EFFECT OF GRANULAR COKE SPECIES ON THE COMPRESSIVE STRENGTH OF PITCH-BASED CARBON COMPOSITES

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Abstract

The pitch-based carbon composites (PCCs) that were reinforced by three kinds of coke particles such as metallurgical coke, pitch coke □ and pitch coke □ were prepared successfully under atmospheric environment using an ordinary hydraulic pressure machine by the new mould pressing and semi-carbonization shaping technology. The as-fabricated PCCs were treated in turn by way of quick baking, one-time densification and graphitization at 2373 K and three correspondent samples are achieved. The effect of the species of granular cokes on compressive strength of PCCs was studied in detail. Results show that the compressive strength of PCCs is closely related to the surface states, microstructure and compressive strength of coke particles. The higher compressive strength, the coarser surface and the more open pores of coke particles demonstrate more remarkable reinforcement to the composites. The PCCs can be achieved through three ways of baking, densification, and graphitization and the PCCs that are fabricated using metallurgical cokes as reinforcement possess the highest compressive strength during each process. Three correspondent strengths are 153.2MPa, 180.3MPa, and 83.5MPa. However, the three strengths of PCCs that are fabricated with pitch coke □ come next and they are 81.2MPa, 142.6MPa, and 76.9MPa. Last come the three strengths of PCCs that are obtained through pitch coke □ and they are 41.6MPa, 102.6MPa, and 38.6MPa.

Keywords: Carbon composites, Coal-tar pitch, Coke, Compressive strength.

Introduction

The pitch-based carbon composites(PCCs) that are reinforced by granular cokes exhibit high temperature resistance, abrasive resistance, chemical corrosion resistance and size stabilization besides their rich raw materials, simple molding process and low production cost , so that they are widely used in the fields of aeronautics, machinery and electricity, metallurgy, chemicals, atomic energy and so on. The coke particles take up 60～80wt% in the composition of the granular coke reinforced pitch-based carbon composites, so their performances influence greatly on the volume

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density and mechanical properties of pitch-based carbon composites. However, little has been reported so far on the research of influence of species of granular cokes as reinforcements over the mechanical properties of pitch-based carbon composites. An ordinary hydraulic machine instead of a hot isostatic pressing machine was used in this work to have prepared PCCs reinforced by coarser particles. The precursor materials were reasonably chosen. The economical and practical mould pressing and semi-carbonization shaping technology (MSCT) was adopted. The influence of species of granular cokes on the compressive strength of the pitch-based carbon composites was investigated.

Experimental

Raw materials

The particles as reinforcements were the smashed pitch coke □(LJ1) provided by Lanzhou Carbon Works, the smashed pitch coke □ (LJ2) made in Shanghai Baostell Group, and the ground metallurgical cokes (YJY) produced in Xi'an Coking Works. The matrix precursor (or adhesive asphalt) was coal-tar pitch made in Taiyuan Iron & Steel Group, and its softening point is 432 K. The particle size of granular cokes and coal-tar pitch consisted mainly of natural smashed particle size. That of the coke particles was smaller than 40 mesh and that of the coal-tar pitch smaller than 70 mesh.

Preparation techniques

Coal-tar pitch occupies 20～22wt% of the whole mixture during preparation. The mixture of coke particles and coal-tar pitch was put into a metal mould at room temperature. An ordinary hydraulic machine and new MSCT technology were adopted to prepare PCCs at atmospheric environment. The pressure inside the mould was approximately 80MPa, and the terminal temperature was between 873 and 893 K. The composites was treated successively through baking (1223 K×2h), one-time densification (pitch impregnation—carbonization treatment), and high temperature graphitization (2373 K×2h). The preparation process of the pitch-based carbon composites was described in details in figure 1.

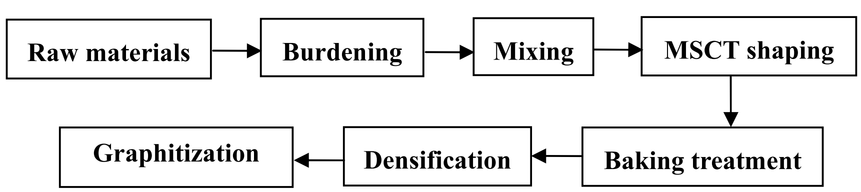


Figure 1. Preparation process of pitch-based carbon composites

For convenient discussion, the PCCs samples achieved through the treatment above are respectively named baked samples, densified samples, and graphitized samples. The former two samples can also be called carbonized samples. In addition, the PCCs manufactured by way of pitch coke Ⅰ, pitch coke Ⅱ, and metallurgical coke are respectively called LJ1 carbon samples (LJ1 baked samples, LJ1 densified samples, or LJ1 graphitized samples), LJ2 carbon samples, and YJY carbon samples.

