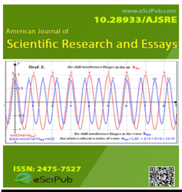
Research Article **AJSRE (2021) 6:1**



American Journal of Scientific Research and Essays (ISSN:2475-7527)

Research status and development direction of controlling factors of graphite mineralization in coal measures

Tian Yuan[1], Li Xiaobo[2], Gong Liubing[1], Li Haihua[1], Yang Rui[1], Xu Bohui[3*]

[1]School of Earth Science and Engineering, Hebei University of Engineering, Handan, Hebei 056038, China. [2]Shandong No.5 Geo-mineral Prospecting Institute, Tai'an, Shandong 271000, China. 3male, associate professor, master's tutor, mainly engaged in research on the processing and utilization of inorganic non-metallic minerals.

Fund Project: Study on the structural order degree of cryptocrystalline graphite and its ore-forming controlling factors in coal measures of Hebei natural fund (D2019402055).

ABSTRACT

Coal-measure graphite mineralization control is affected by many factors. In order to explore the ore-forming control factors and influence mechanism, the paper comprehensively analyzes the influence and mechanism of each factor from five aspects of coal rock composition, coal grade, temperature, pressure and mineralizer, combined with geological examples. The results show that in the process of graphite mineralization in coal measures, the components of coal and rock have the ability of graphitization, but the higher the degree of metamorphism of coal as carbon source, the higher the degree of graphitization of products, the higher the ore-forming temperature, and the higher the degree of graphitization. The development of tectonic movement promotes the graphitization, but the degree of graphitization is different and complicated due to the stress dissipation. Different minerals in coal have different effects on graphite mineralization in coal measures, and its mechanism needs to be further explored. Finally, it is pointed out that the research direction of coal series graphite lies in the different graphitization mechanism of the same rank coal and the different influence mechanism of different minerals in coal.

Keywords: Coal series graphite; Metallogenic mechanism; Graphitization

***Correspondence to Author:**

Xu Bohui

male, associate professor, master's tutor, mainly engaged in research on the processing and utilization of inorganic non-metallic minerals.

How to cite this article:

Tian Yuan, Li Xiaobo, Gong Libing, Li Haihua, Yang Rui, Xu Bohui. Research status and development direction of controlling factors of graphite mineralization in coal measures. American Journal of Scientific Research and Essays, 2021; 6:1

eSciPub LLC, Houston, TX USA.

Website: http://escipub.com/

Introduction

The 21st century is the era of carbon.As an important carbon material, ink is widely used in metallurgy, machinery manufacturing, aerospace industry and other fields with its superior performance, and has been listed as a strategic mineral resource by many countries.In 2004, graphene came out and quickly became a research hotspot. As the main raw material of graphene, the strategic position and resource value of graphene were significantly improved. Many graphene materials have been published and applied widely. Graphene aerogels [1], graphene fiber [2], Graphene liquid crystal [3], graphene film [4], graphene superconductor [5] have emerged, and are gradually applied to oil spill recovery [6], seawater desalination [7] and precision electronic components [8] and other fields.

China is a country with large graphite resources. By the end of 2018, the identified reserves of graphite were about 538 million tons, including 437 million tons of crystalline graphite and 100 million tons of cryptocrystalline graphite [9]. Coal based graphite is an important part of graphite resources, most of which are aphanitic graphite. It has good electrical conductivity, high temperature resistance and other excellent properties. It is mainly used in lubricants, pencil lead, battery electrodes and so on. Due to the lack of in-depth understanding of its metallogenic mechanism and occurrence law, the development and utilization of coal bearing graphite are affected, and its hidden reserves and industrial value are greatly underestimated. Therefore, it is urgent to study the metallogenic mechanism and occurrence characteristics of coal measures graphite. The research on the metallogenic mechanism of graphite in coal measures not only has economic benefits for the development and utilization of graphite resources, but also has important theoretical significance for revealing the evolution law from coal to graphite.

In this paper, from the five aspects of carbon source, coal grade, temperature, tectonic stress and mineralizer, the graphitization process of carbon elements in the laboratory is combined with geological examples to comprehensively analyze the metallogenic mechanism of graphite in coal measures. In order to reveal the evolution process of graphitization of carbonaceous elements and explore the metallogenic mechanism of graphite in coal measures.

1. Graphite and coal series graphite

Graphite is the most common crystal form of carbon in nature. It is allotropic with diamond. Werner, a German chemist and mineralogist, named it in 1789.Natural graphite is mainly composed of carbon and other associated minerals.The microstructure is a special layered structure formed by the stacking of hexagonal ring carbon atoms. The layers are connected by weak van der Waals force, and the carbon atoms are equidistant connected by covalent bonds,The distance between adjacent carbon atoms is 0.142 nm and the bond angle is 120 °;The interlayer spacing of each carbon atom layer is 0.335nm (Figure 1).

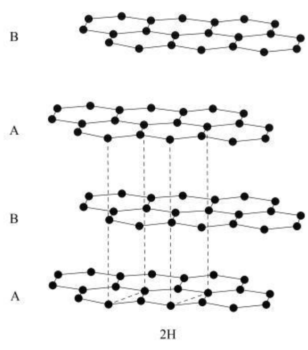


Fig. 1 ideal graphite structure model

Coal measures graphite is an important part of graphite resources, mostly aphanitic graphite, with carbon content of about 60 ~ 80%, similar to coal, black color, bright streaks, gray black, semi metallic luster, greasy feeling, brittle, scaly structure, and sometimes dense block [10,11]. It is mainly formed by metamorphism of coal and carbonaceous shale, and mainly occurs in coal measure strata. It is an important coal measure associated resource.Hunan, Jilin, Shaanxi, Fujian, Anhui and other provinces are the provinces with relatively concentrated coal graphite resources distribution. The type of coal series graphite mineralization and metamorphism is mainly contact thermal metamorphism, mainly experienced four evolution sequences of "anthracite super anthracite semi graphite graphite" (Table 1) [12], There is a transitional relationship in each stage, resulting in the phenomenon of mixed endmembers. Compared with crystalline graphite, coal measures graphite has the characteristics of concentrated ore body, easy development and high grade [13]， the output of coal based graphite accounts for more than half of the output of graphite resources, with an annual output of about 1 million tons. However, only 50% of the output is used in industry, and the rest is used as coal combustion, resulting in serious waste of resources.

Table.1 Graphite and transition stage(Kwiecińska B,2004)

type	d_{002}/nm	Rmax/%	H/C(atom)
graphite	0.3354～0.337	＞9.0	0.005～0.10
Semi graphite	＞0.337～0.338	＞6.5～9.0	＞0.10～0.15
Metamorphic anthracite	＞0.338～0.340	5.0～6.5	＞0.15～0.20
anthracite	＞0.340	＜5.0	＞0.20

2. Controlling factors of graphite mineralization in coal measures

The evolution process of graphitization is influenced by many factors. This paper reviews the influencing factors of graphite mineralization in coal measures from the aspects of carbon source, coal grade, temperature, tectonic stress and mineralizer.

2.1 Carbon source

Coal and carbonaceous shale are the main carbon sources of graphite mineralization [11,13-16]. Coal seams and carbonaceous shale in coal measures strata are the source beds of coal measures graphite.

