Evolution of the Hierarchical Molecular Structures of Tectonically Deformed Coals: Insights from First-Order Raman Spectra

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ABSTRACT: The dynamic metamorphism of tectonically deformed coals (TDCs) is closely correlated with the occurrence of coalbed methane. Here, a Raman detection technique was used to characterize two primary coals and 14 TDCs sampled from the Huaibei coalfield, allowing for profound insight into the dynamic metamorphism caused by tectonic stress in coals. A nine-peak curve fitting method was applied to deconvolute the first-order Raman spectra, and six structural parameters were used to characterize the hierarchical evolution of TDC molecules. The lower $A_2/A_{\text{Total}}$ and $A_5/A_{\text{Total}}$ ratios in TDCs indicate that the cross-links in secondary and aggregated (outer) structures are cleaved by tectonic stress. Once the aromatic structures are released through the cleavage of cross-links, the outer structures can be rearranged into a more ordered configuration, as indicated by the higher $I_G/I_{A_2}$ ratio in TDCs. Additionally, the basic structural units (including aromatic structures and side chains) in TDC are also altered by stress. The increasing values of $A_D/A_G$ and $A_{(D+A_1+A_2)}/A_D$ illustrate that the size of aromatic structures and the ratio of small aromatic structures both increase with increasing coal deformation intensity. The value of $A_C/A_{\text{Total}}$ decreases with increasing deformation intensity, indicating that oxygen functional groups are disassociated by tectonic stress. However, as the basic structural units are commonly rigid and cannot be altered as readily as the outer structures, the evolution of basic structural units is not always obvious in weakly deformed coals (such as cataclastic, mortar, and schistose types) but is more significant in strongly deformed coals (such as granulitic, scaly, and wrinkle types).

1. INTRODUCTION

It is well known that the inner chemical structures of coal can be altered to some degree by tectonic stress 1-3 and that the evolution of these structures directly influences the occurrence and content of coalbed methane (CBM). 4-11 Therefore, it is of great importance to study the evolutionary characteristics and formation mechanisms of molecular structures in tectonically deformed coals (TDCs) as this can provide an important theoretical basis for the exploitation of CBM resources. To date, a number of detection methods have been successfully applied to characterize the evolution of molecular structures in TDCs, including $^{13}$C nuclear magnetic resonance spectroscopy ($^{13}$C NMR), Fourier transform infrared spectroscopy, high-resolution transmission electron microscopy, X-ray photoelectron spectroscopy, and Raman spectroscopy.12-14 Of these, Raman spectroscopy is particularly useful as it is capable of supplying information about specific molecular structures present in coal such as aromatic and amorphous carbon structures.15 Raman spectroscopy is essentially a kind of fast, convenient, and nondestructive detection technique.16-18 It can perform in situ measurements at the microscale, meaning that heterogenous coals containing inorganic minerals do not need to be purified with acid solutions that will attack the molecular structures.19

Additionally, Raman spectroscopy has proved to be sensitive and effective in detecting carbonaceous materials, including amorphous carbon, graphite, graphene, and so forth. 20-22 Coal, being mainly composed of organic carbons, is a kind of natural carbonaceous material; hence, Raman spectroscopy is an important and commonly used technique for studying coal. The Raman spectrum of coal generally includes two hump regions: the first-order region ($\sim 800-1800$ cm$^{-1}$) and the second-order region ($\sim 2100-3400$ cm$^{-1}$).23 To supply useful information about coal molecular structures, the spectra in the two regions are commonly deconvoluted into sub-peaks. The sub-peaks in the second-order region are generally assigned to the overtone or combination of the sub-peaks in the first-order region.20 Therefore, studies about the dynamic metamorphism of TDC normally focus on the deconvoluted sub-peaks in the

