Colloid science of ceramic powders

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Abstract - Several techniques for the preparation of well defined colloidal dispersions consisting of uniform particles of different chemical composition, shape, and size are described. Specifically, the precipitation from homogeneous solutions, phase transformation processes, and reactions with aerosols are used to generate simple, composite, and coated inorganic particles. The effects of the chemical composition of the starting solutions on the morphology and structure of the resulting dispersed solids are discussed and the areas requiring further clarification are indicated.

INTRODUCTION

Modern ceramics incorporates a huge number of materials for countless applications, including engine parts, computer components, sensors, superconductors, catalysts, pigments, magnetic recording particles, drug delivery systems, and many others. The specifications with respect to the performance of such products are becoming more stringent, requiring ceramics of carefully controlled and reproducible characteristics. In the majority of cases these materials are composites, made up originally of much smaller constituents. Thus, it is now widely acknowledged that one of the prerequisites for more successful preparations of solids for high-tech uses is the availability of powders consisting of particles uniform in composition, size, shape, porosity, etc, which on processing will yield products of desired properties. To quote a recent article: "The secret of improving a ceramic material is to control its structure at very small length scales in an early stage of fabrication. Chemistry may be the way to succeed in this goal" (ref. 1).

Obviously, it is necessary to develop techniques for the synthesis of precursor powders with uniform particles of micrometer or less in size. Next, for successful processing one must control their stability and mutual interactions (especially in mixed systems), which are affected by forces acting between primary particles. Finally, depending on application, these powders need to meet certain requirements with regard to their optical, magnetic, charge, conductance, and other properties. All of these aspects of finely dispersed matter are in the domain of classical colloid science. Therefore, it is no surprise that communications between investigators in the disciplines of ceramics and colloids and interfaces have greatly intensified in recent years (refs. 2-5).

Recently, we note substantial progress in the development of techniques and in the understanding of the underlying fundamental principles for production of well defined colloids. Several extensive reviews have been published on this subject, which summarize the accomplishments in the field (ref. 6-10). A large number of simple and complex inorganic, organic, or mixed compounds are now available as dispersions or powders consisting of "monosized" particles. In this work the new results on the preparation of such materials are described with special reference to precipitation from electrolyte solutions and aerosol techniques.

In the case of the former procedure, the emphasis will be on the exploitation of complex chemistry in order to generate particles of different properties. The great sensitivity of the solid phase formation in homogeneous solutions to small changes in the experimental conditions will be illustrated. Yet, by a careful control of the processes, uniform particles of all kinds of chemical compositions and morphologies can be reproducibly generated.

In the use of liquid aerosols for particle preparation chemical processes are constrained to individual droplets, each representing a separate "reaction container", in contact with a vapor that acts as a coreactant.

The so generated dispersions can be used in various studies, such as in the determination of their stability, interactions with solutes and other dispersed matter, as well as in particle adhesion phenomena.

PRECIPITATION TECHNIQUE

A. General considerations

The most common process for the preparation of fine inorganic particles is precipitation from electrolyte solutions. To achieve uniformity of the dispersed matter, it is essential to have a single nucleation stage, followed by a controlled particle growth. The burst of nuclei occurs when critical supersaturation is achieved of particle-forming solutes, which may consist of one or more complex species. The latter depend strongly on the nature
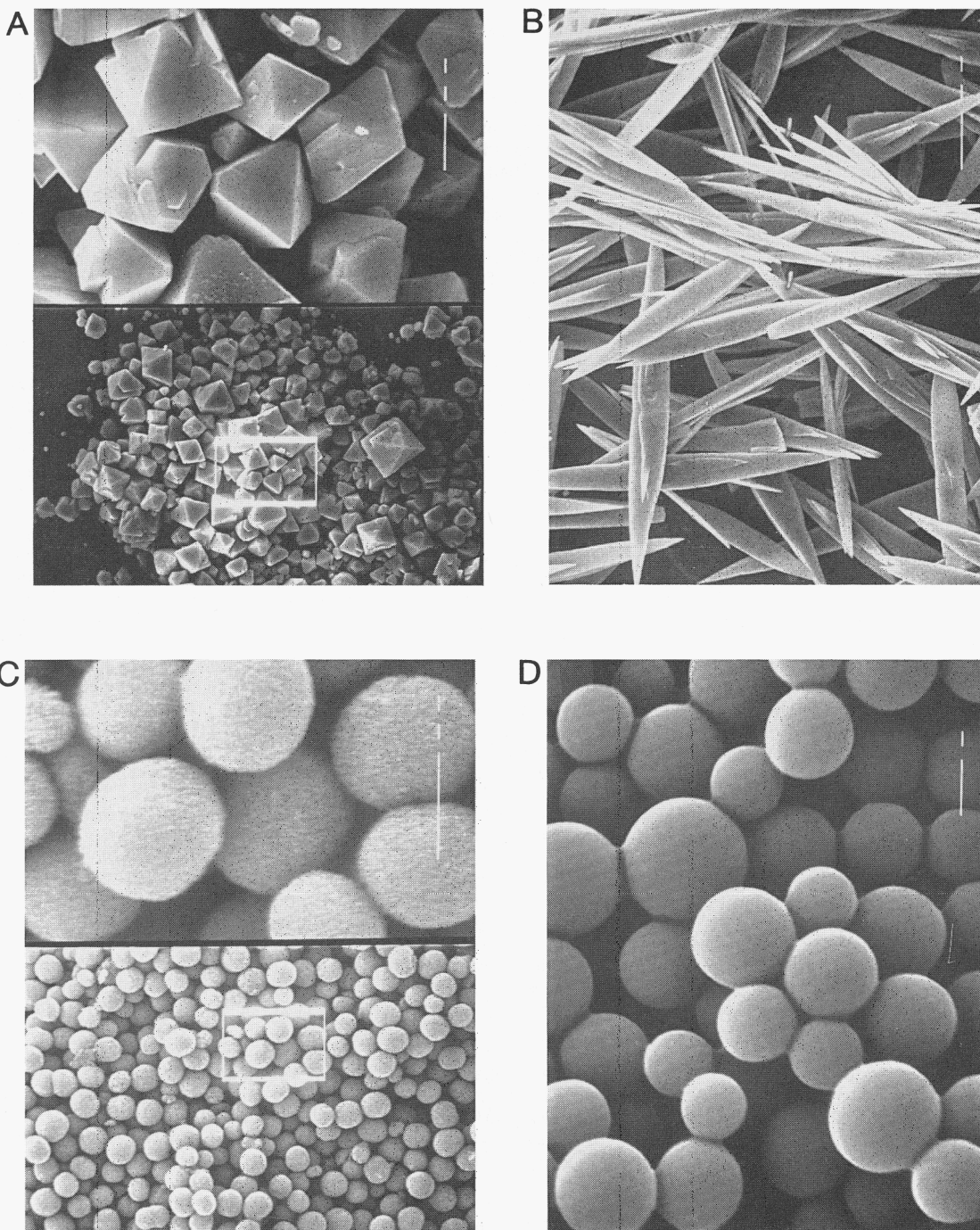