In the early research process, Franklin [17] divided amorphous carbon into graphitized carbon and non graphitized carbon, and its structural model is shown in Figure 2. The non graphitized carbon is difficult to graphitize because of the cross-linking structure formed by the adjacent "microcrystals". Bonnamy [18] and Oberlin[19,20] have found that if the pores generated by the local orientation of molecules are small and large, the growth and development of microcrystals are limited in the process of graphitization evolution, which shows the nature of non graphitized carbon. Qin Yong[21] pointed out that there are differences between vitrinite and inertinite in the process of graphitization. In the peat stage, the aromatic structure of inertinite has been highly condensed, with more oxygen-containing functional groups in the molecular structure and microporous structure in the physical structure. Qin Yong believed that at least in the early stage of graphitization, the inertinite did not form graphite. Li Kuo summarized that the graphitization ability of different coal and rock components is homogeneous, matrix vitrinite > oxidized sericite > pyroxenite [10] Zhang Xiaoxu [22] studied the catalytic graphitization of Shenfu coal and its petrographic components, and found that when the particle size of vitrinite and inertinite of Shenfu coal is less than 75μm When the heating temperature is 2500 ℃, the graphitization ability of inertinite is stronger than that of vitrinite.The results are different from those of Li Kuo and QinYong. The author thinks that the pressure of grinding has made a preliminary transformation on the primary coal rock components during the grinding process of sample preparation, which has an impact on the experimental results. But this view is still to be verified by experiments.

Both vitrinite and inertinite in coal have graphitization potential, but the graphitization behavior of inertinite occurs later.

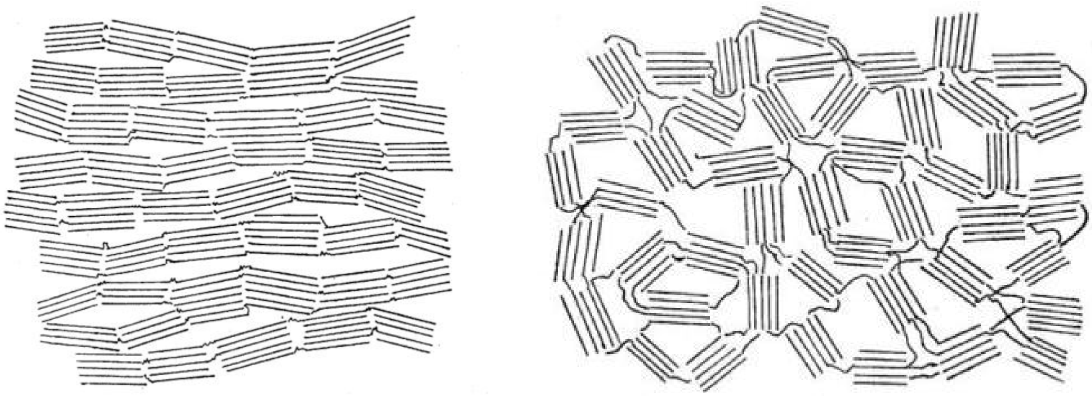


Fig.2 Graphitizable carbon and non-graphitizable carbon（Franklin, 1951）

2.2 Coal grade

In the process of graphitization, high-grade coal is more prone to graphitization during metamorphism, and the temperature required for graphitization is lower than that of low rank coal. Bituminous coal first becomes anthracite during metamorphism [23,24].

In the process of graphitization, the graphitization behavior of coal with different evolution degree is very different, and the graphitization behavior of coal with the same stage is also different.

Anthracite shows the characteristics of non graphitizable porous hard carbon below 2000 ℃. When the temperature exceeds 2000 ℃, some anthracites show graphitizable Welsh anthracite as described by Franklin, but some anthracites do not form true three-dimensional ordered graphite even at 3000 ℃ [25]. This reflects that the graphitization ability of the same rank coal is different due to different coal forming environment. Pusz [26] think that the reason for this phenomenon is mainly due to the various spatial arrangement of basic structural units of coal, and it is found that the structure of metamorphic anthracite will not change under the temperature condition of less than 1000 ℃.Qiu Tian [27] took the dried Taixi anthracite, Anhui Liuzhuang gas fat coal and Shengli lignite as the starting reactants, obtained three different coal based graphite materials after high temperature graphitization, and characterized the three materials by XRD. The final results are shown in Figure 3. In the X-ray diffraction pattern, the spatial orientation of the network aromatic lamellae is (002) peak, and the narrower the (002) peak is, the higher the (002) peak is; the condensation degree of aromatic ring is (100) peak, which is the size of aromatic ring. The larger the size of aromatic layer wafer is, the narrower the (100) peak is[28]. The results show that in the final product, lignite based graphite material is porous honeycomb structure, bitumi -nous based graphite material has a small amount of micropores, anthracite based graphi-te material is polycrystalline graphite with chip size less than 1 micron and irregular microcry-stalline orientation, and the graphitization ability of three kinds of coal grades increases with the increase of coal grade.

Based on the above analysis, the essential reasons for the differences in graphitization behavior of coals with different metamorphic degrees are the differences in the structure of organic macromolecules and the contents of ash and volatile matter.Microscopically, there are less oxygen-containing functional groups in high-grade coal, the process of deoxidation and dehydrogenation in metamorphism consumes less energy and ends earlier, and the product after graphitization is more single; However, the low rank coal contains more oxygen-containing functional groups, which makes it more anisotropic when the coalescence occurs, resulting in more diverse graphitization direc-tions of low rank coal. Macroscopically, anthra-cite has higher metamorphic degree, single physical structure and single graphitization behavior; However, due to the high content of inertinite and clay minerals in low rank coal, the micropore rich structure is retained in the final product when graphitization occurs, resulting in the formation of graphitized carbon with honey-comb structure.

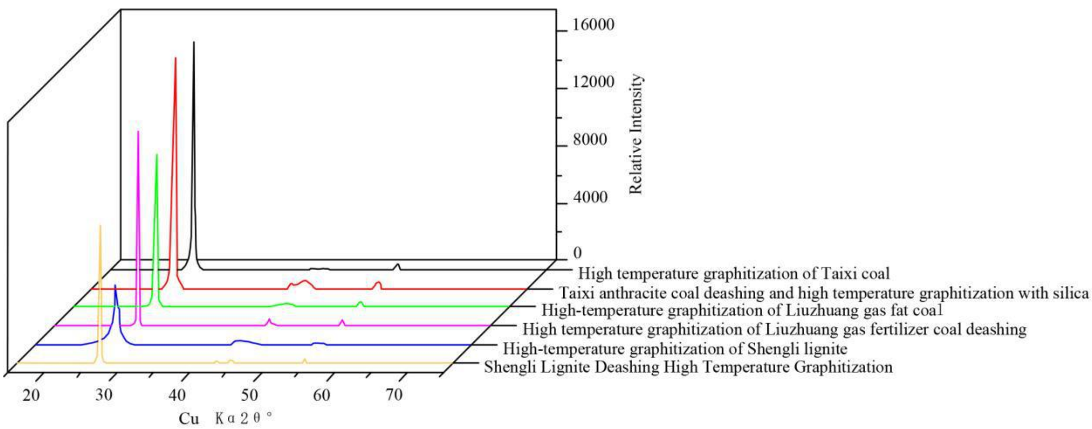


Fig. 3 XRD spectra of coal-based graphite obtained from different raw coal types（Qiu tian, 2019）

2.3 Temperature

Temperature plays a leading role in the process of graphitization, which provides activation energy for the graphitization reaction and make-s the graphitization reaction proceed. Magmatic thermal field and hydrothermal field are the main heat sources of natural graphitization.It is found that the mineralization temperature of crystalline flake graphite is about 600℃~900℃ [13,29-34]. There are relatively few reports on the metallogenic temperature of coal measures graphite, According to the Raman spectrum parameters, Cheng Siyu calculated the metallo-genic temperature range of graphite in Yantong-shan coal measures from 526 ℃ to 622 ℃, with an average of 561 ℃, which is lower than the natural metallogenic temperature of crystalline graphite [35].

