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Atomic force microscopy study on microstructure of various ranks of coals *

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Abstract As a new technology, Atomil Force Microscopy (AFM) is being used in the research of microscopic structure on coal surface in recent years. By this technology, we can observe the nanoscale pore and crack shape of coal surface, and measure some structural parameters. Different metamorphic grades produce different feature of surface microscopic structure of coal. This paper analyzes the surface microscopic structure of different metamorphic grade coal by AFM. The results show that the coal surface microstructure has a trend from rough to smooth with the increasing of metamorphic grade. The low rank coals contain large or medium pores and the high rank coals contain micro pores. The values of surface morphology characteristic parameters (S_q and S_a) nonlinearly decrease with the increasing coal rank. That is, the coal surface becomes smoother during coalification.

Keywords atomic force microscopy (AFM), metamorphic degree, micro-structure, nanoscale pore

Introduction

Coal is a kind of fossil fuel which is very complicated in structure and composition, and at the same time, it is the place of storage and migration of coal bed methane. Degree of coal metamorphism is very different, especially the nanopore structure and the surface morphology characteristics, and it also has a significant impact on storage and adsorption of coal-bed methane. Domestic and foreign scholars have done a lot of researches and won fruitful research results (Clarkson and Bustin 1999a, 1999b; Karacan et al., 2001; Zhang, 2001; Zhang et al., 2002; Jing and Cui, 2007; Yan et al., 2008; Zhang et al., 2011; Pan et al., 2012). In the 1990's, atomic force microscopy (AFM) is introduced to make microscopic study of coal entered to the nanometer scale. Yumura et al. (1993) preliminary observed morphology and characteristics of AFM coal surface. Yang and Pan (1994) using the method of combining the scanning tunneling microscope (STM) and the AFM preliminarily studied the high resolution image of coal surface. It for the first time made the preliminary explanation at the molecular scale of the coal graphitizing mechanism. Through AFM, Gwendolyn et al. (1997) have measured the porosity of maceral. Then Bruening et al. (2005) measured surface properties and oxidation of coal macerals by AFM. Chang et al. (2006) using AFM on coal surface morphology of the three-dimensional measurement, observed in the coal particle and pore. Through the observation of AFM, Wang et al. (2006) analyzed coal particle size, roughness and power spectrum on the surface of coal. Liu et al. (2010) researched the ultrafine pulverized coal particles morphology on the condition of characteristics of AFM research. Yao et al. (2011) studied and explained by using AFM coal nano porosity, pore size distribution and porosity. The AFM research mainly focus on coal maceral or coal surface pore characteristics of the visual description, but not on the surface morphology characteristics in different levels or different differences in quantitative analysis. This paper will use the atomic force micro-scope (AFM) to analyze the coal microstructure (surface morphology, pore structure and form, etc.) and different classes of coal adsorption/desorption ability difference of micro factors in different metamorphic degree.

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1 Sample selection and experiments

The instrument used in this study is the CSPM4000 scanning probe microscope of primitive nano instrument company, which work mode including contact, tapping and phase shift imaging etc, and the maximum scanning range was 0.26 nm horizontal and 0.1 nm vertical (mica calibration), scanning scope biggest can reach 100 μm×100 μm. Experimental sample is showed in Table 1. The natural coal samples were selected to make into the mirror coal or clarain banding proper size and the surface which is smooth, polished coal sample base, making it in the level on the stage. And then wipe coal sample surface with anhydrous alcohol, and remove surface dirt and other impurities. This experiment uses the contact pattern, which the biggest scanning ranges 10 000 nm×10 000 nm, minimum scanning ranges 800 nm×800 nm.