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first-order region. However, the different studies conducted in this area have produced a variety of deconvoluted sub-peaks and characterization parameters. Pan et al. resolved the spectrum in the first-order region into D and G sub-peaks and characterized these sub-peaks in terms of the full widths at half-maximum (FWHM-D and FWHM-G), intensities (I_D/I_G and I_D/I_G), and band positions (W_D, W_G, d_G(Wo)), allowing the structural differences between weakly and strongly deformed coals to be examined in detail. Han et al. deconvoluted the Raman spectra of TDC into four sub-peaks, finding that the molecular structural defects in coal caused by tectonic stress were positively correlated with the fitting area ratio A_D/A_G. Ghosh et al. obtained the sub-peaks D_1, D_2, D_3, D_4, and G through the deconvolution of first-order Raman spectra, and the positions, intensities, and FWHMs of those sub-peaks, along with the ratios I_D/I_G and A_D/A_G were used to evaluate the influence of tectonic deformation on coal molecular structures. Liu and Jiang also demonstrated that the first-order region of TDC spectra could be deconvoluted into four sub-peaks and that the ratio I_D/I_G could be used to characterize the crystallinity of coal molecular structures. Li et al. divided the first-order region spectrum into five sub-peaks and used the structural parameters I_D1/I_G, A_D1/A_G, FWHM-D1, and FWHM-G to reveal the development of structural defects and characteristic aromatic structures present in TDC molecules. Using a similar approach, Song et al. fitted five sub-peaks (D_1, D_2, D_3, D_4, and G) to first-order region spectra and used the I_D1/I_G ratio to investigate the development characteristics of secondary structural defects in different types of TDCs.

The aforementioned studies show that first-order Raman spectra of TDCs normally consist of two to five deconvoluted sub-peaks and that the most commonly used characterization parameters are related to the D (D_1) (1350 cm^-1) and G (~1600 cm^-1) sub-peaks. However, inadequate deconvolution of the two broad hump peaks in first-order Raman spectra will likely lead to the neglect of a lot of useful molecular structural information, and a reasonable deconvoluted peak number is critical to the explanation of the first-order Raman spectra. Further, in addition to the previously mentioned D and G sub-peaks, other parameters can be obtained from first-order Raman spectra to enable even more detailed characterization of the coal molecular structures. For example, Smith et al. resolved the char spectrum in the first-order region into 10 sub-peaks, improving the assignments of those sub-peaks as a result and evaluating the molecular structural evolution of chars based on the deconvolution results. Xu et al. resolved the first-order spectra of 32 kinds of Chinese coals into 10 sub-peaks, enabling the calculation of the additional structural parameters A_(Gr+Vl+Vr)/A_D, A_GL/A_Total, A_S/A_D, A_O/A_Total to clarify the evolution of coal molecular structures with different coal ranks. Guo et al. deconvoluted coal and char spectra in the first-order region into nine sub-peaks and calculated the structural parameters A_D/A_G, A_(Gr+Vl+Vr)/A_D, and A_O/A_Total to estimate the characteristics of coal and char molecular structures. However, the 9 and 10 sub-peaks deconvolution methods have rarely been applied to the study of TDCs. Therefore, it is necessary to systematically explore the Raman spectra of TDC in the first-order region to unlock the full potential of this technique.

Against this backdrop, the present study utilizes a unified deconvolution procedure to obtain more sub-peaks in the first-order Raman spectral region of medium-low ranked TDCs compared with previous studies. To this end, 2 primary structure coal samples and 14 TDC samples with various deformation intensities were collected from the Huaibei Coalfield, Anhui province, China. From the resolved results, the additional structural parameters A_D/A_G, A_(Gr+Vl+Vr)/A_D, and A_O/A_Total were calculated and used to investigate the evolution characteristics of hierarchical molecular structures of TDCs, including the detailed evolution of outer structures and basic structural units.

2. EXPERIMENTAL SECTION

2.1. TDC Samples. To avoid the influence of the micro sedimentary environment, the 2 primary structure coals and 14 TDC samples used in experiments were all collected from the same layer of coal seam 8 in the Zhu Xianzhuang colliery of Huaibei coalfield. The sampling procedure followed the Chinese
standard GB/T19222-2003. The basic information of the 16 coal samples is listed in Table 1. In order to classify TDCs with different deformation intensities, the coal samples were consolidated by injecting epoxy and polished perpendicular to the maceral bedding planes using sandpaper and colloidal solution. Finally, the micro deformation characteristics were observed using a Polarizing Microscope Eclipse LV100N Pol (Nikon) under reflected light.

