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Thermal stability of carbon-MoSi$_2$-carbon composites by thermogravimetric analysis

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A thermal stability of carbon-carbon composites with increase of oxidation resistant filler, MoSi$_2$, have been studied by thermogravimetric analysis during the graphitization process. In this work, the initial decomposition temperature, temperature of maximum rate of weight loss, integral procedure decomposition temperature, and decomposition temperature range for the degradation temperatures, and the activation energy based on Horowitz-Metzger calculating method were characterized in a thermal stability study. It has been found that 12–20 wt% filler on the basis of the resin matrix leads to an improvement of degradation temperature and to an effectively increase of activation energy of the composites. This is probably due to the effect of the inherent MoSi$_2$ properties, resulted from a brittle-to-ductile transition for increasing the interfacial adhesion between fiber and matrix, and a mobile diffusion barrier formation against oxygen attack, in the vicinity of 900–1000°C.

1. Introduction

Carbon-carbon composites (C-C composites) are unique high temperature materials which can maintain their mechanical properties even above 2000 K in oxidizing environments. These composites are commonly made of a carbonaceous matrix reinforced with carbon fibers. Phenolic (or phenol-formaldehyde) resins can serve as starting matrix materials in a liquid impregnation procedure employing pyrolysis and carbonization of the resin contained in the composite and subsequent densification until the desired density is attained [1–3]. Since phenolic resins are easy to handle and give considerable carbon char yield among the various thermoset precursors, such as furan resins, polyvinyl alcohol, polyacrylonitrile, cellulose and epoxy resins [4].

When the resin matrix is exposed to high temperatures, major requirements for the final composite performance are based on the following: (1) thermal stability against thermal isotropic volume shrinkage (2) oxidation resistance sufficient in oxidizing environments (3) high thermal conductivity (CT) and low coefficient of thermal expansion (CTE) against thermal shock, (4) high strength and stiffness in real high temperature applications [2, 5].

In the oxidation resistant filler, we believe that intermetallic MoSi$_2$ used in this work may be more suitable for high temperature structural applications. It has a higher melting point (2020 ± 20°C) than other intermetallics, such as the aluminides of iron, nickel and titanium and has excellent resistance to oxidation [6]. Furthermore, it exhibits brittle-to-ductile transition (BDT) in the vicinity of 900°C, and above this temperature shows significant metallic ductility [7, 8], which can make an important role in the one step manufacturing process avoiding catastrophic the composite failure during graphitization [9].

The objective of the present work is to provide an understanding of the effect of oxidation resistant filler on the thermal stability of the C-C composites. In this work, detailed and precise factors on the thermal stability based on the initial decomposition temperature (IDT), temperature of maximum rate of weight loss (T_{max}), integral procedure decomposition temperature (IPDT), decomposition temperature range, and activation energy (E_a) by thermogravimetric analysis (TGA) are investigated.

2. Experimental

2.1. Materials and sample preparation

The fiber used in this experiment were untreated and unsized polyacrylonitrile (PAN)-based high strength carbon fibers, TZ-307 manufactured by Taekwang of Korea. A typical strength for these fibers was about a 3.5 GPa. The resole type of phenolic resin supplied from Kangnam of Korea was used as the matrix precursors of C-C composites to be studied. MoSi$_2$ powders (<2 μm, supplied from Aldrich Co.) were used as an oxidation resistant filler after pulverization by freezer/mill (Spexcertiprep, spex 6700) in reduce their particle size (or in increase their BET's specific surface area [10]) to about 0.3 μm. These powders were systematically prepared by 0, 4, 12, and 20% by weight of MoSi$_2$ on the basis of resin matrix.

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Composite laminates were prepared using a conventional prepreg method [11]. Individual prepregs were 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 10.5 MPa and 220°C for 120 min in a vacuum bagging composite processing. The bulk fiber volume fraction of the green composites was about 60% (±2%). After the curing of the resin, the laminates were subjected to the carbonization process at 1100°C at a heating rate of 10 $K{\cdot}h^{-1}$ and the graphitization process at 2300°C at a heating rate of 400 $K{\cdot}h^{-1}$ in an inert environment. The retention times after maximum carbonization and graphitization heat-treatment temperatures (HTT) were 2 h and 1 h, respectively.

