Functional ceramics with controlled microstructure were successfully synthesized through metallorganics. The controlled hydrolysis of metal alkoxides yields BaO-TiO₂ powders, which could be sintered to the microwave dielectrics of improved properties. Zirconia toughened ceramics were fabricated by a novel processing using zirconia-coated composite powders of silica or mullite synthesized via cohydrolysis of zirconium alkoxide on dispersed starting powders. Zirconia-mullite composite powders were sintered affording compacts dispersed uniformly with zirconia particles, which showed the increased fracture toughness and designed microstructure. The controlled hydrolysis of lithium and niobium alkoxides was found to form the double alkoxide in a solution, which was converted to stoichiometric LiNbO₃ powders, films and fibers. Crystalline, epitaxial LiNbO₃ films with stoichiometry were prepared on sapphire substrate at 250°C. The orientation and crystallinity of LiNbO₃ films could be controlled by the selection of the crystallographic plane of a substrate as well as the crystallization conditions.

Key-words: Metal alkoxide, Hydrolysis, Surface modification, Heteronanocomposite powder, Zirconia, Silica, Mullite, Lithium niobate, Double alkoxide, Orientation, Epitaxial film, Fiber, Carbon composite, Organometallic polymer, Pressure pyrolysis

1. Introduction

The growing demand for the functionality and performance of ceramics accelerates the development on specific methods for the advanced ceramics. The chemical composition, crystalline state, phase composition, grain size and other factors all influence the actual properties and performances of sintered and monolithic ceramics. Hybrid ceramics with tailored microstructure requires the precise process control for ceramics based upon the suitable starting materials. Metallorganics consist of central metal atom and organic groups bonded to the metal atom. The sol-gel processing using metallorganics offers following advantages: (1) highly pure product, (2) composition control of products, (3) feasible formation of various shapes, such as films and fibers, (4) high homogeneity, (5) low temperature processing.

One of the significant features for the processing using metallorganics is the control of chemical bond of precursor. The bond nature of starting chemicals affects the properties of precursors, which define the characteristics of processing. For example, metal alkoxides are hydrolyzed and condensed yielding ceramic precursors, which are required to have appropriate properties for processing, such as stability, solubility and viscosity. The precursor is shaped into powders, films and fibers depending upon these properties. The subsequent crystallization and microstructure development also reflect the structure of precursors, and are strongly affected by the firing atmosphere as well as the crystallographic
plane of substrate. Thus, the properties of final ceramic materials result from the nature of chemical bond in the parent metallorganics. This paper demonstrates the liquid phase processing involving the precursor synthesized from metallorganics. The first subject is the synthesis of homogeneous powders for sintered Ba-Ti-O ceramics using metal alkoxide. Then, the surface modification of powder is discussed on the processing of composite particles, the hydrolysis of second alkoxides in the suspension of oxide particles yielding hetero-nano-composite powders. The third topic concerns with the preparation of LiNbO₃ films and fibers from double alkoxide solution. Finally, the synthesis of metal-dispersed carbons from organometallic polymers is described, leading to the innovative processing of advanced functional ceramics. Metal-dispersed carbon is also a heteronano-composite consisting of carbon matrix and metal dispersoid.

2. Processing through metallorganics

2.1 Barium titanate ceramics

The monosized, sub-micron, and spherical particles with homogeneous composition for the fabrication of sintered body are synthesized by the sol-gel method.1)-3) The BaO-TiO₂ system includes a variety of phases for useful applications in dielectrics. Ba₂Ti₉O₂₀ ceramics have excellent microwave dielectric properties, such as a high dielectric constant, a low dielectric loss, and a low temperature coefficient of resonant frequency. Usually, Ba₂Ti₅O₁₁ sintered body has been synthesized by the solid state reaction of BaCO₃ and TiO₂ above 1300°C. However, the quality of dielectric properties degrades due to the phase change, and the additives to sinter below the decomposition temperature and the reduction of titanium at high temperatures. Therefore, the low temperature processing of Ba₂Ti₅O₁₁ is required for the synthesis of a dense sintered body.