According to the macro- and micro-deformation characteristics of TDCs, the deformed coal samples were divided into six types based on the structure-genesis classification scheme, namely, cataclastic, mortar, schistose, granulitic, scaly, and wrinkle (Figure 1). Of these, cataclastic, mortar, schistose, and granulitic coals belong to the brittle deformed sequence, scaly coals belong to the ductile deformed sequence, and wrinkle coals belong to the ductile deformed sequence. The stress-strain environments of the different deformation sequences are diverse. For brittle deformed coals, the strain rates of coal deformation are commonly higher than for the other two deformation sequences, as has been demonstrated by actual simulative experiments. Under the action of high deformation strain rates, brittle deformed coals are shattered into fragments (Figure 1m). From cataclastic to mortar to granulitic coals, the shattered particle size becomes smaller and particle roundness increases with increasing brittle deformation intensity. The flaky and scaly structures in schistose and scaly coals indicate a shearing deformation environment in both (Figure 1k,m), while in the latter, the stronger shear stresses directly lead to brittle-ductile deformation. The maceral bands in ductile deformed coals possess the small fold shapes (Figure 1n) that are commonly formed in low-strain rate environments.

2.2. Experimental Methodology. 2.2.1. Raman Spectroscopy. First, the TDCs were dried and ground into powder samples above 200 mesh, which can avoid the deviations of molecular structural characterization caused by coal heterogeneity. The treated and fully mixed powdered coal samples were characterized using a Bruker SENTERRA Raman microscope at an excitation wavelength, λ0, of 532 nm, a laser power of 5 mW, a detection resolution in the range of 9−18 cm−1, and an integration time of 2 s.

2.2.2. Deconvolution Method. Deconvolution is the key to extracting molecular structural information from TDC spectra. As discussed in Section 1, the conventional deconvolution method extracts two to five sub-peaks from the first-order TDC Raman spectra. However, in the present study, the use of this method was not able to produce a perfect fit to the experimental data. When using the two to five sub-peaks methods in the present study, the fitted curves did not coincide with the experimental curve (Figure 2a–c), particularly in the range of 1600−1800 cm−1, indicating that some useful information may be obscured due to inadequate deconvolution. As has been shown by recent studies, it is possible to deconvolute more than 5 sub-peaks from the first-order spectra by employing the 9 sub-peak and 10 sub-peak methods (the only difference between these two frequently used methods being the fitting of a sub-peak (R) in the range of 800−960 cm−1). In the present study, the fitted area ratio of the sub-peak R in the range of 800−960 cm−1 to the total fitting area for the TDC and primary coal samples was less than 5%, and even no sub-peaks could be identified in this range. Additionally, the repeatability and goodness-of-fit of the nine sub-peaks method for the measured data were found to be very high. Hence, the nine sub-peaks fitting procedure was the method of choice in this study (Figure 2d). A linear baseline correction was applied to the acquired TDC Raman spectra, and Gaussian peaks were used to fit the data. The assignment of the nine sub-peaks is detailed in Table 2.

