

Research Article

FTIR and Raman Spectral Research on Metamorphism and Deformation of Coal

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Under different metamorphic environments, coal will form different types of tectonically deformed coal (TDC) by tectonic stress and even the macromolecular structure can be changed. The structure and composition evolution of TDC have been investigated in details using Fourier transform infrared spectroscopy and Raman spectroscopy. The ductile deformation can generate strain energy via increase of dislocation in molecular structure of TDC, and it can exert an obvious influence on degradation and polycondensation. The brittle deformation can generate frictional heat energy and promote the metamorphism and degradation, but less effect on polycondensation. Furthermore, degradation affects the structural evolution of coal in lower metamorphic stage primarily, whereas polycondensation is the most important controlling factor in higher metamorphic stage. Tectonic deformation can produce secondary structural defects in macromolecular structure of TDC. Under the control of metamorphism and deformation, the small molecules which break and fall off from the macromolecular structure of TDC are replenished and embedded into the secondary structural defects preferentially and form aromatic rings by polycondensation. These processes improved the stability of macromolecular structure greatly. It is easier for ductile deformation to induce secondary structural defects than in brittle deformation.

1. Introduction

The study of macromolecular structure and complicated composition of coal is the most difficult and important topic in coal chemistry [1–4]. Effective analytical methods for coal structure and chemical composition research, such as Fourier transform infrared (FTIR) spectroscopy and Raman spectroscopy are, becoming more and more important for coal chemical researchers [5–15]. Previous studies discussed that with the upgrade of metamorphism, the aromatic structure of primary structure coal increased and expanded, whereas the side chain of aliphatic compound and functional group decreased. The hydrogen and oxygen deplete in coals; as a result, the condensation degree gradually improved. Aromatic structure is mainly composed of anthracite, and the condensation degree is further improved [2, 3, 5,

16, 17]. The coal basins in China experienced multiple tectonic movements and developed widely distribution of tectonically deformed coal (TDC) under the strong tectonic deformation environments [18]. Compared with primary structure coal, the evolution characteristics and ways of macromolecular structure of TDC are more complicated [8, 17–21]. The formation of lignite due to diagenesis could experience different degrees of metamorphism under various temperature-pressure conditions during geological history. If the coal seams are apparently affected by tectonic stress, they can produce deformation in certain degrees. For all the deformational coal seams, the process and mechanism of deformation (brittle deformation and ductile deformation) are actually different [17–21]. Many studies have been conducted in order to investigate the relationship between the group absorption frequency of FTIR and the

metamorphic grade of coals, as well as Raman spectral analysis on carbon materials [3–15, 19]; however, products about the studies of different deformation mechanisms and grades of TDC using FTIR and Raman spectrum analysis, and the analysis of evolution process and mechanisms in macromolecular structure of TDC, were rarely reported. Different deformation mechanisms will exert different influences on the macromolecular structure and composition of TDC [6, 7, 18, 19]. Based on the FTIR and Raman spectrum analysis of TDC samples from Huaibei coalfield, the evolution characteristics of macromolecular structure affected by the change of metamorphism and deformation grade are discussed. The aim of this paper is to explain the mechanism of tectonic deformational influence on the evolution of structural defects and chemical composition.

2. Samples and Experimental Methods

The TDC samples with different deformation and metamorphism ($0.7\% < R_{o,max} < 3.1\%$) were collected from Permo-Carboniferous coal bed in Huaibei coal field, which was strongly affected by the Mesozoic tectonic deformation. The coal seams were mainly distributed in graben, especially in syncline. The tectonic deformation altered the structure of coal seams remarkably and formed various types of TDC.

All samples are pretreated through demineralization and vitrinite centrifugation processes in order to better delineate the characteristics of the deformation and metamorphism of TDC samples. The demineralization process utilized HCl and HF to reduce the proportion of mineral matter in each sample (<2%). The vitrinite centrifugation process used benzene and CCl₄ to increase the composition percentage of vitrinite to 80–90%. The group maceral and vitrinite reflectance ($R_{o,max}$) were tested as well.

The FTIR analysis on 32 samples and Raman analysis on 19 samples are conducted to further understand the evolution of macromolecular structure affected by deformation and metamorphism. It can be determined that the type of functional group and its change correlated with deformation and metamorphism in coal by analysis of absorption band, shown on infrared spectrum [7, 9]. The structural analysis and qualitative identification of molecular can be studied by Raman spectrum because the formation of Raman spectra is closely connected with the structure and the ordering degree of coal macromolecule [22]. FTIR was performed on Nicolet 750 microscopic infrared spectrometer in the Analytical Instrumentation Center in Peking University. The scan ranges from 4000 cm⁻¹ to 650 cm⁻¹. Spectra were recorded by coadding 128 scans at a resolution of 8 cm⁻¹ using an MCT/A detector and a KBr/Ge beam splitter. Raman was performed on Renishaw RM-1000 microscopic Raman spectrometer at the State Key Laboratory of Geological Processes and Mineral Resources in China University of Geosciences. The spectral resolution was 2.4 cm⁻¹, slit width was 2.5 cm⁻¹, and laser power on the sample surface was 0.8 mw; measurements were carried out using the 514.5 nm excitation wavelength with Ar⁺ laser; acquisition time was 30 s. The spectra were measured under 25°C temperature.

3. Results and Analysis

Part of experiment results are listed in Table 1.

