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Percolation Evolution and Characteristics in the Formation Process of Pores for Porous Graphite†

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The micro-pore structure and distribution of graphite during the forming process of pores in roasting is developed and the evolution process from a local connection to infinite connectivity of pores is analyzed by percolation theory. The percolation characteristics of micro-structural images are analyzed based on the renormalization group method and the micro-pore structure is measured by mercury injection test. The analysis and experimental results show that the nature of the forming process of pores in roasting is the percolation evolution process from local area and finite clusters to global material and infinite clusters.The area porosity of graphite samples for filtration ranges from 0.541 to 0.588 and the volume porosity ranges from 0.297 to 0.403, which are greater than the threshold and have percolation structure. On the other hand, the area porosity of graphite samples for impregnation ranges from 0.189 to 0.314 and the volume porosity ranges from 0.107 to 0.155, which are smaller than the threshold and have no percolation structure.

Keywords: Porous graphite, Percolation theory, Percolation threshold, Renormalization group.

INTRODUCTION

The graphite materials have the advantages of self-lubrication, stable chemical properties and low expansion rate, while they contain 20-40 % micro-pores, which can reduce its hardness, intensity and other mechanical capacities[1]. There are two commonly used methods for graphite material modification: one is the impregnation technique, through which the pores are filled and the materials are compacted to increase the physical properties of the materials the other one is optimization of the pore structure of the materials and changing its size and distribution, so as to prepare the porous graphite with good connectivity to be applied to filtration and adsorption process. The industry practices have proved that roasting process has the greatest influence on the distribution of the pore structure, which will in turn impact the consequent impregnation and infiltration processes. The pore structure of a well roasted graphite product is rationally distributed and has good long distance connection, which can form the networks running through the materials leading to high quality of impregnation and filtration results. On the contrary, the pore structure of the poor roasted graphite products is irrationally distributed and has inferior long distance connection, which cannot create the mutually connected networks, thus creating a lot of lonely holes. Therefore, it tends to not impregnated in the impregnation process and to be blocked in the infiltration process.

Roasting is the heat treatment on the compression molded green body of graphite under the condition of air-isolation. It enables the asphalt binder to flow when heated and discharge volatiles after pyrolysis and poly-condensation reaction. Then the coking materials will solidify and finally create firm skeletons. The roasting processes involve the heat and mass transfer in the porous media, accompanied with physical changes and chemical reactions. The complexity and the multi-factor combined effects have prevented the researchers from conducting a comprehensive study on the roasting process of the graphite. Teganowa and Litego[2] have studied the temperature gradient of every phase and stress variation on the blanks and has plotted out the curves of the radical and tangential stress in the roasting, setting a good guidance for the roasting system of large size (diameter > 600 mm) blanks. After studying the pyrolytic condensation and rheological properties of the coal tar pitch by TGA and DTG, Xu and Li[3] proposed the variation rules of viscosity of the asphalt vs. temperature. The above mentioned researches only studied the change of a single parameter in roasting, not the combination of changes of the blanks

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in roasting on the whole. Liu *et al.*[4] studied the influences of roasting system on the properties of the graphite products and compared the influence rules of different roasting temperature, roasting time and pressure on various parameters. Their study has considered the influence of the roasting process on the integral properties of the final products. However, the changes of pore structure in roasting process were neglected.

In this work, the heat and mass transportation in the pore forming process of the porous graphite was analyzed with heat and mass transfer theory from the perspective of porous media. Wang[5] proposed that the heat and mass were transferred in the saturated porous media and unsaturated porous media alternatively. By using the Whitaker volumetric average method[6,7], the continuity equation, momentum equation and energy equation for each phase were derived. Unfortunately, since the roasting of graphite must be conducted under high temperatures and closed environment, some key physical property parameters (such as the average density, diffusion coefficient, heat conductivity coefficient and relative permeability coefficient of the volatiles) are difficult to be determined through experiments. Moreover, there are no effective research results or experimental data available. Up to now, the equations from Whitaker volumetric average method could not be efficiently solved by numerical simulation, impeding the research on the pore forming process of graphite materials from the perspective of heat and mass transfer.