3. RESULTS AND DISCUSSION

3.1. Aromatic Structures of TDCs. 3.1.1. Size of Aromatic Structures (A/D). The ratio A/D represents the fitted area ratio of sub-peak D to sub-peak G and corresponds to the size of aromatic structures in coal samples, with a threshold value of 1.52 for the presence of large aromatic structures. In the present study, as the TDC samples collected were of low-medium coal rank, their A/D values ranged from 0.62−1.07 (Figure 3), indicating the presence of small- to medium-sized aromatic structures. Further, A/D was positively correlated with the coal deformation intensity, which indicates that the size of the aromatic structures in the TDCs increased under the action of tectonic stress. This is because the dynamic metamorphism of coals induced by tectonic stress involves two important evolutionary patterns, namely, stress degradation and stress polycrystallization. The process of stress polycrystallization refers to the directional growth of aromatic rings and aromatization of cyclic aliphatic chains, which is the main reason for the increase in A/D.
Furthermore, it is worth noting that the increase in $A_D/A_G$ from cataclastic to mortar coals is not obvious compared with that for granulitic, scaly, and wrinkle coals. For granulitic coals, in particular, the tectonic stress on the coal matrix is significantly stronger than in other brittle deformed coals, leading to a greater accumulation of mechanical and thermal energy; consequently, more advanced metamorphism occurs in these coals. Scaly coals, on the other hand, are formed in a high shear stress environment, which favors the polycondensation of aromatic structures. However, the wrinkle coals are of the ductile deformed type formed in lower-strain rate deformation environments and are therefore capable of generating more strain energy to alter the inner coal chemical structure, resulting in a higher $A_D/A_G$ ratio.

3.1.2. Ratio of Aromatic Structures ($A_D/(D+A_1+A_2$/$A_D$).

The parameter $A_D/(D+A_1+A_2)/A_D$ refers to the ratio of the sum of the fitted areas of sub-peaks $D$, $A_1$, and $A_2$ to the fitted area of subpeak $D'$. Sub-peak $D'$ is assigned to large aromatic clusters (with ring number $> 6$), while sub-peaks $A_1$, $A_2$, and $D$ are assigned to aromatic clusters with five aromatic rings, aromatic clusters with three to five aromatic rings, and poly aromatic hydrocarbons, respectively.
respectively (Table 1). In addition, sub-peaks D, A1, and A2 can all be assigned to the amorphous carbon structures in coal (Table 1). Therefore, the value of \( A_{D+\text{A1+A2}}/A_{D} \) is commonly used to characterize the relative content of small aromatic structures or the development of structural defects.30 The results show that the value of \( A_{D+\text{A1+A2}}/A_{D} \) gradually increased with increasing coal deformation intensity (Figure 4), which indicates an increase in the amount of small aromatic structures or structural defects. This is because strong tectonic stresses can directly lead to the rupture of aromatic structures or the rotation of C–C bonds, both of which increase the ratio of small aromatic structures and the number of structural defects.26,36,37

Figure 4 also shows that the \( A_{D+\text{A1+A2}}/A_{D} \) ratio increase of schistose coal to wrinkle coal is larger than that of cataclastic and mortar coal. However, for granulitic coal, the brittle deformation is stronger than in mortar and cataclastic coals, which directly leads to the generation of more mechanical energy and a higher degree of variation of coal molecules. The schistose and scaly coals, on the other hand, are formed in a high-shear stress environment, which is more favorable to bond breaking and rotation. During the low-rate ductile deformation of wrinkle coal, the strain energy generated from tectonic stress can be released through bond breaking and rotation in the coal molecular structure. Therefore, the long-term action of stress on wrinkle coal can lead to greater generation of small aromatic structures and structural defects.

3.1.3. Degree of Order of Aromatic Structures (\( I_{G}/I_{A2} \)). The parameter \( I_{G}/I_{A2} \) is defined as the ratio of the fitted areas of sub-peak G and shoulder peak A2. Of these two peaks, the former is commonly assigned to the quadrant breathing of aromatic rings, and the latter is assigned to amorphous carbon structures (Table 1). Therefore, \( I_{G}/I_{A2} \) represents the degree of order of aromatic sheets.38 As the coal deformation intensity increases, the value of \( I_{G}/I_{A2} \) significantly increases (Figure 5), illustrating that the order degree of TDC molecules is enhanced under the influence of tectonic stress. The increasing value of \( I_{G}/I_{A2} \) ratio is mainly attributed to the breaking of both noncovalent and covalent bonds in TDCs under the action of tectonic stress, which can liberate the aromatic structures and result in changes in the orientation of aromatic sheets.28