Performance test

The prepared PCCs materials were machined into 10 (±0.04) mm×10 (±0.04) mm×10 (±0.04) mm cubic test samples. The volume—weight method (referring to GB1994.14 - 88 for test method) was adopted to measure and calculate the volume density. Then the compressive strength was measured under a ZD10/90 typed electronic universal machine (referring to GB1994.8 - 88 for test method, the loading direction is parallel to the orientation of the mould pressure). Five samples of the same type were processed and measured and the result was the average value.

Microstructure observation

The fracture surface of the selected RCCs sample was observed and analyzed under a HITACHI S-570 scanning electron microscope.

Results and discussion

Figure 2 shows the influence tendency of reinforcement species on compressive strength of the PCCs samples by way of baking, densification and graphitization.

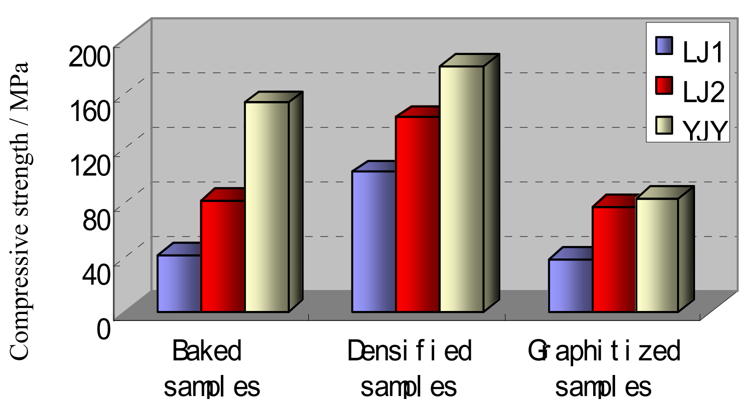


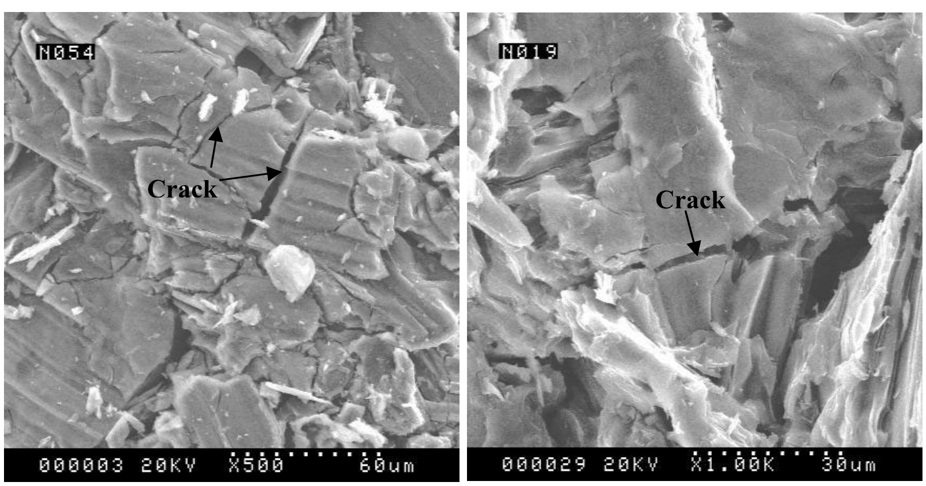
Figure 2. Effect of coke species on the compressive strength of PCCs materials

Compressive strength of carbonized samples

Figure 2 shows that no matter how the PCCs composites are baked samples or densified samples, the carbonized samples made from metallurgical cokes possess the highest compressive strengths. They are 153.2MPa and 180.3MPa. The strengths of the samples made from pitch coke Ⅱ come next and they are 81.2MPa and 142.6MPa. Those of the samples made from pitch coke □ are the lowest and they are 41.6MPa and 102.6MPa.

Among the three kinds of coke particles as reinforcements, the compressive strength coefficient of metallurgical cokes is the highest. Therefore, the density of the composites made from metallurgical cokes is the lowest, but they still exhibit the highest compressive strength. The compressive strength coefficient of pitch coke □ is the lowest, so the reinforced particles in the composites are easily broken under pressure. Besides, the surface of the particles of pitch coke □is even and there are few pores defects, so that its capacity of absorbing or storing adhesive pitch is poorer than that of pitch coke □. Thus, the interface bonding between adhesive pitch carbon and reinforced coke particles is poor after carbonization. That's why the composites made from pitch coke □ possess the highest density, but they exhibit the lowest compressive strengths. The compressive strengths of different carbon samples have much to do with the microstructure of reinforced coke particles and compressive strength coefficient besides with the density.

