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19. ABSTRACT (Continue on reverse if necessary and identify by block number)

The major goal of this project was to address the properties and interactions of fine powders of interest in ceramics. In order to arrive at quantitative conclusions and assure reproducibility of data, the first requirement was to have well defined dispersions consisting of uniform particles of different chemical compositions (simple or mixed) and in different shapes. Thus, one part of the program has dealt with the synthesis of such "monodispersed" powders. Specifically, we have produced colloidal particles of different metals, metal oxides, and silicon nitride. In addition, internally mixed particles of stoichiometrically defined metal ratios (such as metal niobates) and of variable composition have been obtained. Finally, coated particles of inorganic cores covered with shells of either different inorganic compounds or of polymers were prepared. All these systems were characterized in terms of their bulk and surface properties.

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19. ABSTPACT -- Continued

In the other part of the program, we studied, theoretically and experimentally, interactions between unlike particles (i.e., the stability of mixed dispersions), in order to evaluate compaction and sintering effects of such powders. The rate of heterocoagulation was followed in aqueous dispersion of different combinations of particles and the obtained data were compared with expected values based on different theoretical models. The significant discrepancies between the experimentally evaluated and calculated stability ratios could be reconciled, if the surface charge segregation was taken into account.

As a special case of interactions in mixed solids we investigated particle adhesion phenomena, with emphasis on multilayer particle deposition. We developed a theory that made it possible to follow the transition from a single layer to multiple layers and then confirmed the model experimentally.

FINAL TECHNICAL REPORT

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Mr. David Hoffman	Mr. Curtis J. Zimmermann

DEGREES:

With full or partial support, the following students have graduated from Clarkson University during this contractual period.

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Ph.D.

Bar Aiken	Myung Jin Kim
Fazlul Haque	Niels Ryde
Yie-Shein Her	Curtis Zimmermann

SUMMARY OF THE ACCOMPLISHMENTS

The primary objective of this project was to relate fundamental phenomena of colloid and surface science and engineering to the problems related to ceramics. Specifically, the program was designed to:

A. Generate new and better defined powders as precursors for controlled microstructures with special emphasis on materials of interest in a variety of applications, such as electrooptics, acoustooptics, piezoelectrics, semiconductor, and many others.

B. Develop a quantitative understanding of interactions between solids in order to improve compaction, sintering, adhesion, and other properties of powders.

One of the major prerequisites to achieve the above goals is to develop procedures for the synthesis of powders of different, but desired chemical composition, consisting of particles uniform in size, in a variety of shapes.

Once such materials are made available, it is possible to relate their physical properties (optical, magnetic, electric, adsorptive, etc.) to morphological characteristics of the particles, in addition to their chemical composition.

Furthermore, such well defined systems lend themselves for the study of particle/particle and particle/plane interactions, the understanding of which is essential for the development of composite ceramics.

This report, therefore, describes the results as obtained in the major areas:

1. Preparation of well defined ceramic powders, and

2. Solid/solid interactions.

Some of the general aspects of colloid and interface chemistry in ceramics have been described in several review articles (2,3,10,14,23,30,33,36).*

1. Preparation of Well Defined Ceramic Powders

One of the major objectives and accomplishments of this program has been the preparation of ceramic powders, consisting of particles of uniform size and shape. These solids may have simple chemical composition, or they may be made of particles of mixed nature, internally or externally.

The major approach in the preparation of powders has been homogeneous precipitation. The procedure consists of hydrothermal treatment of aqueous metal salt solutions to form solids either by forced hydrolysis or by decomposition of certain solute complexes. The principal investigator has previously shown that such reactions, if properly controlled, can result in the precipitation of exceedingly well defined dispersions which, on separation from the mother liquor, yield powders of known characteristics.

In a limited number of cases a new technique was employed to produce powders, based on chemical reactions in aerosols. In this method droplets of one reactant in an inert gas are exposed to the vapor of a coreactant, which on contact with the droplets produces solids. The procedure yields, as a rule, spherical particles the size of which can be predetermined by the size of the liquid aerosols.