When studying the flow of fluids in network structures, Hammersley[8] proposed that the percolation theory can be applied to analyze the movement or diffusion of fluids in random media and stochastic system. One of its notable characteristics is that particular nature will undergo sudden changes when a parameter is increased to a certain threshold. That is to say the percolation theory focuses on the qualitative changes resulted from the changes of particular variable in the process, sparing the efforts to establish a complicated mathematical formula and its solution and offering a new idea for the research on random phenomenon. In the physics of amorphous solids, Zallen[9] listed many application ranges of the percolation theory. Later this theory was further promoted by numerous scholars, the theories of whom have been applied in such as physics, chemistry, environment, financial, social phenomena and many achievements were obtained[10-13]. By using the percolation theory andrade and Stanley[14,15] studied and reviewed free diffusion, anomalous diffusion, localized vibrations, fluid flow in porous media, connectivity of human behaviours and many other problems. Hunt[16,17] has researched on the seepage phenomenon in porous media using this theory and put up with the fractal expression of hydraulic conductivity. Yanuka *et al.*[18] established the geometrical and topological model in porous media by a three-dimensional joint pore size distribution, which is used to reconstruct the porous structure to analyze the volume-based pore size distribution. Their research findings are of great reference for studying the pore forming process in the roasting of graphite materials. From the perspective of fluid dynamics, the essence of the pore forming process in roasting for the porous graphite is the fluid (which means the volatiles) flow in porous media. With the qualitative changes of the materials brought by pore amount (porosity) (from disconnection to connection), the pores grow out of nothing. Moreover, the change from partial occupancy to infinite connection is the percolation evolution process of the pores in graphite.

EXPERIMENTAL

In order to study the structure evolution of the pore forming process in porous graphite, the green bodies of graphite samples were prepared. Then the samples were roasted and the samples of pore forming process in some key stages were obtained. The evolution process of the pore structure was observed through the micro metallographic. Finally, the percolation structures were analyzed by the measure experiments of pore structure and theoretical results. Coal char particles were used as raw materials. As shown in Table-1, the grain composition of the aggregate particles as follows: 200-400 mesh, 41-52 %; 400-600 mesh, 14-25 % and 600-800 mesh, 4-16 %. Medium temperature coal tar pitch was used as a binder. It was grounded and added to aggregate particles, with 18-32 wt % content. Then the aggregate particles and binder were mixed in a roller for 4 h. The mixtures were heated to 150-170 ºC and kept at the temperature for 1 h. They were kept at 35 MPa for 5 min.

The molding bodies with same specifications from one batch were placed into different calciners for roasting. In order to prevent oxidation of the bodies in the roasting process, the green bodies were placed in a special iron box and the remaining gap was fully filled with coal particles. Then the iron box was sealed and placed in the calciner. In the roasting process, small amount of air in the calciner was exhausted in the oxidation reaction with the peripheral coal particles in the box. So the roasting of the green bodies was completed in an anaerobic environment to avoid oxidation of the surface of the bodies. Fig. 1 shows the heating-up curve of the roasting. In order to study the structure variation at different stages, the calciners were powered off in sequence at different time. The samples were taken out after cooling down.

The surface treatment of the graphite samples is started from removing the coarse particulates on the surface by grinding wheel and sandpaper to get planar samples. Then the samples were polished by a polisher to remove the scratches and until they are polished to the mirror plane. Then the samples were cleaned with alcohol. Finally, the polished samples were put into glassware for corrosion with 4 % natal solution. Once the corrosion finished, the samples were washed

TABLE-1
FORMULAS OF THE AGGREGATE PARTICLES FOR SIX SAMPLES (wt %)

Composition	1#	2#	3#	4#	5#	6#
Particles A (200-400 mesh)	44	50	47	52	44	41
Particles B (400-600 mesh)	20	14	18	18	24	25
Particles C (600-800 mesh)	4	6	7	4	12	16
Pitch	32	30	28	26	20	18