Figure 1. Scanning electron micrographs (SEM) of particles obtained by aging at 90°C for 1 hr the following solutions:
(A) 8×10^{-3} mol dm^{-3} CuCl$_2$ and 2×10^{-1} mol dm^{-3} urea;
(B) 8×10^{-3} mol dm^{-3} CuSO$_4$ and 2×10^{-1} mol dm^{-3} urea;
(C) 2×10^{-3} mol dm^{-3} Cu(NO$_3$)$_2$ and 5×10^{-1} mol dm^{-3} urea (black solids).
(D) 8×10^{-3} mol dm^{-3} Cu(NO$_3$)$_2$ and 2×10^{-1} mol dm^{-3} urea (green solids);
In (A), (B), and (C) the longest bar corresponds to 10 μm, while in (D) to 1 μm.

of the solutions (concentration of the salts, choice of anions for a given cation and vice versa, pH, solvent composition, etc.) and on the conditions (temperature, stirring, size of the volume, etc.) under which the experiments are carried out. It is the complex chemistry of the solutions in each specific case that determines the composition and the morphology of the final products. Obviously, this sensitivity of the precipitation processes to so many parameters can be both beneficial and detrimental in the efforts to synthesize uniform colloids. Establishing the optimum conditions to generate such products is a time consuming and painstaking project. However, the precipitation from solutions offers the opportunity to obtain a variety of particles in terms of their chemical composition, structure, shape, and size. Furthermore, no special equipment is needed; a constant temperature environment, infrequently exceeding 100°C, suffices in most cases.

There are a number of questions which need to be resolved, particularly with respect to the nature of dispersions generated from a given electrolyte solution. In some instances the same reacting components will yield particles of different morphologies and even of different composition when either the concentration of the solutes or the temperature and/or the length of aging the systems is altered. For example, in ferric chloride solutions acidified with HCl and heated for a given period of time, depending on the concentration of the reactants, either β-FeOOH or α-Fe_2O_3 particles are precipitated. While the former appear as rods of varying axial ratios, the latter are of spherical, cubic, or ellipsoidal morphology. The particle shape can be altered by changing the anions; i.e., under identical conditions ferric chloride, nitrate, or perchlorate will result in hematite particles of different shapes (ref. 11).

In other cases the presence of various anions results in entirely different products for the same cationic species. An example of such effects is offered in Fig. 1, which shows electron micrographs of a series of particles precipitated from copper(II) solutions in the presence of urea. Thus, solutions of $CuCl_2$ yield octahedral particles of copper(II) oxychloride (Fig. 1A), while those of $CuSO_4$ result in elongated crystals of copper(II) basic sulfate (Fig. 1B). Electron micrographs 1C and D are of spherical particles precipitated in $Cu(NO_3)_2$ solutions under somewhat different conditions. The solid illustrated in Fig. 1C appears black and that of Fig. 1D is green; the former is essentially a copper oxide, whereas the latter is a basic carbonate (ref. 12). In these examples the emphasis is on the shape of the particles rather than their uniformity.

The sensitivity of the properties of the products to small changes in experimental conditions is illustrated in Fig. 2. The two drastically different kinds of particles were generated from identical solutions of lanthanum nitrate containing urea. The aging of the systems at the elevated temperature that yielded spherical particles was carried out in closed tubes, while those resulting in elongated particles in open tubes with stirring. It should be noted that little loss in the volume of the liquid occurred in the latter case.
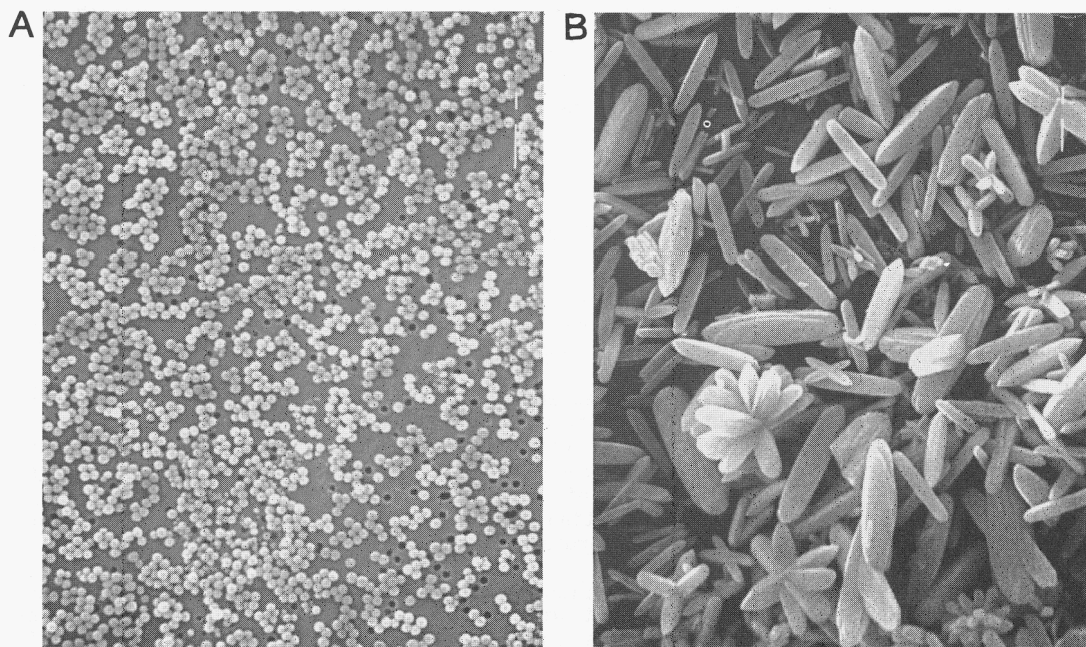