Figures 3, 4, 5 and 6 show, respectively, SEM images of the compressive fracture surface of PCCs baked samples made from pitch coke □, pitch coke □ and metallurgical cokes. From the former three pictures, it can be seen that apparent crack defects appear in the fracture of the samples made from pitch coke □or pitch coke □. The length and width of the cracks in the samples made from pitch coke □are larger than those in the samples made from pitch coke □. In contrast, fewer cracks appear in the compressive fracture surface of the samples made from metallurgical cokes as shown in figure 6. When the figure is amplified as shown in figure 7, cracks can be seen on the fracture. The cracks will accelerate the rupture of carbon samples, so the YJY carbon samples perform the best mechanical properties, LJ2 carbon samples come next, and LJ1 carbon samples rank the last.



(a) ×500 (b) ×1000

As for the PCCs baked samples containing pitch coke □, the crack defects can be seen from the fracture surface in figure 3. The bared reinforced granular cokes (RC) and binding agent carbon (BC) can also be seen clearly in the composites as shown in figure 4. On the fracture surface of PCCs baked samples with pitch coke □ and metallurgical cokes as shown in figure 5 and figure 6, it is hard to see the original coke particles in the composites because the binding agent carbon combines well with the reinforced cokes. Thus, when the total porosity of the coke particles as reinforcements is certain, the coarser surface, the more open pores of the coke particles and larger contact area between coke particles and adhesive pitch coke are more beneficial to the reinforcement of composites.

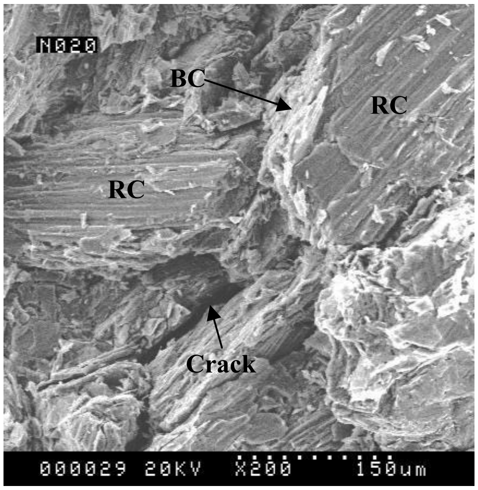


Figure 4. Micrograph of compressive fracture of carbon composites with pitch coke□

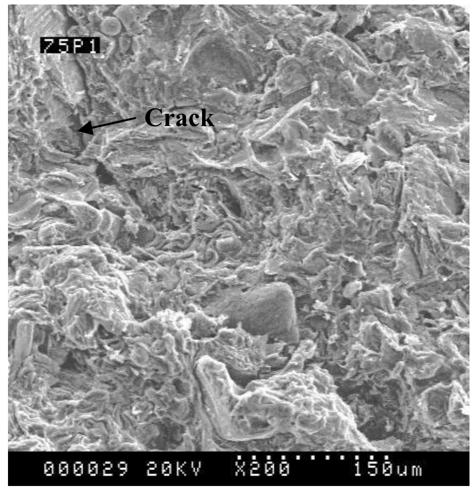


Figure 5. Micrograph of compressive fracture of carbon composites with pitch coke□

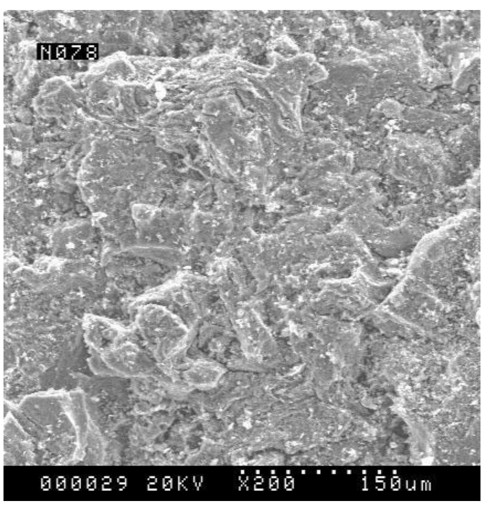


Figure 6. Micrograph of compressive fracture of carbon composites with metallurgical coke

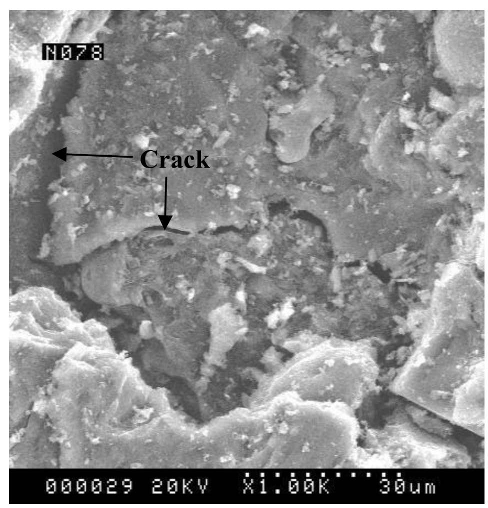


Figure 7. Micrograph of compressive fracture of carbon composites with metallurgical coke