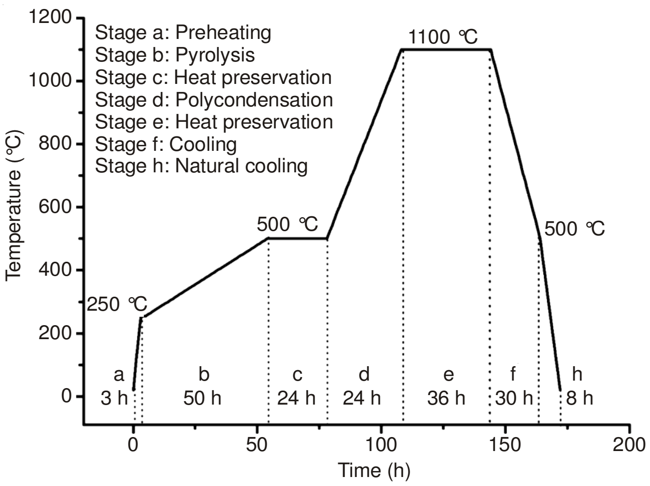


Fig. 1. Heating-up curve of roasting for green graphite body

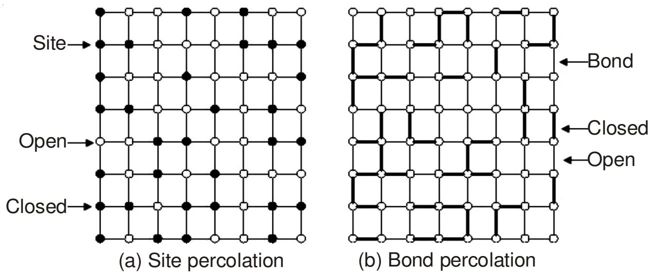


Fig. 2. Site percolation (a) and bond percolation (b) in a square lattice. (Open circles and solid circles represent open sites and closed sites, respectively. Bold solid line and thin solid line represent open channels and closed channels, respectively)

clean and put into a drying oven for drying. After the treatment, the metallic structures of the porous graphite ware obtained by a G51 metallographic microscope (Olympus Inc., Japan). Every sample has three mutually perpendicular planes and every surface is shot with three photos, with the magnification of 100, 200 and 500x, respectively.

The AutoPore IV 9520 automated mercury injection porosimeter (Micromeritics Inc., USA) was used to measure the pore structure. The maximum pressure is 60000psia (Pounds per square inch absolute, 1 psia = 6.896 kPa) and the measuring diameter range is 0.003-1000 μm. First, the sample was weighed and put into the sample tube. Then the sample tube was sealed with a thin layer of sealing resins and then put into the experimental device. The tube was vacuumized to 50μmHg and filled with mercury to increase the pressure for low pressure testing (< 50 Pisa). After the test completed, the mercury was backed out. The sample was weighed again. The step above are repeated to do a high pressure testing (< 60000 Pisa). With the tested data, the pore structure parameters were obtained through Win9500 data analysis software.

RESULTS AND DISCUSSION

Percolation theory: The percolation theory is known as an excellent tool in dealing with the irregular phenomenon and chaotic system in nature. Its outstanding characteristic is long-distance connectivity, a catastrophe or intense phase change in certain nature with the increase of connection degree or certain density, or occupation or concentration, which is presented as the sudden appearance or disappearance of certain behaviour on a macro level[16,19-21]. The basic types of percolation include bond percolation and site percolation.

Fig. 2b shows that the connection of the two crossover points in a two-dimensional square grid is called "bond". Taking the assumption that some of the bonds are connected (open) and some are not (close), the bond percolation studies whether the fluids can circulate from one end to another end in the grid. On the other hand, assume there is connection between two points in the grid and consider whether each point is occupied or not: if occupied, this point is thought to be on smooth; and if not (blocked), the study of whether there is circulated percolation channel from one end to the other end in the grid is called site percolation. The critical value of whether the surface characteristics will change is called the percolation threshold. When the probability of a single parameter reaches to the percolation threshold, there is a sudden change in the nature with the limited clusters to the unlimited ones in the lattice.