The influence of heating rate on Graphitization of coke was studied by Tadao Ishikawa [36]. The results show that the higher the slow heating rate and the final temperature above 2000 ℃, the better the graphitization degree is. The research results of Zhang depin et al. [37] show that the higher the temperature is, the more perfect the graphite crystal structure is. Bustin RM [38] heated anthracite at different temperatures to obtain the final experimental results. The XRD diffraction pattern is shown in Figure 4. With the increase of temperature, the (002) peak becomes narrower and higher, which indicates that the higher the temperature is, the higher the degree of graphitization is. The research of Qiu Tian [27] shows that there is a positive correlation between temperature and graphitization degree, and high temperature is conducive to the stacking of graphite flakes and the development of carbon mesh. Taking Lutang graphite mine as a typical example, there is a graphite semi graphite anthracite transition zone between the graphite seam and the coal seam. The physical and chemical properties of graphite semi graphite anthracite are almost parallel to granite body, and their physical and chemical properties change gradually with the distance from granite body [39]. Hou Dandan found that the closer the ore bed is to the intrusive rock, the higher the degree of metamorphism and graphitization of graphite [40].

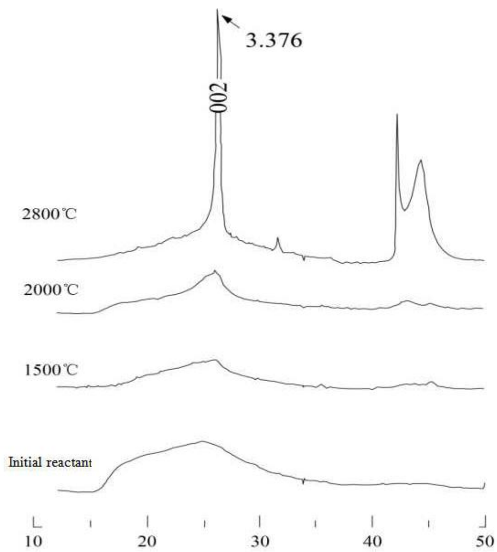


Fig.4 Portion of X-ray diffractograms, traces of starting material, and anthracite heated to 1500℃, 2000℃, and 2800℃. (Bustin R M.1995)

Cui Xianjian [41] analyzed the samples collected from Lutang graphite at different distances from the intrusive rock mass. The distribution of sampling points is shown in Fig. 5 and Fig. 6, and explored the correlation between the degree of graphitization and the distance from the intrusive rock mass. The Raman spectrum is shown in Fig. 7. LP is crystalline flake graphite in Pingdu, Shandong. It is found that the Raman spectra of most carbon materials have two first-order scattering peaks, the G peak near 1580 cm^{-1} and the D peak near 1350 cm^{-1}.At present, the strength ratio r of D peak to G peak is often used to judge the order degree of carbon materials. The smaller the R value is, the higher the order degree is, that is, the higher the graphitization degree is [42,43].

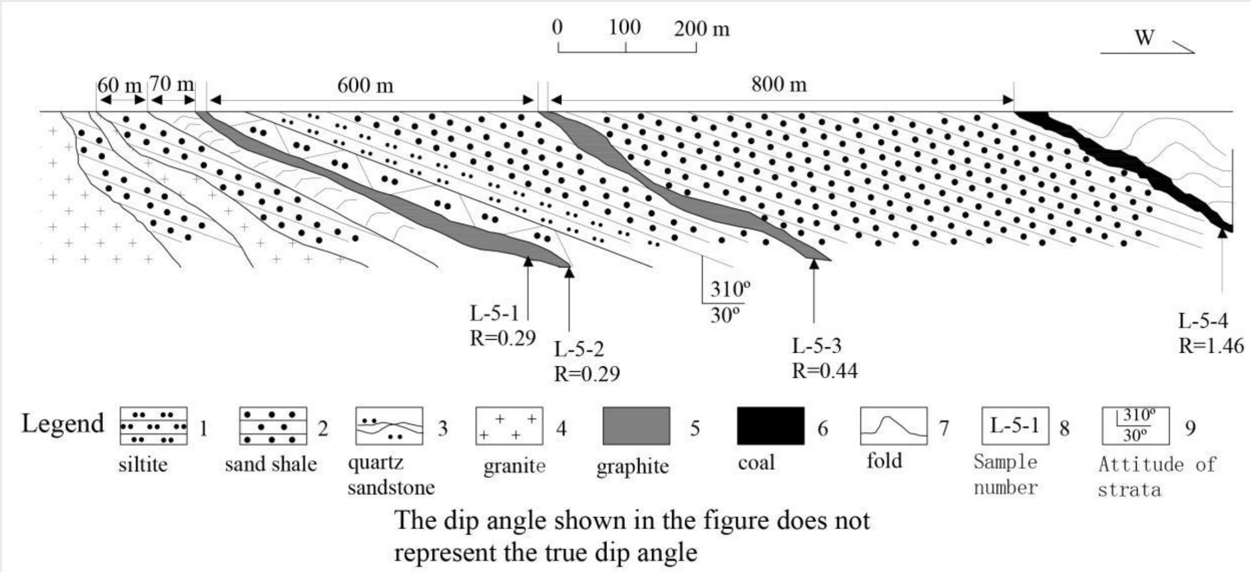


Fig.5 Random section of No.5 mine tunnel and corresponding graphitization degreee R of samples (Cui Xianjian,2018)