Figure 2. SEM of particles prepared by aging a solution 2.5×10^{-2} mol dm^{-3} in $La(NO_3)_3$ and 2.7×10^{-1} mol dm^{-3} urea at 90°C for 1 hr in (A) closed and (B) open tubes and stirred.
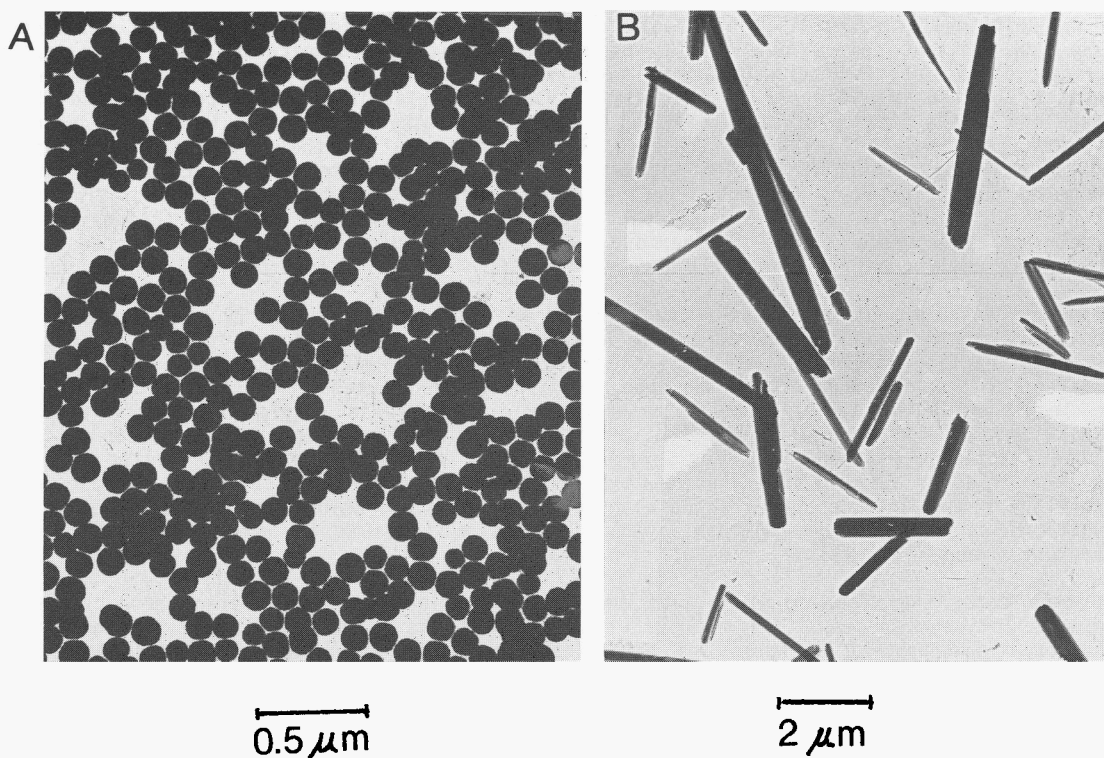
Figure 3. Transmission electron micrographs (TEM) of (A) $Y(OH)CO_3 \cdot H_2O$ particles obtained by aging at 90°C for 2.5 hr a solution 1.5×10^{-2} mol dm^{-3} in YCl_3 and 0.5 mol dm^{-3} in urea; (B) $Y_2(NH_3)(CO_3)_3 \cdot 3H_2O$ particles obtained by aging at 115°C for 18 hr a solution 3.0×10^{-2} mol dm^{-3} in YCl_3 and 3.3 mol dm^{-3} in urea.

Another example of the effect of experimental conditions on the particle composition and shape, generated from solutions of the same reactants, is offered in Fig. 3. The spheres consisting of $Y(OH)CO_3 \cdot H_2O$ were obtained by heating an YCl_3 solution in the presence of urea at 90°C for 2.5 hr (Fig. 3A). Longer aging times at 115°C and somewhat different concentrations of the solutes resulted in rod-like particles of $Y_2(NH_3)(CO_3)_3 \cdot 3H_2O$ shown in Fig. 3B. The difference in the chemical composition (and correspondingly in morphology) can be related to decomposition products of urea, which vary with temperature and reaction time. In order to insure reproducibility, it is necessary to establish the precipitation boundaries that will delineate experimental parameters leading to a given product. Two such domains are illustrated in Fig. 4 for solutions containing $Y(NO_3)_3$ and urea, in which code letters indicate the morphology of the resulting particles (ref. 12).

All described systems have been prepared in the presence of urea, which on heating decomposes to CO_2 and NH_4^+ in acidic aqueous solutions, and to NH_3 and CO_3^{2-} species in basic or neutral solutions. As a consequence either metal ion hydrolysis is promoted to give metal (hydrous) oxides or simple (or mixed) carbonates are formed. Thus, introducing urea gives rise to a large variety of compounds which may precipitate as uniform particles under properly controlled aging conditions. Table I summarizes a number of such diverse products obtained in the presence of urea. Whether hydrous oxides or carbonates will form depends on the relative solubilities of the corresponding compounds.

It should be emphasized that urea is not essential in the preparation of many colloidal metal (hydrous) oxides of narrow size distribution. Indeed, readily hydrolyzable ions will yield such particles by hydrolysis of metal salts solutions without any additives, as it was demonstrated on a number of examples (refs. 6,7,11,22-26). The process is frequently accomplished by adequate heating of metal salt solutions (forced hydrolysis). The addition of urea is essential in promoting hydrolysis of weakly hydrolyzable cations, although in such cases other complexes may form as illustrated in Table I.

It should be noted that the described principles do not apply only to metal (hydrous) oxides or carbonates, which have been mainly dealt with so far. Decomposition of thioacetamide under properly controlled conditions yields uniform metal sulfides (refs. 22-24), while selenourea gives metal selenides (ref. 25).

It is readily rationalized that all described phenomena are due to different complexation reactions in solution which precede the precipitation of a solid phase. A detailed understanding of these processes requires the knowledge of the kinetics of the formation
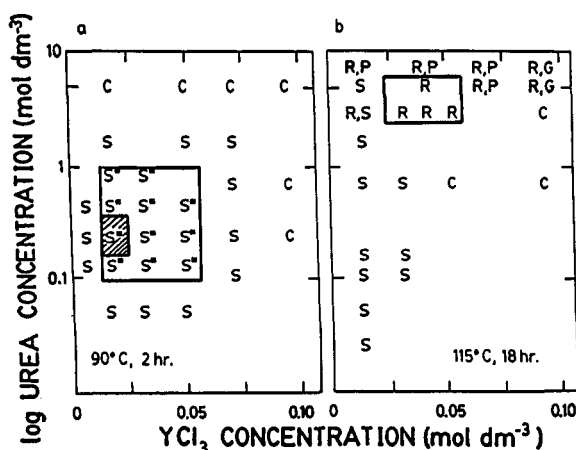
Figure 4. Precipitation domain for systems containing $Y(NO_3)_3$ and urea.
(a) Solutions aged at 90°C for 2 hr. Enclosed clear and shaded areas represent conditions for the formation of uniform spherical particles aged in uncapped and capped tubes, respectively. (b) Solutions aged at 115°C for 18 hr. Enclosed area represents conditions yielding rod-like particles. Symbols: R (rods), S (spheres), S* (uniform spheres), C (coagulated spheres), P (platelets), and G (gel).