Alkoxides of barium and titanium are used for the synthesis of powder for sintering. The precipitates formed by hydrolysis of the direct reaction product from barium metal and titanium isopropoxide were washed with water by ultrafiltration giving filtrate liquid, in which no barium ion was detected. However, the filtrate contained barium ion, when the precipitate were prepared from a mixture of barium alkoxide and titanium isopropoxide. Therefore, the bonding state of double alkoxide of the former is definitely different from that of the latter.

The shape and dispersibility of the as-prepared particles depended strongly on the concentration of alkoxides and the reflux time after hydrolysis.1) As the reflux time for aging increased from 2 h to 24 h, the various shapes of particles with a relatively wide size distribution (0.1 to 0.2 μm) changed to the mono size powder with an average diameter of about 0.2 μm. When the concentration of Ba(OiPr)₂ decreased to 0.0028 M, spheroidal, monosized particles with an average diameter of about 0.2 μm were prepared, but they were aggregated. However, when the concentration of Ba(OiPr)₂ decreased to 0.00028 M, spheroidal monodispersed particles with an average diameter of about 0.3 μm could be synthesized via the Ostwald's ripening. The spheroidal particles formed from the 0.0028 M solution were consolidated and sintered. The single phase Ba₂Ti₉O₂₀ was formed at a temperature as low as 1200°C for 24 h, which is about 150°C lower than that for the preparation by the solid state reaction of BaCO₃ and TiO₂. The relative density of Ba₂Ti₅O₁₁ changed with sintering temperature as shown in Fig. 1, which also shows the densification behavior of Ba₂Ti₅O₁₁ powders formed from BaCO₃ and TiO₂. The sintering proceeds rapidly above 1230°C when the powders formed at low concentration of alkoxide. The Ba₂Ti₅O₁₁ sintered compact was successfully prepared between 1230° and 1300°C. The dielectric constant and Q value of the fully dense sintered body were 40 and 2850 at 10 GHz, respectively.

Ba₂Ti₅O₁₁ is known as a meta-stable phase, and is difficult to synthesize as a single-phase sintered body through the solid state reaction. Monosized and spherical Ba₂Ti₅O₁₁ particles are synthesized from mixtures of corresponding metal alkoxides.2),3) Ba₂Ti₅O₁₁ particles thus prepared were sintered by hot-pressing at 1050°C and 8.5 MPa yielding a single phase compact having a dielectric constant 42 and Q value of 5700 at 10 GHz.

2.2 Zirconia-coated silica and mullite

The second phase of composites should be dispersed homogeneously in the matrix at the proper order of heterogeneity in order to improve the mechanical or electrical properties and the reliability of ceramics. The transformation toughening of zirconia results from the control of the particle size and size distribution of zirconia, and from the uniform dispersion of tetragonal zirconia particles in the matrix.

The surface of particles is modified by the solution method using metal alkoxides.4)-7) When metal
alkoxides are hydrolyzed in the suspension of oxide, the hydrous oxide precipitates from the liquid phase depositing on the surface of oxide particles primarily existed. Thus, the oxide particles of nm size as a second phase do coat surfaces of the larger primary particles as shown in Fig. 2.

2.2.1 Zirconia-modified silica

The surface modification of mono-dispersed spherical silica powders is investigated as a model system. Silica particles were suspended in an alcohol solution of zirconium and yttrium isopropoxide, and then zirconium-yttrium hydrous oxide was precipitated by hydrolysis on surfaces of silica particles. BET surface area of zirconium hydrous oxide/silica composite powders is about 50 m²/g, which is much higher than that of colloidal silica particles of 21.8 m²/g. The increase of surface area derives from the deposition of zirconium hydrous oxide on the silica particles.