2.2. Measurements

To evaluate the weight loss against HTT, the graphitized specimens for the TGA measurements (Du Pont, TGA-2950) were heated from room temperature to 1000°C in an oxidizing environment at a rate of 10 $K{\cdot}min^{-1}$. A wide angle X-ray diffractogram (XRD) of the composites was recorded on a Rigaku Model D/MAX-III B using Cu K_α radiation as the source for characterizing the composite surface elements.

3. Results and discussion

It is generally accepted that reliable degradation temperature and kinetic parameters, such as IDT, T_{max}, IPDT and activation energy, can be used to assess material's lifetime [12, 13]. Fig. 1 shows the schematic diagram of the TGA for determining the IPDT of a major thermal stability of the specimen based on the Doyle's proposition [12], and then the IPDT is calculated as follows:

$$\mathrm{IPDT}(^\circ\mathrm{C}) = AK \cdot (T_f - T_i) + T_i \qquad (1)$$

$$\text{in} \quad A = \frac{S_1 + S_2}{S_1 + S_2 + S_3} \quad \text{and} \quad K = \frac{S_1 + S_2}{S_1}$$

where A is the area ratio of total experimental curve divided by total TGA thermogram, K the coefficient of A, T_i the initial experimental temperature (40°C, in this work), and T_f the final experimental temperature (1000°C).

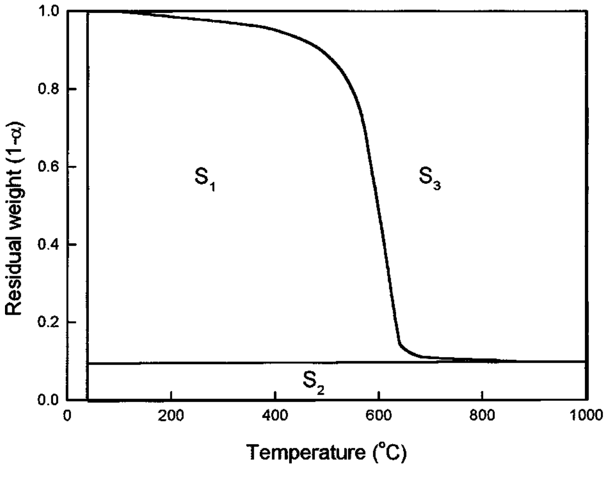

Figure 1 Schematic representation of S_1, S_2 and S_3 for A and K.

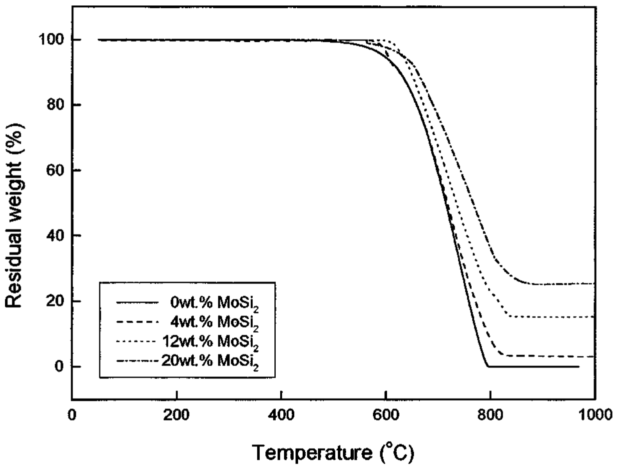

Figure 2 TGA thermograms of the C-C composites studied.

The activation energy, E_a, for the decomposition of C-C composites in oxidizing environment is calculated from TGA thermogram as shown in Fig. 2, by the integral method of based on the Horowitz-Metzger [14] according to the following equation:

$$\ln\{\ln(1-\alpha)^{-1}\} = \frac{E_a \cdot \theta}{RT_{max}^2} \qquad (2)$$

where α is the decomposition ratio, θ the $T - T_{max}$, and T_{max} the temperature of maximum rate of weight loss, and R the ideal gas constant.