The stronger structural deformation in granulitic coals compared with other brittle deformed coals (cataclastic, mortar, and schistose) indicates the presence of stronger tectonic stresses. This can result in more bond breaking and more aromatic structures being liberated. Consequently, the rearrangement of aromatic structures is more obvious in granulitic coals. The presence of higher-order aromatic structures in schistose and scaly coals is mainly caused by the strong shearing deformation environment, which proves to be conducive to the rearrangement of aromatic sheets once the sheets are released and allowed to move freely. On the other hand, for wrinkle coal, a lower-strain rate deformation provides a different molecular evolution mechanism (as the ductile deformation transforms mechanical energy into strain energy),36 leading to a more ordered molecular configuration.

3.2. Oxygen Functional Groups of TDCs (\( A_{C}/A_{\text{Total}} \)). Sub-peak C of the coal samples is assigned to the carbonyl oxygen functional groups (Table 1). As the coal deformation intensity increased, the value of \( A_{C}/A_{\text{Total}} \) gradually decreased (Figure 6), indicating that tectonic stress could result in the dissociation of these functional groups. Further, simulative coal deformation experiments have shown that under the action of stress, oxygen functional groups (particularly carbonyl) can be dissociated into gases.39–41 It should be noted that the average \( A_{C}/A_{\text{Total}} \) values of scaly coals are lower than that of wrinkle coal, which indicates that higher shear stresses are likely to facilitate the dissociation of oxygen functional groups. Furthermore, the dissociation of oxygen functional groups can also break the hydrogen bonds connected with them,28 thereby increasing the motion and rearrangement of aromatic structures. Therefore, the dissociation of oxygen functional groups plays a key role in the molecular evolution of TDCs.

3.3. Cross-Linking Density of TDCs (\( A_{S}/A_{\text{Total}} \)). The S peak is closely correlated with the C(aromatic−Calkyl) content (namely, the hydro-atomic structure or aromatic substituents) in the coal molecular network (Table 1). Hence, a higher value of \( A_{S}/A_{\text{Total}} \) usually indicates a higher cross-linking density of the coal.
molecular network. The \( A_s/A_{Total} \) of TDCs gradually decreased with increasing coal deformation intensity (Figure 7), implying that tectonic stress can destroy the network structures. As is well known, the bridge bonds of coal molecular structures include both covalent and noncovalent bonds. Previous research has shown that tectonic stresses can directly act on and break these chemical bonds, particularly the weaker noncovalent bonds. Once the cross-linking of coal molecular network structures is broken, the movable structures can be further rearranged under the action of tectonic stress. Hence, the variation in the cross-linking density of TDC is consistent with the evolution of aromatic structures and functional groups.

The ratio \( A_s/A_D \) is usually used to evaluate the degree of development of disordered molecular structures (including hydro-aromatic structures) in coal. As the coal deformation intensity increases, the value of \( A_s/A_D \) gradually decreases (Figure 8), indicating that the proportion of disordered structures decreases as well. The substituents of aromatic structures are usually aliphatic chains and functional groups with heteroatoms. The dynamic metamorphism of TDCs is believed to take place through heteroatom expulsion and an increase in aromaticity. Compared with aromatic structures, aliphatic chains and functional groups are more easily affected by tectonic stress; therefore, these impure and unstable side-chain structures are ultimately disassociated under the action of stress, thereby lowering \( A_s/A_D \).

### 3.4. Dynamic Metamorphism of TDCs as Revealed by Raman Spectra

#### 3.4.1. Dynamic Metamorphism Sequence of TDC Molecules

The dynamic metamorphism of TDC is explained based on knowledge of the molecular network structures in coal. According to Zeng and Xie and Robert, the coal molecular structure is hierarchical. In the hierarchy of coal molecular structures, the primary structure refers to the basic (monomer) structural unit, and the basic structural units in same coal are different from each other in terms of structural composition, configuration, and size (Figure 9a). Additionally, the basic structural units are commonly rigid structures. The secondary structure refers to the macromolecules that are composed of basic structural units (Figure 9b) and can further coalesce to form aggregated structures (Figure 9c). Among them, the basic structural units are defined as inner structures, and secondary and aggregated structures are defined as outer structures. The response of coal molecular network structures to tectonic stresses is reflected at all the three levels. The Raman spectra revealed that both the basic structural units and cross-linked networks were altered by the tectonic stress.