The zeta potential of powders by the electrophoresis analysis demonstrates the surface modification of silica powders as shown in Fig. 3. The colloidal silica particles show a negative value over the whole pH range examined (> pH 3). The change of zeta potentials for yttrium-zirconium hydroxide/silica particles against pH is definitely different from that of silica particles themselves. The isoelectric point of the modified silica particles is pH 6.5, which is very close to that of yttrium-zirconium hydroxide colloids.

The suspension of yttrium-zirconium hydroxide/silica of pH 4 was consolidated by centrifuging. The green body exhibits highly homogeneous microstructure composed of uniformly packed composite particles with narrow distribution in pore size. The consolidated body was sintered at 1100°C for 2 h to dense bodies of 98% relative density. The fracture toughness of sintered silica increased by the addition of 4.2 vol% 3Y-ZrO₂ from 1.6 to 2.0 MN/m³² due to the dispersion toughening of zirconia.

2.2.2 Zirconia-modified mullite

Mullite is one of the most attractive temperature-resistant materials. The dispersion of zirconia particles in mullite matrix has been attempted to improve the sinterability and the fracture toughness of mullite. Mullite particles are coated with zirconium hydrous oxide by the same cohydrolysis method as described in the Section 2.2.1. The zeta potential of powders by electrophoresis analysis for yttrium-zirconium hydroxide/mullite system reveals a difference between modified and unmodified particles. The isoelectric point of pH 7 for the modified mullite particles is almost the same as that of yttrium-zirconium hydroxide. The specific surface area increases from 18 to 200 m²/g after the surface modification.

The fracture toughness of sintered bodies of zirconia–mullite composites was remarkably improved to 4.0 MN/m³², compared with that of the sintered body of mullite itself (2.2 MN/m³²).

The composite powders of 10 vol% 4Y-ZrO₂/mullite calcined at 450°C were ultrasonically redispersed in water of pH 4, and consolidated into a green compact by colloidal processing. The calcined powders were also pressed uniaxially into the compacts. The sintering conditions and the properties of sintered compacts by the colloidal filtration (CF) and the uniaxial pressing (UP) are summarized in Table 1. The 4Y-ZrO₂/mullite composite powders were sintered to reach the density of higher than 99% of theoretical density. The sintered 10 vol% 4Y-ZrO₂/mullite from the consolidated compact through the CF method has a toughness of 4.2 MN/m³², which is...
higher than that of the sintered body by UP. The colloidal filtration combined with the surface modification of powder affords the microstructure in which submicron zirconia particles are homogeneously dispersed in the mullite matrix.

2.3 Lithium niobate ceramics

LiNbO$_3$ has useful applications for piezoelectric materials, especially for SAW devices and electro-optic devices. Single crystals of LiNbO$_3$ have been grown by the Czochralski method not from the stoichiometric melt, but from the congruent melt (48.45 mol% Li$_2$O). The sintered bodies from the solid-state reaction of Li$_2$CO$_3$ with Nb$_2$O$_5$ encounter several problems, e.g. the evaporation of Li$_2$O and the microcracking due to anisotropic thermal expansion. Since the important physical properties of LiNbO$_3$ vary sensitively with Li$_2$O content, bulk crystals or films with homogeneous and well-controlled composition have been required. Therefore, this chapter focuses on the synthesis of stoichiometric, crystalline LiNbO$_3$ using double alkoxides by the controlled chemical reaction in solvents.