3.1. Parameter of FTIR Analysis. The types of functional group in TDC samples collected from Huaibei coal field are basically the same with other researchers [3, 7, 23]. But the peak positions and the changes of absorption peaks with the increase of metamorphic grade are different from others (Figure 1). The biggest difference between TDC and the primary structure coal showed on FTIR spectrum is reflected in the change of relative absorption strength but not the absorption frequency.

3.1.1. Evolution of Characteristic Frequency of Aromatic Structure. The characteristic frequency of aromatic structure includes the absorption strength of (1) 3049 cm⁻¹ related to stretching vibration of CH in aromatic ring, (2) 1600 cm⁻¹ related to vibration of C=C in aromatic ring, and (3) 749 cm⁻¹, 810 cm⁻¹, and 871 cm⁻¹ related to the plane deformation vibration of CH in aromatic rings. With the increase of metamorphic grade, the absorption strength of 1600 cm⁻¹ has little change in brittle deformational coal but decreases first and increases later in ductile deformational coal, and with the range from 0.994 to 1 (Figure 2(a)).

Generally, the change of absorption strength of 1600 cm⁻¹ was not so obvious compared with the other frequencies. The absorption strength of 749 cm⁻¹, 810 cm⁻¹, and 871 cm⁻¹ related to the plane deformation vibration of CH in aromatic ring is correlated with independent, two and more adjacent hydrogen atoms state, respectively. The strongest absorption strength of these frequencies is in the middle metamorphic grade and then in the higher and lower metamorphic grades it is the weakest (Figure 1). Figure 2(b) shows that this change is influenced by brittle and ductile deformation. The strongest absorption strength of 3049 cm⁻¹ related to stretching vibration of CH in aromatic ring is also in the middle metamorphic grade and gradually decreases towards lower and higher metamorphic grades.

With the increase of deformational intensity (brittle and ductile deformation), the absorption strength of 1600 cm⁻¹ increases at first and then decreases, which is inversed with the variation of absorption strength of 749 cm⁻¹ (Figures 2(c) and 2(d)).

3.1.2. Evolution of Characteristic Frequency of Aliphatic Structure. The frequency of aliphatic structure includes absorption strength of (1) 2923 cm⁻¹ and 2862 cm⁻¹ related to the asymmetric stretching vibration of CH₂ and symmetrical stretching vibration of CH₃, shown as shoulder absorption of 2923 cm⁻¹ in aliphatic structure. These frequencies are the weakest in the middle metamorphic grade and increase in the lower and higher metamorphic grades and (2) 1442 cm⁻¹ related to the asymmetric deformation vibration of CH₂ and CH₃ in alkane structure. With the increase of metamorphic grade, the change of absorption strength of 1442 cm⁻¹ range from 0.8 to 0.99.

TABLE 1: Part of experiment results of TDC samples.

Series of deformation	Sample ID	$R_{o,max}/(\%)$	$R_{o,min}/(\%)$	$\Delta R_o/R_{o,max}^1$	FTIR					Raman ²	
					CH ₃ CH ₂		C=C	CH ₃ CH ₂	C-H	A _G	A _D
					2923	2826	1600	1442	749		
Brittle deformation coal	LHM06	0.98	0.83	0.15	0.557	0.326	0.991	0.815	0.317	113967	55594
	HZM03	1.93	1.67	0.13	0.344	0.220	0.994	0.822	0.348	515720	286732
	SK04	1.00	0.91	0.09	0.522	0.372	0.998	0.920	0.369	115158	58378
	HZM02	1.93	1.67	0.13	0.323	0.199	0.998	0.935	0.420	—	—
	LHM12	1.37	1.13	0.18	0.579	0.383	0.998	0.933	0.385	215980	131925
	STM02	1.41	1.12	0.21	0.647	0.403	0.994	0.806	0.380	272570	153720
	TYM04	0.95	0.8	0.16	0.504	0.354	1.000	0.895	0.176	137498	64296
	SK03	0.98	0.88	0.10	0.363	0.264	0.996	0.886	0.548	174251	78056
Ductile deformation coal	LHM04	1.40	1.18	0.16	0.657	0.414	0.988	0.893	0.450	394537	202143
	LHM09	1.39	1.12	0.19	0.599	0.406	0.996	0.951	0.362	—	—
	LLM04	0.83	0.60	0.28	0.547	0.378	0.999	0.918	0.282	324725	164211
	HZM10	2.62	2.02	0.23	0.671	0.406	0.996	0.913	0.301	461139	157064
	LHM02	1.38	1.08	0.22	0.582	0.38	0.998	0.946	0.385	—	—
	LHM03	1.58	1.18	0.25	0.555	0.351	0.988	0.840	0.406	420961	229994
	STM05	1.66	1.12	0.33	0.491	0.312	0.997	0.992	0.455	511926	306591
	XTM08	1.92	1.63	0.15	0.260	0.180	1.000	0.910	0.500	499840	260745

¹ $\Delta R_o = R_{o,max} - R_{o,min}$, ²The data of Raman was cited in [22].