TABLE 1. Dispersions of narrow size distribution obtained by forced hydrolysis with urea

Final Products		Particle Shape	Particle Size (μm)	Anion	Final pH	Ref
Metal Hydrous Oxides	$Al(OH)_3$	spheres	0.1-0.6	SO_4^{2-}	7-9	14
	$Cr(OH)_3$	"	0.1-0.6	SO_4^{2-}	7-9	14
	$Cd(OH)Cl$	rods		Cl^-	5.5	15
Metal Basic Carbonates	$Cu_2(OH)_2CO_3$	spheres	0.3-1.0	NO_3^-	6-8	12
	$Zr_2(OH)_6CO_3$	"	0.3-0.7	SO_4^{2-}	6-8	13
	$Y(OH)CO_3$	"	0.1-0.5	NO_3^- or Cl^-	6-8	13
	$La(OH)CO_3$	"	0.1-1.0	NO_3^- or Cl^-	6-7	12
	$Sm(OH)CO_3$	"	0.05-0.4	NO_3^- or Cl^-	6-8	16
	$Eu(OH)CO_3$	"	0.1-0.4	NO_3^- or Cl^-	6-8	16
	$Gd(OH)CO_3$	"	0.1-0.6	NO_3^- or Cl^-	7-9	16
	$Tb(OH)CO_3$	"	0.1-0.3	NO_3^- or Cl^-	6-8	16
	$Ce_2O(CO_3)_2$	ellipsoidal platelets		NO_3^-	6-8	16
Metal Carbonates	$CdCO_3$	cubes		NO_3^- or Cl^-	7-10	15
	$Y_2(CO_3)_3NH_3$	rods		NO_3^-	9-10	13
Metal Basic Sulfates	$Zr_2(OH)_6SO_4$	spheres	0.3-0.8	SO_4^{2-}	2.2	18
	$Al_x(OH)_{3x-2y}(SO_4)_y$	"	0.2-0.8	SO_4^{2-}	<6	14
	$Cr_x(OH)_{3x-2y}(SO_4)_y$	"	0.2-0.8	SO_4^{2-}	<6	14
	$Fe_3(OH)_5(SO_4)_2$	hexagonal or monoclinic crystals		SO_4^{2-}	---	17
Metal Phosphates	$Mn_3(PO_4)_2$	spheres	0.2-0.5	SO_4^{2-}, PO_4^{3-}	6-8	19
	$CO_3(PO_4)_2$	"	0.2-0.5	SO_4^{2-}, PO_4^{3-}	6-8	20
	$Zn_3(PO_4)_2$	"	0.3-0.8	SO_4^{2-}, PO_4^{3-}	6-8	21
	$Cd_3(PO_4)_2$	"	0.3-0.8	SO_4^{2-}, PO_4^{3-}	6-8	19
	$Ni_2(OH)PO_4$	"	0.1-0.4	SO_4^{2-}, PO_4^{3-}	6-8	19
Composite Compounds	$Al_xCr_{1-x}(OH)_3$	spheres	0.1-0.6	SO_4^{2-}	6-8	14
	$Ce_xY_{1-x}(OH)CO_3$	"	0.05-0.2	NO_3^-, SO_4^{2-}	5.5-8	13
	$ZrY_x(OH)_{3+x}(CO_3)_{0.5+x}$	"	0.2-0.7	NO_3^-, SO_4^{2-}	6-8	18

and disappearance of all solutes before and during the nucleation and particle growth stages, which is by no means an easy task. Once such solution complex chemistry is known, it is possible to explain why certain solids appear in a given crystal habit. A more difficult task is the elucidation of the reasons for different morphologies of particles of the same chemical composition, generated either in solutions of the same reactants under often slightly different conditions, or by changing anions while cations remain the same.

Spherical particles precipitated from aqueous electrolyte solutions deserve special comments. In some cases such dispersions consist of amorphous materials, exemplified by aluminum or chromium (hydrous) oxides, which are obtained simply by forced hydrolysis of the corresponding metal sulfate solutions (refs. 26,27). However, spherical particles of cerium(IV) oxide, iron(III) oxide, cadmium sulfide, zinc sulfide, etc., precipitated by the same procedure, show distinct X-ray patterns characteristic of known crystalline materials or minerals of the same chemical compositions (refs. 11, 28-30). It is obvious that such a method of preparation cannot yield spherical <u>single</u> crystals. Indeed, it was documented by low angle X-ray analysis and by electron microscopy that these spheres were built up of subunits of much smaller size, hence having internally composite structure.

Figure 5 shows a series of electron micrographs which clearly demonstrate the aggregation of very small particles into larger uniform spheres (ref. 30). The process can be followed by optical means, as demonstrated in Fig. 6, which gives the change in the light scattering intensity as a function of time in a solution of zirconium sulfate aged at 50, 80, and 90°C. The increase in turbidity is due to nucleation and growth of "primary" particles. After a given induction period, turbidity decreases again indicating the onset of the aggregation process, whereby the number of particles is drastically reduced while the size of the resultant spheres increases.

B. Particles of mixed cation composition

It was shown in the previous section that many solids generated in a metal salt solution actually have a mixed chemical composition with respect to the incorporated anions. This effect is due to the formation of solute complexes, such as hydrolyzed cations, which also coordinate another anion. Precipitated particles contain this anion along with the hydroxide ion, either in stoichiometric or nonstoichiometric ratios.
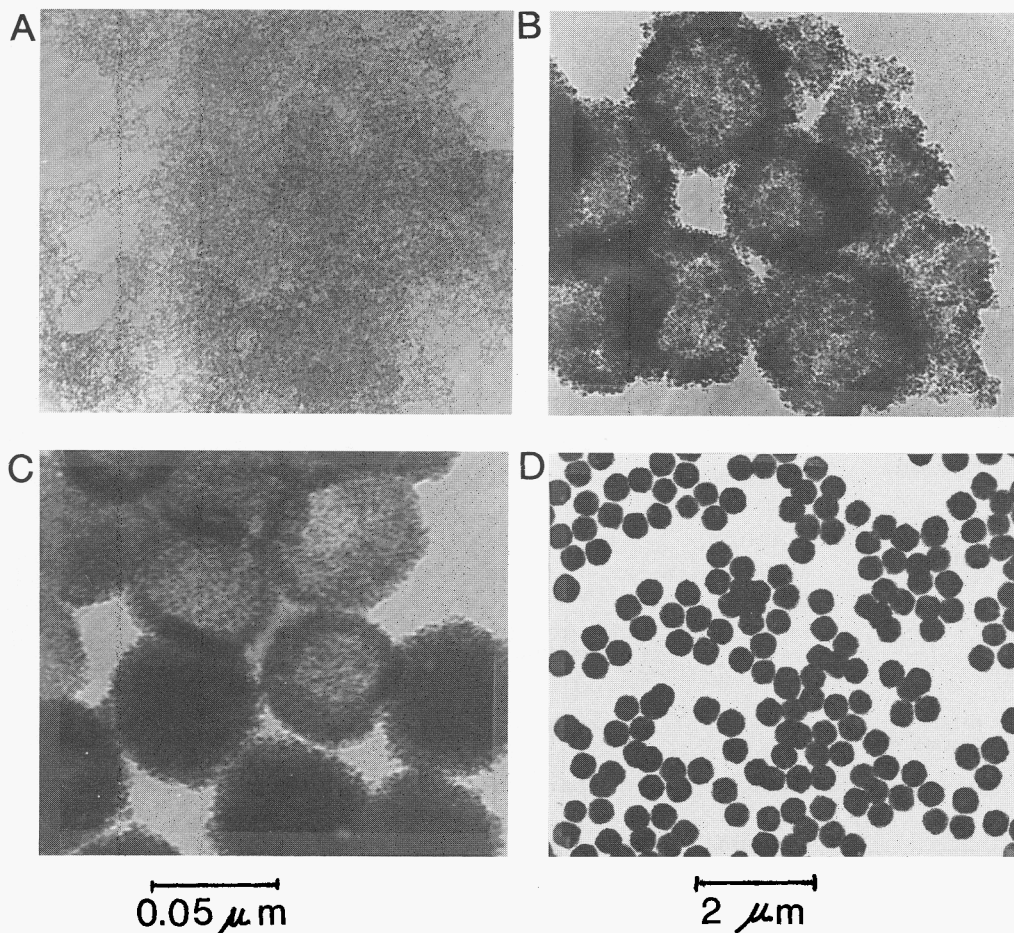