Table 1 Characteristics of the samples

Samples	Deformation type	Coal rank	$R_{0,\max}$ (%)
DLT01	Undeformed coal	Lignite	0.48
BD01	Undeformed coal	Long flame coal	0.75
SJZM05	Fragmented coal	Fat coal	1.15
PMBK07	Fragmented coal	Coking coal	1.28
HBM04	Fragmented coal	Lean coal	1.80
XZM05	Fragmented coal	Meager coal	2.37
FH03	Fragmented coal	Anthracite	3.77

2 Experimental results and discussions

2.1 Surface morphology characteristics description and analysis

First of all, AFM can well reflect the coal kind of microscopic molecular arrangement structure. Fig.1 is lean coal (XZM05) in different scanning range of AFM topography. The coal sample is smooth in the naked eye, and its microstructure is uneven. There are some visible dark and highlighting pore, in which the part of highly bright is coal particles and the dark area is pore. In the larger scan range (10 000 nm×10 000 nm), the sample surface can only observe protuberance of coal particles and notching scratches (may be caused by rupture); in narrow scanning range (5 000 nm×5 000 nm), we gradually can see black pore. In smaller scanning range (1 500 nm×1 500 nm, 800 nm×800 nm), although the accuracy can not beyond the reach of atomistic level, but in AFM figure we can see because of the coal molecular overlay deposit, coal microstructure shows ring molecules in the form of group. These light and shade of different macro-molecular globular structure interconnections show chain arrangement, and between these molecules there are a large number of micropores making coal adsorption capacity greatly improved.

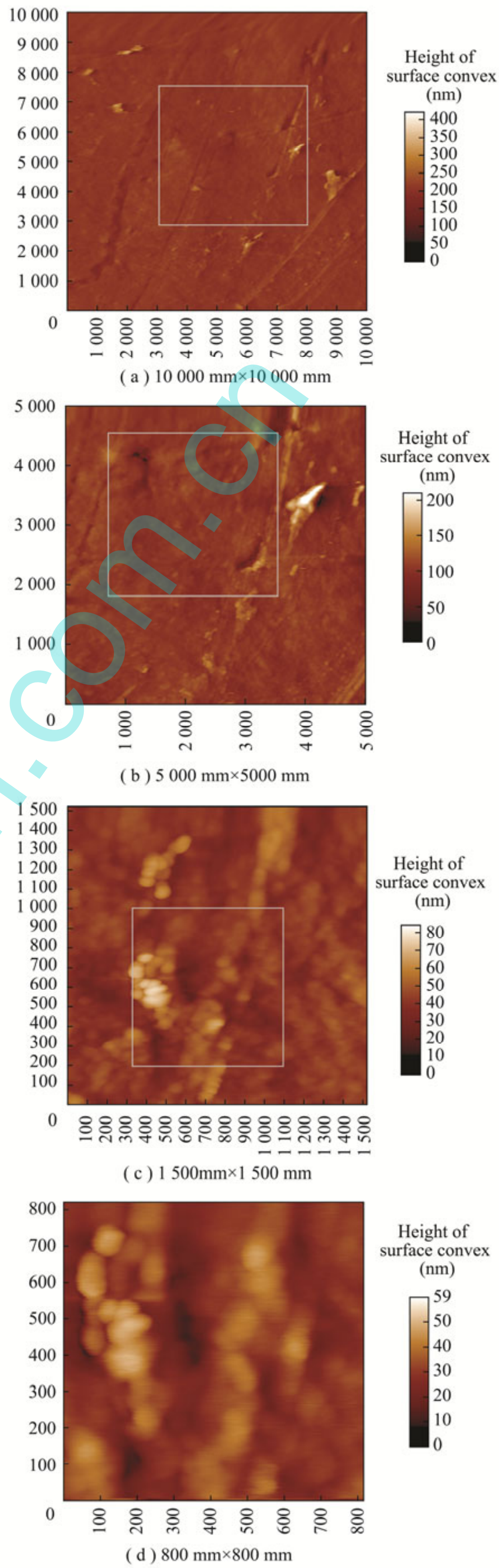

Fig.1 AFM image of a series of scanning range of the sample XZM05

For the same structure of different metamorphic degree of coal samples, we did the AFM scanning and got a series of different metamorphic grade coal AFM scanning chart (Fig.2).

