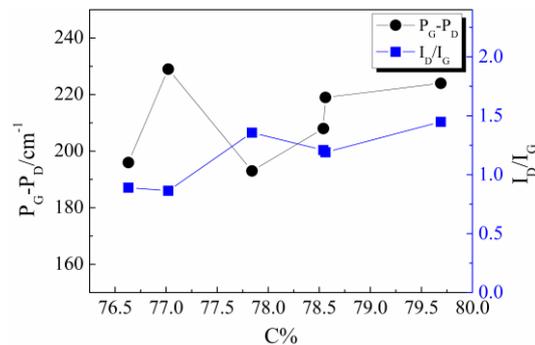


Fig. 3 Relationship of deconvoluted peak position difference $P_G - P_D$ & I_D / I_G with carbon content

And deconvoluted parameters (such as $P_G - P_D$, I_D / I_G , W_D , W_G) were introduced to explain the relationships.

Fig. 2 showed the relationship of position of deconvoluted D band & G band with carbon content. In fig. 2, when carbon content was less than 78% the intensity of D band decreased with the increasing of carbon content firstly and then increased. When carbon content was higher than 78%, the intensity of D band decreased slowly.

However, G band showed opposite to D band. It may be concluded that slight change of carbon content may have the same effect on D band and G band.

Fig. 3 showed the relationship of deconvoluted peak position difference $P_G - P_D$ & I_D / I_G with carbon content. I_D / I_G meant the area ratio of D and G band. $P_G - P_D$ presented the gap of intensity of G band and D band. Fig. 8 showed that $P_G - P_D$ increased in principle with carbon content increasing. But I_D / I_G increased firstly and then decreased with the increasing of carbon content when carbon content was less than 78%. I_D / I_G increased slowly with the increasing of carbon content when carbon content was higher than 78%. It further verified the conclusion of Fig. 2.

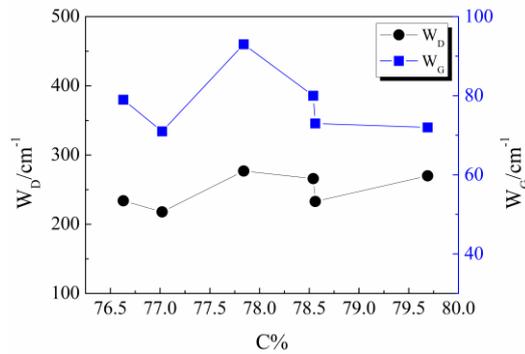


Fig. 4 Relationship of the width (FWHM) of deconvoluted G& D band with carbon content

Fig. 4 showed the relationship of the width (FWHM) of deconvoluted G band and D band with carbon content. W_D meant the FWHM of the deconvoluted D band, which was cooperated with the disordered and defect carbon. Meanwhile, W_G represented the FWHM of the deconvoluted G band, which was related with the degree of graphitization of carbonaceous materials.

Fig. 4 showed W_G decreased firstly and then increased when carbon content was less than 78%. But when carbon content was higher than 78%, W_G decreased slowly. And W_D showed the same tendency compared to W_G . Combined Fig.3 and Fig.4, it could conclude that 78% was the critical point of carbon content. When carbon content was less than 78%, the disorder sp^3 carbon species increased which brought the vibrational wavenumber of D band to increase. While carbon content was higher than 78%, sp^2 increased on the contrary, which implied that relative area of G band appeared to increase.

It should be mentioned[17] that the whole process is accompanied by the volatilization and decomposition of the organics. W_G decreased slowly because of its stable graphite. Relative density of sp^3 bondings in small molecules increased while the low-carbon organics precipitating, most sp^3 bondings in low-carbon organics emerged as unified species as a prominent contribution to the decreasing of the W_D when carbon content was higher than 78%. It meant that the spectrum contained more information of low-carbon organics instead of the remaining coal.

***In-Situ* High Temperature Results and Discussion**

Fig. 5 showed the *in-situ* temperature dependent Raman spectra[18] of C1 in Ar atmosphere. Ar gas flow rate was controlled by bubbles test in water, about 160 bubbles per minute. When the temperature was lower than 473 K, the heating rate was 30 K per min. When the temperature was higher than 473 K, the heating rate was 50 K per min. When the temperature was lower than 873 K, the integral time and frequency was 20x20. When the temperature was higher than 873 K, the integral time and frequency was 30x30. Yellow substance was observed in the temperature of 673 K. This yellow substance was tar oil by analysis[19]. The spectrum labeled as 873 K-2 was the second determination after 40 minutes pyrolysis at 873 K and cleaning the optical silica glass at room temperature followed re-heating back to 873 K. All cooling rate was 50 K per minute.