Percolation evolution in forming process of the pores: Fig. 3 shows the microscopic images of the body which are not roasted after compression moulding. Figure showed that the distribution of the aggregate particles is relatively uniform and there is no cluster of large size particles. The distribution of the binder is sound, the aggregate particles are primarily wrapped by the binder and there is a continuous phase in the binder. Because the aggregate particles have no flow ability, the volatile matter can only flow along the pore between the particles, which are similar to the bonds in bond percolation. If the volatile matter can overcome the stress among the pores and flow through local pores, it indicates that the bond connections are smooth; if it cannot flow through the pores between particulars, it indicates that the bonds in the limited clusters are blocked. Therefore, the perfect graphite blank moulding is as showed in Fig. 3c. Moreover, it is more reasonable to study the percolation evolution through the bond percolation model.

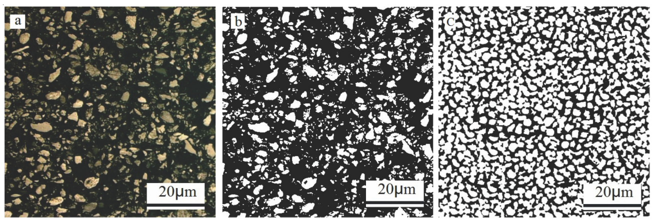


Fig. 3. Images of a green body after compression moulding. The particles are white and the asphalt adhesive is black; Fig. 3b is the binarization image by Photoshop and Fig. 3c is an ideal model of bond percolation for porous graphite

Fig. 4 shows the microstructure image of the pores for the finished products after roasting. The pores are clear in outline and the aggregate particles are excellent in the solidification of asphalt coking materials. Intuitively, the pore distribution in the black area is rather rational with no particular thick and large particles but good connection, basically forming the mutually connected network structure and finally constituting the unlimited percolation clusters. In fact, the percolation clusters do not include all the capillary pores contained in the

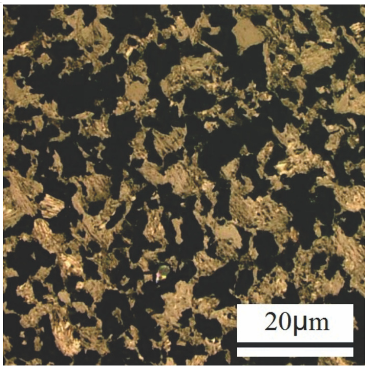


Fig. 4. Micro-structure of porous graphite after roasting process according to the heating-up curve of roasting in

blanks, which are called "lonely holes or dead holes". There are two reasons. Firstly, in the roasting process, although the volatile matter with a poor connection can be discharged once heated, these open small size pores in the heating stage may close again in the cooling stage, for the volatile channel is circuitous on a small scale, so they may form isolated pores. Secondly, the partially connected small clusters do not connect with percolation clusters, so they do not belong to the part of percolation clusters. Many experiments have proved that in order to get a sound flowing and solidifying effect, the heating rate in the pyrolytic process (250-500 ºC) should be slowed down. 5 ºC/h is suitable and continued time should not be less than 24 h when it is at the highest temperature (500 ºC). The continued time should be 36 h in solidifying stage (1110 ºC) so as to ensure the excellent solidifying effect. In the cooling stage, the cooling rate can be slightly increased. When the temperature is reduced to 500 ºC, the natural cooling method could be adopted[5].

Fig. 5 shows the binarization images of the microstructure of porous graphite in every phase of roasting. When the temperature reaches 250 ºC, preheating is over and the phase of binder changes, wrapping most part of the aggregate particles. Then the pitch begins to flow and goes through the pyrolytic volatilization. From the figure, it could be observed that there is a greater reduction of aggregate particles (white) than the one before roasting (Fig.3b) and most of them are covered by the molten asphalt binders. In the pyrolytic volatilization stage (250-500 ºC), due to the continuous heat absorption and the significant increase of volatile matter energy, the volatiles permeate along the path that could be easiest permeated, which is always of irregularity and locality. Because the outside of the blanks is fast to absorb heat, so the energy needed to create the permeating channel is relatively smaller than the inside. Therefore, the pore channel is first formed outside the blanks and then the partially connected channel begins to form as is shown in Fig. 5b. When the temperature reaches 600 ºC after a long time heating, the pyrolytic process becomes slower and the volatile amount begins to reduce. Due to the delay of heat transfer, pyrolytic process is yet to complete and the poly-condensation reaction begins at the same time. Fig. 5c and 5d showed that in the later stage of the pyrolytic process, the relatively large pores appear, forming a large amount of partially connected pore clusters. However, for the poly-condensation reaction just begins, the aggregate particles expand when heated and the coking materials are yet to be solidified, blocking the partially connected pores clusters to form a connected blank within a long-range connective percolation cluster. Theoretically, the poly-condensation reaction finishes, but in the real experiment, the poly-condensation reaction is not finished because of the delay of heat transfer. So the solidifying effect is not ideal. Therefore, when the samples are continued to be heated to 1100 ºC (Fig. 5e) and undergone coking under high temperature, the poly-condensation effect of the aggregate particles is relatively obvious. Under the wrapping and poly-condensation of binders, the surrounding area with the large size aggregate particles as the centre began to poly-condense to a whole part and the prototype of the skeleton begins to appear. During this time, the pore structure is forming the unlimited percolation cluster. Fig. 5f shows the microstructure of porous graphite for the finished products after complete roasting process. The aggregate particles have solidified to a relatively strong skeleton with a clear outline. The network structure goes through the whole blank to form an unlimited percolation cluster.

