EFFECT OF FILM THICKNESS ON GRAPHITIZATION AND OXIDATION BEHAVIOR OF CARBONIZED POLYIMIDE FILMS

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INTRODUCTION

Although polyimide carbon is known as non-graphitizing type carbon, Y. Hishiyama et al [1, 2] reported that highly orientated and well-crystallized graphite film could be obtained from heat-treatment of the polyimide thin film. Hatori et al [3] reported influence of the film thickness on in-plane orientation and graphitizability of polyimide films. This research also aimed to know carbonization and graphitization behavior of commercially available polyimide films with different thickness and to investigate their oxidation behaviors.

EXPERIMENTAL

Film samples of 30 mm x 30 mm size with thickness of 25 μm and 125 μm cut from large area polyimide films (Kapton-100H and Kapton-500H) were used in this experiment. The films were heat-treated up to 1000°C in N_2 with heating rate of 5°C/min and the holding time of 1 hr for carbonization. Graphitization was carried out by heating of the carbonized films at 1500°C, 2000°C and 2500°C in Ar gas with heating rate of 20°C/min and the holding time of 1 hr. Carbon yield, linear shrinkage along the film surface, change of X-ray parameter and morphological change with heat-treated temperature were investigated.

Oxidation tests of the heat-treated carbon films were carried by TG and the oxidized films were observed by SEM to know the influence of the thickness.

RESULTS AND DISCUSSION

Carbon yields of the films were almost same as about 57 wt% after carbonization at 1000°C for both films. With increase of heat-treated temperature the values decreased, but the difference between them was observed above 1500°C. That is, carbon yield of 52 wt% for the film with 125 μm thickness and about 46 wt% for the film with 25 μm thickness. Shrinkage once occurred after carbonization for both films, and the shrinkage was about 20% for the 125 μm-film and about 24% for the 25 μm-film. Those were agreed well

Table 1 d(002), d(004), Lc(002) and Lc(004) of polyimide carbon films with thickness of 25μm and 125μm.

H.T.T. / °C	film thickness / μm	d (002) / Å	d (004) / Å	Lc (002) / Å	Lc (004) / Å
2000	25	3.411	——	26	——
	125	3.430	——	27	——
2500	25	3.374	3.370	>1000 (2190)	470
	125	3.373	3.371	410	370

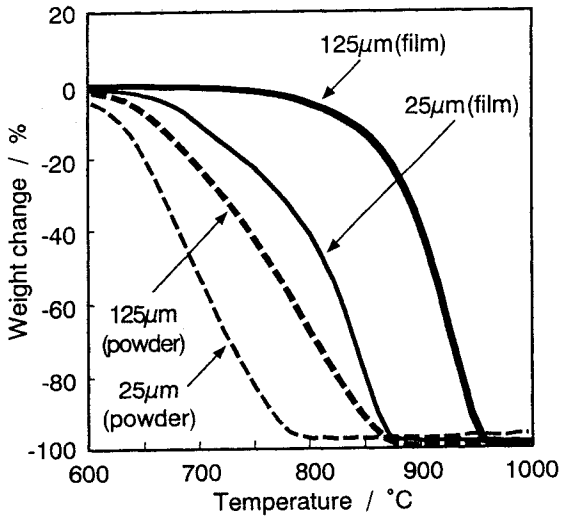

Fig. 1. TG curves of heat-treated polyimide films at 2000°C with difference thickness and those for the powders.

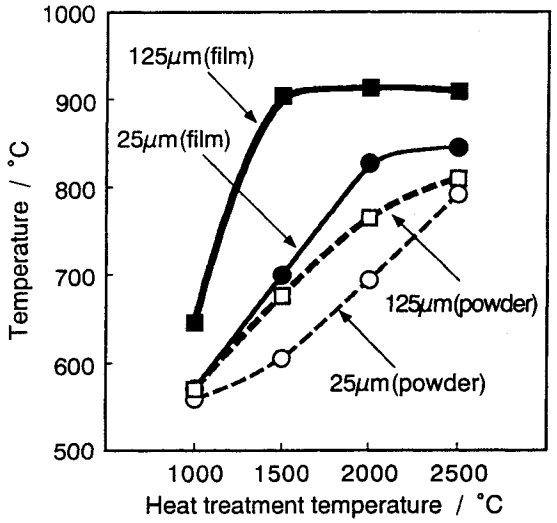

Fig. 2. 50% weight loss temperature of heat treated polyimide films with different thickness and those for the powders.

the data reported by Inagaki et at [3]. However, by heat-treatment of the carbonized film above 2000°C expansion was observed for both films. Expansion in length after 2500°C was about 10% from 1000°-1500°C treated films. The expansion was thought to occur by progress of preferred orientation of crystallite with increasing temperature.

Table 1 shows d(00 ℓ) spacing and crystallite size, Lc(00 ℓ) of the films with different thickness. No significant difference was observed in d-values, but growth of Lc value was apparently proceeded for the 25 μm-film after 2500°C treatment. The remarkable morphological difference was observed between the films after 2500°C. The 25 μm-film showed flat surface, while rough surface and some voids which formed by out-gas from the inside were observed for the 125 μm-film. This suggested that some gas such as N_2 still remained in the 125 μm-film up to 2500°C.

The TG curves with oxidation temperature showed that the films heat-treated at 2500°C had higher oxidation resistance than the film heat-treated at 2000°C. However, the 125 μm-films showed higher oxidation resistance than the 25 μm-films of both 2000°C and 2500°C treatments, although the 25 μm-film had higher graphitization degree. Figure 1 shows weight changes of heat-treated polyimide films at 2000°C with a different thickness and those for the powders. This behavior was thought to be caused by different surface area between the films. Therefore TG curves of the powder forms of the films were also investigated. But the tendency of oxidation behavior did not changed between them even for the powder. Figure 2 shows 50% weight loss temperature of the heat-treated films with different thickness and the powders. Formation of many pits by oxidation appeared on the surface of the films. However, the pit size was much bigger for the 125 μm-film than that for 25 μm-film.

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