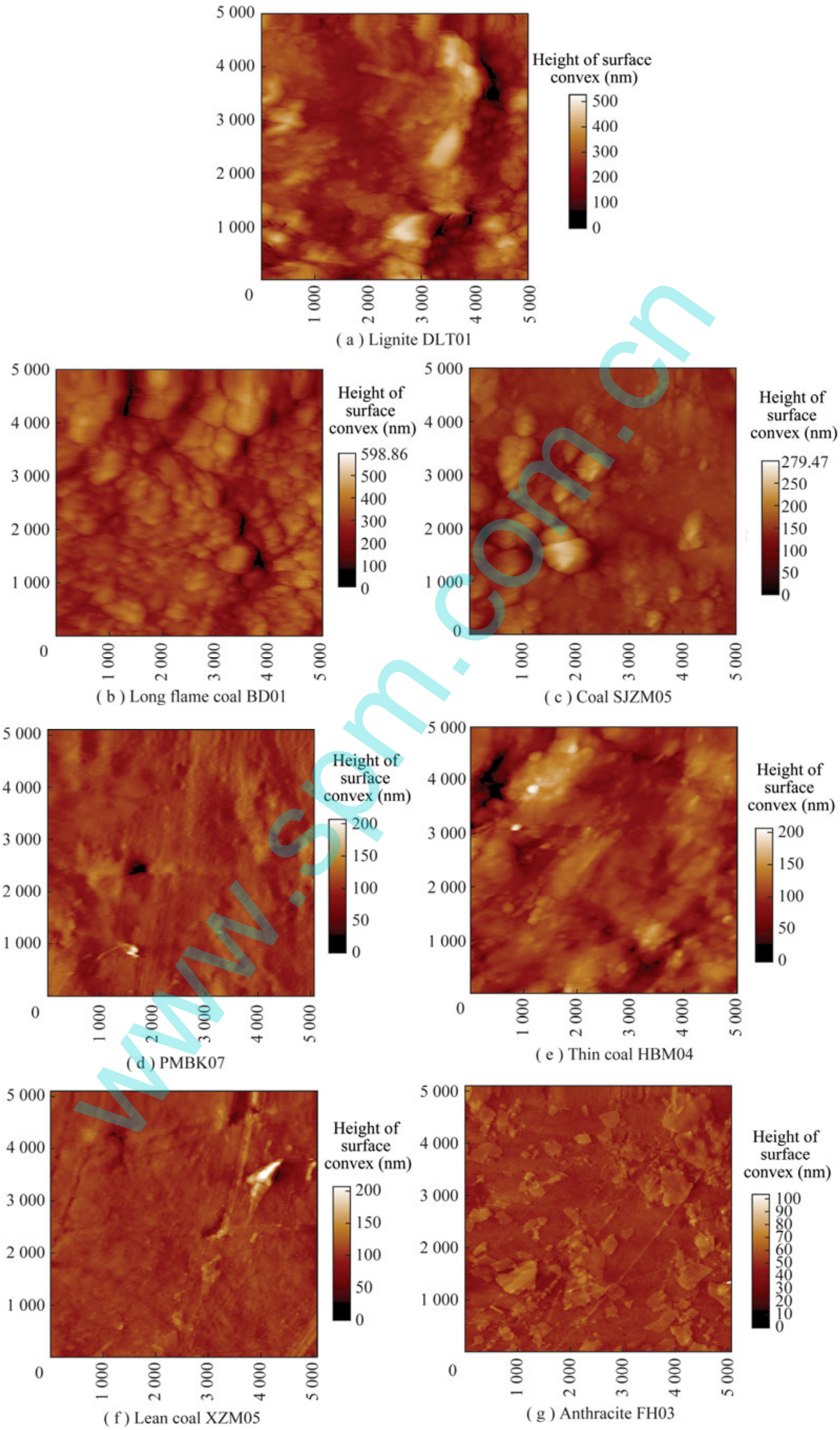

Fig.2 AFM images of different ranks of coal

In Fig.2(a), lignite DLT01 shows a complicated surface morphology, a bigger ups and downs and different pore shapes; (b) Long-flame coal BD01 particle shows massive characteristics. The visible crack is strip, existing at the particles; (c) The surface of fat coal SJZM05 is relatively flat, and there are some outstanding coal large particles; coking coal; (d) PMBK07, the surface begins to have some ups and downs, a round pore can be observed; (e) Thin coal HBM04, there is a bigger ups and downs on the surface of the sample. Due to the influence of tectonic stress, pore is elongated; (f) Sample surface of lean coal XZM05 which shows compact shape, the pore has a closed state and the number of micro porous begin to increase; (g) FH03 anthracite, sample surface has a lot of irregular flake of coal particles, the pores of which are smaller. It shows the trend of transformation from anthracite to graphite.