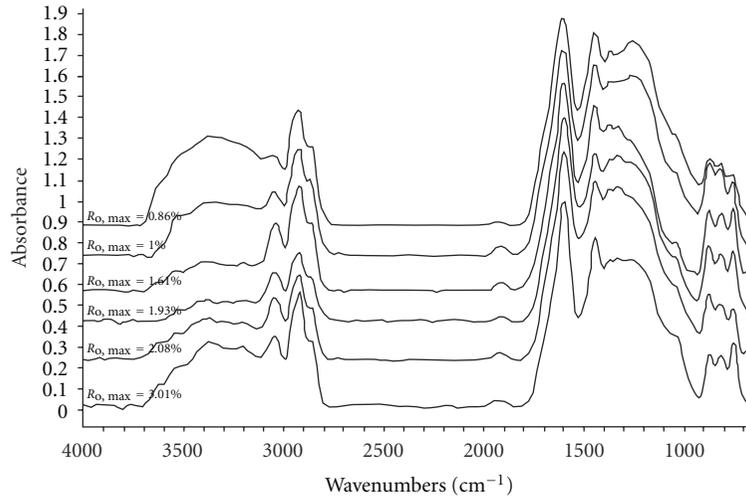


FIGURE 1: The infrared spectrum of TDC with different metamorphic stage.

With the increase of metamorphic grade, the absorption strength of aliphatic structure is much more complicated (Figures 2 and 3). The absorption strength of 2923 cm^{-1} increases first and then decreases in brittle and ductile deformational coal, but absorption strength change of 1442 cm^{-1} is not obvious. It is indicated that the aliphatic structure is gradually degraded with the increase of metamorphic grade in these two deformational mechanisms and this results in the decrease of aliphatic structure.

With the increase of deformational intensity, under the lower metamorphism grade, the absorption strength of 2923 cm^{-1} increases first and decreases later, which is

contrary to the absorption strength variation of 1442 cm^{-1} in brittle and ductile deformational coal (Figures 3(c) and 3(d)). Under the lower deformational intensity, the aliphatic functional groups, alkane branched chains, and a few aromatic rings break off at first, which promotes the metamorphism because of the brittle deformation. In the meantime, the dropped small molecules have not got enough time to form aromatic structure because of the rapid strain rate [19–22]. Part of dropped alkane branched chains are transformed into aliphatic functional groups, and others are turned to free macromolecules. Under the slow strain rate of ductile deformational coal [22], the dropped small

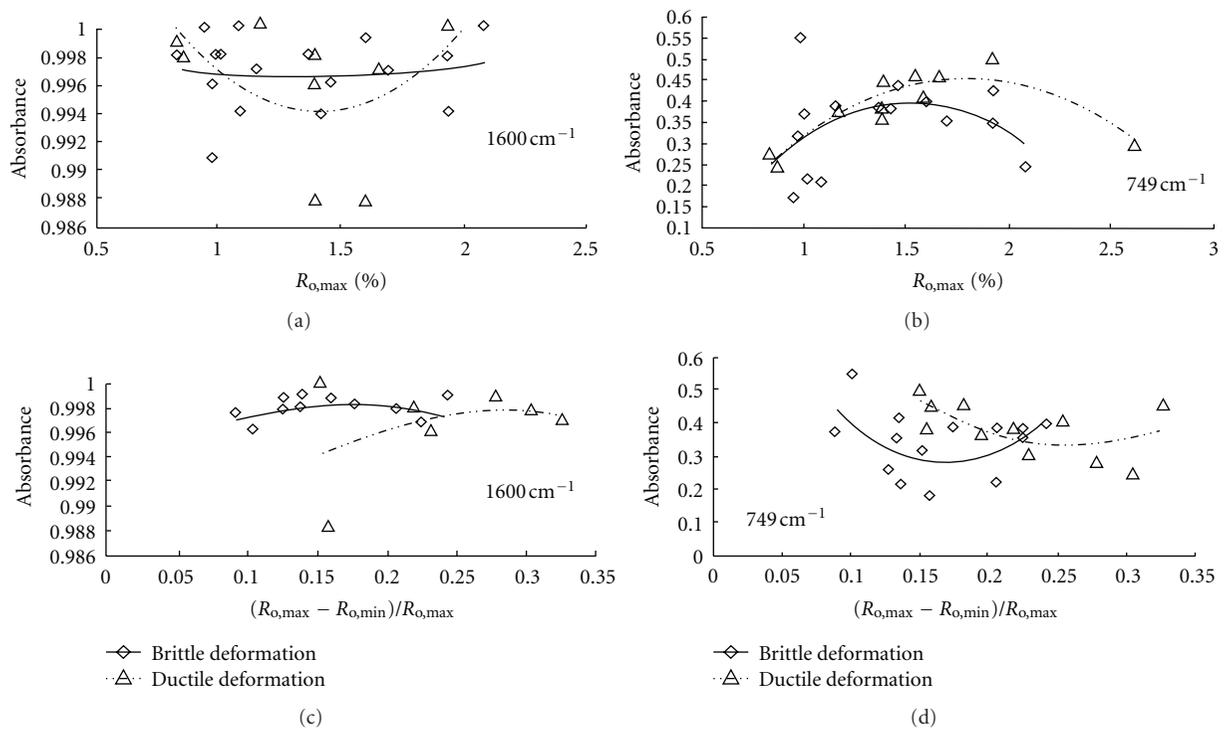


FIGURE 2: Relationship of aromatic absorbance peaks of TDC with different metamorphic and deformation stages. (a) and (b) relationship between aromatic absorbance peaks and metamorphic stages. (c) and (d) relationship between aromatic absorbance peaks and deformation stages.

