

POSTER

POROUS SURFACE LAYER IN FURAN RESIN-DERIVED CARBON

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INTRODUCTION

Thermosetting resins are known as the materials to form hard carbons via a solid state carbonization. The hard carbons have the liquid or gas impermeable property. Yamada[1] reported that the specific surface area of furan resin-derived carbon powder of 80–100 μm in diameter against heat treatment temperature(HTT) in the range up to 1300°C, increased up to 800°C with increasing HTT and then decreased, but gas impermeability of bulk material was maintained.

Recently, a few studies[2,3] reported on graphitization behavior in non-graphitizable carbons that skins of 100–300nm in thickness were graphitized, but the inside texture remained amorphous.

In this study, microstructural development in furan resin-derived carbon was discussed in the viewpoint of polymerization process and graphitization process.

EXPERIMENTAL

Furan resin was hardened with polymerizing agent, paratoluene sulfonic acid, for one week in ambient air, followed by post curing at 100°C for 96hrs in drying oven. The polymerized specimens were cut into dimensions of 10x10x(2–3)mm³. Carbonization was carried out at 1000°C for 2hrs in flowing Ar, followed by heat-treatment at 2600°C for 0.5hr in flowing Ar. The specimens, carbonized at 1000°C and heat-treated at 2600°C were characterized by the measurements of specific surface area with different levels of burn-off from 0% to 36% in air. The specific surface area was measured by BET plots from adsorption-desorption curve of N₂(and/or Kr) gas at liquid nitrogen temperature, Raman spectroscopy(Ar laser, 514.5 nm), powder XRD analysis and SEM.

RESULTS AND DISCUSSION

Specific surface area is shown in figure 1 as a function of burn-off for the carbonized specimens. As the amount of burn-off increased to 2% in the carbonized specimens, specific surface area increased, and then decreased drastically to 10% of burn-off. The value slightly increased again up to 36% of burn-off. The surface of the 1000°C-treated specimen burned-off about 2% observed with SEM was shown in figure 2. Surface layer of about 60 μm in thickness was peeled off from the inside body. The surface layer was microporous but the inside was not. Taking into consideration the amount of microporous surface layer of 60 μm is 6% in weight, hence, the change in specific surface area could be divided into 2 steps. The first one is the step for the extinction of microporous surface layer, and the second the step for the formation of pit by oxidation of inside body.

The specific surface area of the carbonized specimen after polishing of about 0.2mm in thickness of both sides extremely decreased to 2 orders of magnitude as shown in figure 1 by open circle. These facts indicate that the formation of microporous layer was determined before carbonization. In order to confirm the origin of the formation of the microporous layer during carbonization, the resin was hardened in flowing Ar gas, and polymerized and carbonized by the same way as the case of hardening in ambient air. As a result, polymerization in flowing Ar gas resulted in disappearance of microporous layer after carbonization. It suggests that the formation of microporous layer after heat treatment at 1000°C was almost determined by chemical reaction in early polymerizing stage with air. Oxygen probably made an important role for the formation.

Specific surface area decreased extremely to 3 orders of magnitude, by heat treatment at 2600°C. The values were less than 200cm²/g, regardless of the amount of burn-off. Figure 3 is Raman scattering spectra obtained on the specimen surface heat-treated at 1000°C and 2600°C. The

intensity ratio (I_{1350} to I_{1580}) is known to be closely related to the mean crystallite size L_a along the a -axis. The ratio changed from unity for the surface of the specimen heat-treated at 1000°C to almost zero for that at 2600°C . It means that microporous layer with amorphous structure was rearranged into graphitic layer. Considering that only negligible amount of graphite was recognized for the specimen heat-treated at 2600°C through powder XRD analysis using (002) diffraction and that the penetration depth of the laser beam in carbon materials estimated to be 100nm [4], the as-treated surface is consisted of graphite layers with large L_a in submicrometric thickness.