Finally, sometimes it is not possible to directly generate a powder of a desired chemical composition or a given shape. In these cases one may synthesize a precursor material of required morphological characteristics and then chemically manipulate it to obtain the necessary product. Such treatments can be generally designated as phase transformations.

Below, the results of a number of studies dealing with the preparation of well defined powders by these techniques will be summarized, while the details can be found in the cited published papers.

A. Monodispersed powders of simple chemical composition

Dispersions of uniform particles of pure metals are difficult to obtain by precipitation. Instead, it is possible to prepare metal oxides, which are then reduced to pure metals either in liquid dispersions by the addition of appropriate reducing agents or by reacting dry powders with hydrogen. If such processes are performed with sufficient care, the particle integrity and

*The numbers in parentheses refer to the list of publications supported by this contract.

morphology can be preserved. Using the described approach, a variety of colloidal metal powders have been prepared, including copper, nickel, cobalt, iron, ruthenium, and palladium (26). In most cases spherical particles were so obtained, although other particle shapes could be achieved, such as cubic copper (13).

Homogeneous precipitation has been employed to generate different metal oxides, including platelet-type hematite (α-Fe_2O_3) (9), spherical tin oxide (7), spherical hafnium oxide (11), and several copper compounds of various morphologies (13,17). In all these cases the solids were generated by heating at moderate temperatures (< 100 °C) aqueous solutions of the corresponding metal salts, either directly or in the presence of urea or formamide. It was shown that anions played an important role in determining the chemical composition, shape, and size of the resulting particles (3,30,33).

Considerable effort was invested into designing procedures for continuous precipitation of monodispersed particles. A plug-flow type reactor was constructed, which yielded uniform yttrium basic carbonate particles over extended periods of time (4,31,37). The same equipment was also employed to produce uniform silica particles of different modal diameters.

The aerosol technique was used in the preparation of tin oxide by generating droplets of $SnCl_4$ and interacting them with ammonia vapor (16). The aerosol method was shown capable of generating silazane polymers, which served as precursors for the silicon nitride synthesis. For this purpose droplets of methyldichloro-silane were reacted with ammonia gas. The so obtained white silazane powder yielded on calcination spherical particles of α- and β-Si_3N_4 (25).

Many of the so obtained dispersions were characterized by different techniques to evaluate their properties. For example, the magnetic properties and interactions of platelet-type hematite particles were investigated in detail (9,15).

B. Composite materials

a. Internally composite solid particles

In many applications the properties of powders can be drastically changed when more than one metal ion is present. The actual composition of such solids may be stoichiometric or variable. We have produced materials of both kinds.

Specifically, we have established conditions to produce uniform particles of lead, magnesium, and potassium niobates of different shapes, including spheres (18,27). These materials have been characterized in terms of their properties and the mechanisms of formation were elucidated.

Much effort was invested into the studies of coprecipitation phenomena from mixed metal salt solutions. Specifically, composite copper(II)-yttrium(III), copper(II)-lanthanum(III) (1), aluminum–yttrium(III) (24), and zirconium(IV)–yttrium(III) (5) oxides have been prepared and evaluated. It was shown that uniform amorphous spherical particles made up of both metal oxides can be obtained, but that they are not internally homogeneous. The molar ratio of constituent metal ions changed with the particle growth and differed from that in solution, until the entire reaction was brought to completion. On calcination, such final powders transform into crystalline solids of defined stoichiometry, yet retain their spherical shape. The so prepared calcined samples of mixed composition show enhanced stability as in the case of the zirconia/yttria system (5).

Aerosol technique was also used to prepare colloidal magnesium–aluminum silicates (cordierite and fosterite) by reacting droplets of a mixed metal alkoxide with water vapor (8).

b. Coated particles

For many reasons it is useful to coat one kind of particles with a layer of a different chemical composition. In doing so one may alter optical, magnetic, and conductive characteristics, as well as surface reactivity, sinterability, and other properties of a powder. It is also possible to produce particles of a desired shape by using a core of a given morphology and cover it with a compound of interest.