According to the Equation 2, the activation energy is given by the straight line corresponding to the $\ln\{\ln(1-\alpha)^{-1}\}$ versus θ, as shown in Fig. 3, with a constant correlation coefficient, $R = 0.987$ for the specimen containing 12% by weight of $MoSi_2$ on the basis of resin matrix. All experimental results of the degradation temperatures of the C-C composites studied as a function of $MoSi_2$ filler are listed in Table I, and the evolution of the activation energies of the composites versus $MoSi_2$ content is shown in Fig. 4. These results indicate that the degradation temperatures including IDT, T_{max}, and decomposition temperature range largely increase in increasing the $MoSi_2$ content, especially IPDT greatly increases from 702 °C for the composites unfilled to 1147 °C for the composites containing 12% by weight of $MoSi_2$, as increasing the A and K described in Equation 2. Similar result can be observed in the evolution of activation energies of the composites, 144 $kJ{\cdot}mol^{-1}$ for the unfilled composites and 167 $kJ{\cdot}mol^{-1}$ for the specimen containing 12% by weight of $MoSi_2$. This behavior is clearly due to the presence of brittle-to-ductile transition fillers which can improve the degree of adhesion at interfaces

TABLE I Effect of $MoSi_2$ filler on the thermal stabilities of the C-C composites studied

$MoSi_2$ content (wt%)	IDT (°C)	T_{max} (°C)	A	K	IPDT (°C)	temp. range (°C)
0	480	739	0.69	1.00	702	650–750
4	568	742	0.71	1.04	749	650–800
12	588	768	0.75	1.25	940	650–800
20	563	784	0.79	1.46	1147	650–800

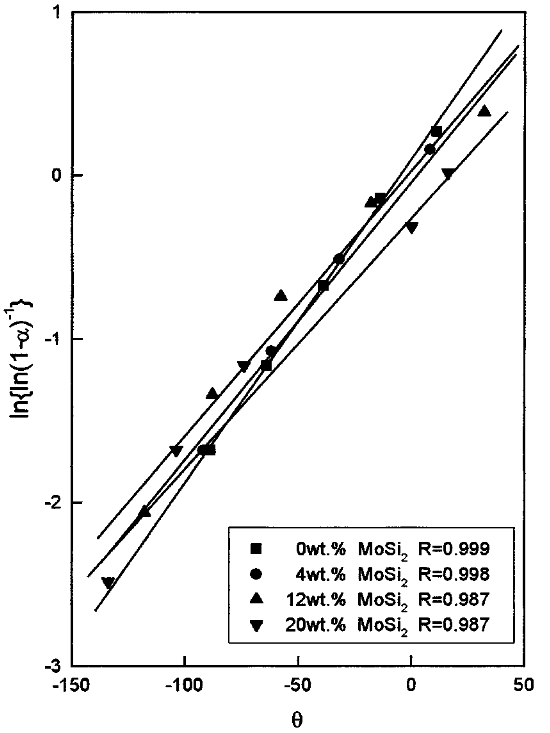

Figure 3 Plots of $\ln\{\ln(1-\alpha)^{-1}\}$ vs. θ for the C-C composites studied.

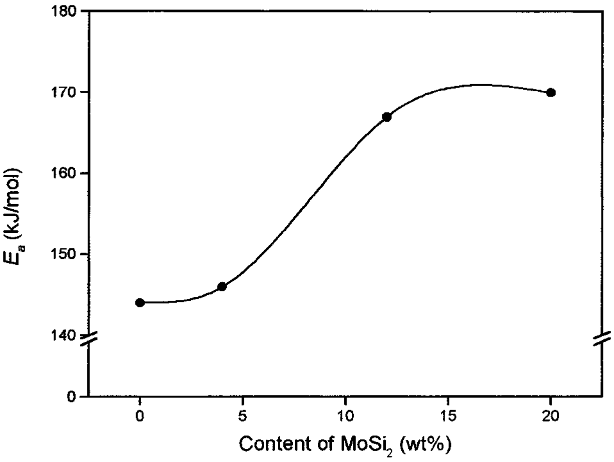

Figure 4 Evolutions of the activation energy as a function of $MoSi_2$ content of C-C composites.

between fiber and matrix during the graphitization process.