Through the contrast we found that, with the increase of metamorphic grade, surface morphology characteristics have apparent changed. In lignite DLT01 (Fig.2(a)), micro-particle structure descrambled, microscopic particles present crumb, strip, and primary pore many of which are macropores and mesopores level. Because coal is the product of diagenesis stage, which the metamorphic degree of coal is low, the formation of lignite overburden pressure is small, and the ground temperature is low (less than 40–60 ℃), Therefore, lignite in aromatic ring layer is small and is random in distribution, molecular structure change is not big, mainly for the compaction, dehydration and dropout of functional groups, for the loose and descrambled of the performance of the molecular structure. At the same time pressure mercury trials shows that the lignite pore in mesopores (100–1 000 nm) and macropores (more than 1 000 nm) is given priority place, and microporous and pore surface area is relatively small (Bustin, 1995).

In the long flame coal BD01 (Fig.2(b)), microscopic particles is massive structure in distribution, but the particle contacts between are not close. There are elongated pore between particles. In fat coal SJZM05 (Fig.2(c)), the sample surface have bossed coal particles. Pore length is relatively short, and the scanning range most are relatively flat. In coking coal PMBK07 (Fig.2(d)), sample began to have some ups and downs, which can be observed the circular pore, from pore form constructive for pore (Zhang, 2001). Thomas and Damberger (1976) interpreted this phenomenon in this stage as: the asphaltenes formed in the light brown coal stage to fat coal stage (namely $R_{o,\ max}$=0.5% to $R_{o,\ max}$=1.3%) makes the coal porosity increase greatly due to temperature increase, venting from coal pore in the later period of calcification. In thin coal HBM04 (Fig.2(e)), the sample surface morphology is greatly ups and downs, and pore is elongated, this is due to the use of the coal sample for cataclastic coal, so the surface morphology and pore form may be formed because of the metamorphic process by tectonic stress (mainly for the shear stress). In the lean coal XZM05 (Fig.2(f)), the sample surface grain structure shows close contact relation, the overall present a compact form, and pore has a closed state.

Anthracite FH03 (Fig.2(g)), there are a lot of irregular flake of coal particles in the sample surface, and the pore is smaller. At the same time, it shows than lean coal XZM05 showed significantly more dense feeling, which reflects the trend of transformation of coal to graphite. Previous research results show that coal is composed of micro crystal ink slice and aromatic nucleus composition, whose size is 0.1–70 nm (Tao, 1983; Zhang and Xian, 1993). After high temperature thermal effect, the aromatic nucleus gradually grow up and change to graphite. In addition, Franklin (1951) used X-ray diffraction to find that in the simulation of coal environment, temperature below 2 000 ℃, the structure of anthracite is compact, and the pore is small. But in more than 2 500 ℃ temperature after treatment, the carbon atom layer spacing quickly becomes narrow, closed to ideal graphite, and it becomes graphitizing. This may be because of anthracite coal carbon atom levels of preferred orientation, and it makes anthracite can be in high temperature graphitization.

