

THERMAL STABILITY OF CARBON-CARBON COMPOSITES FILLED WITH MOLYBDENUM DISILICIDE

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Introduction

Carbon fiber-reinforced carbon matrix composites (carbon-carbon composites) are potentially useful materials in applications requiring strength and toughness, at high temperatures combined with low weight. Potential uses range from those in aircraft, hypersonic aerospace vehicles and the automotive industry, to biomedical and refractory applications. These composites retain their strength, modulus and mechanical properties to temperatures higher than those tolerated by other materials [1,2].

Strong covalent bonding gives a low carbon atom diffusibility which, combined with the highly anisotropic graphite crystal structure, suggests exceptional creep resistance for graphitic carbons. However, the rapid reaction of carbon with oxygen at temperatures as low as 500°C causes rapid degradation of the composites and thus effective thermal stability for carbon-carbon composites at temperatures of 1000°C and above must be developed. However, no such study is available on the carbon-carbon composites based on thermosetting resin matrix mixed by suitable filler, resulting in increasing the thermal stability of carbon-carbon composites at high temperature [3].

The objective of the present work is to provide an understanding of the effects of inorganic fillers on the thermal stability of the carbon-carbon composites with and without addition of molybdenum disilicide (MoSi_2) powders in the matrix, and describes the changes in these properties resulting from graphitization of the composites to 2300°C.

Experimental

Polyacrylonitrile (PAN) based high-strength carbon fibers (Taekwang Ind., TZ-307, 12K) were used in the filament fibers of which were no sizing and no surface

treatments. The resole type of phenolic resin (Kangnam Chem. Co.) was used as the matrix precursors of carbon-carbon composites to be studied. The MoSi_2 powders (<2 μm , supplied from Aldrich Co.) were used as oxidation inhibitors after pulverization by freezer/mill (Spexcertiprep Co., spex6700) in reduce their particle size (about 0.4 μm). Especially, these materials exhibit a brittle-to-ductile transition (BDT) in the vicinity of 900°C, and above this temperature shows significant metallic ductility [4]. So, we believe that this ductility makes important roles in improving the thermal stability, and in resulting the one liquid impregnation step without a catastrophic composite failure during graphitization. The composites were systematically prepared with MoSi_2 powders of 0, 4, 12 and 20wt% on the basis of resin matrix.

Composite laminates were obtained by the prepreg method. Individual prepreg was first made by uniformly mixing fibers and the phenolic resin of a controlled composition by a drum-winding machine. The green composites were prepared in a hot-press at 10.5MPa and 220°C for 120min as vacuum bagging method. After the curing of the resin, the laminates were subjected to the carbonization process at 1100°C at a heating rate of 10°C/hr and the graphitization process at 2300°C at a heating rate of 400°C/hr. The bulk fiber volume fraction of the composites was about 60% ($\pm 2\%$) for all composites.

The thermal stability of the carbon-carbon composites in air atmosphere was investigated by using TGA (Du Pont, TGA-2950) at a heating rate of 10°C/min.

Results and Discussion

Thermal stabilities given by initial decomposition temperature (IDT), the temperature of maximum rate of weight loss (T_{max}), and the integral procedural decomposition temperature (IPDT) show the increase according to the increasing concentration of MoSi_2 in carbon-carbon composites (Fig. 1, Tab. 1) [5].

Energy of activation for the decomposition of the carbon-carbon composites in air atmosphere was calculated from TGA curves by the integral method of Horowitz-Metzger according to the following equation [6]:

$$\ln[\ln(1-\alpha)^{-1}] = \frac{E\theta}{RT_s^2}$$

where α is the decomposed fraction, E the energy of activation, $\theta = T - T_s$, T_s the reference temperature at which dw/dt is maximum, and R is the gas constant.

The plots of $\ln[\ln(1-\alpha)^{-1}]$ vs. θ are shown in Fig. 2, and straight lines were obtained. From the slope of these lines, the activation energy (E) of decomposition was calculated. The activation energy ranges between 102-129 kJ/mol (Tab. 1) in carbonized composites.

As a result, the activation energy increases in increasing both the HTT and concentration of MoSi_2 . This result is explained by the fact that the addition of MoSi_2 in the composite system leads to the increase of the interfacial adhesion between fiber-filler-matrix, especially in the higher manufacturing temperature, which can be shown in BDT behavior.

References

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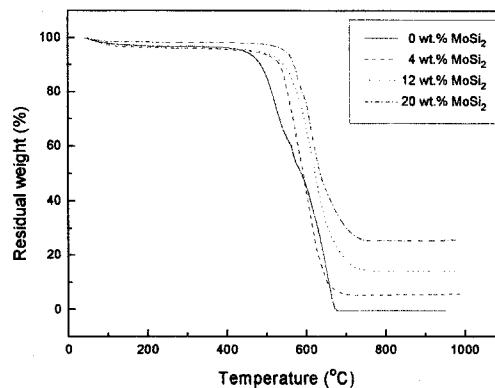


Figure 1. Thermogravimetric traces of carbon-carbon composites.

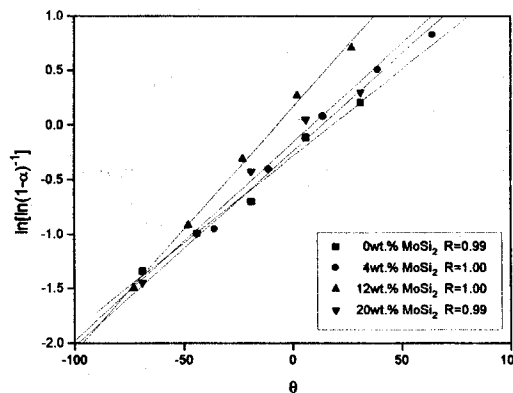


Figure 2. Plot of $\ln[\ln(1-\alpha)^{-1}]$ vs. θ for carbon-carbon composites.

Table 1. Effect of MoSi_2 on the thermal stabilities of the composites studied

Composites	Conc. of MoSi_2 (wt%)	IDT (°C)	T_{\max} (°C)	IPDT (°C)	Temp. range (°C)	E (kJ/mol)
Green Composites	0	324	569	539	500-600	94
	4	360	586	600	550-650	110
	12	376	623	720	550-650	119
	20	390	619	881	550-650	146
Carbonized Composites (HTT 1100 °C)	0	390	530	564	500-600	102
	4	410	600	638	550-650	106
	12	420	620	820	550-650	129
	20	480	630	951	600-700	147
Graphitized Composites (HTT 2300 °C)	0	480	739	702	650-750	144
	4	568	742	749	650-800	146
	12	588	768	940	650-800	167
	20	563	784	1147	650-800	170