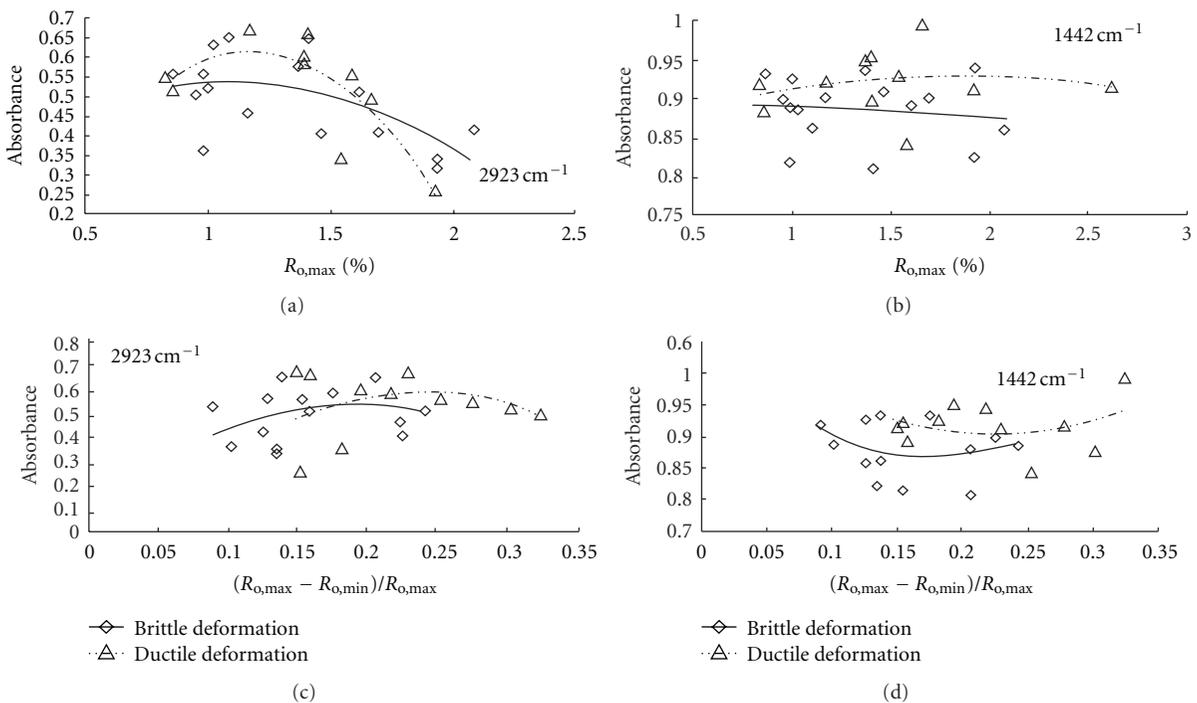


FIGURE 3: Relationship of aliphatic absorbance peaks of TDC with metamorphic and deformation stages. (a) and (b) relationship between aliphatic absorbance peaks and metamorphic stages. (c) and (d) relationship between aliphatic absorbance peaks and deformation stages.

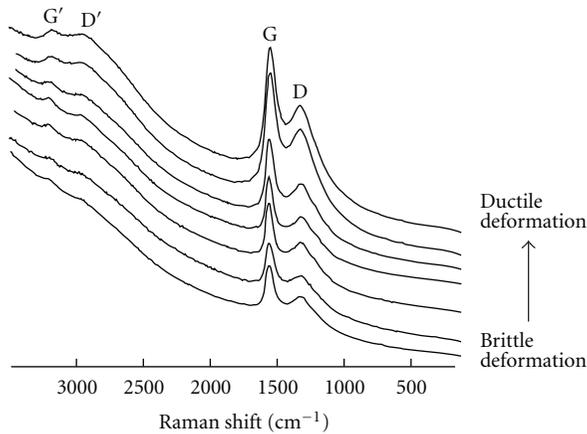


FIGURE 4: The Raman spectrum of TDC with different deformation mechanisms (from [22]).

molecules are combined to aromatic rings and increase the absorption strength of aromatic structure.

3.2. The Raman Spectral Analysis. Nakamizo studied the grinded graphite and graphitized coke applying Raman spectrum and found that the peak G in Raman spectrum is related to the deformation vibration of $C=C$ on aromatic plane; the peak area of G (A_G) stands for the total number of aromatic rings [24, 25]. The grinding process could form structure defects. It is also suggested that secondary structural defects are produced by exogenic action like grinding process. Previous researchers suggested that the tectonic shear stress process and the grinding process were similar under the geological environment; both could generate secondary structural defects in coal graphite [26].

3.2.1. Evolution of the Peak Area of G (A_G). Two peaks (G and D) are observed in Raman spectrum in TDC samples from Huainan-Huaibei coal field, which are in the range from 1590 cm^{-1} to 1600 cm^{-1} and the range from 1340 cm^{-1} to 1356 cm^{-1} , respectively (Figure 4).

