

Preparation of bulky glassy carbon bodies from phenolformaldehyde resin

When many high polymers are heated in an inert atmosphere to temperatures above 300°C they lose much of their non-carbon content as gases and change to forms of carbon in a process which is termed carbonization. The process by which the non-carbon content is eliminated is completed at temperatures which exceed 1000°C. Above this temperature the material is termed polymeric carbon [1]. In particular, many thermosetting polymers pyrolyse to form high yields (40 to 60%) of disordered non-graphitizing carbons with glass-like properties [2]. These glassy carbons have been studied extensively recently because of their isotropic properties, low gas permeability, high temperature stability, and chemical inertness [2, 3].

Glass-like carbons are now produced commercially under a variety of trade names by Japanese, French, British, and US manufacturers. Typical glassy carbon wares are susceptors, crucibles, beakers, dishes, electrodes and medical implants [1]. Glassy carbons with low apparent porosity (0 to 12%) have moderately high bulk density (1.3 to 1.55 g cm⁻³) and good compressive strength (1000 to 7000 kg cm⁻²) [2]. However, it is impossible to make non-porous glassy carbon artefacts thicker than 3 mm because of fissuring which takes place at temperatures where one observes the greatest evolution of gaseous pro-

ducts [1]. This is a strong limitation to the widening of applications of glassy carbon. It is also possible to manufacture bulky, porous carbon samples with low bulk density (0.1 to 0.4 g cm⁻³) [4], but these have poor mechanical properties (resistance to crushing 5 to 20 kg cm⁻² [4]).

The methods of manufacturing strong glassy carbons are slow and hence expensive. When pure resin is used as the starting material a slow rate of heating must be used, because in the case of rapid heating the high pressure of the evolving pyrolysis gases would damage the partially carbonized body [5, 6].

In this communication we report a new, rapid method of manufacturing bulky glassy carbon samples of moderate porosity and good compressive strength using as a starting material liquid phenolformaldehyde resin, which is hardened prior to being carbonized in an inert atmosphere. An additive (ethyl alcohol) which does not take part chemically in the hardening reaction is mixed with the resin before hardening. This additive evaporates in the post-curing stage and/or at the beginning of carbonization leaving submicroscopic pores into the polymer matrix.

The following example illustrates the manufacturing process: 40 g "Tammer F3" phenolformaldehyde resin (Aaltosen Tehtaat Oy Sarvis, Finland) and 9 ml 99.5% (wt/wt) ethyl alcohol were mixed. The mixture was filtered and 4 ml 4-toluenesulphonic acid was added. The mixture was vacuum degassed and mixed until homogeneous. The

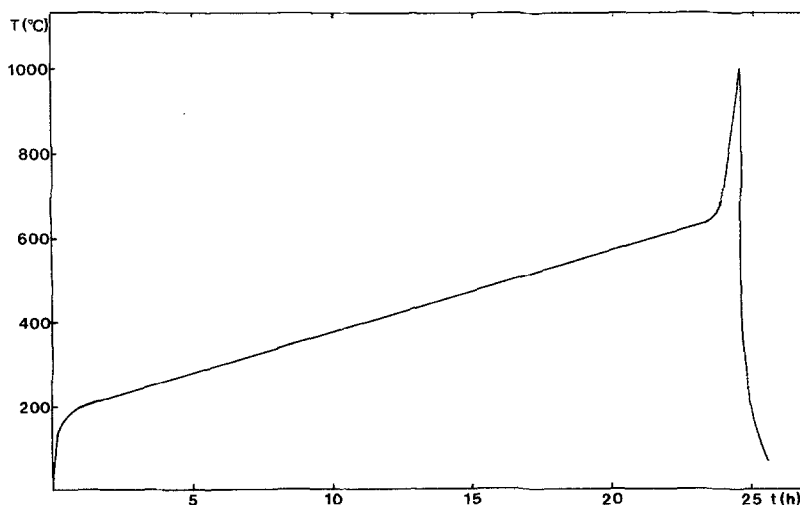


Figure 1 The heat-treatment diagram in carbonization of phenolformaldehyde resin.