2.3.1 Lithium niobate powder

Figure 4 shows the flow diagram for the preparation of LiNbO$_3$ powders and films. Lithium ethoxide is reacted with niobium ethoxide in a refluxing ethanol for 24 h yielding a homogeneous solution. The change of the absorption bands due to Nb-O bond in the IR spectra shows the different coordination of niobium-oxygen polyhedron in solution from that of the starting niobium ethoxide itself. Also, the $^1$H NMR spectra of the solution show that the methylene proton of ethoxy group undergoes the change of signal from three quartets to one quartet, which shows the formation of double alkoxide. This chemical coordination of ions was confirmed recently by Eichorst et al. The solution of the double alkoxide was hydrolyzed with 2.5 times equivalent amount of water to afford the precipitate, which crystallized in single phase LiNbO$_3$ of high crystallinity at low temperature as low as 250°C in a flow of water vapor/oxygen. On the other hand, the alkoxide solution refluxed less than 4 h gave a mixture of LiNbO$_3$, LiNb$_3$O$_8$ and Li$_3$NbO$_4$ after heat treatment at 350°C. This result shows the distinct effect of the formation of double alkoxide on the low temperature and single phase synthesis. The calcining atmosphere is also critical to the low temperature crystallization of LiNbO$_3$. The as-precipitated powder was calcined in a water vapor/oxygen atmosphere to give a crystalline phase at 250°C, while no crystallization was observed at 250°C in a flow of oxygen. The former contains no IR absorption of carbonate, the latter exhibits the absorption of carbonate. Water vapor can effectively remove the carbonate generated during calcination to promote the crystallization at 250°C, which is the lowest temperature among them ever reported. Mole ratio of Li$_2$O and Nb$_2$O$_5$ in the precipitates from equal molar solution alkoxides was analyzed to be 1.000±0.001 by an atomic absorption spectroscopy and a wet chemical analysis.

2.3.2 Lithium niobate film

The synthesis of LiNbO$_3$ films is one of the typical examples of the low temperature synthesis of highly oriented, crystalline films. The double alkoxide solution is partially hydrolyzed with an equivalent mole of water in order to avoid the precipitation of oxide. After refluxing for 24 h, the precursor solution is concentrated to the concentrations from 0.2 to 0.6 mol/l yielding a homogeneous solution. Films were fabricated using the precursor solution by dip-coating on Si or sapphire substrates of various crystallographic orientations. The crystalline film was prepared after firing under various conditions above 250°C.

The crystallization of LiNbO$_3$ film is influenced by the crystallinity of the preapplied film on a substrate. The underlying LiNbO$_3$ film developed by first dip-coating was heat-treated at 250° and 400°C. The film prepared by second dipping on the less-crystalline thin film heated beforehand at 250°C can crystallize in LiNbO$_3$ at 400°C. In contrast to these films, films on the thin film, crystallized beforehand at 400°C, can crystallize readily at a temperature as low as 250°C.

The orientation and quality of films depend strongly on the lattice parameters and thermal expansion coefficient of films and substrates. The XRD profiles of LiNbO$_3$ film oriented on silicon and sapphire sub-

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**Table 1.** Mechanical properties of mullite and 10 vol% 4Y-ZrO$_2$/mullite sintered bodies.

<table>
<thead>
<tr>
<th>Method</th>
<th>10vol% 4Y-ZrO$_2$/Mullite</th>
</tr>
</thead>
<tbody>
<tr>
<td>UP</td>
<td>C.F.</td>
</tr>
<tr>
<td>Sintering condition</td>
<td>1630°C, 5h</td>
</tr>
<tr>
<td>Relative density</td>
<td>100</td>
</tr>
<tr>
<td>Hv (GPa)</td>
<td>10.4</td>
</tr>
<tr>
<td>Toughness (MNm$^{3/2}$)</td>
<td>11.9</td>
</tr>
</tbody>
</table>

*U.P.: Uniaxial press, C.F.: Colloidal filtration*
strate are shown in Fig. 5. Films on sapphire showed highly preferred orientation at 400°C according to each orientation, such as (0001), (1120) and (0112). However, films on Si (100) were polycrystalline and had the same XRD profiles as that of LiNbO₃ powder, even at 400°C. The crystal symmetry of Si is cubic, while sapphire (α-alumina) and LiNbO₃ have the same type of oxygen packing. Films orient preferentially along the oxygen packing layer. The mismatches between LiNbO₃ and α-alumina at 400°C along the a-axis and c-axis are 8.59% and 6.50%, respectively. The films carefully crystallized on sapphire substrates exhibited the epitaxial growth feature as examined by RHEED.

