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GRAIN CONFIGURATION OF ONE WORM AFTER INDIVIDUAL COMPRESSED

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Abstract

The surface photograph of one individual compressed expanded graphite worm was investigated by Metalloscope, obtaining an image like the metal metallurgical structure. Boundaries between particles was reconstructed and mean grain size was analyzed by the granularity analyze software. Results showed that the mean grain size could not be influenced by original granularity (32 mesh, 50 mesh, 100 mesh) and process (different oxidizers, different expansion temperatures and different presses), the values of it is 30～45μm . XRD, SEM and AFM were used to carry on further analysis that there was a sub-structure in particles. The graphite crystal of sub-structure is perfect, the parameter of crystallite size is, La3～8μm Lc30～80nm,respectively. Data from XRD profiles were used to calculate the orientation index, ratio of peak and background and other indexes then studied the pressure's influence to orientation. The result is that orientation index value $\rho > 1$, this shows that along the perpendicularity pressure surface the orientation degree of expanded graphite particles is high.

1 Introduction

Although expanded graphite has appeared for many years, it is also studied by many groups and many new applications are discovered, such as bio-medical materials, sorption of viscous heavy oils [7,4], etc. Many researchers have investigated appearance and structure of expanded graphite [1]. For example, Gao-lin had studied effect of expansion time on the microstructure of expanded natural flake graphite [2]. The natural flake graphite was expanded for five times and results show that only the first expansion is obvious then the differences in the bulk density get smaller and smaller with increasing expansion time. This gave some information about natural graphite and indicated that the expansion mechanism may be different form the traditional one and this need further study.

In the present work, when Metallurgical Microscope was used to study the compressed expanded graphite, we occasionally discovered a metallurgical metallic structure in images which magnified for 200～500 time. “Particles” are encircled by network grain boundary and results of repeat experiments showed that the phenomenon exactly existed. Mean grain size was analyzed and results suggested that the mean grain size could not be influenced by original mesh, acidification and expansion process. Because crystallization temperature of

graphite is above 2800℃ and grain size can not so large so we deduced that these particles must be from natural flake graphite but not from preparation process. These observed flake can not damaged by acidification process and high expansion temperature and only when it was pressed the flake oriented. In order to make sure whether the flake still has typical graphite structure and the mean of grain boundary, XRD, AFM, and SEM were used to make a further analysis.

In addition, structure parameter (ratio of peak and background [5] and orientation index [8]) derived from XRD was used to represent the degree of orientation and laws were also summarized.

2 Experimental

2.1 Raw material

Flake graphite used was prepared in an industry and Tab.1 shows its ash content.

Tab 1. Ash content of flake graphite

	32 Mesh	**50 Mesh**	**100 Mesh**
Ash content (%)	1.2195	5.5336	8.4409

2.2 Instrument

Metallurgical Microscope NIKON EPIHOT 200; XRD XPert MPD（40 mA, 40 kV ）; SEM（日立 S-3000N）; AFM (SPA4000); DY-30 electric tablet machine

2.3 Preparation of sample

Expanded graphite is prepared with H_2SO_4 as an intercalate and HNO_3 as an oxidant, react 3h, then rinse, filter and were dried in a circulation oven at 85℃ for to remove the moisture. Expansion and exfoliation occurred during the heat treatment at 900℃. Then measuring cylinder is used to obtain the expansion volume.

Another method to get expanded graphite is that it is prepared with H_2SO_4 as intercalate, $KMnO_4$ as oxidant and process is the same as above. In addition, expanded graphite is prepared at different temperatures700℃, 800℃, 900℃, 1000℃, then observe the difference of their structures.

Single whole worm-like expanded graphite was put on a clean micaceous sheet and covered by another clean micaceous sheet then pressed it with a uniform power and made it stick to the micaceous sheet. Metallurgical Microscope was used to observe expanded graphite and the clear images were treated with the granularity analyze software.

In order to control the power, variety of single worm-like expanded graphite was press by electric tablet

machine directly with 5MP and 10MP. In contrast experiment many expanded graphite worms was pressed in the modal and XRD was used to observe compressed expanded graphite.