Figure 5. (A-C) Formation of CeO_2 particles by forced hydrolysis of an acidic (4.0×10^{-2} mol dm^{-3} H_2SO_4) solution of $Ce(SO_4)_2$ (1.0×10^{-3} mol dm^{-3}) heated at 90°C during a 6 hr period. (D) TEM of this dispersion at the completion of aging after 48 hr.

In many applications it is desirable to have particles with more than one cation, in order to modify their properties (catalytic, magnetic, optical, electrical, etc.). It is shown here that the precipitation technique can be applied to this end. A mixture of metal salt solutions in different molar ratios may yield on aging uniform particles under conditions similar to those applied to individual systems when treated separately. The more similar the chemical properties of the two cations, the more easily are formed composite solids.

In some cases the content in cations in the solid phase reflects almost exactly the composition of the solution from which the particles are precipitated. Figure 7 illustrates two such dispersions, i.e., an Y(III)/Ce(III) and an Y(III)/Zr(IV) basic carbonate. The
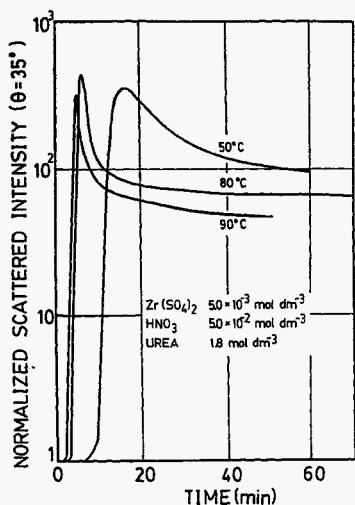
Figure 6. Change in optical density (arbitrary scale) with time of systems consisting of 5.0×10^{-3} mol dm^{-3} Zr(SO$_4$)$_2$, 5.0×10^{-2} mol dm^{-3} HNO$_3$, and 1.8 mol dm^{-3} urea at 50, 80, and 90°C, respectively.
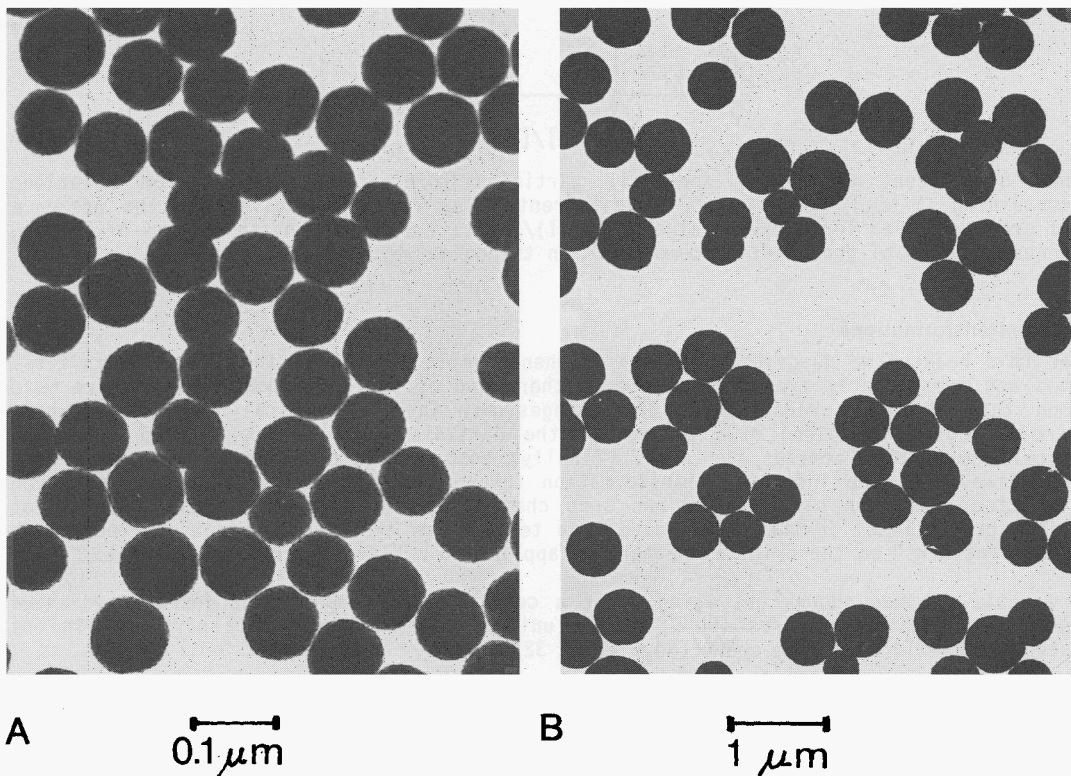

Figure 7. TEM of mixed colloidal particles obtained by aging the following solutions: (A) 5.1×10^{-3} mol dm^{-3} Ce(NO$_3$)$_3$, 1.5×10^{-2} mol dm^{-3} Y(NO$_3$)$_3$, and 0.5 mol dm^{-3} urea kept at 90°C for 2 hr. (B) 5.0×10^{-3} mol dm^{-3} Zr(SO$_4$)$_2$, 4.0×10^{-3} mol dm^{-3} Y(NO$_3$)$_3$, 1.8 mol dm^{-3} urea, 5.0×10^{-2} mol dm^{-3} HNO$_3$, and 3% (v/v) polyvinylpyrrolidone (PVP), kept at 80°C for 5 hr.

chemical compositions of these solids are determined to be $Y_{0.75} Ce_{0.25}(OH)CO_3 \cdot H_2O$ and $ZrY_{0.8}(OH)_{3.8}(CO_3)_{7.3} \cdot 0.8H_2O$, respectively (refs. 13,18), which correspond to the molar ratios of the cations in the respective solutions. In both examples amorphous spherical particles of narrow size distribution are obtained. On calcination at elevated temperatures (e.g., 650°C) the same solids are converted to crystalline metal oxides, yet the spherical shape is preserved.