Based on a large number of AFM image statistical study, low-rank coal pore is macropores and mesopores mainly, high-rank coal pore is small pore mainly (Tang et al., 2008). Conclusion accords with the previous research on different metamorphic degree of coal pore development understanding. In the lignite stage, molecular structure is disordered, aromatic lamellar space is bigger, side chain is longer, and it shows loose space structure, and it has the larger porosity. With the deepening of degree of coalification, condensation ring increases significantly, side chains and functional groups began to decrease, and coal molecular orientation arrangement, and anisotropic improved significantly. Aromatic lamellar spacing decreases, and pore ratio decreased, the specific surface area increased. In the stage of anthracite, because of macromolecular group's close accumulation, aromatic lamellar spacing is greatly reduced, the main chain skeleton of branched chain and functional group off form the oval and rectangular primarily pores and micropores, making the anthracite coal adsorption ability greatly improved

Because of the restrict of the experimental condition, this paper does not research the influence of tectonic stress and microstructure, but the tectonic stress of coal microstructure influence cannot be ignored. The scholars in this respect have different understanding, Jiang et al. (1998) pointed out the influence factors of deformation is various, even though the temperature is an important factor of structure and orderly development of the coal. Cao et al. (2006) also pointed out that tectonic stress can be regarded as coalification "catalyst", which improves the sedimentary organic matter evolution rate; but Ju et al. (2005) thinks that compared to the increase of temperature has not much influence on the structure of nanoscale pore, structural stress influence on the parameters of pore structure plays a decisive role. So far, the influence of structure on the coal micro pore and nanometer pore is still in the Stage of observation and description mechanism exploration. Different deformation mechanism of nanoscale pore control mechanism research remains to be further studied (Hou et al., 2012), and this will be the next step of AFM research focus.

2.2 Microscopic particle analysis

In the macroscopic particle aspect, it is generally thought that, the smaller the particle size, surface area of coal is bigger, and so does the adsorption capacity of coal, which namely that coal adsorption ability is greater than the lump coal adsorption ability. Wang et al. (2005) thinks medium coal has larger surface area and good pore connectivity that its ability of absorption increases. At a micro level, the relationship of research between nanoparticles dimension and the ability of the ability of adsorbed gas is less. This paper using own software of instrument to analyze nanoparticles dimension, the quantity and the diameter and some information of the surface of nanoparticles. In the particle analysis (Fig.3) we can found, along with coalification process, the coal surface nanoparticles number general trend is gradually increasing and particle is in diameter, presenting grain refinement trend. This shows that in the coalification process, due to the overburden pressure and tectonic stress effect, large coal particles was broken into small particles. Thus makes the contact getting closer, the micro porous starting to increase and the macropores and the middle pore reducing. The coal body structure became "compact" from "loose", this is in conformity with the pore structure in the face of pore description.

2.3 Surface roughness parameter statistics and analysis

Surface roughness are of great influence for many physical properties. With the development of research, people began to pay attention to 3 d surface roughness parameters (Pancewicz and Mruk, 1996). This paper uses 3 d roughness parameters, making different metamorphic degree coal surface microstructure characteristics can be researched and quantitative measurement. By using Amplitude parameters (Li and Dong,

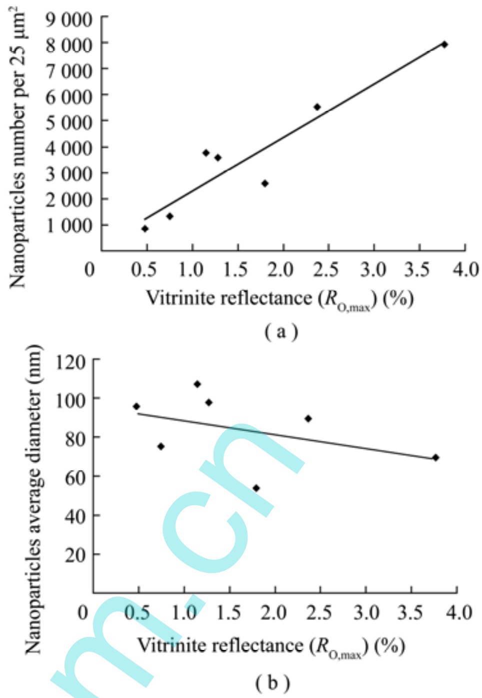

Fig.3 The relationship between the number of particles, the average particle diameter and the maximum reflectance of vitrinite