3 Results and discussion

3.1 The structure of expanded graphite obtained by Metallurgical Microscope

Although many studies have been published concerning structure of expanded graphite [3], little research has been done on single compressed expanded graphite worm. In this paper, Metallurgical Microscope was used to study the variety of expanded graphite which pressed with single worm and images were modified for 500 times as shown in Fig 3-1.

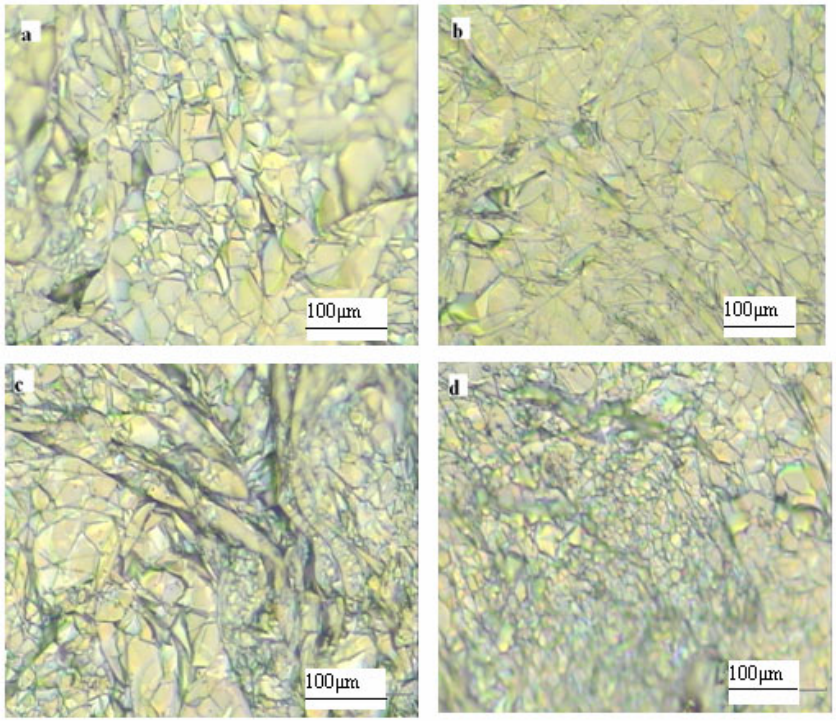

Fig 3-1. The phase diagram of expanded graphite at different specification (500×) (a,b Expanded graphite of 32 mesh; c Expanded graphite of 50 mesh; d Expanded graphite of 100 mesh)

As show in Fig 3-1, the structure of different expanded graphite is almost the same. All of them have inhomogenous flakes which may be from original flake graphite or caused by their different orientation in press process. In this process, layers may slide, overlay or be pushed down so we may observe a whole flake or apart.

$KMnO_4$ is a common oxidant; images of expanded graphite prepared with $KMnO_4$ are shown in Fig 3-2.