Fig. 6 showed that the *in-situ* temperature dependent Raman spectra of C4 in Ar atmosphere. The integral time and frequency was 30x30 in the heating process. The experimental conditions of C3, C4, C5 and C6 were as the same as that of C4.

From all the *in-situ* temperature dependent Raman spectra of all samples, it could be observed that D band was decreasing with the increase of temperature. It implied that graphitization degree became higher with the increase of temperature.

In the same time, a sharp peak could be observed at around 1559 cm^{-1} in nearly all the individual spectrum at different temperature. This sharp peak which was a plasma line could help to find out the variation of the G peak position with the increase of temperature clearly. G peak position would shift blue and the intensity would become weaker with the increase of temperature due to the decreasing volatile contents in the samples. It demonstrated that G peak position was effected by the volatile occupying and adsorption on the surface of coal.

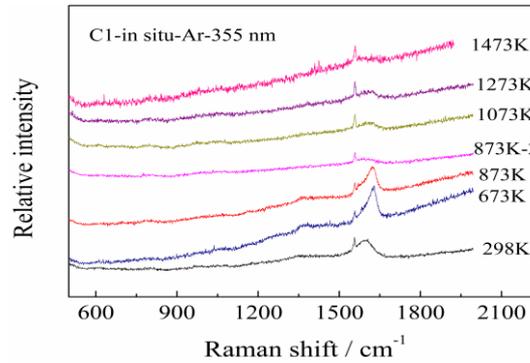


Fig. 5 *In-situ* temperature dependent Raman spectra of C1 in Ar atmosphere

The spectrum of C2, C3 and C6 showed the same phenomenon as that of C4 at 673 K. The spectrum at 673 K seemed strange and unique, which was quite different to all other spectrums. It implied that the liquid substance had emerged on the surface of coal because of the extension of

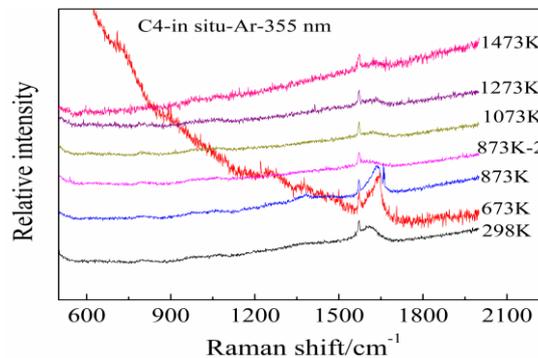


Fig. 6 *In-situ* temperature dependent Raman spectra of C4 in Ar atmosphere

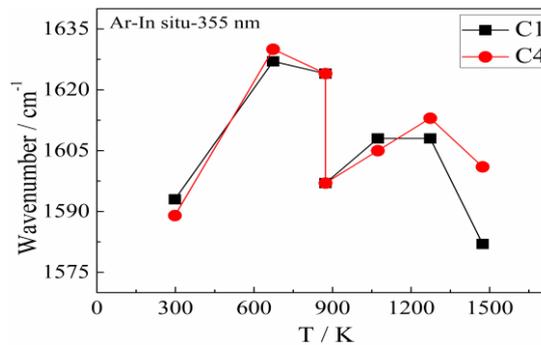


Fig. 7 *In-situ* temperature dependent peak position of G band for C1 and C4 pyrolysis in Ar atmosphere

Rayleigh line[20]. When the temperature exceeded the curing temperature 873 K, it might appear adhesion phenomena and form to char. It showed *in-situ* temperature dependent peak position variations of G band for C1 and C4 pyrolysis in Ar atmosphere in figure 7. By the experimental observation and G band peak position variations of coals, it could be concluded that low-carbon organics precipitate considerably and begin to volatilize at the temperature of 673 K, and some of them would stay on the surface of coal grain as liquid state. There was also a critical point at the temperature of 873 K[21]. When the temperature was higher than 873 K, most high-carbon organics would start precipitating and volatilizing. At the same time, the peak positions of G band at 1073 K and 1273 K were also larger than that of second value at 873 K. It proved that most high-carbon organics precipitate and volatilize from inside to surface of the coal from 873 K to 1273 K and

mostly decompose at 1473 K rapidly. Meanwhile, it was observed that C2, C3, C5 and C6 behaved as the same as C1 and C4.