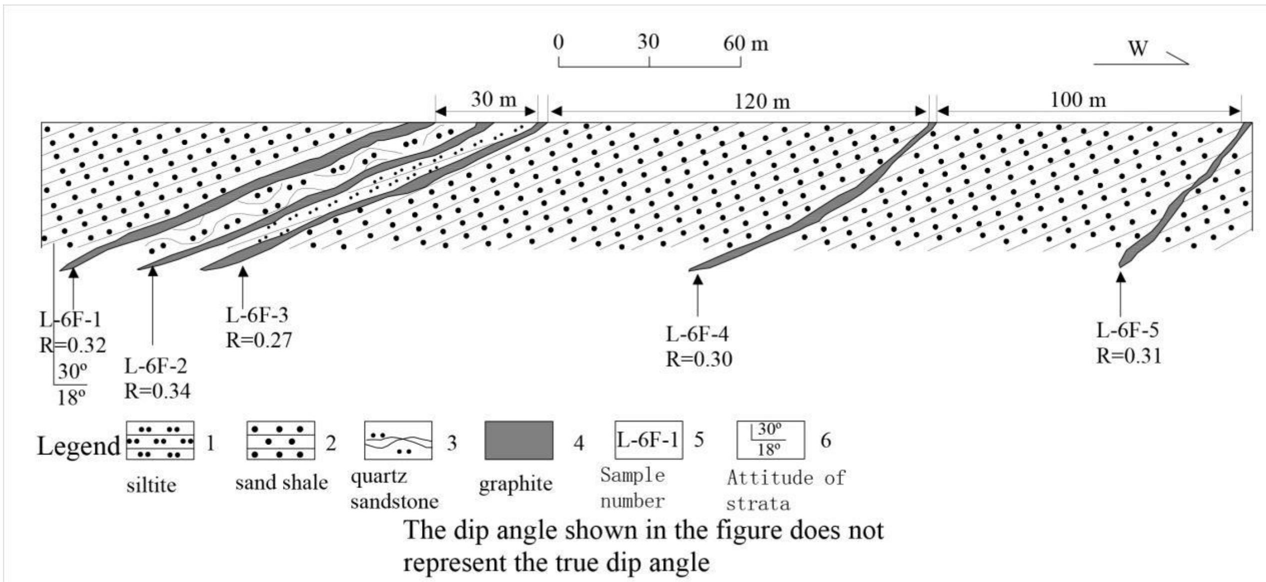


Fig.6 Random section of No.6 mine tunnel and corresponding graphitization degreee R of samples (Cui Xianjian,2018)

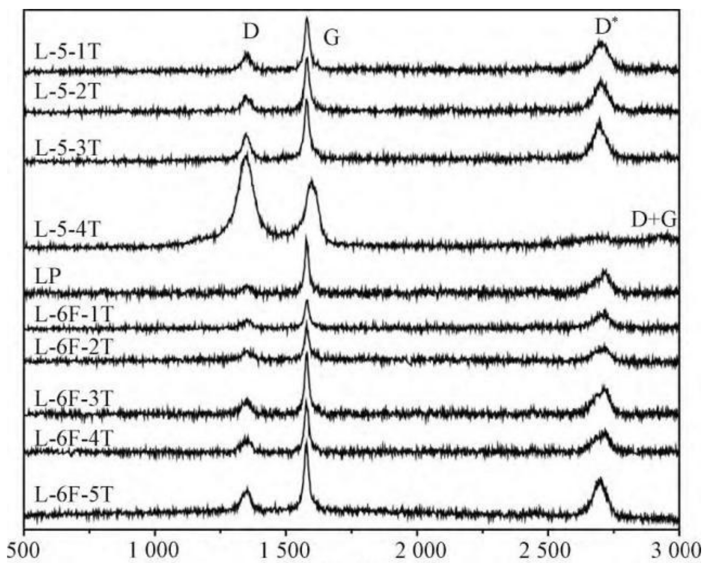


Fig.7 Raman spectra of graphite and coal samples (Cui Xianjian,2018)

According to the analysis of Fig. 5, FIG. 6 and Fig. 7, with the distance from the intrusive body from far to near, the degree of graphitization gradually decreases, which indicates that the closer the distance from the intrusive body is, the higher the temperature is, and the higher the degree of graphitization is.

2.4 Stress

The experimental kinetic data show that it takes 10^{40} minutes to Synthesize Graphite from amorphous carbon even at 700 ℃ [44-47]. The results of laboratory synthetic graphite show that graphite structure appears when the carbon material is heated to 2800 ℃, and the mineralization temperature of natural graphite is far lower than this temperature.Therefore, it can be judged that besides temperature leading, the coal-bearing graphite mineralization is also affected by other external factors.R. Professor M. Bustin's team heated anthracite for graphitization after shear test. It was found that the samples after shear test began to show graphitization structure at 600 ℃, and most of the samples were completely graphitized at 900 ℃ [38]. Directional pressure plays a key role in the process of enhancing the order of basic structural units of coal, and is a necessary condition for graphitization. This view has been proved in high temperature and high pressure experiments and graphitization experiments of high metamorphic coal [48,49].

The promotion mechanism of pressure on Metamorphism can be summarized into three viewpoints: friction heat viewpoint, strain energy viewpoint and mechanochemical viewpoint. According to the viewpoint of friction heat, the tectonic movement makes the coal seam slide mechanically, and the friction heat produced provides the heat energy needed for graphitization. Anthracite coalification on the reverse fault plane of the Rockies and graphitization of coal in parts of the Alps are regarded as typical cases of the frictional heat viewpoint [50,51]. The essence of friction heat viewpoint is still the effect of temperature on graphitization, and the friction heat generated by mechanical displacement of coal seam driven by tectonic stress is its heat source. According to strain energy, strain energy or kinetic energy is the main energy source of organic matter structure evolution without thermal energy. Ross [52] and Bustin [38] proposed the mechanism of strain energy transformation of kerogen graphitization. Bustin [38] explored the effects of shear stress, coaxial stress and hydrostatic stress on the graphitization process, and found that shear stress has better catalytic effect. The team believes that the mechanism of stress action is mainly due to the collapse of the hole wall caused by the strain energy and the steering and directional arrangement of the basic mechanism units. The mechanochemical point of view is based on the chemical transformation of organic polymer under mechanical action. It is considered that the micro shear stress is concentrated in individual segments of polymer. When the shear stress exceeds the critical stress, the polymer chain breaks and splits into small molecular hydrocarbons [53]。

Lutang coal mine in Hunan Province is a typical coal measure graphite deposit. The occurrence state of "different minerals in the same layer" provides a good condition for the study of coal measure graphite mineralization. Wang Lu [54] found that in the Lutang Graphite Deposit, from south to north, the degree of graphitization is mainly affected by the structure, the strength of structural deformation is enhanced, and the degree of graphitization becomes higher. In the middle area, the structure is complex and the degree of graphitization is quite different. Mo Jiafeng [55] explained this phenomenon as stress loss caused by over development of structure, which affected the degree of graphitization.