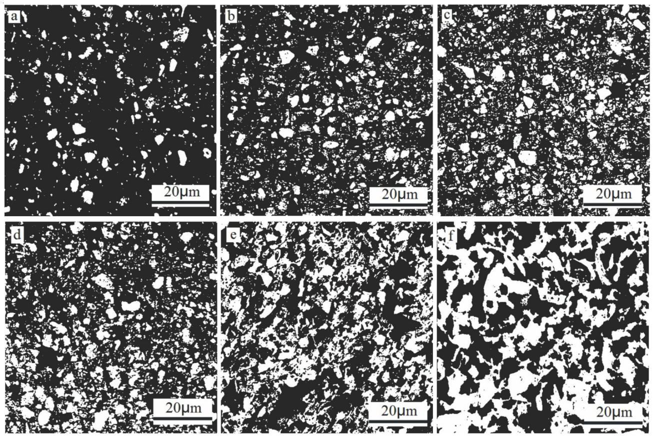


Fig. 5. Binarization images of pore structure during different stage in roasting process. The particles and skeleton are white and the adhesive and holes are black. 5(a) is the microstructure of graphite at 250 ºC; 5(b) is the micro-structure of graphite at 500 ºC; 5(c) is the micro-structure at 600 ºC; 5(d) is the micro-structure at 800 ºC; 5(e) is the micro-structure at 1100 ºC; 5(f) is the micro-structure of graphite after finishing roasting process according to the heating-up curve in Fig. 1

Analysis on the percolation characteristics of the pore structure in porous graphite: Wilson[22] and Uwe[23] first applied the renormalization group theory to the critical phase transition and suggested that the correlation length at the critical point of the percolation model goes to infinity and the whole system is of scale invariance. The system should be reconstructed and be observed with the scaling up (reduce the resolution) process. The relations between the parameters before and after the reconstruction are found and the relevant information around the critical point is obtained. The renormalization group method plays a great role in studying the fields of rock failure, material damage and the permeability of asphalt[24,25]. By establishing the fractal and percolation model in the course of rock destruction, Liang and Tang[26] discovered that the fracture process changes from the random distribution to orderly concentrated one. Moreover, the destruction clusters evolve from partially small amounts to the large mutually connected clusters through researching on the fractal and percolation characteristics of gradually damaged rocks.

Take the two dimensional lattice percolations as an example. Assuming there is an 8 × 8 lattice, renormalize the 2 × 2 lattice as a single grid of the cell. When there are three grids occupied (1) in four grids, the new grid is deemed to be occupied (1), which is of connectivity. Then a 4 × 4 lattice is obtained. Continue to renormalize the cell through 2 × 2 lattice until it is renormalized into one grid. If there is a cluster running through one end to the other end of the cell, then the renormalized grid is the occupied grid with percolation channel connected (Fig. 6).