Figure 8 deals with mixed Y(III)/Cu(II) systems. The ordinate gives the percent of Cu^{2+} in spherical particles for different Cu(II)/Y(III) ratios in the salt solutions in which the precipitation took place. The full line is calculated for solids having the composition $Y(OH)CO_3 \cdot H_2O + (x/2) \ Cu_2(OH)_2CO_3$. Circles are analytical data obtained for particles generated from solutions containing Cu(II) to Y(III) salts in different ratios, while several points for the same value of the abscissa refer to different concentrations of metal salts. In all cases urea was present, but its concentration varied in individual experiments. It would seem that the composite particles of essentially the same stoichiometry precipitated in all these systems (ref. 31).
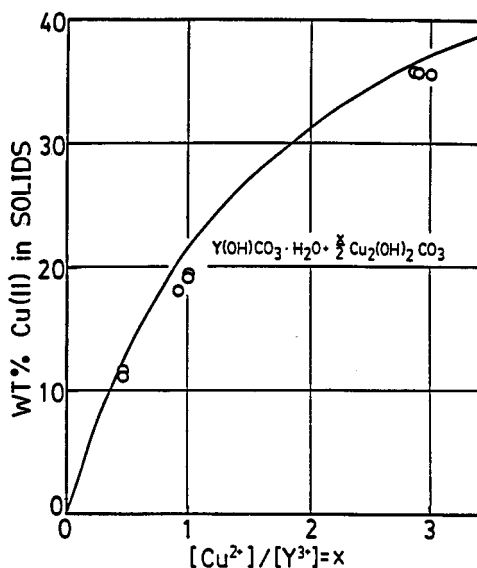

Figure 8. Percent Cu(II) in spherical particles (ordinate) obtained from solutions containing $Cu(NO_3)_2$ and $Y(NO_3)_3$ in different molar ratios (abscissa) in the presence of urea. Circles for a given value of Cu(II)/Y(III) = x correspond to systems of varying concentrations of the reacting components in the aging solutions.

C. Phase transformations

Under this heading we describe a variety of phenomena in which one kind of solids is first formed and subsequently transformed into another kind of solids. Such processes are more common than generally recognized. The changes may involve chemical composition while the morphology is retained or, conversely, the particle shape may be altered while the chemical composition remains the same. Finally, both the composition and the shape can be modified. In some instances transformation takes place spontaneously and may not even be detected, while in other situations such changes are induced to produce particles of specific properties. In the latter case high temperature treatment, oxidation, reduction, or other "attacks" on the original matter are applied to achieve a different product.

For example, it was shown that aging under a certain set of conditions ferrous hydroxide gels at moderate temperatures (90°C) yields uniform spherical magnetite particles in the presence of a mild oxidizing agent (NO_3^-) (ref. 32).

Ellipsoidal maghemite can be obtained from hematite particles of the same shape by a sequence of reduction and re-oxidation processes (Fig. 9A) (ref. 33), while complete reduction results in pure iron of the same morphology (Fig. 9B) (ref. 34).

Phase transformation may take place spontaneously, sometimes just by changing the liquid environment. Figure 10A shows spherical amorphous particles of lanthanum basic carbonate which, when separated and suspended in pure water, crystallize into platelets displayed in the electron micrograph 10B. The latter crystallites do not further change on
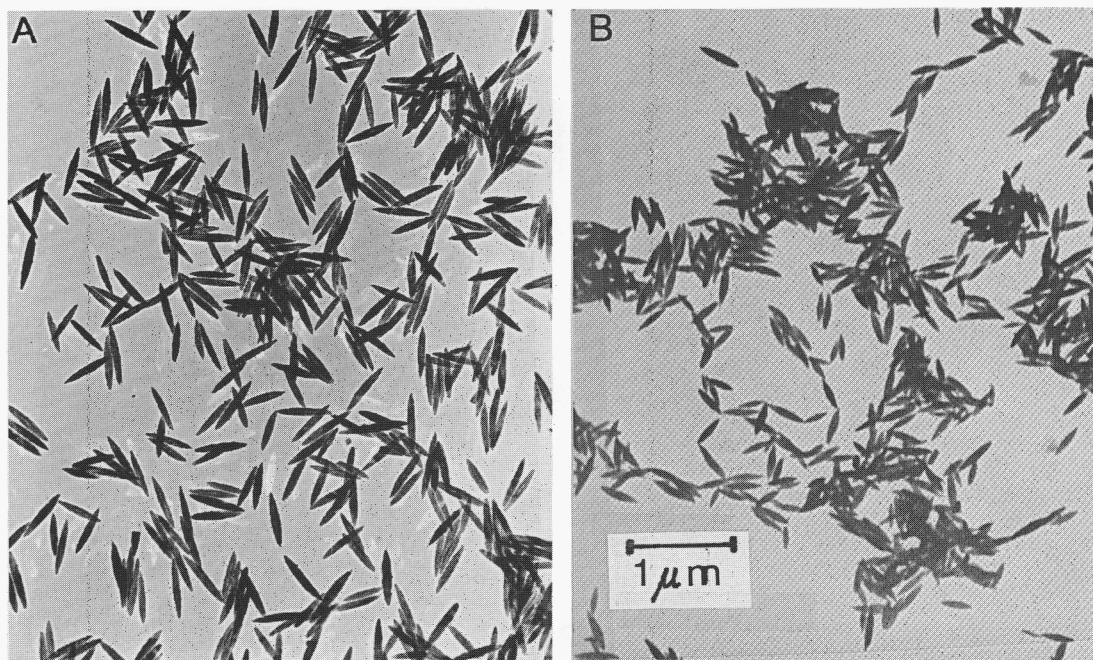
Figure 9. (A). TEM of γ-Fe$_2$O$_3$ (maghemite) particles obtained by first reducing α-Fe$_2$O$_3$ (hematite) particles of the same shape in hydrogen to Fe$_3$O$_4$ (magnetite) at 340–400°C and reoxidizing in air at 240°C to maghemite (ref. 33). (B) Iron particles obtained by reduction of hematite in hydrogen at 400°C (ref. 34).