Summary

In room temperature, 78% was the critical point of carbon content. When carbon content was less than 78%, the disorder sp^3 carbon species increased which resulted in the vibrational wavenumber of D band to increase. While carbon content was higher than 78%, sp^2 increased on the contrary. *In-situ* high temperature dependent experiment, the sharp peak around 1559 cm^{-1} which was a plasma line could help to find out the variation of the G peak position with the increase of temperature clearly. G peak position would shift blue and the intensity would become weaker with the increase of temperature due to the decreasing volatile contents in the samples. Peak position variations of G band could help to conclude that low-carbon organics precipitate considerably and begin to volatilize at 673 K and some of them would stay on the surface of coal as liquid due to the extension of Rayleigh line. The temperature at 873 K was a critical temperature.

Acknowledgments

This work was supported by the key project of Chinese National Natural Science Funds (50932005), Chinese National Natural Science Funds (20973107 & 40973046), the Shanghai Committee of Science and Technology and CSIRO Minerals Down Under Flagship of Australia. You Jing-lin e-mail address: jlyou@staff.shu.edu.cn

References

- [1] Y.Z. Yongjin, and Shanying Hu, Journal of chemical industry and Engineering, 63 (2012) 3-8.
- [2] J. Chen, Shandong chemical industry, 34 (2005) 23-25.
- [3] Z.B.Y.Y.L.L.e. al, Clean Coal Technology, 21 (2015) 79-82.
- [4] N.M. S. Potgieter-Vermaak, N. Wagner, et al, Journal of Raman Spectroscopy, 42 (2011) 123-129.
- [5] P.D. Green, C.A. Johnson, K.M. Thomas, Fuel, 62 (1983) 1013-1023.
- [6] F. Tuinstra, J.L. Koenig, The Journal of Chemical Physics, 53 (1970) 1126-1130.
- [7] R.A. Friedel, G.L. Carlson, Fuel, 51 (1972) 194-198.
- [8] C.A. Johnson, J.W. Patrick, K. Mark Thomas, Fuel, 65 (1986) 1284-1290.
- [9] R. Hinrichs, M.T. Brown, M.A.Z. Vasconcellos, M.V. Abrashev, W. Kalkreuth, International Journal of Coal Geology, 136 (2014) 52-58.
- [10] J.N. Rouzaud, A. Oberlin, C. Beny-Bassez, Thin Solid Films, 105 (1983) 75-96.
- [11] K. Angoni, Carbon, 31 (1993) 537-547.
- [12] C.L. Xiaojiang Li, Journal of Fuel Chemistry and Technology, 33 (2005) 385-390.
- [13] C. Sheng, Fuel, 86 (2007) 2316-2324.
- [14] X. Liu, Y. Zheng, Z. Liu, H. Ding, X. Huang, C. Zheng, Fuel, 157 (2015) 97-106.
- [15] X. Qi, D. Wang, H. Xin, G. Qi, Energy & Fuels, 27 (2013) 3130-3136.
- [16] A. Tselev, I.N. Ivanov, N.V. Lavrik, A. Belianinov, S. Jesse, J.P. Mathews, G.D. Mitchell, S.V. Kalinin, Fuel, 126 (2014) 32-37.
- [17] L. Liu, Y. Cao, Q. Liu, Fuel, 146 (2015) 103-110.

- [18] YOU Jing—lin, JIANG Guo-chang, ZHOU Dong-ming, et al. Chinese Journal. of light scattering, 17 (2005) 4-6.
- [19] Y.J. YU Liwang, WANG Yuanyuan, et al, Journal of Fuel Chemistry and Technology, 43 (2015).
- [20] G.-C.J. J.-L. You, H.-Y. Hou, et al JOURNAL OF RAMAN SPECTROSCOPY, 36 (2005) 237-249.
- [21] Y.J. Liu Xiaofei, Wang Yuanyuan, et al, Journal of Fuel Chemistry and Technology, 42 (2014) 270-276.