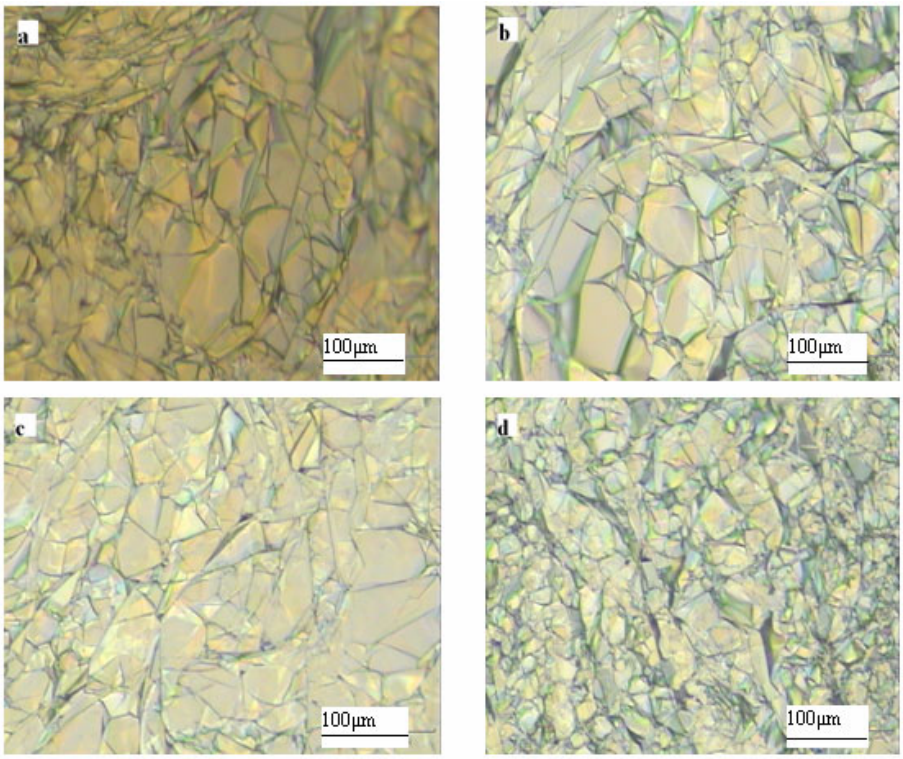

Fig 3-2. the phase diagram of the expanded graphite when the quantity of $KMnO_4$ is different（500×）(a addition quality is 0.1g;b addition quality is 0.2g;c addition quality is 0.3g;d addition quality is 0.6g)

As show in Fig 3-2, the structure of different expanded graphite prepared with different qualities of $KMnO_4$ is similar and it is also similar to expanded graphite prepared by mixed acid. Metallurgical metallic structure is the main trait of these images. The grain size was analyzed and results were show in Fig 3-4.

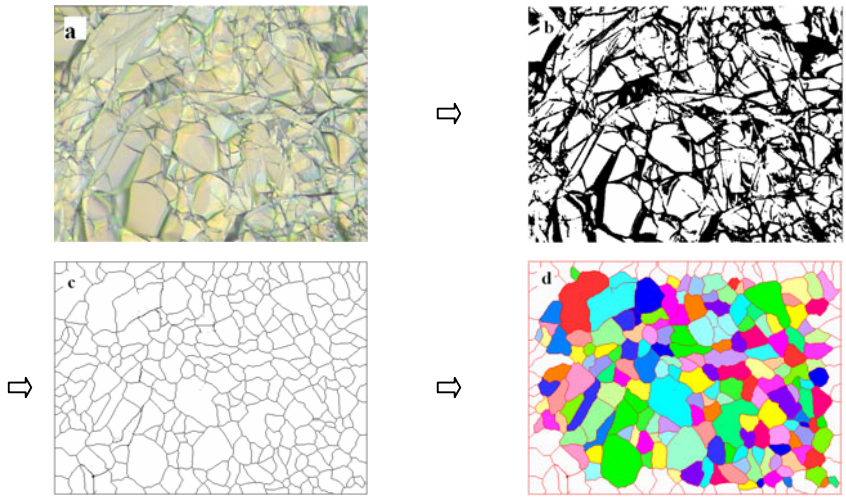

Fig 3-3 Procedure images of grain-size analysis（a original image ; b threshold division ; c crystal boundary reconstruction ;d Rating (area method)

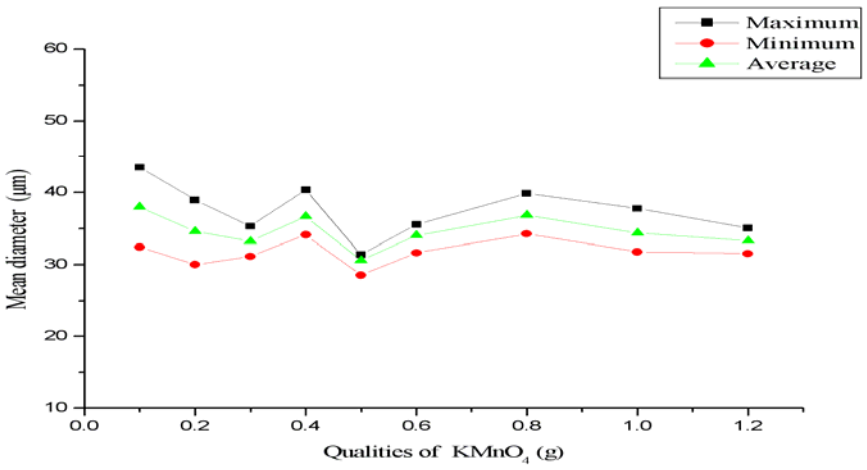

Fig 3-4. The mean diameter of expanded graphite (32 mesh)

In Fig 3-3, procedures of grain-size analysis were listed and mean diameter of expanded graphite was shown in Fig 3-4. As shown in image, the mean diameter of expanded graphite is different but steady between 30～45μm. To analyses Fig3-1, the mean diameter is about 30μm so this shows that mean diameter can not be influenced by mesh of natural graphite and qualities of $KMnO_4$.