Peak G in Raman spectrum is related to the deformational vibration of $C=C$ on aromatic plane; A_G means peak area of G , the total number of aromatic rings [22, 26]. With the increase of metamorphic grade, for brittle deformational coal, the values of A_G increase but change gently like a convex curve in ductile deformational coal which is always higher than the values in brittle deformational coal (Figure 5(a)). It is indicated that the total number of aromatic rings increase in brittle deformational coal, but increase first and decrease later in ductile deformational coal when metamorphic grade increases. The FTIR data show that the change of total aromatic rings are relatively slight, but the absorption strength of every frequency band is changed which means that the undulatory property on the whole aromatic structure is caused by fracture, abscission, and cyclization of aliphatic structure in macromolecular structure of coal. With the increase of deformational intensity, the value of A_G increases in brittle deformational coal, but

first decreases and then increases in ductile deformational coal (Figure 5). The total number of aromatic rings formed in brittle deformational coal are relatively less than in ductile deformational coal. It is indicated that the ductile deformation played a more important role in the process of polycondensation in macromolecular structure of coal.

3.2.2. Evolution of the Peak Area of D (A_D). The Peak D is related to the lattice vibration of irregular hexagon in disordered sp^2 carbonaceous material connected with secondary structural defects between molecular structures [22, 25, 26]. A_D refers to peak area of D and reflects the change of secondary structural defects in the macromolecular structure and the degree of structure order. With the increase of metamorphic grade, the change of A_D is the same as A_G . The values of A_D increase in brittle deformational coal, but increase first and then decrease in ductile deformational coal (Figure 6(a)).

Previous research discussed that there were two types in D peak of Raman spectrum; the first one is induced by defects of primary structures (1370 cm^{-1}), and the other is induced by secondary structural defects (1360 cm^{-1}) which are also related to tectonic stress [26]. The peak D in Huaibei TDC samples is all distributed at 1360 cm^{-1} , indicating that the secondary structural defects generated by tectonic stress exist in TDC. With the increase of metamorphic grade, the secondary structural defects increase rapidly in brittle deformational coal, but increase prior to decrease in ductile deformational coal.

With the increase of deformational intensity, the value of A_D increases in brittle deformational coal, but decreases prior to increases in ductile deformational coal (Figure 6(b)). It is suggested that with the increase of deformational intensity, the secondary structural defects increase in brittle deformational coal, but decrease first and then increase in ductile deformational coal. However, the secondary structural defects in brittle deformational coal are always fewer than in ductile deformational coal. The increasing and accumulating of unit dislocation may transform the stress into strain energy in ductile deformational coal [19, 20, 22, 27], which is easier to generate the secondary structural defects in macromolecular structure of TDC.

4. Discussion

Compared with primary structure coal [2–7, 16, 17, 23, 25, 26], the difference of macromolecular structure shown by FTIR and Raman data of TDC is obvious with the increase of metamorphic grade. Ju et al. studied the different metamorphism-deformation environments and ultrastructure of various TDC using XRD and Nuclear magnetic resonance methods and observed the ultrastructure directly by High-resolution transmission electron microscope [28, 29]. The results reveal that the temperature and tectonic deformation could affect the metamorphism-deformation environment as shown by the change of the stacking of the basal structural units (BSU) layer L_c and the ratio of extension and stacking of the BSU layer L_a/L_c . Under the effect

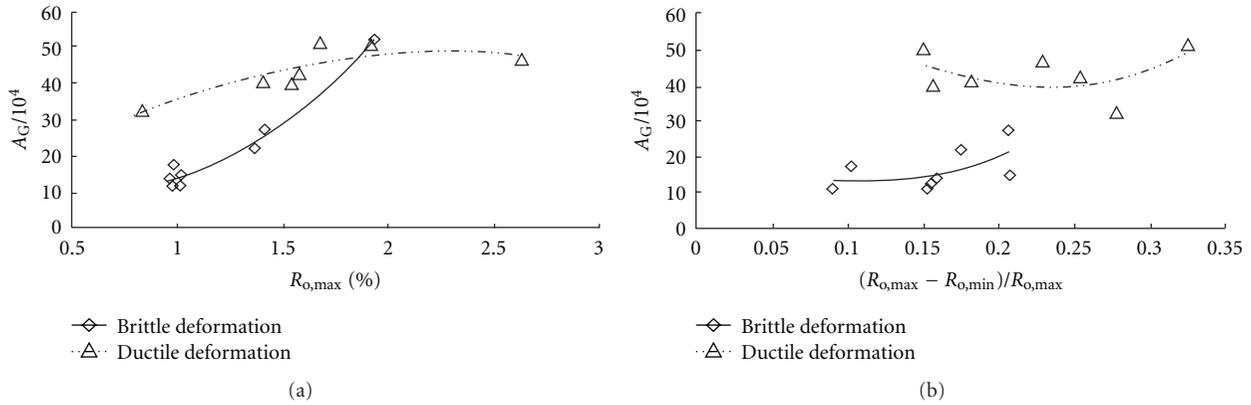


FIGURE 5: Relationship of A_G of TDC with their metamorphic and deformation stages: (a) relationship between A_G and metamorphic stages, (b) relationship between A_G and deformation stages.