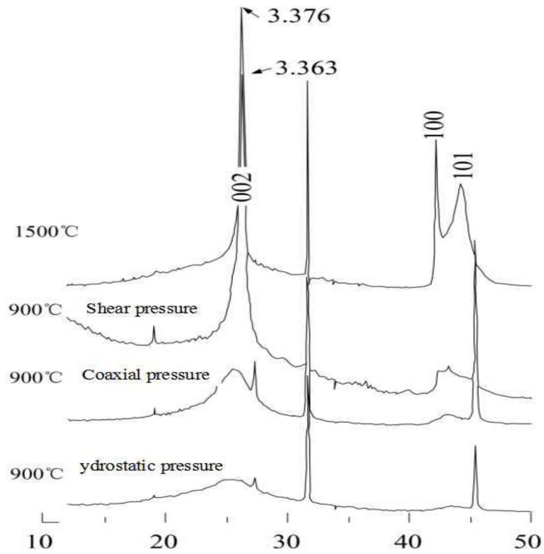


Fig.8 Portion of X-ray diffractograms of anthracite tested at 900℃ in hydrostatic, coaxial, and simple shear configurations and sample heated to 2800℃ HTT（Bustin R M.1995）

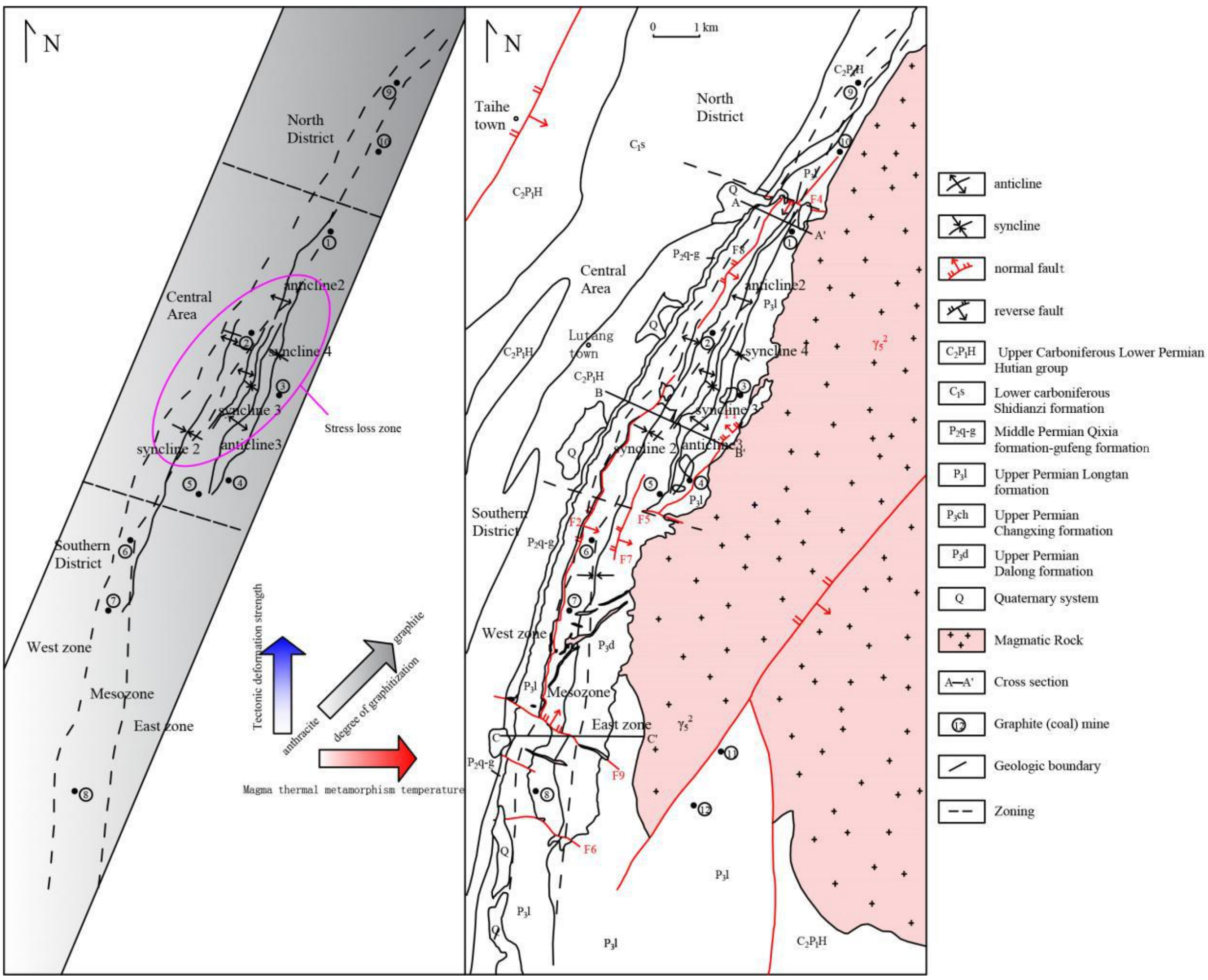


Fig.9 Metallogenic model diagram and Sketch division of tectonic unites in Lutang minning area (Adapted from Wang Lu, 2018)

2.5 Mineralizer action

In the study of the influence of elements in coal on graphitization, it is found that the coal sample containing manganese, iron, calcium and boron is easier to graphitize [56-59]. There are few experiments on the mechanism of Mineralizer in the process of coal measure graphite mineralization, but a large number of experiments have been carried out to explore the role of Mineralizer in the process of graphitization evolution of carbonaceous materials. It is found that the elements with catalytic effect on the graphitization process are mainly B, Ti, Al, V, Cr, Fe, Co, Ni, W, y, La, etc [60-69].

Table.2 Catalytic effects of various metals on the graphitization process of carbon materials

Catalysis	element
Eliminate disordered layer defects and promote homogeneous graphitization	B
Catalytic formation of graphite	Si、Ge、Mg、Ca、Cu
Catalytic formation of graphite and disordered graphite	Fe、Co、Ni、Al、Ti、V、Cr、Mn
No catalysis	Zn、Ag、Cd、Au、Sn、Pb、Hg

At present, the mechanism of mineralizer catalysis is mainly composed of two mechanisms: dissolution and re-precipitation and carbide conversion. The former thinks that the mineralizer can dissolve carbon and form co-melts at high temperature. When the solubility of carbon reaches saturation, carbon materials will be precipitated in the form of graphite with low energy level; The latter thinks that the mineralizer enters the carbon group and carbon substance to form carbides at high temperature, and the carbide decomposes at high temperature to form graphite and new mineralizer.

Early studies suggested that the catalytic mechanism of transition metal elements was due to the existence of 2-5 electrons in the outermost layer structure, which formed a strong covalent bond with carbon, and the decomposition and rearrangement of metal carbides at high temperature to form graphite and new metal atoms [60]. However, the electronic configuration of early studies can not perfectly explain the catalytic ability of non transition metals.

It is found that Fe, Ni, Mo, Mn, Cr, Ti and Zr react according to the mechanism of dissolution and precipitation [73-84]. Li h found that during the process of iron catalyzed graphitization, iron particles adhered to the surface of carbon particles, then heated at high temperature, iron particles melted and wrapped the carbon particles. After continuous heating, iron interacted with carbon to form graphite structure, and no iron carbide was found in the final productSilicon reacts with carbon at 1800 ℃ to form silicon carbide. When the temperature rises to 2800 ℃, silicon carbide decomposes to form graphite and silicon [27]. In the process of graphitization, boron replaces the carbon in the lattice and promotes the process of graphitization [82].

Among the associated minerals in coal measures, quartz, ankerite, illite and kaolinite can promote the graphitization of coal. D Gonz á Liz [84] thought that illite, ankerite and siderite had better catalytic effect than kaolinite. Qiu Tian [29] found that when the temperature is 1800 ℃, the primary quartz and clay minerals in coal react to form graphitization intermediate silicon carbide. As the temperature continues to rise to 2800 ℃, silicon carbide decomposes to form highly regular graphite crystals. The higher the content of clay minerals in raw coal sample, the higher the graphitization degree of final product, but the higher the content of silicon impurities in the product.