1999), characterization of 3 d surface roughness parameters is used to describe the parameters of the surface morphology characteristics (Gadelmawla et al., 2002). The three characteristics of the height of the main parameters of the surface characterization: (1) statistical properties; (2) the extreme characteristics; (3) height distribution shape (Wang et al., 2006). The average roughness S_a (the average roughness) shows the average distance of the datum from surface; Root mean square value S_q (the root mean square roughness) shows the root mean square deviation datum surface planting (Poon and Bhushan, 1996; Chen et al, 2009). The formula is as follows:

$$S_a = \frac{1}{MN}\sum_{j=1}^{N}\sum_{i=1}^{M}\left|Z(X_i, Y_j)\right|$$

$$S_q = \sqrt{\frac{1}{MN}\sum_{j=1}^{N}\sum_{i=1}^{M}Z^2(X_i, Y_j)}$$

where M, N are discrete sampling points of sampling area to X and Y; $Z(x, y)$ is surface height deviation.

From Fig.4 we can see that with the increase of the degree of metamorphism, S_q value and S_a value of the overall trend are downward which indicates that in the coalification process, the coal surface becomes more "flat". The greater is the value of surface roughness parameter, the more complicated is the coal sample surface structure. With the decrease of the surface roughness parameters, the surface structure becomes simpler, pore becomes flat and aperture decreases. Namely, the micro pore is in the major place, the surface area is increased and the adsorption capacity is improved. This is because in the process of coalification, the initial overlying pressure and the surrounding rock confining pressure cause deformation; in the later period of coalification, along with the increase of buried depth, overlying pressure increase gradually, making the coal molecular arrangement gradually regulated, the structure close and the surface to smooth.

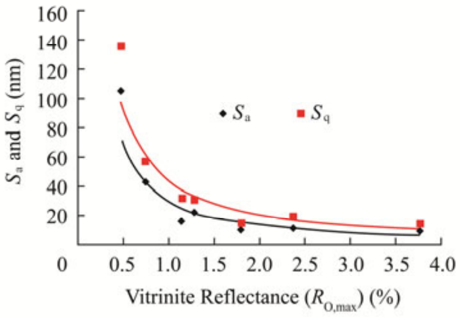

Fig.4 The different ranks of coal the average roughness (S_a) and the root mean square roughness (S_q) change trend

3 Section analysis of AFM

Morphological characteristics of coal such as porosity, pore size and pore depth affect the adsorption and desorption of coalbed methane. So Scholars are interesting in the morphological characteristics of coal pore, but previous studies indirectly inferred pore morphology using mercury ejection curve or nitrogen adsorption isotherm, not showing the true pore morphology. AFM provides measurement to directly observe the pore morphology and pore density. It is a good visual reference for the morphological study of coal nanopore structure. Section analysis allows the operator to select the location of a transect line taken across the sample. In addition, section analysis provides information related to vertical distance (topography) and roughness along the section (Bruening and Cohen, 2005).

In section analysis, the surface topography of the samples have very different that there are various pore and the pore wall undulates irregularly. In low-rank and mid-rank coal, the mesopores and small pores mainly on the coal surface. With coalification degree increasing, small pores of surface is in major place. At the stage of anthracite, number and density of coal micropore began to increase gradually. Height difference of surface is smaller which indicates that the coal surface microstructure has a trend that it became rough to smooth with the increasing of metamorphic grade

4 Conclusions

(1) With the increase of the degree of metamorphism, surface morphology characteristics have apparent changed. low-rank coal pore is macropores and mesopores mainly, high-rank coal pore is small pore mainly.

(2) With the increase of the degree of metamorphism, S_q value and S_a value of the overall trend is down which indicates that in the coalification process, the coal surface becomes more “flat”.

(3) In the coalification process, due to the overburden pressure and tectonic stress effect, large coal particles was broken into small particles. Thus makes the contact getting closer, the micropores starting to increase and the macropores and the mesopore reducing. The coal body structure became “compact” from “loose”.

(4) In section analysis, explain that changes of pore microstructure in the coalification process. With coalification degree increase, micropores are in major place and coal surface microstructure has a trend that it become rough to smooth.

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