irradiated surface. The expansion was uniform across the whole plane perpendicular to the c-axis, even though the switching beam was smaller than this plane. The rise and fall times were ~15 s. The origin of the optomechanical effect is the reversible exfoliation of the near surface region of the intercalated graphite.

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Discussion of the formation of nanometric texture in spherical carbon bodies

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One of characteristics of carbon materials is a wide variety of texture. The author has presented a proposal to classify the texture on a nanometric scale on the basis of the scheme and the degree of preferred orientation of the hexagonal carbon layers of basic structural units (BSUs), as shown in Fig. 1 [1,2]. These textures are known to govern the graphitization behavior [3] and also various properties [2]. In axial and point orientation schemes, carbon layers are preferentially oriented along the reference axis and point, respectively, and result in the formation of various carbon fibers and carbon spheres. In these orientation schemes, radial and concentric arrangements of the carbon layers are possible (Fig. 1). In practice, it is well known that the mesophase-pitch-based carbon fibers can have different textures such as radial and concentric textures in their cross-sections. In carbon blacks, carbon layers are oriented statistically in a concentric manner, as can be seen in various structural models in which the details of the arrangement of each layer are little different from each other. In mesophase spheres, however, the orientation scheme of carbon layers is known to be radial, at least near the surface, as many authors have confirmed since Brooks and Taylor [4].

However, there has been no explanation and even no discussion on the reason why these textures are formed, as far as the author is aware. Why do most of the mesophase spheres have a Brooks-Taylor type texture and why not a concentric one? Why do the carbon blacks have a concentric texture, in contrast to the mesophase spheres?

In this note we shall discuss the reason why these two kinds of arrangement of carbon layers, radial and concentric, are possible by focusing on spherical carbon bodies.

In Table 1, a brief description of the formation conditions and the phases involved at the interface between carbon spheres and their surroundings during thermal decomposition and subsequent carbonization processes are summarized, together with the resultant texture in carbon spheres in six different materials.

The spherical carbon bodies can be classified into three from their nanometric texture, concentric, radial and random arrangements of carbon layers. If we draw our attention to the interface between the sphere and its
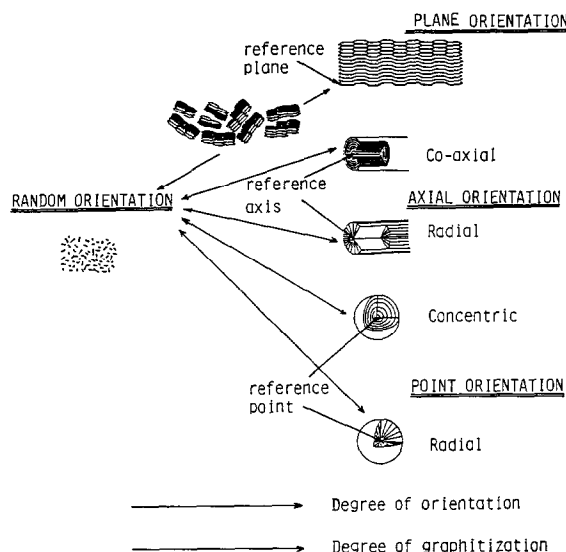

Fig. 1 Classification of nanometric texture in carbon materials based on the preferred orientation of the carbon layers in BSUs.

surroundings at the moment of formation, we can understand that the concentric texture in spherical bodies is caused always when the interface between different phases is either liquid/gas, solid/liquid or solid/gas. On the other hand, the formation of carbon spheres with radial texture occurs with a liquid/liquid interface. This correspondence seems to be reasonable because of a strong interaction between the spheres and their surroundings during their formation.

The fundamental theory of nucleation and growth of crystals tells us that the critical radius of a nucleus depends on the interfacial energy. This interfacial energy is related strongly to the difference in surface energies between the two phases in contact at the interface. During the formation of these spherical particles, BSUs are composed of a parallel stacking of condensed aromatic rings. In these units, the anisotropy may be supposed to be similar to that in graphite layers. If so, the basal plane of BSUs has much lower surface energy than the edge plane.

Table 1 Texture in spherical carbon bodies.

Carbon	Formation conditions	Interface	Texture
Carbon blacks	thermal decomposition of hydrocarbon gases	liquid/gas	concentric
Fluid cokes	decomposition of oil onto carbon nucleus	solid/liquid & liquid/gas	concentric
Graphite nodules	precipitation in molten cast iron	solid/liquid	concentric
Mesophase spheres	segregation in molten pitches	liquid/liquid	radial
Carbon spherules	decomposition & carbonization under pressure	liquid/liquid	radial
Glass-like carbon spheres	solid carbonization of organic precursors	solid/gas	random

In carbon blacks, the interface is located between liquid and gas, according to the droplet mechanism, [5] and so the interfacial energy is reasonably supposed to be large. In this case, the determining factor for the formation of nanometric texture is to have a minimum surface energy of the particles , which can be attained by facing the basal planes of BSUs to the surroundings, leading to the concentric texture. In the particles of fluid cokes, a similar concentric arrangement of carbon layers have been reported [6].