TABLE I Properties of glass-like porous carbon

Bulk density	1.20 g cm ⁻³
Apparent porosity	34%
Compressive strength	44 000 ± 8000 N cm ⁻²
Vickers microhardness	> 225 (~ 270) kg mm ⁻²
Electrical resistivity	260 × 10 ⁻⁴ Ω cm

mixture was poured into a test tube (i.d. 15 mm) and hardened at a temperature of 50 to 60° C for 2 h and then allowed to cool to form a rod. The rod was cut into cylindrical pieces (height 15 mm). These were kept at a temperature of 190° C for 5 h.

The cured samples were carbonized in a tube furnace by heating to 1000° C in a nitrogen atmosphere. The heat-treatment diagram is given in Fig. 1.

The compressive strengths of 6 to 14 glassy carbon samples were measured using an Instron 1115 TT-DM-L tester, at a test speed of 1 mm min⁻¹ and hardness estimations were made using the microscope hardness meter PMT-3 with a load of 30 g. The apparent porosity of samples was estimated modifying the method ASTM C 373-72 (the samples were impregnated in boiling water for about 3 weeks until their weight remained constant; the porosity was calculated from the weight increment). X-ray diagrams were recorded using the JEOL JDX-7S diffractometer, and electrical resistivity was measured using Fluke 8600 A Digital Multimeter and Hg as electrodes.

The microstructure of samples and of fracture surfaces was studied by a transmission electron JEOL JEM-200A microscope and by a scanning electron JEOL JSM-U3 microscope.

The linear shrinkage of phenolformaldehyde samples during carbonization was 25%. The carbon yield was ~50%. X-ray diagrams were taken of carbon samples to detect any traces of graphite. Reflections of graphite were totally absent, therefore it was concluded that the samples were amorphous by nature.

The measured properties of the prepared carbon are given in Table I. According to the results given in Table I the prepared carbon shows good compressive strength, especially when the degree of porosity of the sample is taken into account [1]. This may be due to the uniform distribution of pore sizes in samples. The pore structure was studied by transmission electron microscopy (Fig. 2).

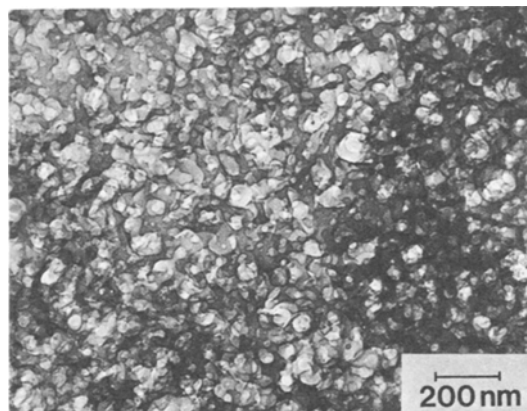


Figure 2 TEM micrograph of a carbonized specimen.

Fig. 2 shows that the samples contain a large amount of small, comparatively uniformly distributed pores (sizes typically between 10 and 100 nm). Evidently the formation of small pores is a consequence of the addition of ethyl alcohol to the resin mixture.

Comparing the experimental conditions of carbonization in this work to earlier work [1] it can be concluded that the presence of pores during carbonization is an essential requirement in preparing bulky glassy carbon samples because the pores allow the rapid removal of pyrolysis gases.

The high porosity may be advantageous in some applications (e.g. in filters and in lubricant-impregnated bearings) but in many cases it is disadvantageous. It is well known that the number of pores can be diminished by heat-treatment [7]. On the other hand, it seems evident that the amount of additive (ethyl alcohol) is correlated to the number of pores. Therefore, studies concerning the effects of heat-treatment and of additive amounts upon the porosity are in progress in our laboratory.