In Fig 3-5, the mean diameter of different expanded graphite expanded at different temperature is compared. Although volume of expanded graphite increase with temperature increased, grain size do not change obviously, between 30～40μm. Grain size can not influence by expansion temperature.

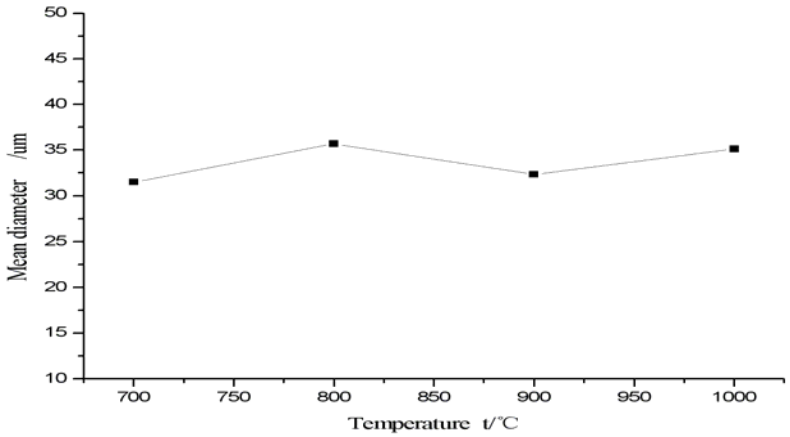

Fig 3-5. The mean diameter of the expanded graphite under different temperature

3.2 Single compressed worm observed by SEM

In order to prove the image like the metal metallurgical structure was not find by accident, SEM was

used to investigate the same sample and the images were shown in Fig.3-6.

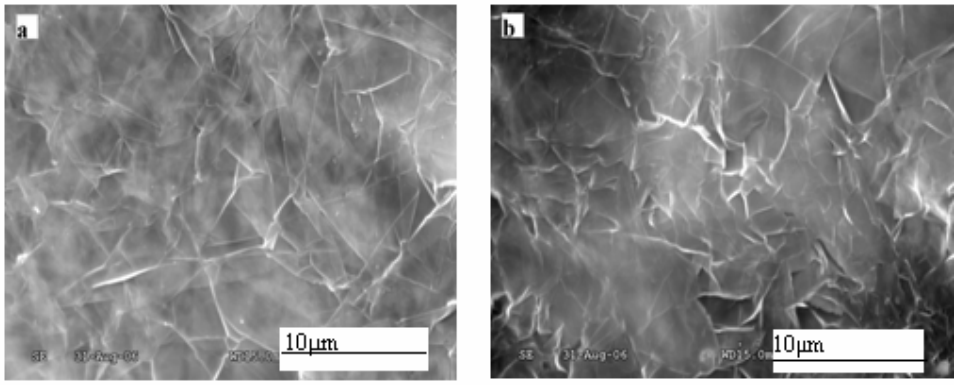

Fig 3-6. SEM photos of compressed expanded graphite（a　4000×；b　5000×）

As show in the images, metallurgical metallic structure is seen, grain boundary is clear and the particle size is nonuniform so result is analogous to that obtained by Metallurgical Microscope. Mean diameter is obtained by lineation method, only 4um, which is not accord with that get by the Metalloscope. The explanation is that there is substructure inside particles but resolution of Metalloscope is at a low level so it can not see this substructure. It is very interesting, as we know, many alloys have substructure. Now the exact mean of substructure and grain boundary is not clear so XRD was used to do further analysis.

3.3 Single compressed worm observed by XRD

In this article, XRD was used to study texture of expanded graphite and orientation of expanded graphite pressed by different force.