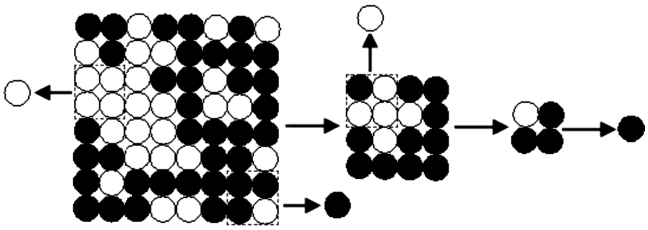


Fig. 6. Schematic diagram of renormalization group for two-dimensional lattice

Based on the percolation theory, the flowing process of fluids in the porous media is actually the process of the fluids to occupy the pore spaces. The key factor in this process is the space distribution of the pores, or depending on the probability of the pores in the lattice model. Zhou and Xie[27] proposed that with regard to the porous media, no matter how complicated the pore structure is, it could always be transformed to the accumulation network model through renormalization group process; and the percolation probability of two-dimensional lattice based on the twice the scale is:

$$P = p_0^4 - 4p_0^3(1 - p_0) \quad (1)$$

where p_0 is the probability of the pores in the lattice model. The percolation probability of 3 × 3 lattice derived by Trucotte[28] is:

$$p_{3\times3} = p_0^9 - 6p_0^8 + 14p_0^7 - 9p_0^6 - 6p_0^5 + 4p_0^4 + 3p_0^3 \quad (2)$$

In fact, it is difficult to get the percolation threshold for most of the random structures. Table-1 shows a few percolation thresholds of the geometric structure which could be rigorously solved. For the porous carbon in the two-dimensional plane, the porous structure could be transformed into a two-dimensional lattice. In this way, the study of the two-dimensional porous structure of porous graphite can be transformed to the study of the percolation characteristics of its corresponding two-dimensional lattice.

From the perspective of computer graphics, all the graphics are stored and transferred in the form of the matrix and the essence of the graphic treatment is the processing of the corresponding matrix. Therefore, the analysis and processing of the micrographics of the porous graphite should be transformed to the analysis and processing of their corresponding matrix. Firstly, the analysis area with the pixel as a unit is selected to be read by Photoshop. The micrographics are converted to black-white graphics with the white skeleton and black pores by the binarization method. Secondly, the program is developed to calculate the thresholds and transform the black-white value graphics into two-dimensional lattice into 0, 1, with the white grid as 0 and black grid as 1. The cells are renormalized in 2 × 2 lattice by Matlab programming until it gets the renormalization results.

In order to analyze the percolation characteristics by renormalization group method, 6 samples of different formulas are selected. First, the renormalization results are obtained by aforementioned method; second, the area porosity of each sample can be solved through Matlab programming. The renormalization results can be testified by comparing with the percolation thresholds of the square; and whether the two-dimensional section of the porous media is of percolation structure can be analyzed. Through mercury injection test, the volume porosity of each sample is tested. Comparing with the percolation thresholds of the simple cubes in classic geometry (Table-2), whether the three-dimensional cube of the porous structure is of percolation structure can be analyzed and the results are shown in Table-3.

TABLE-2
PERCOLATION THRESHOLDS OF SOME TYPICAL STRUCTURES[9]

Lattice	Site percolation	Bond percolation
Square	0.594	0.500
Honeycomb	0.698	0.653
Triangle	0.500	0.347
Simple cube	0.311	0.249
Body-centered cubic	0.245	0.178
Face-centered cubic	0.198	0.119

It can be seen from Table-3 that the porosity of 1-4# samples is lower than the site percolation threshold of square, but larger than the bond percolation threshold, so the renormalization group result is 1. The analysis on the evolution