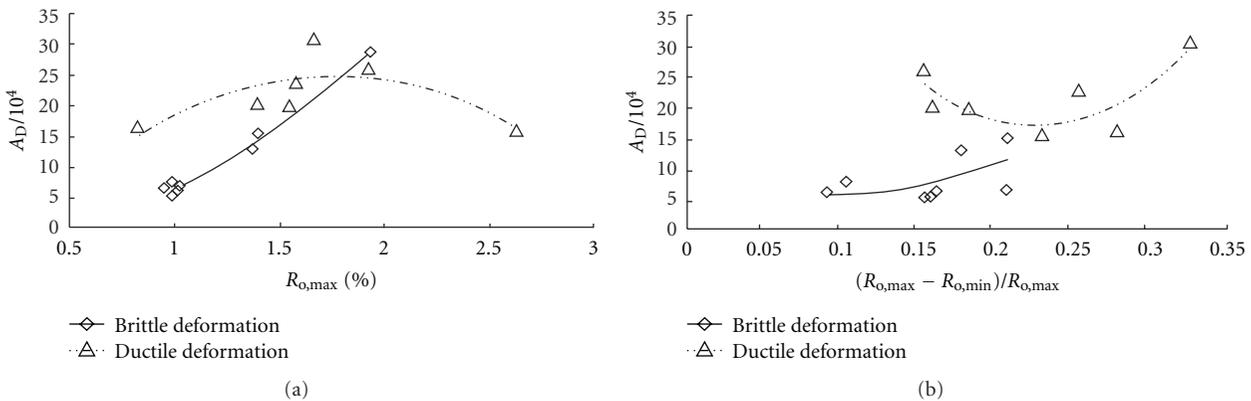


FIGURE 6: Relationship of A_D of TDC with their metamorphic and deformation stages: (a) relationship between A_D and metamorphic stages, (b) relationship between A_D and deformation stages.

of oriented stress, the orientation of the macromolecular structure becomes locally stronger, and the ordering degree of C-nets as well as the arrangement of the BSU is obviously enhanced. It is suggested that the temperature is not the only reason that results in carbonification process of coal, but also the tectonic deformation plays a very important role in this process [17, 28].

With the increase of metamorphic grade, the aliphatic structure and functional groups break off, and the aromatic structure is enriched in ductile deformational coal. However, for brittle deformational coal, the increase of aromatic structure is not obvious. It is indicated that the ductile deformation could produce apparent effect on degradation and polycondensation, and the increased metamorphic grade could promote the ductile deformation and the polycondensation process. The brittle deformation can only produce apparent effect on degradation and has little influence on polycondensation. The absorption strength of aromatic structure is developed as complementary to the aliphatic structure bands compared to the absorption peaks of aromatic and aliphatic structure. In lower metamorphic grade, there is much more aliphatic structures in TDC. Because of the fracture, abscission and cyclization of aliphatic

functional groups and alkane branched chains made the aromatic structure increase with the metamorphic grade rise.

With the increase of deformational intensity, the brittle deformation transforms the stress into frictional heat energy [19, 20, 22, 27], increases the kinetic energy, and promotes the degradation. The aliphatic functional groups and alkane branched chains break off first because of the high strain rate, and the residual of them will be transformed into aromatic structure so that the rangeability of aromatic structure in brittle deformation is relatively low. The ductile deformation transforms the stress into strain energy by increasing and accumulating of unit dislocation [19, 20, 22, 27], which promotes the polycondensation. In lower metamorphism stage with degradation as the main reaction, the aliphatic functional groups and alkane branched chains break off by ductile deformation. The dropped small molecules have enough time to form aromatic rings because of the slow strain rate, which results in more and more aromatic structure enrichment in ductile deformational coal.

Raman data show that the D peak of Raman spectrum is observed around 1360 cm^{-1} , indicating that secondary structural defects in TDC samples from Huaibei coal field are induced by tectonic deformation. In lower metamorphic

grade, the increase of the total number of aromatic rings and secondary structural defects are induced by brittle and ductile deformation, whereas by ductile deformation in higher metamorphic grade. This feature suggests that lower metamorphic grade is a benefit to brittle deformation, while the higher metamorphic grade can promote the ductile deformation. The FTIR spectrum shows that the ductile deformation can produce apparent effect on degradation and polycondensation, but brittle deformation exerts little influence on polycondensation. It is observed that degradation is the main reaction for macromolecular structure formation in lower metamorphic grade, instead of polycondensation in higher metamorphic grade. With the increase of deformational intensity, fewer secondary structural defects exist in brittle deformational coal than in ductile deformational coal, indicating that the ductile deformation can produce the secondary structural defects easier than brittle deformation.

To summarize, different deformational mechanisms change the chemical structure and produce the secondary structural defects, which are the main reason for various structure evolution of TDC compared with primary structure coals. Based on the XRD test about those TDC samples we studied early [29], with the increase of deformational intensity, the degradation is the main effect under brittle deformational coal. The brittle deformation can transform stress into frictional heat energy, increase the kinetic energy, and accelerate the movement of molecule (functional group) [19, 27, 29, 30]. The aliphatic functional groups and alkane branched chains break off by brittle deformation and promote the degradation as well, shown by decrease of L_c and L_a . With increasing deformation and accumulating thermal energy, the cyclization and aromatization of aliphatic functional groups increase and form aromatic rings and make the L_c and L_a increase. Meanwhile, for the ductile deformational coal, the aliphatic functional groups, alkane branched chains, and a fraction of aromatic rings break off by ductile deformational in the lower metamorphism stage shown by the decrease of L_c . The accumulating of unit dislocation may transform the stress into strain energy and the slow strain rate [19, 27, 29, 30]; parts of dropped small molecules have enough time to form aromatic rings and make L_a increase. In the higher-middle metamorphism stage, with the polycondensation as the main effect, this promotes more dropped small molecules to form aromatic rings and the polycondensation on the other side. With the increase of ductile deformation and accumulating of unit dislocation, the secondary structural defects are generated in this stage which can reduce the structural stability of TDC. The secondary structural defects make the aliphatic functional groups, alkane branched chains, and a fraction of aromatic rings break off selectivity shown by decrease of L_a . With more secondary structural defects and small molecules dropped, these small molecules started to fill into secondary structural defects to stabilize the macromolecular structure. So the dropped small molecules splice and embed preferentially in secondary structural defects or residual aromatic structures and form aromatic rings to make the macromolecular structure of much stability.