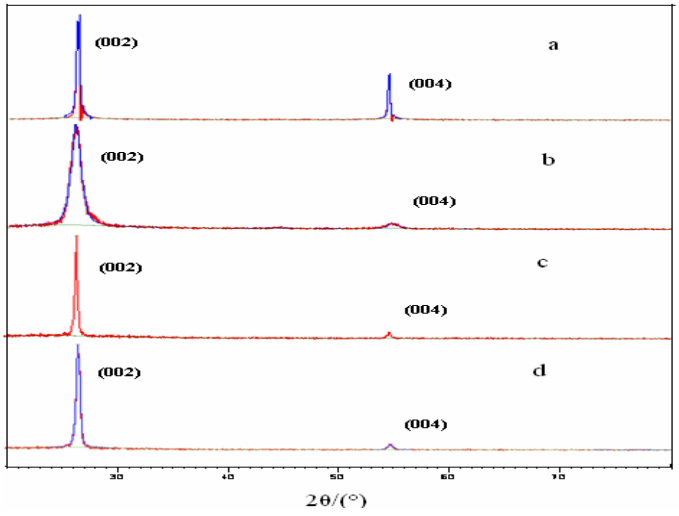

Fig 3-7. XRD patterns(a Flake graphite, b Graphite oxide, c Expanded graphite compressed by 5MP, d Expanded graphite compressed by 10MP)

XRD patterns of flake graphite, graphite oxide and compressed expanded graphite pressed by different

force, 5MP and 10MP, respectively, are compared in Fig3-7.As shown Fig3-7 a, the pattern of flake graphite is accord with the standard one. For graphite oxide in Fig3-7 b, the 002 diffraction profile become broader and relative intensity of 004 profile decreases, except for these 101 profile appears at 43° in 2θ. These may cause by intercalates in graphite oxide flakes become random orientation. After press, 101 profile disappears but 002 profile does not change and this indicates that compressed expanded graphite also has graphite structure. The profiles are coincident with profiles of expanded graphite worms. All of this proves that in press process it will not produce crystal but only crystals orientate again.

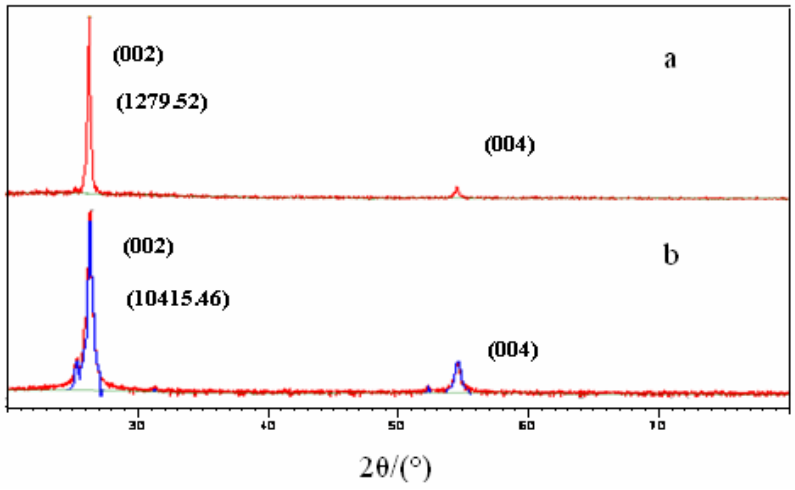

Fig 3-8. XRD patterns of expanded graphite compressed by different methods

In Fig3-8a, XRD pattern of expanded graphite pressed with single worm is shown and Fig3-8b is pressed with many worms. In order to compare with each other, the same force was used. Two patterns indicate 002 profile and 004 profile have the same position but CPS data show that in Fig3-8b, 002 and 004 profiles are stronger than that in Fig3-8a and this is because the amount of worms increase in the latter method so the particles which precipitate in diffraction also increase and that cause the peak become more obvious. In Fig3-9b, a small peak appears at 52° in 2θ,102 diffraction profile, and this may caused by interaction between worms in press process.