Figure 2 also shows that all the mechanical properties of the three PCCs baked samples have improved remarkably after densification process. The compressive strength of LJ1 carbon samples even increases by 145%. This is because that cracks or pores to some extent exist in the baked samples prepared by MSCT process. After pitch impregnation–carbonization densification treatment, various defects that have been formed during the mould pressing and semi-carbonization shaping and baking process can be modified. Therefore, the densification treatment, particularly, the first densification process can improve the mechanical performances greatly.

Based on the test results above, we know that the compressive strength of metallurgical samples by way of MSCT technology is far beyond the lowest strength of various carbon blocks in accordance with the Chinese Criterion. Additionally, the metallurgical cokes are rich in resources and low in cost. It is of promising commercial prospect to use metallurgical cokes or part of them as reinforcements to prepare different pitch-based carbon composites such as corrosion resistance lining plates and carbon blocks of high-temperature furnace.

Compressive strength of graphitized samples

From figure 2, it can be seen that the mechanical properties of the PCCs reinforced by three coke particles are all declined apparently after graphitization process at 2373 K. Among the three graphite samples, PCCs composites reinforced by metallurgical cokes possess the highest compressive strength, about 83.46MPa (density1.69 g/cm3), those reinforced by pitch coke □ are of the second, approximately 76.85MPa (density1.84 g/cm3), and those reinforced by pitch coke □are of the last, 38.61MPa (density1.88 g/cm3). The compressive strength of carbon samples made from metallurgical cokes decreases most greatly after graphitization process, which is caused by the declining of density.

The graphitization degree of carbon materials is usually characterized with XRD. Generally, the smaller d_{002} of the layer distance, the stronger diffraction, and the narrower width of half-height are more beneficial to the higher graphitization degree. Consequently, the graphitization degree of graphite samples reinforced by three coke particles is measured by XRD method. The result is listed in Table 2.

Table 2. Test results of graphitization degrees of three graphitized samples

Species of graphitized samples	**Pitch coke□**	**Pitch coke□**	**Metallurgical coke**
Diffraction strength (Kcps)	14.25	5.30	4.64
Width of half height (°)	0.40	0.70	0.82
d_{002} (nm)	0.34103	0.34104	0.34082
2θ (°)	25.84	25.90	25.88

It can be seen from the table 2 that the graphitization degree of LJ1 sample is the highest and that of the LJ2 sample is almost the same as that of the YJY sample. The density of the LJ1 graphitized sample is the highest, but the compressive strength is the lowest. The density of the YJY graphitized sample is obviously lower than that of LJ2 graphitized sample, but the compressive strength is higher than the later. Under certain graphitization process, the mechanical properties of the graphitized samples are not only related to the graphitization degree, but to their density and original strength. The lower graphitization degree, the higher density, and the stronger original strength will lead to the better mechanical properties of the graphitized samples.

It can also be seen from figure 2 that under the same graphitization process , the variation tendency of the mechanical properties of the three graphitized samples made respectively from metallurgical cokes, pitch coke □ and pitch coke □is nearly the same as that of the compressive strength coefficient of the three reinforced particles. Therefore, we can say that the species of the reinforcement not only exert great influence on the mechanical performances of PCCs, but also have some inheritance in the strength of the reinforced particles in the composites.

Conclusion

(1) The species of reinforcement not only influence greatly on the mechanical properties of PCCs, but inherit their original strength to some extent. No matter how the composites are made through baking, densification or graphitization, those made from metallurgical cokes are of the highest strengths, which are 153.2MPa, 180.3MPa, and 83.5MPa, respectively. The strengths of those made from pitch coke □ come next, which are 81.2MPa, 142.6MPa, and 76.9MPa, respectively. And the strengths of those made from pitch coke □are the lowest, which are 41.6MPa, 102.6MPa, and 38.6MPa, respectively.

(2) Under the circumstances of the same preparation techniques and the same raw materials, the compressive strength of different PCCs is not only related to the volume density and densification process, but closely related to the compressive strength, microstructure, and surface state of the granular cokes. The higher compressive strength, the rougher surface, and the more pores of the granular cokes will reinforce obviously the pitch-based carbon composites.

(3) Under the same graphitization process, the mechanical properties of different graphitized samples are not only by affected the graphitization degree, but by the volume density and the original strength of the graphitized samples. The lower graphitization degree, the higher volume density and higher original strength are beneficial to the improvement of the mechanical properties.

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