5. Conclusions

- (1) With the increase of deformation and metamorphism, the change of FTIR and Raman spectrum shows different ways. The tectonic deformation made a very important role which affects the macromolecular structure of TDC. Different deformational mechanism induced different evolution process of macromolecular structure of TDC. The ductile deformation can produce apparent effect on degradation and polycondensation, but brittle deformation has little influence on polycondensation in lower metamorphic grade. In higher metamorphic grade, polycondensation is the main reaction in macromolecular structure of coal. It means that the degradation is the main effect under brittle deformation and the polycondensation under ductile deformation.
- (2) Tectonic deformation can produce the secondary structural defects in macromolecular structure of TDC. The increase of total number of aromatic rings and secondary structural defects is mainly caused by brittle deformation in lower metamorphic grade, but ductile deformation in higher metamorphic grade. Furthermore, the ductile deformation can produce the secondary structural defects easier than brittle deformation.
- (3) The existence of secondary structural defects reduces the stability of macromolecular structure in TDC. Brittle deformation promotes the degradation and makes the aliphatic functional groups and alkane branched chains break off selectively in lower metamorphic grade. With the increase of deformation and metamorphism, more secondary structural defects are produced and small molecules are dropped; the ductile deformation promotes the polycondensation, so the dropped small molecules splice and embed preferentially in secondary structural defects or residual aromatic structures and form aromatic rings to make the macromolecular structure of much stability.

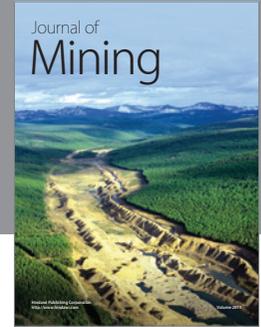
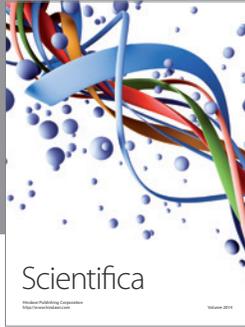
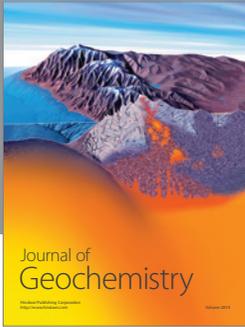
Acknowledgments

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References

- [1] J. R. Levine and A. Davis, "The relationship of coal optical fabrics to alleghanian tectonic deformation in the central Appalachian fold-and-thrust belt," *Pennsylvania Geological Society of America Bulletin*, vol. 101, no. 10, pp. 1333–1347, 1989.
- [2] D. Y. Cao, S. R. Zhang, and D. Y. Ren, "The influence of structural deformation on coalification: a case study of