In additional, in the present work, 50mesh and 100mesh were also observed, and changes of expanded graphite were analyzed by parameters, ratio of peak and background and orientation index. In the industry production, the latter press method was used. Because many expanded graphite worms overlay with each other we can not see clear boundaries between particles by Metalloscope this may be the reason why no one can obtain clear Metalloscope images by far.

3.3.1 Grain size

L_a and L_c are structure parameters derived from X-ray diffraction which are used to differentiate two directions, parallel and perpendicular to the hexagonal. The crystallite size L_c can be calculated from the full width at the half maximum intensity β of each line by Scherrer's equation [6],

$$L_{hkl}=K\lambda/\beta\cos\theta \qquad (1)$$

Where λ=0.15406nm is the wavelength of X-ray used, K=0.94 is a constant and θ is the diffraction angle of the line. The results are listed in Tab2.

Tab2. Lc data of different meshes expanded graphite

	Expanded Graphite of 32 Item	**Expanded Graphite of 50 Item**	**Expanded Graphite of 100 Item**
Pressure 5Mp	53.4 nm	51.3 nm	79.2 nm
Pressure 10Mp	32.9 nm	54.8 nm	73.5 nm

With the mesh of graphite changes, Lc changes obviously. The flake graphite has typical layered structure and L_c is larger than L_a. As we know, the measurement range of X-ray diffraction is 0～100 nm, Lc has approach to the limitation so XRD can not used to calculate La. With the fact the ratio between La to Lc is 60～80, we suppose the ratio of La：Lc=100 then we can obtain La is about 3～8μm so it is coincident with result obtained by SEM.

3.3.2 AFM images of expanded graphite

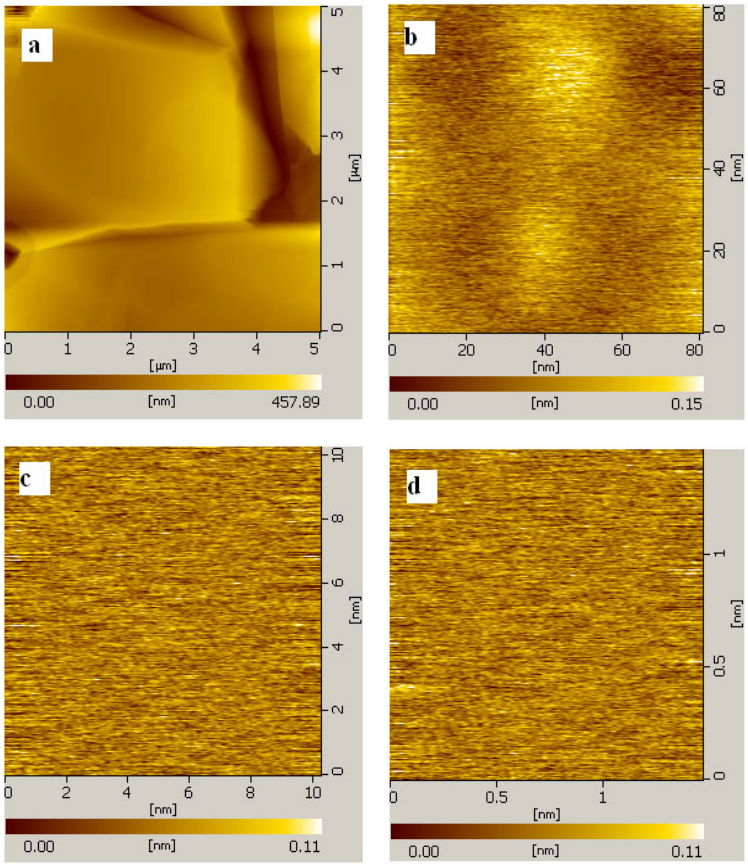

Fig 3-9. AFM scanning images of expanded graphite：（a 600nm×600nm ； b 80nm×80nm ； c 10nm×10nm ； d 1.5nm×1.5nm.）

AFM scanning images of expanded graphite with different resolution are shown in Fig3-9. Scanner area become smaller and smaller from a～d, the most smooth location was chose to magnify. Scanner area of Fig3-9a is 5μm, according to the size of substructure, the appearance of deep trenches is the main trait at this level of resolution but we have not known its exact mean and need further investigation. Avoid the defect then we magnify the image, as shown in Fig3-9d, the surface is so smooth that we think this is the perfect atom surface because artificial surface is not so smooth. But unluckily, for the instrument is not steady we did not get images of atom as clear as HOPG.