Generally, stress action occurs from the outer to the inner structure of coal (i.e., from the aggregated structures to the secondary structures and to the primary structures). The molecular segments of aggregated and secondary structures are cross-linked or entangled via noncovalent bonds, namely, hydrogen bonding, van der Waals interactions, \( \pi-\pi \) interactions, and chain entanglements, and covalent bonds, namely, ether linkages and methylene chains. Compared with the basic structural units, such cross-linked structures are more easily cleaved by tectonic stresses; hence, the configurations of outer structures are changed first. Lower \( A_s/A_{Total} \) and \( A_s/A_D \) values indicate that the cross-links in the outer structures are cleaved by tectonic stress, leading to the greater release of low-molecular weight segments. The released free radicals can be rearranged under the action of tectonic stress, further increasing the degree of order of aromatic structures, as is reflected in the increased \( I_G/I_{A_2} \) value of the TDCs.

As mentioned previously, the rigid basic structural units in TDCs are commonly altered under the influence of tectonic stress after the outer structures have already been altered. Two types of structures in basic structural units are typically characterized by Raman spectra, namely, aromatic structures and side chains. Of these, the oxygen functional groups (a kind of side chain) were first cleaved by the tectonic stress, as
demonstrated by the decreasing $A_d/A_{Total}$ value. This is because the oxygen functional groups tend to be much weaker than other basic structural units. Further, as the disassociated oxygen functional groups are mainly responsible, their cleavage will directly decrease the cross-linking density of outer structures.

Second, although more stable than oxygen functional groups, the aromatic structures present in TDCs can also be changed by tectonic stress, in terms of their size, ratio, and even hexagonal structure, through the rotation and cleavage of C–C bonds. The tectonic stress can drive the freely mobile aromatic structures to merge together; however, the breaking of C–C bonds also ruptures the aromatic rings and increases the ratio of small aromatic structures. Thus, the $A_{(D+A1+A2)}/A_{Dx}$ of TDCs is commonly higher than that of primary coals. Additionally, as the tectonic stress-induced rotation of C–C bonds can destroy the integrity of large aromatic structures, the increase in the value of $A_{(D+A1+A2)}/A_{Dx}$ is also due in part to the increase in secondary structural defects arising from rotation and breaking of C–C bonds.

3.4.2. Dynamic Metamorphism Related to the Stress–Strain Environment. The sampled TDCs were classified into three deformation sequences according to the structure-genesis classification scheme, namely, brittle, brittle–ductile, and ductile. The evolution of TDC molecular hierarchy is sensitive to different stress–strain environments. The cross-links in the secondary and aggregated structures of brittle deformed coals are significantly influenced by the tectonic stress, as demonstrated by the decreasing $A_s/A_{Total}$ and $A_s/A_D$ values. However, the variation of $I_G/I_A$ in cataclastic and mortar coals is not very significant, indicating that the stresses in these two types of TDCs are capable of breaking the cross-links but cannot change the orientation of the outer structures. On the other hand, the $I_G/I_A$ in schistose and granulitic coals is higher than that of primary coal, which indicates that the outer structures are altered by tectonic stress. The schistose coal is formed in a shear stress environment that is more beneficial to the change of outer structures, while the stronger crushing and grinding effect of granulitic coal leads to increased generation of mechanical and thermal energy, which can also promote molecular motion. For the brittle–ductile deformation sequence, the scaly coal is formed in a strong shear stress environment, meaning that the cross-linking and orientation of outer structures can be significantly altered, while the lower strain environment of wrinkle coal can accumulate more strain energy, which can be partially released by changing the orientation of outer structures.

