Brief Communications

Polyadamantane as a source of diamond-like carbon

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The literature data concerning the effect of high pressures (9 GPa) and temperatures (1800 °C) on polyadamantane is revised. A new diamond-like carbon is formed, whose structure is similar to that of natural skeletal diamond.

Key words: adamantane, polyadamantane, diamond, carbon.

The synthesis of cross-linked polyadamantane[1] by repeated debromination of brominated polyadamantane derivatives was one of numerous attempts to obtain diamond-like carbon at atmospheric pressure (Scheme 1).

The X-ray diffractogram of amorphous polyadamantane is characterized by an intense halo with a maximum corresponding to the period ~4.9 Å.[1] Heating of this polymer at 400 °C *in vacuo* resulted in a white polycrystalline powder containing ~99% carbon with density ~2 g cm^{-3}. Distinct diffraction lines of the crystalline phase, which correspond to interplanar distances 4.54, 2.84, 2.47, 1.86, 1.66, 1.43, and 1.38 Å, were observed in the diffractogram of this product. The data obtained are consistent with the structural model of polyadamantane in the form of an assembly of carbon nuclei of adamantane C_{10} linked by single C—C bonds.

Previously, the transition of α-carbyne and polyadamantane into β-carbyne at 9 GPa at 1800 °C has been reported.[2] However, this information raises objections, because β-carbyne is an unstable polymorphous form of carbon and its generation seems improbable

Scheme 1

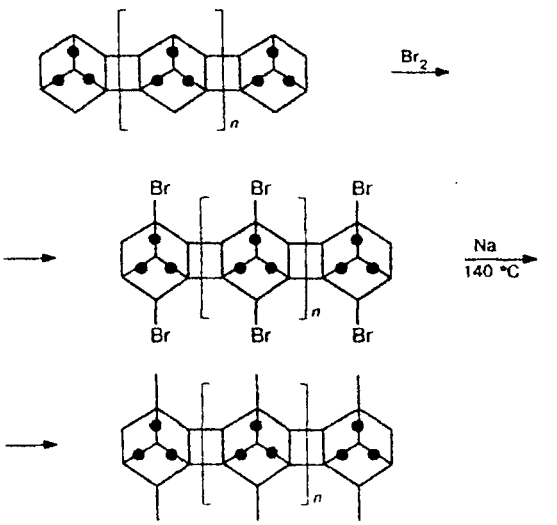

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Table 1. Interplanar distances for carbyne, polyadamantane, and skeletal diamond

Chaoite[7]			α-Carbyne (9 GPa, 1800 °C [2])			Polyadamantane (400 °C [1])			Polyadamantane (9 GPa, 1800 °C [2])			Skeletal diamond[5]			Diamond-like carbon[6]	
d/Å	*I*	hkl	*d*/Å	*I*	hkl	*d*/Å	*I*	hkl	*d*/Å	*I*	hkl	*d*/Å	*I*	hkl	*d*/Å	*I*
4.47	v.s	110	—	—	—	4.94	s	100	—	—	—	—	—	—	4.43	m
4.26	v.s	111	—	—	—	—	—	—	—	—	—	—	—	—	4.27	s
4.12	v.s	103	4.13	s	110	—	—	—	4.12	m	110	—	—	—	4.04	s
3.71	m	201	3.72	w	201	—		—	3.73	m	201	3.41	—	—	3.80	m
3.22	m	104	—	—	—	—	—	—	3.64	m	—		—	—	3.27	w
3.03	w	203	—	—	—	—	—	—	—	—	—	—	—	—	3.07	w
2.94	w	210	—	—	—	2.84	m	110	2.87	w	211	2.69	—	—	—	—
2.55	s	301	2.54	w	211	2.47	m	200	2.85	w	—	2.54	w		2.57	w
2.46	m	213	—	—	—	—	—	—	—	—	—			—	2.47	w
2.28	m	205	—	—	—	—	—	—	—	—	—	2.28	m	—	2.20	w
2.24	m	220	—	—	—	—	—	—	2.24	w	103			—	—	—
2.10	m	304	—	—	—	—	—	—	2.07	w	220	2.06	s	111	2.05	w
1.98	w	206	—	—	—	—	—	—	1.85	w	310	—	—	—	1.98	w
1.91	w	461	1.81	w	222	1.88	w	210	1.80	w	310	—	—	—	—	—
1.37	w	416	1.37	w	330	1.66	m	300	—	—	—	—	—	—	—	—
1.28	w	600	—	—	—	1.43	w	220	1.27	w	0.06	—	—	—	—	—
1.26	w	336	1.26	w	426	1.38	w	310	—	—	—	1.26	s	—	—	—
1.19	m	337	1.22	w	116	—	—	—	—	—	—	1.19	m	—	—	—
1.18	m	427	—	—	—	—	—	—	—	—	—	—	—	—	—	—
1.08	w	41.10	—	—	—	—	—	—	—	—	—	1.08	m	—	—	—
0.86	w	41.14	—	—	—	—	—	—	—	—	—	—	—	—	—	—

Note. Conditions of treatment of carbonaceous materials are given in parentheses

under such severe conditions. Quantum-mechanical calculations showed that β-carbyne can be transformed into diamond.[3] Later this transition was realized by heating amorphous β-carbyne in the presence of small amounts of highly disperse diamond as a seed.[4]

As a matter of fact, under the conditions reported earlier[2] the formation of new diamond-like carbon occurs, which is similar to "skeletal diamonds" found in the Kumdykol' deposit.[5] This follows from a comparison of interplanar distances of the polyadamantane heated at 400 °C and the polyadamantane subjected to the action of high pressures and temperatures, natural diamond, chaoite at the site of a meteorite fall, and diamond-like carbon obtained by heating β-carbyne at 360 °C[6] (Table 1). It is seen from Table 1 that interplanar distances for the diamond-like carbon and chaoite[7] coincide and are close to those for "skeletal diamond."

Skeletal diamonds are known to be abnormal crystalline forms[8] that are formed under conditions of deficient carbon "feeding" for the normal growth of crystals. Such diamonds are characterized by one-direction ordering [111], they have imperfect structure and contain much amorphous phase.

Thus, a new diamond-like carbon is formed as a result of the action of high pressures and temperatures on polyadamantane. Its structure is close to that of the natural skeletal diamond rather than to β-carbyne as has been stated earlier.[2]

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