Fig. 5. XRD profiles of films crystallized at 400°C on (a) silicon (100) and (b) sapphire substrates of (0112), (1120) and (0001).
kinds of metal alkoxides. The double alkoxide is hydrolyzed with controlled amount of water yielding the oligomeric precursor composed of M–O–M' bonds. The precursor of appropriate molecular structure, ligands and molecular weight, gives a homogeneous solution necessary for the following processing. Powders, films and fibers are formed from the homogeneous solution including the molecular building blocks during the formation of three-dimensional network. After the gelation is completed, the precursor of desired shape is fired under the controlled atmosphere producing ceramics. The growth of films on a substrate proceeds according to its crystallographic plane. The fundamental condition of crystal growth with high orientation is a reasonable matching of crystal lattice between films and substrates. The firing atmosphere of precursor should be carefully selected to produce a dense and highly crystalline films at low temperatures.

3. Synthesis of carbon-metal composites from organometallics

Organometallics composed of metal–carbon bonds are versatile as starting materials for the synthesis of metal-dispersed carbon. Metal-dispersed carbon composites of controlled morphology have many applications such as magnetic materials, catalysts and pigments. Metal particles, such as iron,15),16) cobalt,17) nickel,18) cementite,15),19),20) magnetite,21) Ni-ferrite,22) Fe-Co alloy,23) boron,24) and platinum,25) can be dispersed in a carbon matrix by the pressure pyrolysis of organometallic polymers.

This processing for the synthesis of metal-dispersed carbon has similar advantages to the sol-gel process, (1) highly pure product, (2) high dispersion of metallic compounds in carbon matrices. In addition, the remarkable superiorities of the pressure pyrolysis to usual carbonization methods are the controllability of morphology for carbon matrix and high yield of carbon. The objectives of the processing are the control of both carbon morphology and the size and crystallinity of nm-sized metal particles.

3.1 Pressure pyrolysis of polydivinylbenzene

The pressure pyrolysis of polydivinylbenzene (poly-DVB) gave a variety of morphologies, including isotropic spherulites, depending upon the pyrolysis pressure and temperature.20),27) The carbon spherulites are optically isotropic, hard and nongraphitizable at 2000°C. The isotropic properties of the resultant carbon result from the disordered three-dimensional cross-linkage of the starting poly-DVB. The thermal breakdown of cross-linked poly-DVB affords low molecular weight oligomers at the initial stage of pyrolysis. The oligomers of different molecular weight undergo the liquid–liquid microphase separation of immiscible phases, which leads to the morphological control of resultant carbons.

3.2 Synthesis of carbon composite

3.2.1 Synthesis of organometallic copolymers

Organometallic compounds consisting of only metal, carbon and hydrogen are used as starting compounds to disperse pure metals or metallic compounds during pyrolysis, since the carbonization is carried out in a closed system under pressure. The organometallic compounds should be soluble in the monomer compounds for molecular-level mixing.

The organometallic compounds are copolymerized with unsaturated monomers, such as divinylbenzene (DVB) and styrene (St), at 300°C and 100 MPa. Also, an unsaturated monomer solution containing the organometallic compound is polymerized under pressure, yielding polymers dispersed with organometallic compounds at the molecular level.

3.2.2 Pressure pyrolysis of the organometallic polymers below 400°C

Vinylferrocene (VF) is copolymerized with DVB or St, to form organoiron copolymers. The DVB-VF copolymer has a cross-linkage via benzene rings, since DVB has two vinyl groups on a benzene ring. However, St with one vinyl group does not give such a three-dimensional cross-linked structure via polymerization.