Meanwhile, an interesting XRD result of the composites made with different heat treatment temperatures in a given retention time of 20 hs is shown in Fig. 5. These clearly indicate that the specimen prepared with the 12 wt% $MoSi_2$ received at 1000 °C shows an intensity spectra of SiO_2, while the same specimen prepared at 600 °C identify the $MoSi_2$ spectra. Therefore, it is found that a new formation of oxygen protection layer, SiO_2, of C-C composites during graphitization makes an important role in a mobile diffusion barrier at high temperatures, resulting in increasing thermal stability of C-C composites, based on the following either Equations 3 or 4 [15]:

$$2MoSi_2 + 7O_2 \rightarrow 2MoO_3 + 4SiO_2 \quad (3)$$

$$5MoSi_2 + 7O_2 \rightarrow Mo_5Si_3 + 7SiO_2 \quad (4)$$

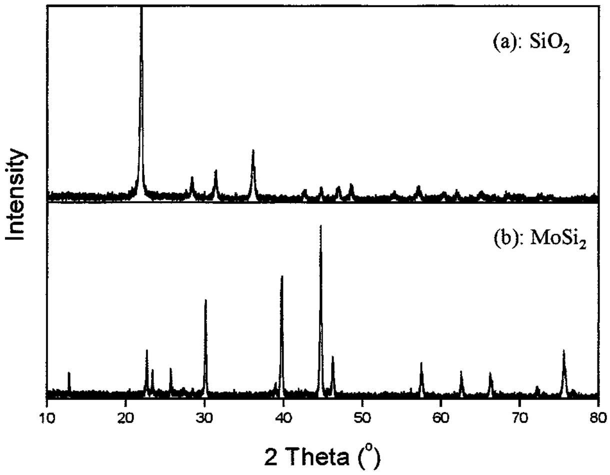

Figure 5 XRD patterns of the C-C composites made with different HTT in a given retention time of 20 hs, (a): 1000 °C and (b): 600 °C.

4. Conclusion

In this work, more detailed and precise thermal stability factors of C-C composites based on the IDT, $T_{\max}$, IPDT, decomposition temperature range, and activation energy are investigated in terms of dynamic TGA in oxidizing environment. As an experimental result, the increasing of pulverized $MoSi_2$ filler of C-C composites leads to an improvement in thermal degradation temperatures and activation energy, if the filler content is in the range of 12–20 wt%. This behavior can be mainly resulted in the inherent $MoSi_2$ properties which are correlated with the followings i) presence of the brittle-to-ductile transition, for the increased interfacial adhesion at interfaces among fiber, matrix and filler, and ii) formation of the protective layer acting as a diffusion barrier for oxygen at high temperature.

References

1. C. R. THOMAS, "Essential of Carbon-Carbon Composites" (Royal Society of Chemistry, Cambridge, 1993).
2. E. FITZER, *Carbon* **25** (1987) 163.
3. S. J. PARK and J. R. LEE, *J. Mater. Sci.* **33** (1998) 647.
4. G. SAVAGE "Carbon-Carbon Composites" (Chapman, London, 1993).
5. J. D. BUCKLEY, *Ceram. Bull.* **67** (1988) 364.
6. J. M. YANG and S. M. JENG, *J. Mater. Res.* **6** (1991) 505.
7. J. J. PETROVIC and R. E. HONNELL, *J. Mater. Sci.* **25** (1990) 4453.
8. S. JANDHYALA, *J. Am. Ceram. Soc.* **76** (1993) 226.
9. S. J. PARK, M. S. CHO, J. R. LEE and P. K. PAK, *Carbon*, in press.
10. S. BRUNAUER, P. H. EMMETT and E. TELLER, *J. Am. Chem. Soc.* **60** (1938) 309.
11. J. M. CHARRIER, "Polymeric Materials and Processing" (Hanser, Munich, 1990).
12. C. D. DOYLE, *Anal. Chem.* **33** (1961) 77.
13. X. G. LI and M. R. HUANG, *J. Appl. Polym. Sci.* **71** (1999) 565.
14. H. H. HOROWITZ and G. METZGER, *Anal. Chem.* **35** (1963) 1464.
15. E. W. LEE, J. COOK, A. KHAN, R. MAHAPATRA and J. WALDMAN, *JOM.* **43** (1991) 54.

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