We have demonstrated that inorganic shells of different thicknesses can be produced on inorganic cores such as in coating of zirconia with yttria (5) or copper oxide with silica (13). In the latter case, it was possible to reduce the cores with hydrogen to pure copper, which was protected by the outer silica layer.

In another project we were able to coat inorganic cores with polymers. Specifically, shells of polypyrrole were produced on iron(III) and cerium(IV) oxides by first adsorbing the organic monomer on the metal oxide cores with subsequent polymerization (19). In these systems the cores played a double role, i.e., as carriers of the polymer coating and as polymerization catalysts. The resulting particles, thus, consisted of nonconducting cores and conducting coatings (35).

In still unpublished work, we have produced silica particles coated with yttria and vice versa, and used such powders in compaction and sintering studies. Solids of clearly different properties were obtained on calcination of these composite precursors, which depended on the nature and the thickness of the outer layers relative to the cores.

2. Solid/Solid Interactions

In any ceramic processing the quality of the final products depends not only on the characteristics of the precursor powders, as described above, but also on the types of interactions between the particles. Of special interest are such interactions in systems of unlike particles, which are more often found in the "real world" than matter of simple composition. The study of mixed dispersions represents a special challenge, both from theoretical and experimental points of view.

A. Heterocoagulation

The theory of the stability of dispersions consisting of different kinds of particles has been a rather controversial subject. Several models have been proposed in order to explain and predict the properties of such mixed systems. For this reason we have performed a rather comprehensive analysis of different theoretical formulations and carried out computations based on these models for different conditions, with special emphasis on the validity of certain simplified assumptions. The results of this study have been described in a detailed review article (34).

Once we established the regions of applicability of the theoretical expressions for heterocoagulation in terms of various parameters, a systematic investigation was undertaken to compare the experimental results with the theoretical calculations. Dispersions of uniform spherical particles are best suited for such investigations, since the essential parameters for the evaluation of data can be ascertained.

Specifically, we have followed the kinetics of heterocoagulation in mixed systems consisting of spherical particles of different chemical composition and surface properties in media of varying ionic strength. Significant deviations between the theory and experiments were encountered in all cases. The causes of these discrepancies were analyzed in depth, and it was established that they can be accounted for, if the surface charge segregation is taken into consideration (29,32).

B. Particle adhesion

The problems of particle deposition on solid surfaces from a liquid environment and their removal from such substrates is of importance in numerous situations of technological significance.

Theoretically, the problems of particle adhesion represent a special case of interactions in mixed dispersions. One needs to consider that one kind of particles is much larger than the other kind. It should also be emphasized here, that the particle deposition and detachment are not reversible processes.

In this research, we paid special attention to the problems of multiple particle deposition phenomena, which we have treated theoretically (20) and experimentally (21,28). It was possible to demonstrate that the measured particle attachments fit well the theoretical model, and that it was possible to identify conditions which led to a change from monolayers to multilayers. Again, the analysis of data and the comparison with the theory were made possible, because we were able to work with appropriate well defined dispersions developed in our laboratory.

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Abstract

The major goal of this project was to address the properties and interactions of fine powders of interest in ceramics. In order to arrive at quantitative conclusions and assure reproducibility of data, the first requirement was to have well defined dispersions consisting of uniform particles of different chemical compositions (simple or mixed) and in different shapes. Thus, one part of the program has dealt with the synthesis of such "monodispersed" powders. Specifically, we have produced colloidal particles of different metals, metal oxides, and silicon nitride. In addition, internally mixed particles of stoichiometrically defined metal ratios (such as metal niobates) and of variable composition have been obtained. Finally, coated particles of inorganic cores covered with shells of either different inorganic compounds or of polymers were prepared. All these systems were characterized in terms of their bulk and surface properties.

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