THE EFFECT OF BORON ADDITIVES UPON THE PROPERTIES OF CARBON FIBERS

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Introduction

The attractive mechanical and physical properties of carbon fibers and its applications at high temperatures are applied in aerospace, turbine structural components and the utility communities because of their light weight and high performances. They even possess specific strengths and moduli which are greater than other materials at elevated temperatures. However these applications of carbon fibers and C/C composites have been limited by carbon oxidation. the disadvantage of oxidation loss in air restricts their high temperature applications to those in vacuum or/and inert atmosphere. To protect from oxygen attack, the most commonly performed method is a SiC-coating. but the difference on thermal expansion coefficient between the SiO_2 layer on the SiC coating and the carbon substrate causes cracking of coating surface. to solve this problem, multi-layered coatings have been studied and it has been found that they can provide reliable oxidation protection. The problem is that once the coating barrier is destroyed, oxidation protection cannot be sustained. In this regard, oxidation inhibitors to protect the oxidative procedure have been studied. Addition of boron has been found to be one of the most effective solutions in reducing oxidation loss[1,2] C/C composites are protected through the addition of B_2O_3 , which melts at relatively low temperatures and flow to fill cracks in the matrix, providing a diffusion barrier in the composite.

The focus of this experiment was to study the influence of substitutionally doped boron in oxygen attacks, physical properties and mechanical behavior of typical pitch carbon fibers.

Experiment

sample preparation-The examined carbon fiber was based on ployacrylnitrile(PAN) based fiber and was carbonized at 1350℃, and its properties was summarized in Table I. The fibers were impregnated in boric oxide solution B_2O_3. After the impregnation, the fibers were dried and then heated at changed temperatures(1500℃, 1800℃, 2000℃, 2200℃, 2600℃ and 2800℃). On the other hands, six samples were prepared by different heating temperatures without B_2O_3 treatment.

TGA-Dupont Model 951 Thermogravimetric analyzer(TGA) was used to study the oxidation resistance of fibers in air. Fiber oxidation was conducted dynamically at temperatures ranging from 25℃ to 1000℃ with 40cc/min of gas flow rate.

XRD-Hi-Star Area detector of BRUKER AXX was used to examine the fiber crystallite parameters of interlayer spacing, d, and crystallite size, Lc

Mechanical tests-LLOYD LR 30K was used to examine the basic mechanical properties(tensile strength and modulus) of fibers

Results and discussion

Change in tensile strength and modulus of boron-doped and non-doped carbon fiber with increasing of HTT is shown in Table 1. it shows that there is a little change in tensile strength and modulus from 1500 to 2200℃HTT. However from above 2600℃ it shows dramatically decreasing of tensile strength and increasing of modulus. It is because tensile strength of carbon fiber heat treated above 2600℃ may due to the formation of large crystalline grains and destruction of carbon fibers, which allows easy crack propagation. Fig 3 and Table 2 show the influence of substitutional boron to improve the graphitization in carbon fiber above 2600℃ HTT. It is well known that carbon fiber can be doped substitutionally with boron by heating it with boron above 2500℃ [3]. In Fig 3 the oxidation resistance of boron-doped sample from 2600℃ to 2800℃shows slightly changed trends to that of non-doped sample. There is a liquid phase at 2350℃ in the carbon-boron system and it is considered that boron vaporized rather easily at such a high temperature and allowed boron to dope in carbon fiber substitutionally although remaining little boron oxide on carbon fiber surface to reduce oxidation.

Table 2 shows that non-boron-doped samples below 2200℃ HTT have almost same trends of oxidation resistance, which shows oxidation loss reveals that the influence of boron coating layer is more predominant factor than that of crystallization to reduce the active sites. The analysis of boron contents in each carbon fiber is not performed yet. However after the analysis, all the results will be clear.