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Aluminides of non-magnetic transition metals

The intermetallic compounds are of considerable interest from both the scientific and practical points of view [1, 2]. An important class of intermetallics is the aluminides of transition metals, and among them the simpler group of aluminides of non-magnetic transition metals. Interesting examples of the latter group represent, for instance, compounds VA_{10} having anomalously large atomic volume [3] and heat capacity [4], Nb_3Al (having high superconductivity transition temperature) $NpAl_2$ and $NpAl_3$ (ferromagnetic compounds, although both components are non-

magnetic [5]), Zr_3Al (a promising structural material for nuclear reactors), etc.

It was recently shown that a certain interrelation exists between the values of the deviations of atomic volume from additivity and the physical properties of the components [6–12]. The aim of the present note is to present the data of the deviations of atomic volumes from additivity (and in addition also the data of superconducting transition temperatures T_c [13]) for known aluminides of non-magnetic transition metals.

The percentage deviation (K) of atomic volume (V) from the sum of its components ($\Sigma\Omega$) was calculated by the formula [6–12]:

TABLE I Aluminides of transition metals with 3 and 4 outer electrons

Compound	Structure	$\frac{\Delta V}{V} \times 100$	T_c (K)	Compound	Structure	$\frac{\Delta V}{V} \times 100$	T_c (K)
YAl	CsCl	-2	—	HfAl	CrB	+3	—
LaAl ₃	Ni ₃ Sn	-2	<1.3	ScAl	CsCl	+4	—
Zr ₂ Al	CuAl ₂	-2	—	Sc ₂ Al	Ni ₂ In	+4	—
Hf ₂ Al	CuAl ₂	-2	—	LaAl ₂	Cu ₂ Mg	+4	3.2
LaAl ₄	BaAl ₄	-1	<1.1	Ti ₃ Al	Ni ₃ Sn	+4	—
LaAl	CeAl	0	<0.4	Zr ₄ Al ₃	hexag.	+4	—
La ₃ Al ₁₁	orthor.	0	<1.3	Hf ₄ Al ₃	Zr ₄ Al ₃	+4	—
YAl	CrB	+1	<1.1	Zr ₂ Al ₃	orthor.	+4	—
Zr ₅ Al ₃	W ₅ Si ₃	+1	—	Hf ₂ Al ₃	orthor.	+4	—
Zr ₅ Al ₃	Mn ₅ Si ₃	+1	—	ZrAl ₃	tetrag.	+5	<1.0
Zr ₃ Al ₂	tetrag.	+1	—	TiAl	AuCul	+5	—
Hf ₅ Al ₃	Mn ₅ Si ₃	+1	—	HfAl ₃	ZrAl ₃	+5	—
Zr ₅ Al ₄	Ti ₅ Ge ₃	+2	—	TiAl ₃	TiAl ₃	+6	<1.0
La ₃ Al	Ni ₃ Sn	+2	6.2	HfAl ₃	TiAl ₃	+6	—
Hf ₃ Al ₂	Zr ₃ Al ₂	+2	—	TiAl ₂	Ga ₂ Hf	+6	—
Y ₃ Al	Cu ₃ Au	+3	<1.1	YAl ₃	Ni ₃ Sn	+6	—
Zr ₃ Al	Cu ₃ Au	+3	0.73	YAl ₃	BaPb ₃	+6	—
Y ₂ Al	PbCl ₂	+3	<1.1	ScAl ₂	Cu ₂ Mg	+7	<1.0
Y ₃ Al ₂	Zr ₃ Al ₂	+3	<1.1	ZrAl ₂	MgZn ₂	+7	<0.3
LuAl ₂	Cu ₂ Mg	+3	<1.0	ScAl ₃	Cu ₃ Au	+8	<4.2
Zr ₂ Al	Ni ₂ In	+3	—	HfAl ₂	MgZn ₂	+8	—
ZrAl	CrB	+3	—	YAl ₂	Cu ₂ Mg	+9	<0.3