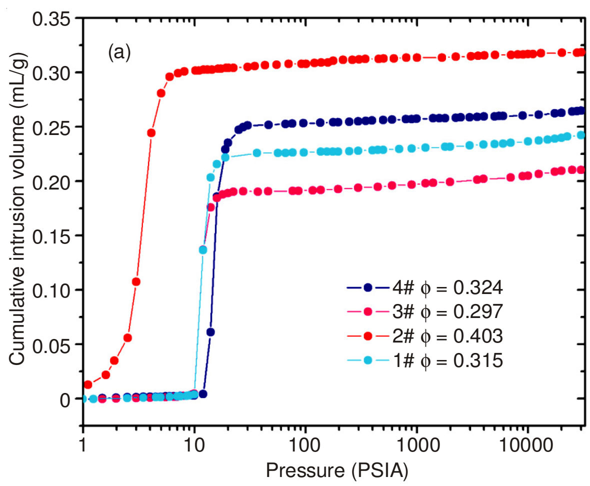
TABLE-3
RESULTS OF PERCOLATION ANALYSIS FOR GRAPHITE STRUCTURE

Samples No.	1#	2#	3#	4#	5#	6#
Analysis region (pixel)	512 × 512					
Area porosity	0.541	0.588	0.549	0.575	0.314	0.189
Average pore diameter (nm)	405.1	477.8	318.6	399.8	104.4	66.2
Threshold (square, site)	0.594					
Threshold (square, bond)	0.500					
Result of renormalization	1	1	1	1	0	0
Volume porosity	0.315	0.403	0.297	0.324	0.155	0.107
Threshold (cube, site)	0.311					
Threshold (cube, bond)	0.249					
Percolation structure	Yes	Yes	Yes	Yes	No	No

process of pores by the bond percolation model indicates that 1-4# samples are of percolation structure based on the two-dimensional sections. When compared with the volume porosity from the data of mercury injection test, the volume porosity of 1# and 4# samples are greater than the bond and site percolation thresholds of single cube. So it can be determined to be of percolation structure. Although the volume porosity of 2#,3# sample is a little less than the site percolation threshold, it is greater than the bond threshold obviously, which indicates that 1-4# samples have same percolation structures. Therefore the 1-4# samples have long-distance connective percolation structure. No matter from the perspective of area porosity or the volume porosity, the thresholds of 5-6# samples are lower than the bond (or the site) percolation and the renormalization group result is 0, indicating that 5-6# samples have no long-distance connective percolation structure. Pores just form the partially connected clusters and do not form the unlimited clusters.

Percolation characteristics of porous graphite in mercury injection test: The AutoPore IV9520 mercury injection porosimeter in combination with Win9500 mercury injection data analyzing software were used to do the mercury injection test and to analyze whether the samples have percolation structure. Fig. 7 clearly shows the percolation in the course of mercury injection. From the beginning of pressurization, it does not reach the certain value to break into the pores due to low pressure. With the intrusion volume around 0.002 mL/g, it can be considered that there is no intrusion. When the pressure reaches the certain threshold, the intrusion value suddenly increases. Among them, 1-4# samples are the porous media for filtration. When the pressures are 13.97, 5.91, 13.95 and18.96 Pisa, the cumulative intrusion volume will increase to 0.2031, 0.2966, 0.1857 and 0.2324 mL/g, respectively. At this time, the mercury in these pores forms the percolation network and the mercury volume increases a little with the increase of pressure subsequently. So the curve is rather flat; and even when it reaches the maximum pressure of 30000 Pisa, the increased values of cumulative intrusion volume are 0.0392, 0.0216, 0.0792 and 0.0353 mL/g, respectively. However, they are negligible compared to the general mercury volume.

The percolation theory can be used to better understand the curve of the cumulative intrusion volume *vs*. the changes of pressure, *i.e*., when the pressure does not reach the



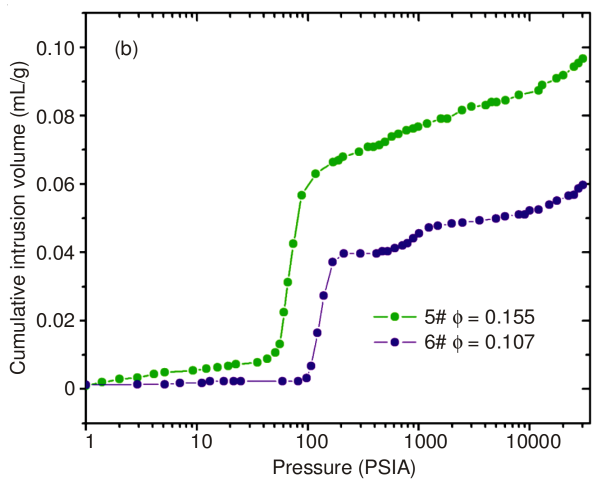


Fig. 7. Relationship between the pressure and the cumulative intrusion of sample 1#-6# with the volume porosities being 0.315, 0.403, 0.297, 0.324, 0.155 and 0.107, respectively. (1 psia = 6.896 kPa)