Cheng Siyu [35] tested the Raman spectra of graphite along the direction perpendicular to the boundary between pyrite and graphite. The results showed that the Raman parameters of graphite changed with the distance from pyrite. The closer the distance from pyrite, the higher the degree of graphitization. Through the spatial distribution relationship between pyrite and graphitization degree, it is confirmed that iron plays a catalytic role in the process of graphitization.

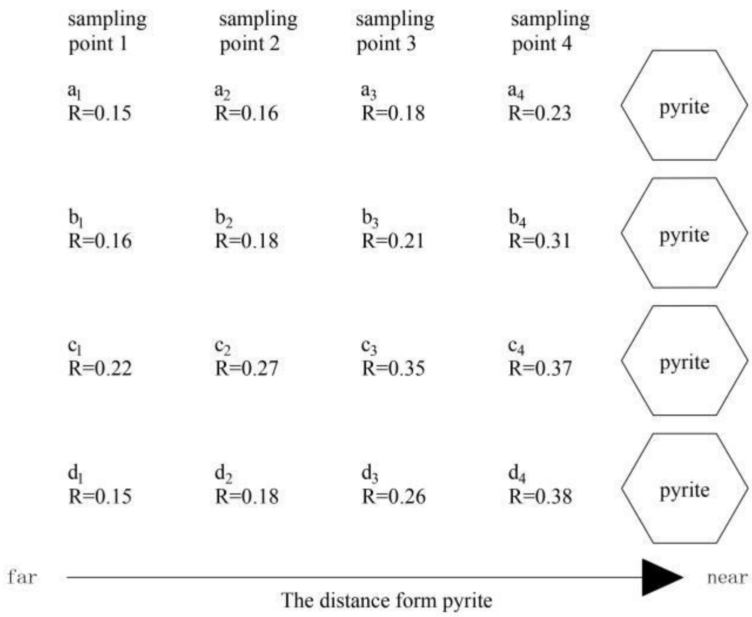


Fig.9 The spatial distribution of pyrite and graphitization degree (Adapted from Chen Siyu,35)

3. Metallogenic characteristics of coal series graphite

The influencing factors of graphite mineralization in coal measures are complex, which leads to the obvious difference of graphitization degree in different spatial distribution of ore bodies. Combined with the above research results, the distribution of graphite in coal measures meets the following rules：1）The closer the ore body is to the intrusive body, the higher the degree of graphitization. The degree of graphitization tends to decrease from the intrusive body to the outermost edge, and the ore body is dominated by anthracite. Mo Jiafeng [56] thinks that the influence range of metamorphism directly caused by intrusive ore body is about 350m. Beyond 350m, the comprehensive influence of high temperature and structure of ore body is more conducive to the formation of graphite. 2）The stronger the intensity of structural deformation, the higher the degree of graphitization. From north to south, with the weakening of tectonic movement, the degree of graphitization shows a weakening trend, until it is dominated by anthracite. 3）The larger the longitudinal buried depth, the higher the graphitization degree of ore body, but the small gap in graphitization degree, indicating that static pressure has a positive effect on graphitization, but it has little influence on the mineralization process. 4）The closer to the iron bearing minerals, the higher the graphitization degree of ore body. In the aspect of macro mineralization, it is mainly associated with metallic ore and graphite ore.

4. Existing problems and future research direction

Great achievements have been made in the exploration of the metallogenic mechanism of coal measures graphite, but there are still some problems and shortcomings:

（1）There is no detailed exploration experiment and micro explanation about the graphitization behavior difference of different coal rock components in coal;

（2）There is a lack of in-depth study on the micro explanation and evolution law of graphitization behavior differences caused by different coal rank structures;

（3）The shear pressure plays a significant role in promoting the graphitization behavior of coal, but its mechanism and the necessity of pressure in the process of graphitization of coal measures need to be further studied;

（4）The influence of the associated mineral elements in coal on the graphitization of coal measures was ignored in the early experiments. The influence of different mineral elements on the graphitization behavior and its mechanism need to be further explored;

（5）For example, aluminum has been proved to be a catalytic element for graphitization in the laboratory, but it is found that aluminum rich minerals have no obvious catalytic effect on the process of graphitization in mineral geological research [85].

For the existing problems, the future development direction of coal measures graphite metallogenic mechanism research is proposed:

（1）In view of the different graphitization behaviors of different coal and rock components, lignite with high inertinite content and high metamorphic anthracite with high vitrinite content are used as raw materials for the research experiment;

（2）This paper analyzes the graphitization behavior of coal under the same temperature and different pressure, and analyzes the effect and mechanism of pressure on the graphitization behavior of coal;

（3）The effect of minerals in coal on coal graphitization behavior was studied, and the mechanism of various minerals in coal on coal graphitization behavior was analyzed .

（4）The effect of mineralizer pressure temperature coupling on coal graphitization behavior was studied to explore the natural mineralization mechanism of coal measures graphite.

References

[1] Worsley M A, Pauzauskie P J, Olson T Y, et al. Synthesis of graphene aerogel with high electrical conductivity[J]. Journal of the American Chemical Society, 2010, 132(40): 14067-14069.

[2] Li X, Zhao T, Wang K, et al. Directly drawing self-assembled, porous, and monolithic graphene fiber from chemical vapor deposition grown graphene film and its electrochemical properties[J]. Langmuir, 2011, 27(19): 12164-12171.

[3] Behabtu N, Lomeda J R, Green M J, et al. Spontaneous high-concentration dispersions and liquid crystals of graphene[J]. Nature nanotechnology, 2010, 5(6): 406.

[4] Li D, Müller M B, Gilje S, et al. Processable aqueous dispersions of graphene nanosheets [J]. Nature nanotechnology, 2008, 3(2): 101.

[5] Uri A, Grover S, Cao Y, et al. Mapping the twist-angle disorder and Landau levels in magic-angle graphene[J]. Nature, 2020, 581 (7806): 47-52.

[6] Bi H, Xie X, Yin K, et al. Spongy graphene as a highly efficient and recyclable sorbent for oils and organic solvents[J]. Advanced Functional M-

aterials, 2012, 22(21): 4421-4425.

[7] Cohen-Tanugi D, Grossman J C. Water desalination across nanoporous graphene[J]. Nano letters, 2012, 12(7): 3602-3608.

[8] Wang Y, Wang L, Yang T, et al. Wearable and highly sensitive graphene strain sensors for human motion monitoring[J]. Advanced Functional Materials, 2014, 24(29): 4666-4670.

[9] Ministry of natural resources. National mineral resources reserve bulletin (2018) [R]. Beijing: Ministry of natural resources, 2019:147 – 148

[10] Li Kuo.Investigation on the structural ordering of natural coaly graphite from Xinhua,Hunan Provience,China.[D].China university of mining & technology-Beijing.2019

[11] Dong Yeji, Cao Daiyong,Wang Lu， et al. Indicators for partitioning graphite and anthracite in coal measures during geological exploration phase[J]. ,2018,46(01):8-12.Coal Geology & Exploration

[12] Kwiecińska B, Petersen H I. Graphite, semi-graphite, natural coke, and natural char classification—ICCP system[J]. International Journal of Coal Geology, 2004, 57(2): 99-116.