Conclusion

The treatment of boron in carbon fibers below 2200℃ did not show the improvement of tensile strength and modulus except for the improvement of oxidation resistance. and B_2O_3 coating layer more contribute than that of crystallization of carbon fiber in terms of reducing the active sites from oxygen attacks. In cases of boron-doped carbon fiber above 2600℃, carbon fibers are doped substitutionally with boron, which accelerate the graphitization of carbon fibers and also being improved oxidation resistance.

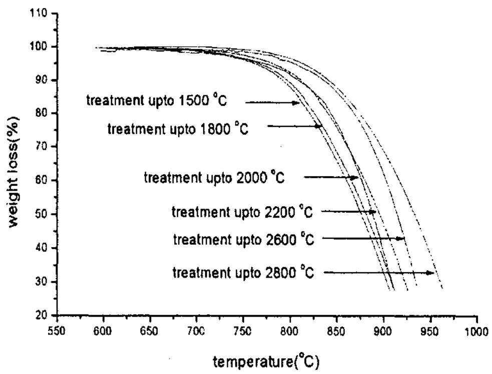

Fig 1. TGA diagram of boron-doped carbon fibers

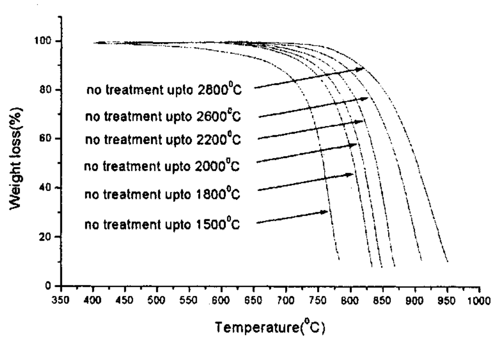

Fig 2. TGA diagram of non-boron-doped carbon fibers

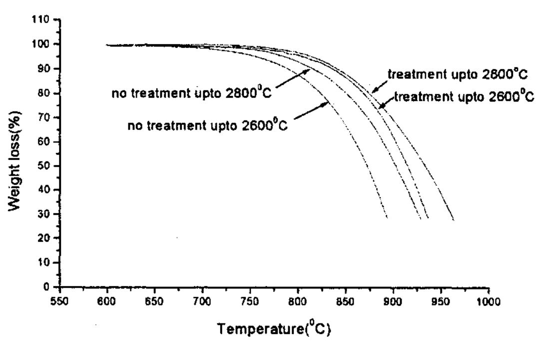

Fig 3. TGA diagram of comparison between boron-doped and non-boron doped carbon fibers

References

1. H. W. Huggins and C. H. Pitt, Ceram. Bull. **46**, 266 (1967)
2. E. Fitzer and D. Kehr, Thin Solid Films **39**, 55(1976)
3. Lowell C., J.Am. Cer. Soc. **50**, 142(1967)

Table 1. Physical properties of boron-doped carbon fibers and non-boron-doped carbon fibers (N/mm^2)

Sample		Boron-doped sample	Non-boron-doped sample
virgin	Strength	3438	
	Modulus	209915	
1500℃	Strength	3034	3032
	Modulus	216700	235552
1800℃	Strength	2879	3239
	Modulus	260576	260576
2000℃	Strength	3078	3170
	Modulus	274338	271825
2200℃	Strength	2718	3232
	Modulus	312131	292650
2600℃	Strength	2514	2689
	Modulus	300566	293878
2800℃	Strength	2368	2598
	Modulus	321275	298083

Table 2. d_{002} and Lc of boron-doped carbon fibers and non-boron-doped carbon fibers (Å)

Sample		Boron-doped	Non-boron-doped
virgin	d_{002}	3.583	
	Lc	36.77	
1500℃	d_{002}	3.470	3.531
	Lc	54.00	54.22
1800℃	d_{002}	3.462	3.491
	Lc	52.54	60.49
2000℃	d_{002}	3.448	3.455
	Lc	80.26	76.69
2200℃	d_{002}	3.448	3.505
	Lc	93.96	88.92
2600℃	d_{002}	3.431	3.450
	Lc	135.4	101.2
2800℃	d_{002}	3.414	3.434
	Lc	140.5	104.9