For the brittle deformation sequence, the basic structural units in cataclastic and mortar coals are relatively unaffected by tectonic stress, while in the case of schistose and granulitic coals, the aromatic structures and oxygen functional groups can be altered. Hence, the differences in the evolution of structural units between the different coal types are mainly due to the different stress environments.

The shear stresses acting on schistose coals can promote the preferential growth of aromatic structures and lead to the formation of larger aromatic sheets, as revealed by the higher value of $A_D/A_s$. Simultaneously, some of the aromatic structures are also ruptured by the shear stress, as indicated by the higher value of $A_{(D+A1+A2)}/A_{Dx}$. In addition, compared with cataclastic and mortar coals, more of the oxygen functional groups in schistose coals are cleaved by shear stress. For granulitic coals, however, stronger brittle deformation leads to the generation of more mechanical and thermal energy that can facilitate the evolution of basic structural units and also leads to higher values of $A_s/A_G$ and $A_{(D+A1+A2)}/A_{Dx}$, which reveals that the size growth and rupture of aromatic structures are more intense in these coals. Similarly, the disassociation of oxygen functional groups is faster in granulitic coals, as indicated by the lower $A_C/A_{Total}$.

The scaly coals, which belong to the brittle–ductile deformation sequence, are formed in strong shear stress environments, which is more beneficial to the evolution of basic structural units. Under the influence of strong shear stress, the preferential growth of aromatic structures in scaly coals is significantly enhanced compared with schistose coals. As there are more large aromatic structures being ruptured into smaller aromatic structures, this increases $A_{(D+A1+A2)}/A_{Dx}$. Meanwhile, the free aromatic structures can be merged into larger aromatic structures, the growth direction of which is commonly along the shearing direction. The oxygen functional groups in scaly coals are more frequently disassociated by strong shear stresses, as can be inferred from the sharply decreasing $A_C/A_{Total}$.

Last, wrinkle coals are classified as being of the ductile deformed type, which are formed in low-strain rate environments. The low-strain rate deformation can transform the mechanical energy into strain energy. Through changing the molecular structures, strain energy is released, which leads to ductile deformation. The basic structural units in wrinkle coals can be significantly altered as well because the aromatic structures are merged into larger ones due to the release of strain energy, and the C–C bonds are rotated and broken, leading to the disintegration of aromatic rings. In addition, the oxygen functional groups are also significantly disassociated under ductile deformation.

4. CONCLUSIONS

In this study, a Raman detection method was applied to characterize the dynamic metamorphism of TDCs. It was found that the nine-peak curve fitting method fit the experimental data better compared to conventional curve fitting methods with fewer sub-peaks. As a result, additional structural parameters of TDC molecules could be acquired from the deconvolution results, including $A_D/A_G$, $A_{(D+A1+A2)}/A_{Dx}$, $I_G/I_A$, $A_C/A_{Total}$, $A_s/A_D$, and $A_s/A_G$. Using these parameters, the evolutionary characteristics and evolution mechanism of TDC molecular structures were elucidated based on the hierarchical structure theory, which holds that the evolution of TDC molecules commonly occurs from the outer to the inner hierarchical structure (i.e., from the aggregated to the secondary to the basic structural units). The aggregated and secondary structures of coal molecules are commonly cross-linked and entangled via weaker intermolecular bonds, which can be altered through the action of tectonic stress. The adjustment of these two outer structures causes the coal molecules to adopt a more ordered configuration. The basic structural units, on the other hand, are more rigid and less likely to be transformed by tectonic stress. Therefore, the evolution of these units is more significant in more strongly deformed TDCs. Due to the stability differences between inner and outer structures, the molecular evolution of the hierarchical structures varies depending on the deformation sequence, with the stress-induced evolution of basic structural units being more obvious in the latter two deformation sequences. Furthermore, alteration of the inner structures can promote the evolution of outer structures; for example, the disassociation of oxygen functional groups can decrease the amount of hydrogen bonds, which affects the cross-linking of outer structures.
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**Notes**

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