The changes of magnetization with temperature are shown in Fig. 7 for DVB-VF and St-VF including 3.0 wt% iron.19) The magnetization of the heat-treated product increased with increasing heat treatment temperature. Since DVB, St and VF are all diamagnetic, this increase of magnetization is attributable to the formation of paramagnetic species by bond scissions of iron–carbon bond followed by their aggregation. The observed increase in magnetization derives from the facility of aggregation of paramagnetic species in a polymer matrix. DVB-VF becomes paramagnetic above 350°C, while St-VF is already paramagnetic at 300°C. Therefore, the aggregation of paramagnetic species is more favorable in the St copolymer than in the DVB copolymer. The three-

Fig. 7. Change of magnetization for organoiron copolymer containing 3.0 wt% iron with heat treatment temperature.

○DVB-VF; ●St-VF.
dimensional matrix of poly-DVB prevents the aggregation of metal particles more effectively than poly-St.

The pyrolysis process of DVB-VF is also compared with the DVB-ferrocene (Fc) system in order to elucidate the effect of the carbon–carbon bond between ferrocene and DVB on the properties of the product.20) The vinyl group of vinylferrocene is effectively used for copolymerization with DVB. On the other hand, Fc is mixed uniformly in the DVB polymer without any bond formation. The chemical bond between the polymer matrix and ferrocene also plays an important role in preventing the aggregation, since the increase of magnetization in DVB-Fc is more rapid than that in DVB-VF with temperature range above 350°C.

The effect of thermal stability of cobalt–carbon bonds of starting organometallic compounds on the properties of cobalt-dispersed carbon is investigated.17) The cobalt–carbon bond of cobaltocene (Cp₂Co) is thermally more stable than that of phenylallylcobaltocene (PACo). The more rapid increase of magnetization is observed in DVB-PACo including the thermally more unstable cobalt–carbon bond. In addition, the use of two organocobalt polymers of different thermal stability results in the difference in the crystallinity of the cobalt particles dispersed in the carbonized products. The well-crystallized cobalt particles are formed from DVB-PACo having a thermally unstable cobalt–carbon bond.

3.2.3 Particle size of metal compounds dispersed in carbon

The pressure pyrolysis of the organoiron copolymer at 125 MPa above 550°C yields carbons dispersed with cementite. The size distributions of cementite in the carbon matrices formed at 550°C and 125 MPa are shown in Fig. 8.19) The size of cementite particle synthesized from DVB-VF was less than 60 nm, while particles up to 120 nm were dispersed in the carbon matrix formed from St-VF. The median diameter of the cementite particles formed from DVB-VF is about 15 nm, which is about one-half of that from St-VF. The different three-dimensional structures of the starting polymers result in the difference of the size of the metal particles. The particle size dispersed in the resultant carbon after pyrolysis originates in the nature of the bond in the parent organometallic polymers.

Figure 9 shows the microstructure of iron-dispersed carbon formed at 650°C and 125 MPa. The magnetic particles less than 50 nm are dispersed homogeneously in the carbon matrix.

For the synthesis of carbons dispersed with fine particles, the starting organometallic copolymer should have (1) a three dimensional cross-linked polymer matrix, (2) carbon–carbon bond strength enough for fixing organometallic compound to polymer matrix, and (3) thermally stable carbon–metal bond in organometallic compounds.

3.3 Magnetic properties of metal particles dispersed in carbon

Figure 10 summarizes the saturation magnetization of cementite-dispersed carbon synthesized from organoiron polymers at 550°C and 125 MPa.19) The saturation magnetization shows a linear relationship against the content of iron in carbon. When the concentration of iron was the same, the saturation magnetization of the cementite-dispersed carbon was constant regardless of the starting organoiron compound. The cementite particles of comparable crystals...
The metal particles dispersed in the as-carbonized carbon matrix have a low crystallinity, when pyrolysis was conducted below 700°C and at 125 MPa. As-prepared metal-dispersed carbon contains fine particles below 10 nm, which are superparamagnetic. Also, the lower saturation magnetization than the calculated value is attributed to the low crystallinity of metal particles. However, the saturation magnetization reaches the calculated value after subsequent heat treatment. For example, the heat treatment of the as-prepared cobalt-dispersed carbon at 800°C enhances the crystallinity of the metal particles, which increases the saturation magnetization from 50% to 95% of the calculated value.17) The increases both in the size and the crystal perfection of the superparamagnetic and ferromagnetic particles by heat treatment raise the saturation magnetization.