[13] Cao Daiyong, Zhang He,Dong Yeji,et al. Research status and key orientation of coal-based graphite mineral geology[J].Earth Sciene Frontiers, 2017,24(5):317-327.

[14] Wang Lu，Dong Yeji，Zhang He，et al． Factors affecting graphitization of coal and the experimental validation［J］. Journal of Mining Science and Tech- nology，2018，3(1):9 — 19. DOI:10. 19606 /j. cnki. jmst. 2018. 01. 002

[15] Gered R， Wolfgang L， Evelin F. On the discrimination of semi-graphite and graphite by Raman spectroscopy[J]. International Journal of Coal Geology，2016(159): 48-56

[16] LI Yang，Wang Lu，Cao Daiyong，et al. The discovery and geological significance of coal-formed graphite in Chongyi coal mine in Jiangxi Province[J]. Coal Geology & Exploration，2019，47(5)：79–85

[17] Franklin R.E Crystallite growth in graphitizing and nongraphitizing carbons [J].Proceedings of the Royal Society A Mathematical Physical & Engineering Sciences,1951,209(1097):196-218）

[18] Bonnamy S, Oberlin A. Heat-treatment of two heavy petroleum products containing vanadium and nickel[J]. Carbon, 1982, 20(6): 499-504.

[19] Oberlin A, Terriere G. Graphitization studies of anthracites by high resolution electron microscopy[J]. Carbon, 1975, 13(5): 367-376.

[20] Oberlin A, Oberlin M. Graphitizability of carbonaceous materials as studied by TEM and X‐ray diffraction[J]. Journal of Microscopy, 1983, 132(3): 353-363.

[21] Qin Yong,Zhang Yousheng, Liu huanjie. Evolution track of coarse grain reflectivity of high coal grade coal[J].Coal Geology & Exploration，1994(05):13-18

[22] Zhang Xiaoxu. Study on Catalytic graphitization of Shenfu coal and macerals[D],Xi`an University of Science and Technology,2014.

[23] Bustin R M，Ross J V，Rouzaud J N．Mechanisms of graphite formation from kerogen: experimental evidence[J]. 1995, 28(1):1-36.

[24] Wilks K R, Mastalerz M, Ross J V, et al. The effect of experimental deformation on the graphitization of Pennsylvania anthracite[J]. International journal of coal geology, 1993, 24(1-4): 347-369.

[25] González D, Montes-Morán M A, Garcia A B. Graphite materials prepared from an anthracite: a structural characterization[J]. Energy & fuels, 2003, 17(5): 1324-1329.

[26] Pusz S, Duber S, Kwiecińska B K. The study of textural and structural transformations of carbonized anthracites[J]. Fuel processing technology, 2002, 77: 173-180.

[27] Qiu Dian. Research on the graphitization process of coal and the migration rule of coal-derived minerals[D].China university of mining&technology,2019.

[28] Li W, Zhu Y. Structural characteristics of coal vitrinite during pyrolysis[J]. Energy & fuels, 2014, 28(6): 3645-3654.

[29] Cao Daiyong, Wang Lu, Liu Zhifei, et al.The research status and prospect of coal-based graphite in China[J/OL].Coal Geology & Exploration,2020,48(01):1-11.

[30] Petrakakis K. Metamorphism of high-grade gneisses from the Moldanubian zone, Austria, with particular reference to the garnets[J]. Metamorph Geol, 1986, 4: 323-344.

[31] Petrakakis K. Evolution of Moldanubian rocks in Austria: review and synthesis [J]. Metamorph Geol, 1997, 15:203-222.

[32] Echtler H P, Ivanov K S, Ronkin YL, et al. The tectono-metamorphic evolution of gneiss complexes in the Middle Urals, Russia: A reappraisal[J]. Tectonophysics, 1997, 276: 229-251.

[33] Jöns N，Schenk V. The ultrahigh temperature granulites of southern Madagascar in a polymetamorphic context: Implications for the amalgamation of the Gondwana supercontinent [J]. Eur J Mineral, 2011, 23: 127-156.

[34] Huang Bojun.Graphitization of carbonaceous materials metamorphic rocks[J].Acta Mineralo-

gica Sinica,1986,6(4):350-353.
[35] Cheng Siyu, Chuan Xiuyun, Yang Yang, et al. Mineralogical Characteristics of Aphanitic Cryptocrystalline in Yantongshan and Its Significance for Origin[J/OL].Acta Scientiarum Naturalium Universitatis Pekinensis:1-13.
[36] Tadao Ishikawa, Shizawa Shiro, Huang Chengyuan.Effects of heating rate, heating time, repressurization of semi-finished products and increasing forming pressure on graphitization [J].Foreign Light Metals,1965(05):31-35.
[37] Zhang Deping, Yin Xintang. Research on graphitization of metallurgical Coke [J]. Carbon, 1982(04):7-13.
[38] [38] Bustin R M, Rouzaud J N, Ross J V. Natural graphitization of anthracite: experimental considerations[J]. Carbon, 1995, 33(5): 679-691
[39] Liu Jian. Moving toward the application and industrialization of graphene:processes of graphite formation and graphitic crystal chemistry[D]. China University of Geosciences (Beijing), 2017.
[40] Hou Dandan. nfluence of order degree of coal-based graphite on structure change og graphene(Beijing),2019.
[41] Cui Xianjian, Liu Qinfu, Li Kuo,et al. Mineralogical Characteristics of Coal-based Cryptocrystalline Graphite in Lutang Area, Hunan Province, China[J].Acta Mineralogica Sinica, 2018,38(02):142-151.
[42] Bokobza L, Bruneel J L, Couzi M. Raman spectroscopic investigation of carbon-based materials and their composites. Comparison between carbon nanotubes and carbon black[J]. Chemical Physics Letters, 2013, 590: 153-159.
[43] [43] Wang Y, Serrano S, Jorge J Santiago-Avilés. Raman characterization of carbon nanofibers prepared using electrospinning[J]. Synthetic Metals, 2003, 138(3):423-427.
[44] Fischbach DB (1963) Kinetics of graphitization of a petroleum coke. Nature 200:1281–1283.
[45] Fischbach DB (1971) The kinetics and mechanism of graphitization. In: Walker PL (ed) The chemistry and physics of carbon 7. Marcel Dekker, New York, pp 1–154.
[46] Walker PL (ed) The chemistry and physics of carbon 7. Marcel Dekker, New York, pp 1–154
[47] Bustin RM, Ross JV, Rouzaud JN (1995) Mechanisms of graphite formation from kerogen: experimental evidence. Int J Coal Geol 28:1–36.
[48] Cao Daiyong, Li Xiaoming, Deng juemei. Coupling effect between coalification and tectonic -thermal events——Geological records of geodynamics[J]. Earth Science Frontiers,2009, 16 (04):52-60.
[49] Ju Yiwen, Lin Hong, Li Xiaoshi, et al. Tectonic deformation and dynamic metamorphism of coal[J]. Earth Science Frontiers,2009,16(01): 158-166.
[50] Bustin R M. Heating during thrust faulting in the Rocky Mountains: friction or fiction?[J]. Tectonophysics, 1983, 95(3-4): 309-328.
[51] Suchy V, Frey M, Wolf M. Vitrinite reflectance and shear-induced graphitization in orogenic belts: a case study from the Kandersteg area, Helvetic Alps, Switzerland[J]. International Journal of Coal Geology, 1997, 34(1-2): 1-20.
[52] Ross J V, Bustin R M. The role of strain energy in creep graphitization of anthracite[J]. Nature, 1990, 343(6253): 58-60.
[53] Liu W, Xu Y, Zhang S. A new kind of mechanism for hydrocarbon generated-mechanochemistral function and experimental prove[J]. Acta Sedimentologica Sinica, 2000, 18(2): 314-318.
[54] Wang Lu, Peng Yangwen, Cao Daiyong, et al. The tectonic framework and controlling mechanism of coal-based graphite in Lutang mining area, Hunan Province[J].Coal Geology & Exploration, 2020,48(01):48-54.
[55] Mo Jiafeng, Zhao xunlin, Zhu Wenqing, et al.Metallogenic law and prospecting direction of coal-based graphite in Hunan Province[J].Coal Geology & Exploration,2020,48(01):18-26.
[56] Mochida， Ohtsubo R， Takeshita K， et al. Catalytic graphitization of graphitizable carbon by chromium， manganese and molybdenum oxides[J]. Carbon，18(1)：25–30.
[57] Fitzer E，Weisenburger S. Evidence of catalytic effect of sulphur on graphitization between 1 400 and 2 000℃[J]. Carbon， 1976， 14(4)： 195–198.
[58] Inagaki M I. Natural graphite： Experimental evidence for its formation and novel applications[J]. Earth Science Frontiers， 2005， 12(1)：171–181.
[59] Gonzalez D，And M M，Garcia A B. Influence of inherent coal mineral matter on the structural characteristics of graphite materials prepared from anthracites[J]. Energy & Fuels， 2005， 19(1)：235–240.
[60] Ōya A, Ōtani S. Catalytic graphitization of carbons by various metals[J]. Carbon, 1979, 17(2): 131-137.
[61] Ōya A, Marsh H. Phenomena of catalytic graphitization[J]. Journal of Materials Science, 1982, 17(2): 309-322.
[62] Ōya A, Yamashita R, Ōtani S. Catalytic graphitization of carbons by borons[J]. Fuel, 1979, 58(7): 495-500.