- carboniferous coal measures in the Northern foothills of the dabie orogenic belt," *Geological Review*, vol. 48, no. 3, pp. 313–317, 2002.
- [3] D. J. Zhang and X. F. Xian, "I.R. spectroscopy analysis of the groups in coal macromolecule," *Journal of Chongqing University*, vol. 13, no. 5, pp. 6–7, 1990.
- [4] X. D. Zhu, Z. B. Zhu, and C. J. Han, "Quantitative determination of oxygen-containing functional groups in coal by FTIR spectroscopy," *Journal of Fuel Chemistry and Technology*, vol. 27, no. 4, pp. 335–339, 1999.
- [5] J. Ibarra, E. Muñoz, and R. Moliner, "FTIR study of the evolution of coal structure during the coalification process," *Organic Geochemistry*, vol. 24, no. 6-7, pp. 725–735, 1996.
- [6] Y. W. Ju, B. Jiang, G. L. Wang et al., *Tectonically Deformed Coals: Structure and Physical Properties of Reservoirs*, China University of Mining and Technology Press, Xuzhou, China, 2005.
- [7] Y. W. Ju, B. Jiang, Q. L. Hou, and G. L. Wang, "FTIR spectroscopic study on the stress effect of compositions of macromolecular structure in tectonically deformed coals," *Spectroscopy and Spectral Analysis*, vol. 25, no. 8, pp. 1216–1220, 2005.
- [8] J. Jehlička, O. Urban, and J. Pokorný, "Raman spectroscopy of carbon and solid bitumens in sedimentary and metamorphic rocks," *Spectrochimica Acta A*, vol. 59, no. 10, pp. 2341–2352, 2003.
- [9] C. P. Marshall, E. J. Javaux, A. H. Knoll, and M. R. Walter, "Combined micro-Fourier transform infrared (FTIR) spectroscopy and micro-Raman spectroscopy of proterozoic acritarchs: a new approach to Palaeobiology," *Precambrian Research*, vol. 138, no. 3-4, pp. 208–224, 2005.
- [10] S. Bernard, O. Beyssac, K. Benzerara, N. Findling, G. Tzvetkov, and G. E. Brown, "XANES, Raman and XRD study of anthracene-based cokes and saccharose-based chars submitted to high-temperature pyrolysis," *Carbon*, vol. 48, no. 9, pp. 2506–2516, 2010.
- [11] A. Cuesta, P. Dhamelincourt, J. Laureyns, and J. M. D. Tascón, "Comparative performance of X-ray diffraction and Raman microprobe techniques for the study of carbon materials," *Journal of Materials Chemistry*, vol. 8, pp. 2875–2879, 1998.
- [12] O. Beyssac, L. Bollinger, J. P. Avouac, and B. Goffé, "Thermal metamorphism in the lesser Himalaya of Nepal determined from Raman spectroscopy of carbonaceous material," *Earth and Planetary Science Letters*, vol. 225, no. 1-2, pp. 233–241, 2004.
- [13] J. Jehlička, O. Urban, and J. Pokorný, "Raman spectroscopy of carbon and solid bitumens in sedimentary and metamorphic rocks," *Spectrochimica Acta A*, vol. 59, no. 10, pp. 2341–2352, 2003.
- [14] J. Jehlička and C. Beny, "First and second order Raman spectra of natural highly carbonified organic compounds from metamorphic rocks," *Journal of Molecular Structure*, vol. 480-481, pp. 541–545, 1999.
- [15] O. Urban, J. Jehlička, J. Pokorný, and J. N. Rouzaud, "Influence of laminar flow on preorientation of coal tar pitch structural units: Raman microspectroscopic study," *Spectrochimica Acta A*, vol. 59, no. 10, pp. 2331–2340, 2003.
- [16] Y. Qin, *Micropetrology and Structural Evolution of High-Rank Coals in P. R. China*, China University of Mining and Technology Press, Xuzhou, China, 1994.
- [17] Y. W. Ju and X. S. Li, "New research progress on the ultrastructure of tectonically deformed coals," *Progress in Natural Science*, vol. 19, no. 11, pp. 1455–1466, 2009.
- [18] Y. W. Ju, B. Jiang, Q. L. Hou, and G. L. Wang, "The new structure-genetic classification system in tectonically deformed coals and its geological significance," *Journal of China Coal Society*, vol. 29, no. 5, pp. 513–517, 2004.
- [19] Y. W. Ju, G. L. Wang, B. Jiang, and Q. Hou, "Microcosmic analysis of ductile shearing zones of coal seams of brittle deformation domain in superficial lithosphere," *Science in China D*, vol. 47, no. 5, pp. 393–404, 2004.
- [20] Y. W. Ju, H. Lin, X. S. Li et al., "Tectonic deformation and dynamic metamorphism of coal," *Earth Science Frontiers*, vol. 16, no. 1, pp. 158–166, 2009.
- [21] D. Y. Cao, X. M. Li, and S. R. Zhang, "Influence of tectonic stress on coalification: stress degradation mechanism and stress polycondensation mechanism," *Science in China D*, vol. 50, no. 1, pp. 43–54, 2007.
- [22] H. Lin, Y. W. Ju, Q. L. Hou et al., "Raman spectra of tectonically deformed coals in brittle and ductile deformation mechanisms and its response to structural components," *Progress in Natural Science*, vol. 19, no. 10, pp. 1117–1125, 2009.
- [23] D. J. Zhang and X. F. Xian, "The study of the macromolecular structure of coal by FTIR spectroscopy," *Spectroscopy and Spectral Analysis*, vol. 9, no. 3, pp. 17–19, 1989.
- [24] M. Nakamizo, R. Kammereck, and P. L. Walker Jr., "Laser Raman studies on carbons," *Carbon*, vol. 12, no. 3, pp. 259–267, 1974.
- [25] M. F. Li, F. G. Zeng, F. H. Qi, and B. L. Sun, "Raman spectroscopic characteristics of different rank coals and the relation with XRD structural parameters," *Spectroscopy and Spectral Analysis*, vol. 29, no. 9, pp. 2446–2449, 2009.
- [26] Z. Zheng and X. H. Chen, "Raman spectra of coal-based graphite," *Science in China B*, vol. 38, no. 1, pp. 97–106, 1995.
- [27] Q. L. Hou, J. L. Li, S. Sun et al., "Discovery and mechanism discussion of supergene micro-ductile shear zone," *Chinese Science Bulletin*, vol. 40, no. 10, pp. 824–827, 1995.
- [28] Y. W. Ju, B. Jiang, Q. L. Hou, G. Wang, and S. Ni, "¹³C NMR spectra of tectonic coals and the effects of stress on structural components," *Science in China D*, vol. 5, no. 9, pp. 847–861, 2005.
- [29] X. S. Li, Y. W. Ju, Q. L. Hou et al., "Structural response to deformation of the tectonically deformed coal macromolecular," *Acta Geologica Sinica (English Edition)*, In press, 2012.
- [30] Q. L. Hou and D. L. Zhong, "The deformation and metamorphism in the wuliangshan ductile shear zone in Western Yunnan, China," in *Memoir of Lithospheric Tectonic Evolution Research*, pp. 24–29, Seismology Press, Beijing, China, 1st edition, 1993.



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