The maximum coercive force of cementite-dispersed carbon formed from DVB-VF is 950 Oe, which is about twice that from St-VF at 2.0 wt% iron.19) The smaller coercive force of the specimen from St-VF than DVB-VF results from the larger size of cementite particles of the former which have multiple magnetic domains. Therefore, the decrease in coercive force is due to the formation of multiple magnetic domains in the large particles.

The saturation magnetization of metal-dispersed carbon reflects the crystallinity and size of metal particles. The size distribution of metal particles is responsible for the coercive force of metal-dispersed carbon.

3.4 Dispersion of alloy particles in carbon matrix

The organometallic polymers containing more than two kinds of metals can be pyrolyzed to disperse alloy and nickel ferrite particles.20),21) Fe·Co alloy has the highest saturation magnetization among transition metal alloys, and remains ferromagnetic at high temperature of 800°C. DVB containing vinylferrocene and cobaltocene derivative was pyrolyzed under pressure yielding carbons dispersed with Fe·Co alloy particles. The alloying between Fe and Co proceeds during pyrolysis. The formation of Fe·Co in as-prepared carbon was confirmed by the thermomagnetic measurement. Carbons dispersed with Fe·Co alloy particles show the saturation magnetization of alloy itself corresponding to the ratio of Fe to Co.

3.5 Morphology of carbon matrix

The morphology of the carbon matrix depends on the concentration of the metals and the pyrolysis conditions such as temperature and pressure. Spherulites and coalescing spherulites are formed by pressure pyrolysis of poly-DVB itself.26),27) On the other hand, the representative morphology of metal-dispersed carbon is coalesced polyhedra of irregular shape. The morphology changes from coalesced polyhedra to fibrous carbon as the concentration of the metal and the pyrolysis temperature increase.15) The polymer matrix decomposes to give liquid phases of various molecular weights at around 400°C under pressure, and then produce carbon above 500°C. The morphology of carbon is affected by the liquid–liquid microphase separation. Metal particles formed by aggregation during pyrolysis change the phase separation from homogeneous to heterogeneous. When the organometallic polymer is pyrolyzed in the presence of water, carbon spherulites dispersed with ferrite particles can be synthesized as shown in Fig. 11.21),22) Supercritical water is considered to act as a low molecular weight component giving a homogeneous microphase separation system. The metal particles are oxidized by water during the pyrolysis producing ferrite particles.

3.6 Synthesis conditions for metal-dispersed carbon

The pressure pyrolysis of organometallic polymers undergoes the liquid phase of oligomers, which is responsible for the morphology of carbons. The size and the morphology of the carbon matrix can be controlled by the selection of the pyrolysis conditions as well as the amount of coexistent water and the metal concentration in the copolymers. The magnetic properties of metal-dispersed carbon are attributed to the crystallinity and the particle size of the metals, which have been found to depend strongly on the properties of both the carbon–metal bond of the organometallic compounds and the carbon–carbon bond of the polymer matrix. This processing affords a novel method for producing carbon nanocomposites with controlled microstructure and morphology.

4. Conclusions

The controlled properties of ceramics originate in the properties of starting materials and precursors including appropriate molecular building blocks, which can be synthesized not only from double alkoxides of metal-organics but also from metallocene polymers of organometalics. The structure of
precursor in solution or in liquid phase is an important key for the successful control of microstructure in the final products. Especially, the selection of chemical bonds in the starting materials is critical for the control of morphology of μm size as well as that of the nm-sized dispersoid. The highly oriented crystal growth is based upon the properly selected nucleation and growth site on a substrate. The underlying feature of the chemical processing in liquid phase is leading to the molecular designing of ceramic materials at the molecular level.

References
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