[63] Thambiliyagodage C J , Ulrich S , Araujo P T , et al. Catalytic graphitization in nanocast carbon monoliths by iron, cobalt and nickel nanoparticles[J]. Carbon, 2018:S0008622318303476.

[64] Tzeng S S. Catalytic graphitization of electroless Ni–P coated PAN-based carbon fibers[J]. Carbon, 2006, 44(10): 1986-1993.

[65] Tzeng S S, Lin Y H. The role of electroless Ni–P coating in the catalytic graphitization of PAN-based carbon fibers[J]. Carbon, 2008, 3(46): 555-558.

[66] Dhakate S R, Mathur R B, Bahl O P. Catalytic effect of iron oxide on carbon/carbon composites during graphitization[J]. Carbon, 1997, 35(12): 1753-1756.

[67] Yi S, Fan Z, Wu C, et al. Catalytic graphitization of furan resin carbon by yttrium[J]. Carbon, 2008, 2(46): 378-380.

[68] Yi Shoujun, Tang Zilong, Xia Xiaodong, et al. [J]. Catalytic graphitization of furan resin carbon by lanthanum[J].Journal of Central China Normal University (Natural Sciences), 2012,46(5): 582-585.

[69] Chen Li, Lv Chunxiang, Jiang Junqi,et al. Lv Yonggen. Effect of polyacrylonitrile gel fiber Boronizing on the graphitization process of carbon fiber [J]. new carbon material, 2019,34 (01): 95-104.

[70] Lu Reaction chemistry of organometallic compounds[M]. Beijing: Chemical Industry Press. 2000:60-62,79-87,112-117.

[71] Ma Shengming.Modern organic synthetic reactions involving metals[M]. Guangzhou: Guangdong Science and Technology Press, 2001:10-25.

[72] Tian Yuan, Yang Rui, Lin Ruihua, et al. Influencing Factors and Catalytic Mechanism of Catalytic Effect in Catalytic Graphitization[J]. Material Science,2020,10(1):40-46.

[73] Li H, Zhang H, Li K, et al. Catalytic graphitization of coke carbon by iron: Understanding the evolution of carbon Structure, morphology and lattice fringes[J]. Fuel, 2020, 279: 118531.

[74] Chen Chao, Wang Ao, Sun Kang,et al. Graphitization of Biomass Catalyzed by Ni[J]. Chemistry and Industry of Forest Products, 2019,39(03):94-100.

[75] Sevilla M, Fuertes A B. Catalytic graphitization of templated mesoporous carbons[J]. Carbon, 2006, 44(3): 468-474.

[76] Brockner W, Ehrhardt C, Gjikaj M. Thermal decomposition of nickel nitrate hexahydrate, Ni (NO3) 2· 6H2O, in comparison to Co (NO3) 2· 6H2O and Ca (NO3) 2· 4H2O[J]. Thermochimica Acta, 2007, 456(1): 64-68.

[77] Marsh H, Warburton A P. Catalytic graphitization of carbon using titanium and zirconium[J]. Carbon, 1976, 14(1): 47-52.

[78] Ōya A, Mochizuki M, Ōtani S, et al. An electron microscopic study on the turbostratic carbon formed in phenolic resin carbon by catalytic action of finely dispersed nickel[J]. Carbon, 1979, 17(1): 71-76.

[79] Mochida I, Ohtsubo R, Takeshita K, et al. Catalytic graphitization of non-graphitizable carbon by chromium and manganese oxides[J]. Carbon, 1980, 18(2): 117-123.

[80] Karatas C. Catalytic enhancement of graphite-CO2 reaction by in situ reduced chromium and nickel from their oxides Cr2O3 and NiO over the temperature range 850-1100° C[J]. Mineral Processing and Extractive Metallurgy, 2004, 113(1): 19-24

[81] Bin Y, Oishi K, Koganemaru A, et al. Catalytic effect of nickel under carbonization of polyimide films[J]. Carbon, 2005, 43(8): 1617-1627.

[82] Rastegar H, Bavand-Vandchali M, Nemati A, et al. Catalytic graphitization behavior of phenolic resins by addition of in situ formed nano-Fe particles[J]. Physica E: Low-dimensional Systems and Nanostructures, 2018, 101: 50-61.

[83] Wang Hua. Effect of BN catalytic graphitization on structure and mechanical properties of carbon fibers [D]. Donghua University, 2016

[84] WANG Hua.The catalytic effect of boron nitride on the structure and mechanical properties of polyacry lonitile-based carbon fiber[D].Dong Hua University,2016.

[85] González D, Montes-Morán M A, Garcia A B. Influence of inherent coal mineral matter on the structural characteristics of graphite materials prepared from anthracites[J]. Energy & fuels, 2005, 19(1): 263-269.

[86] Nyathi M S, Clifford C B, Schobert H H. Characterization of graphitic materials prepared from different rank Pennsylvania anthracites[J]. Fuel, 2013, 114: 244-250.