There is another spherical carbon body of graphite which is formed in molten cast iron, the so-called graphite nodules [7]. The important role of these graphite nodules in steels for their toughening is well known. Since the formation of these nodules is due to the precipitation of carbon from its supersaturated solution of molten iron, the surface of these nodules at their formation stage must be surrounded by liquid iron, and therefore the interface is reasonably supposed to be located between solid graphite and liquid molten iron. In this case again, interfacial energy enough for the segregation of nodules can be reached by concentric arrangement of hexagonal graphite layers.

The surface energy of molten pitches seems to be rather low, close to that of the basal plane of condensed aromatic rings. The interfacial energy between mesophase spheres and the matrix isotropic pitch was predicted to be quite small [8] and was proved to be such by theoretical calculation [9]. In order to segregate mesophase spheres in the molten pitch by forming an ordered assembly of stacks of aromatic rings and to keep a certain amount of interfacial energy, the edge plane must face towards the molten pitch. Supposing a concentric texture in the particles, there can not be expected to be a surface energy difference between the segregated part and the surrounding matrix. Therefore, the only way to keep a certain amount of interfacial energy must be the case of radial arrangement of condensed aromatic rings. At the same time, the segregated part must be of spherical shape to keep their surface energy a minimum. During sphere growth, the radial texture has to be kept, because the interface is still located between two liquids. As a consequence, we have Brooks-Taylor type texture in mesophase spheres.

In some pitches, minute particles, some of them having ellipsoidal shape, where the layers of BSUs align parallel were observed to coexist with Brooks-Taylor type mesophase spheres [10,11]. In this case, BSUs arrange their basal planes perpendicular to the principal axis of the ellipsoid, as shown in Fig. 2. This nanometric texture in minute particles is also the only

way to have a certain interfacial energy, as explained earlier. The arrangement of basal planes of aromatic rings parallel to the principal axis of the ellipsoid is considered to be less probable because the perpendicular arrangement allows an easier exposure of the edges to the interface.

On the other hand, the formation of mesophase spheres with a concentric arrangement of carbon layers has been reported in pitches with added carbon blacks [12,13]. The difference between these two spheres, Brooks-Taylor type and the new one, was clearly shown by polarized-light microscopy. The authors [13] observed a preferential precipitation of the added carbon black particles at the surface of the segregated mesophase
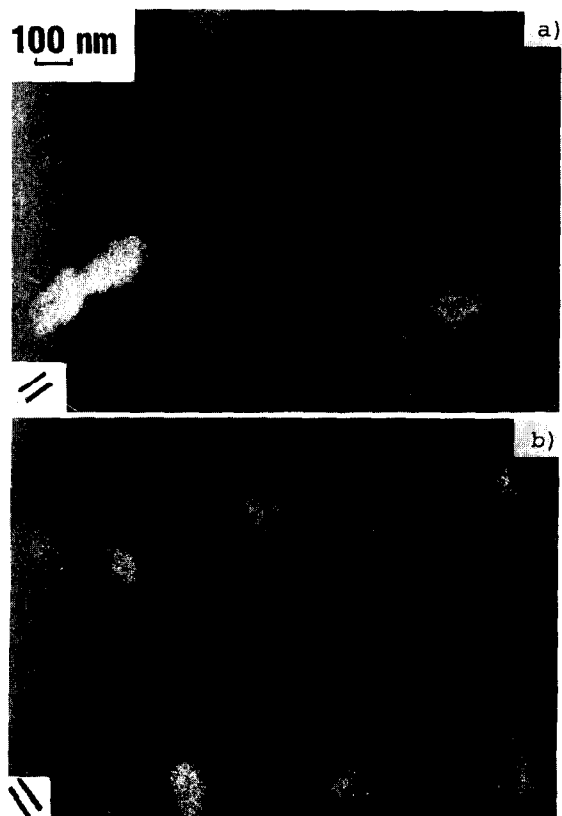

Fig. 2 Anisotorpic particles observed in a pitch (by courtesy of Mme. S. Bonnamy). (a) and (b) orthogonal 002 dark field images. The orientation of the carbon layers is shown by double bars.

spheres, and thus the interface must exist between liquid mesophase and solid carbon black. In this situation, a concentric texture is formed. This result clearly shows the importance of the interface for the formation of nanometric texture in spherical carbon bodies.

We may recall that Brooks and Taylor [4] reported that the mesophase was formed on graphite flakes by ordering its aromatic rings parallel to the graphite surface. This result may be understood by the existence of a large difference in surface energy between liquid mesophase and solid graphite flake.

By the carbonization of some organic precursors under pressure, spherical carbon bodies (carbon spherules) were synthesized [14,15]. The nanometric texture in these spherules is determined to be radial, even at their center [16]. During formation of these carbon spherules under pressure, we found a change in nanometric texture. When there are some solid impurities present, for example SiO_2, the carbon layers tend to align by arranging their basal planes parallel to the surface of the solid [17]. After covering the surface of the solid, the orientation of basal planes of aromatic rings tends to change to a radial one, because the interface is located between two liquids, the deposited and the surrounding one.

In the case of glass-like carbon spheres, there is no interaction between the sphere already formed at the stage of precursor, such as phenol resin, and the surroundings, because of solid state carbonization. Therefore, the nanometric texture of spherical bodies is determined *a priori*, that is a random arrangement of minute BSUs.

In conclusion, the interfacial energy is reasonably supposed to govern the nanometric texture of spherical carbon bodies at the stage of their formation.

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