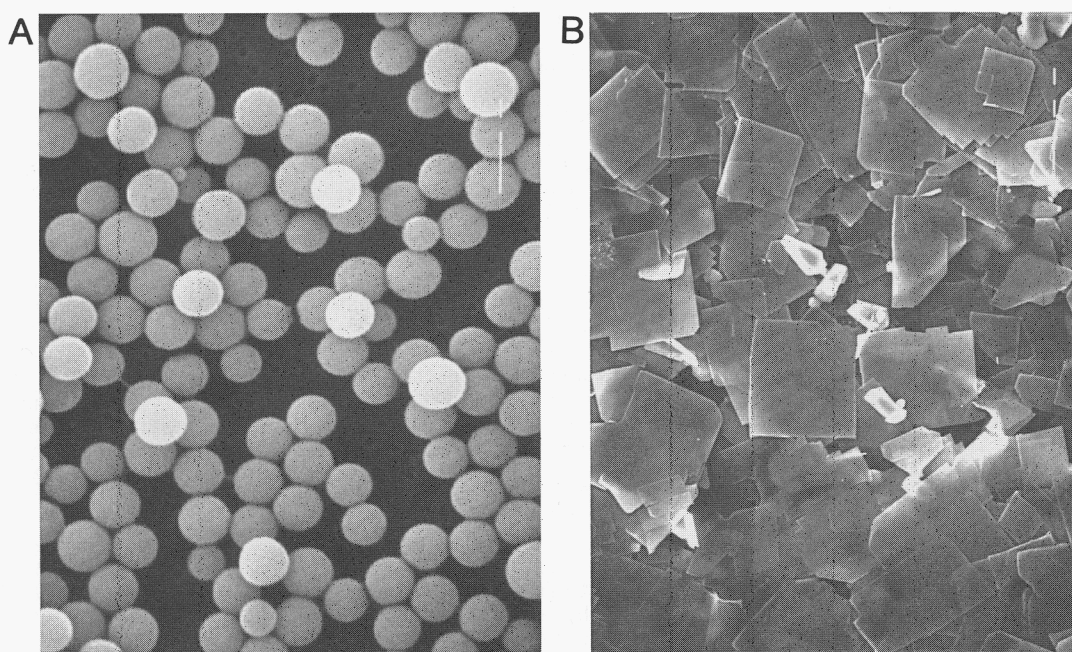Figure 10. (A) SEM of lanthanum basic carbonate particles obtained by aging at 90°C for 1 hr a solution 3 x 10^{-3} mol dm^{-3} in LaCl$_3$ and 1 x 10^{-1} mol dm^{-3} in urea. The longer bar = 1 μm. (B) The same system after the particles were resuspended in water for 4 hr. The longest bar = 10 μm.

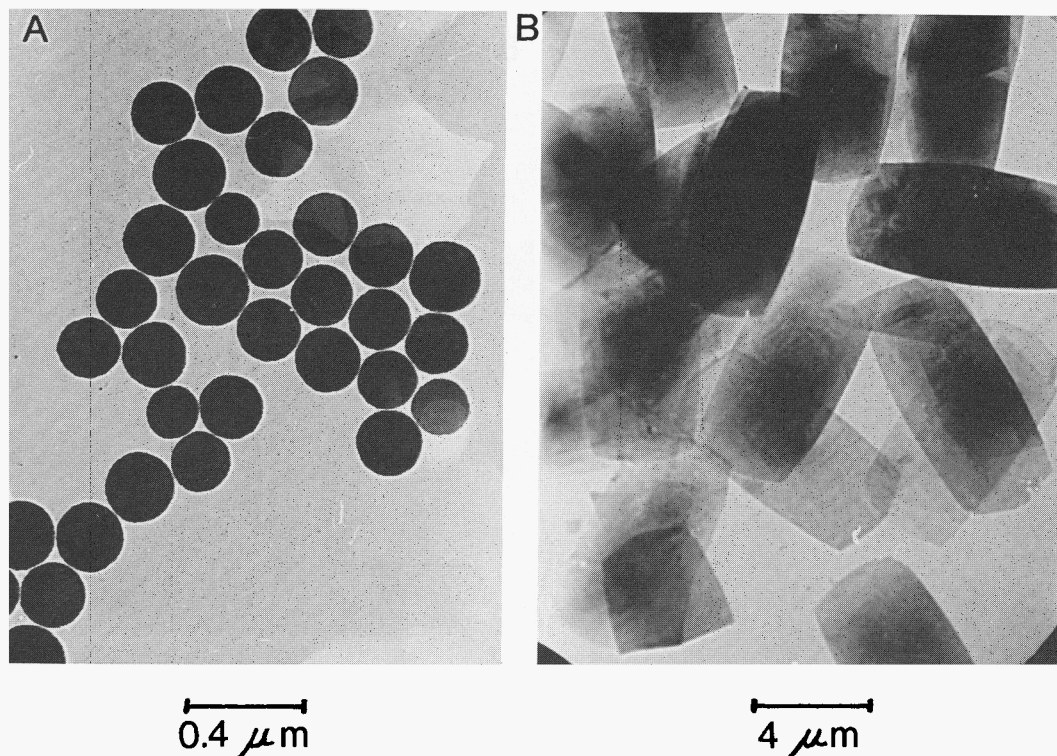Figure 11. (A) TEM of $Mn_3(PO_4)_2 \cdot x\ H_2O$ particles obtained by aging at 80°C for 1 hr a
solution 5×10^{-3} mol dm^{-3} in $MnSO_4$, 5×10^{-3} mol dm^{-3} in H_3PO_4, 1.0 mol dm^{-3} in
urea, and 1×10^{-2} mol dm^{-3} in sodium dodecylsulfate. (B) The same system after the
particles were resuspended in distilled water for two days at room temperature.

calcination at 800°C (ref. 35). Similarly $Mn_3(PO_4)_2 \cdot xH_2O$ spheres (Fig. 11A) resuspended
in distilled water transform into prismatic crystals (Fig. 11B) on standing at room
temperature, while the composition remains the same (ref. 36).

These selected examples clearly indicate that different dispersed matter can be prepared
by manipulating certain solids in order to change their composition, shape, and size.
In many cases the reasons for such transformations are not understood; the elucidation
of these processes represents a genuine challenge for scientists in this field.

D. Coated particles

Another approach in modifying properties of a powder is to coat the particles with a
material of a different chemical composition. Again, it is possible to achieve a uniform
layer by precipitation from aqueous solutions.

Figure 12 illustrates ellipsoidal hematite particles coated with yttrium oxide (ref. 37).
The originally deposited surface layer consists of yttrium basic carbonate, which on
calcination changes to the corresponding oxide. The core dispersion was chosen because
of the particle shape. In excess of the coating material yttrium basic carbonate not
only covers hematite, but also precipitates as separate spheres. Thus, one can usually
detect extraneous particles, simply by inspecting the electron micrographs.

Using various modifications in the procedure, different core particles (chromium hydrous
oxide, hematite, titania) were coated with aluminum oxide (ref. 38), or hematite with
chromium hydrous oxide (ref. 39). The last example is used to illustrate that surface
characteristics of the solids are altered by such deposits, i.e., the coated particles
behave as the coating material itself. Figure 13 shows that the differential scanning
calorimetry curves for chromium hydrous oxide particles and for hematite coated with the
same material are identical, but differ from that of the pure core material.