percolation threshold, the mercury is dotted less among the pores, not forming the mutually connected large clusters. When the pressure reaches the threshold (13.97, 5.91, 13.95, 18.96 Pisa for 1-4# samples), the mercury volume springs up; the mercury breaks through the obstruction of the pores, presenting the long-distance connection in the porous distribution and forms an unlimited network cluster with typical percolation characteristics. After the mercury forms the percolation clusters among the pores, the mercury volume does not increase even if the pressure is increased to the maximum value, for it has an unlimited connectivity. Due to the increased pressure, the new intruded mercury will push the mercury exited in the pores to flow out from the other end of the network, but the total mercury volume kept in pores generally remains unchanged, which proves that 1-4# samples are of percolation structure.

The 5-6# samples are porous media for impregnation. After comparing its cumulative intrusion volume-pressure relations with 1-4# samples, a common point is that all of them have pressure thresholds and the mercury volume is rather small below the thresholds. When the pressure reaches the threshold, the mercury volume will increase linearly. The differences are: (1) the mercury volume is obviously lower than the 1-4# samples with the maximum values for 5# and 6# of 0.0967 and 0.0597 mL/g, respectively; (2) the pressure threshold is rather high. The mercury volume of 5# sample surges from 0.0132 mL/g (pressure: 56.10 Pisa) to 0.0567 mL/g (pressure: 88.05 Pisa) and the mercury volume of 6# sample surges from 0.0165 mL/g (pressure: 122.14 Pisa) to 0.0397 mL/g (pressure: 211.07 Pisa), whose pressure threshold is greater than 1-4# samples. This could be attributed to the low porosity of the samples (the area porosity of 5# and 6# are 0.314 and 0.189, respectively), so the average pore diameter is low (104.4 nm for 5# and 66.2 nm for 6#); and in turn it needs more pressure to break through these porous obstruction.

For 5-6# samples, it continues to increase when the pressure reaches the threshold, while the mercury volume increases significantly without plat trend. This is due to the heterogeneous distribution and different diameters of the pores. So the porous structures of 5-6# samples are not connected and are of long-distance connective percolation structure, only partially forming the limited number of clusters. When the pressure continues to increase, the mercury is able to intrude smaller pores with larger resistance, while the mercury volume remains at a low level. Even when the pressure reaches the highest value, the cumulative intrusion volume does not reach 0.1 mL/g, which indicates that the mercury in the pores does not form a percolation distribution. 5-6 # samples are not of percolation structure, which is in consistent with the previous analysis. The bond and site percolation thresholds of the simple cube are 0.249 and 0.311, respectively; and the volume porosities of 5-6# are 0.155 and 0.107, respectively.

Although 5-6# samples are not of percolation structure, they still show some abrupt changes in the course of mercury injection, similar to the phenomenon of mercury injection test by Xie *et al.*[29] researches on the porous rocks. When the pore amount of certain diameter takes a significant proportion of the porous media, there will be a large amount of mercury entering the pores of these current pore diameters; once the pressure breaks into the resistance of this pore structure, the obvious abrupt changes are shown in mercury intrusion volume.

Conclusion

The forming process of pores in the porous graphite can be regarded as the flow of volatiles in porous media. In the roasting progress, the percolation evolution of the pore structure is "pores appearance-limited porous cluster-partially limited clusters-unlimited porous clusters-network structure". The porous structure of graphite can be characterized by the bond percolation model. The renormalization of the structural images indicates that the graphite structure for filtration is of the long-distance connection and the graphite structure for impregnation is not of the long-distance connection, for pores just form partially connected limited clusters.

Through the mercury injection test, the pressure thresholds and porous structure parameter of each sample were tested. The area porosity of graphite for filtration ranges from 0.541 to 0.588 and the volume porosity ranges from 0.297 to 0.403, which is of percolation structure. The area porosity of graphite for impregnation ranges from 0.189 to 0.314 and the volume porosity ranges from 0.107 to 0.155, which is not of the percolation structure. Consequently, the above results are consistent with the results of renormalization group method.

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