3.3.3 Ratio of peak and background and Orientation index

Ratio of peak and background, X, is a parameter which respect the probability of atoms at one location, the larger of the ratio, the better of atom regularity. The ratio of 004 profile at different conditions is calculated by the following equation,

$$X（\%）=100\times(P/p)_{sample}/(P/p)_{std} \quad (2)$$

Where P is height of profile peak and p is height of profile background, in additional, flake graphite was chose as the standard, results were listed in Tab3.

Tab3 The ratio of peak and background of graphite oxide and expanded graphite

	Graphite Oxide	**Expanded Graphite Compressed by 5MP**	**Expanded Graphite Compressed by 10MP**
Ratio of peak and background（%）	0.639	0.769	1.011

As shown by the data in Tab.3, the ratio of graphite oxide is smaller than others, as the force increase, the regularity of atoms increase and the orientation of the flake become more obvious.

Orientation index is also a common parameter derived from XRD, which means the amount of oriented flake according to the testing surface and $\rho > 1$ means flake graphite has a good orientation. The orientation index of 002 diffraction profile was calculated by the following equation,

$$\rho_{hkl}=（I_{hkl}/\Sigma I_{hkl}）/（I^{0}_{hkl}/\Sigma I^{0}_{hkl}） \quad (3)$$

Where I_{hkl} is relative intensity of one profile, $\sum I_{hkl}$ is relative intensity of all profiles, I^{0}_{hkl} and $\sum I^{0}_{hkl}$ is relative intensity of sample profiles, respectively. As shown in Tab.4, the compressed expanded graphite has a good orientation.

Tab 4. The orientation index of different item expanded graphite

Orientation Index	32 Item	50 Item	100 Item
5（MP）	1.52	1.50	1.58
10（MP）	1.41	1.57	1.55

4 Conclusions

(1) When studied the structure of expanded graphite by Metallurgical Microscope, a metallurgical metallic structure was observed, to analyze mean grain size with the granularity analyze software and results suggested that the mean grain size could not be influenced by original types and expansion process, the mean diameter was about 30～45μm. The real grain size obtained by XRD is La3～8μm. All of this proved the investigation of SEM was right and there was substructure inside the particles.

(2) Parameters ratio of peak and background and orientation index derived from XRD were used to evaluate the orientation degree of flake and observed the degree of orientation become higher with the press increase.

(3) Images of compressed expanded graphite on the atomic scale were obtained by AFM.

References

[1] Anabel Lopez-Macipe,Jaime Gomez-Morales.Nanosized hydroxyapatite precipitation from homogeneous Calcium/Citrate/Phosphate solutions using microwave and conventional heating[J].Advanced Materials,1998,1:49-53.

[2] GAO Lin, GONG Yin-xiang, MA Ling. Effect of expansion time on the microstructure of an expanded natural flake graphite[J]. New carbon materials,2006,21(2):139-143.)

[3] LI Yi-hui, LIU Shu-feng.The study of pore structure and adsorption ability of expanded graphite[J]. Non-Metallic Mines,2004,27(4):44-45.

[4] Michio INAGAKI, Tomoya NAGATA, Taisuke SUWA, et al. Sorption kinetics of various oils onto exfoliated graphite[J].New carbon materials,2006,21(2):97-101.

[5] Michio Inagaki,Kang Fei-yu.Carbon Meterials Science and Engineering[M].Bei Jing:Tsinghua University Press,2006.113-117.

[6] QIU Ying-hua, WANG Tong-hua, SONG Cheng-wen, et al. The influence of pyrolysis atmosphere on the microstructure of a carbon membrane produced from polyacrylonitrile[J].New carbon materials,2006,21(2):162-163.

[7] SHEN Wan-ci, WEN Shi-zhu, CAO Nai-zhen, et al. Expanded Graphite A New Kind of Biomedical Material[J].Carbon,1999,37:351-358.

[8] Wu Gang. Token and application token of material structure[M]. Bei Jing: Chemical industry press,2002.