Well defined inorganic colloidal particles can be used as carriers for organic compounds.
The electron micrograph in Fig. 14A shows chromium hydrous oxide particles covered with
ovalbumin. For this purpose the protein was added to an aqueous dispersion of the solid
particles and the system equilibrated by tumbling at room temperature. The uniform coating
layer was made visible by staining with tungstophosphoric acid.

0.5 μm   Fig. 12

Fig. 13

Figure 12. TEM of ellipsoidal hematite particles coated with yttrium basic carbonate. A dispersion of hematite (0.1 g dm^{-3}) containing 5.0 x 10^{-3} mol dm^{-3} Y(NO$_3$)$_3$ and 1.8 mol dm^{-3} urea was heated at 90°C for 2 hr.
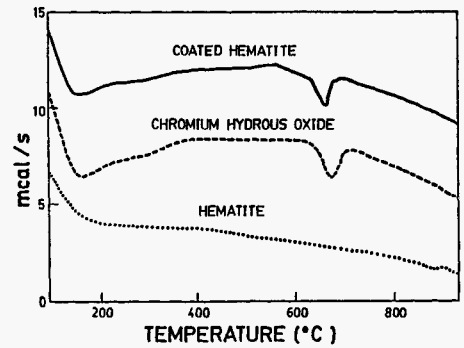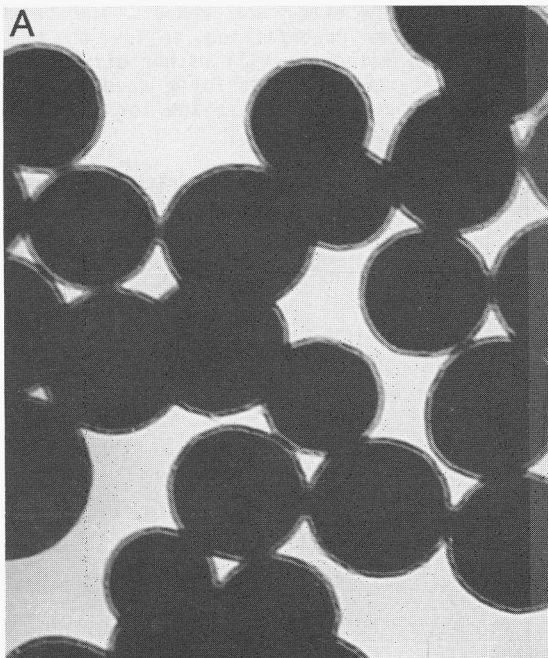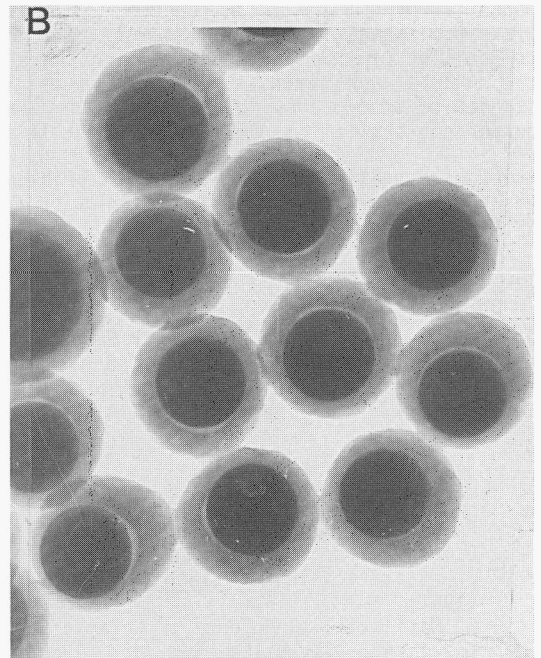
Figure 13. Differential thermal analysis data for ellipsoidal hematite particles (dotted line), for spherical chromium hydrous oxide particles (dashed line), and for the same hematite coated with chromium hydrous oxide (solid line) (ref. 39).

0.5 μm

0.5 μm

Figure 14. (A) TEM of chromium hydrous oxide particles coated with ovalbumin. 6.25 mg of solids and 5.0 mg of the protein in 5 cm^3 solution of pH 5.5. were equilibrated (under tumbling) at room temperature for 24 hr. The coated layer was stained with tungstophosphoric acid. (B) TEM of titania particles coated with polyurea using the aerosol technique. Titania particles were first prepared by exposing droplets of titanium(IV) ethoxide to water vapor. The resulting particles were wetted in the aerosol phase with hexamethylenediisocyanate and subsequently exposed to ethylenediamine vapor.

AEROSOL TECHNIQUE

An entirely different principle is applied in the production of particles by chemical reactions with aerosols. Droplets of one reactant are contacted with a vapor of a coreactant to give a desired powder. With this technique the predominant majority of particles appear as spheres, the size of which can be predetermined by selecting the proper droplet diameters. The method is equally suitable for the preparation of inorganic or organic particles of simple or mixed composition. In the latter case the droplets are most conveniently generated by nebulization of liquids of a desired chemical content which will yield final products of known composition. With simple liquids uniform aerosols can be obtained by the vaporization/condensation process.

For example, spherical titania and aluminum particles were generated by hydrolysis of the corresponding alkoxide droplets with water vapor (refs. 40,41). Polymer colloids could be obtained either by exposing monomer droplets to an initiator in the gas phase, such as in the case of polystyrene (ref. 43) and divinylbenzene (ref. 42), or by interacting monomer droplets with a gaseous coreactant, as was achieved with polyurea (ref. 44).

More recently, coated particles were also prepared by the aerosol technique. Figure 14B illustrates spherical colloidal titania coated with polyurea (ref. 45). In a continuous process the titania aerosol was generated from Ti(IV)-ethoxide onto which hexamethylenediisocyanate was condensed; this aerosol was then exposed to ethylenediamine to form the polyurea coating. Similarly silica coating on titania can be achieved by condensing $SiCl_4$ on titania followed by hydrolysis with water vapor.

CONCLUDING REMARKS

The purpose of this short review is to document the feasibility of the preparation of powders consisting of exceedingly well defined particles. Since these solids can be of simple, mixed, or coated composition, both inorganic and organic, the number of applications in many areas of ceramics is self-evident.

From the scientific point of view the availability of these uniform dispersions has offered the opportunity to study the relationship of various properties of matter (optical, magnetic, electric) as a function of particle composition, size, and shape. The task of establishing the dependence of the morphology of the precipitated solids on the composition of the solutions in which these are generated, although still rather difficult, can now be undertaken. Finally, the described systems can be successfully used in the studies of adsorption, heterocoagulation, and adhesion phenomena as they allow for a better comparison between the experimental results and theoretical expectations.

Numerous investigations dealing with problems mentioned above have been reported in recent years. However, owing to the restriction in space, these could not be dealt with in this write-up.

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