CONCLUSIONS

Microporous layer of about $60\mu\text{m}$ in thickness was formed for the specimen of furan resin-derived carbon heat-treated at 1000°C , when furan resin was polymerized in

air. The phenomenon is associated with the chemical reaction between the resin and ambient air, especially oxygen. The microporous layer was rearranged into graphitic layers by heat-treatment at 2600°C , but the inside remained amorphous.

REFERENCES

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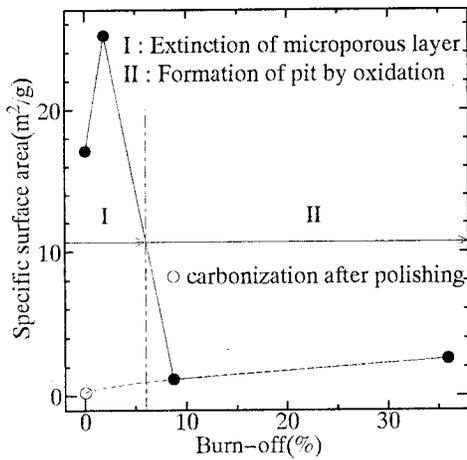


Figure 1 Change in specific surface area as a function of burn-off(%) in carbonized specimens

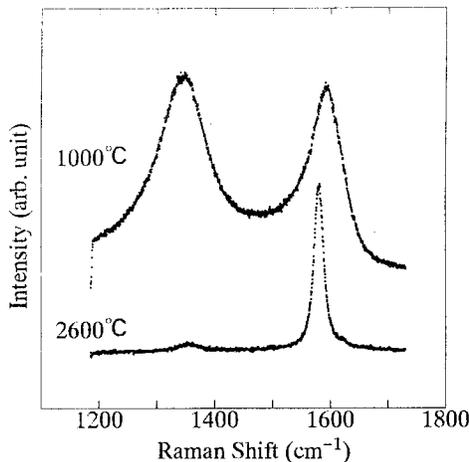


Figure 3 Raman spectra for the surfaces of the specimens heat-treated at 1000°C and 2600°C

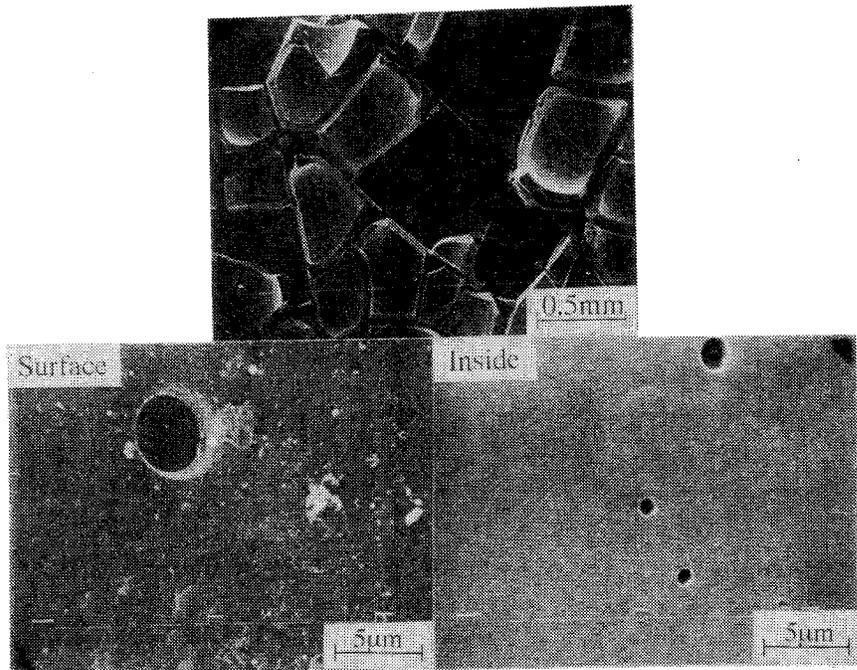


Figure 2 Surface of carbonized(1000°C) specimen burned-off 2%