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SECURITY CLASSIFICATION OF THIS PAGE

AD-A227 932

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REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified

1b. RESTRICTIVE MARKINGS

2a. SECURITY CLASSIFICATION AUTHORITY

2b. DECLASSIFICATION / DOWNGRADING SCHEDULE

3. DISTRIBUTION / AVAILABILITY OF REPORT Approved for public release; distribution unlimited.

4. PERFORMING ORGANIZATION REPORT NUMBER(S)

5. MONITORING ORGANIZATION REPORT NUMBER(S) ARO 23792.1-MS-F

6a. NAME OF PERFORMING ORGANIZATION Northwestern University

6b. OFFICE SYMBOL *(If applicable)*

7a. NAME OF MONITORING ORGANIZATION U. S. Army Research Office

6c. ADDRESS *(City, State, and ZIP Code)*
633 N. Clark Street
Evanston, IL 60208

7b. ADDRESS *(City, State, and ZIP Code)*
P. O. Box 12211
Research Triangle Park, NC 27709-2211

8a. NAME OF FUNDING / SPONSORING ORGANIZATION U. S. Army Research Office

8b. OFFICE SYMBOL *(If applicable)*

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER DAAL03-86-G-0054

8c. ADDRESS *(City, State, and ZIP Code)*
P. O. Box 12211
Research Triangle Park, NC 27709-2211

10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.

11. TITLE *(Include Security Classification)* Plasma Synthesis and Sintering of Advanced Ceramics (Unclassified)

12. PERSONAL AUTHOR(S) Timothy D. Fletcher* and D. Lynn Johnson (*Now with Case Western Reserve Univ.,Cleveland O

13a. TYPE OF REPORT Final Report

13b. TIME COVERED FROM 9/15/86 TO 9/14/89

14. DATE OF REPORT *(Year, Month, Day)* 1990/09/15

15. PAGE COUNT 24

16. SUPPLEMENTARY NOTATION The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

17. COSATI CODES

FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)* Colloid; Plasma; Processing;Ceramic

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

The feasibility of using a gas plasma to inhibit ultrafine ceramic powders from agglomerating during processing was explored. The agglomeration that usually occurs after formation and during collection of ultrafine ceramic powders is one of the largest obstacles to their widespread use. By immersing the particles into a plasma immediately after they are formed, it is believed that a sufficient charge can be imparted onto the particle surfaces to generate enough inter-particle repulsion to stop or greatly reduce particle agglomeration. The mechanisms by which a plasma can charge the surfaces of particles and affect the agglomeration behavior of particles suspended in a gaseous medium are discussed.

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OCT 24 1990
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20. DISTRIBUTION / AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL D. Lynn Johnson

22b. TELEPHONE *(Include Area Code)* 708/491-3584

22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR — 83 APR edition may be used until exhausted. All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE
UNCLASSIFIED

PLASMA SYNTHESIS AND SINTERING OF ADVANCED CERAMICS

Final Report

by

Timothy D. Fletcher and D. Lynn Johnson

Covering Period

15 September 1986 to 14 September 1989

U. S. ARMY RESEARCH OFFICE

Grant No. DAAL03-86-G-0054

Department of Materials Science and Engineering
Northwestern University
Evanston, Illinois 60208-3108

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OBJECTIVES

The original objective of this study was to investigate plasma synthesis of SiC, Si_3N_4, and other advanced ceramics utilizing the hollow cathode discharge (HCD) and microwave induced plasmas (MIP). With the recognition that particles in plasmas carry electrostatic charge, the concept of colloidal plasma processing of ceramics was conceived. The modified objective was to investigate the feasibility of colloidal plasma processing of ceramics.

COLLOIDAL PLASMA PROCESSING: CONCEPTS

It is well known that ultrafine particles prepared in gas plasmas agglomerate during collection, rendering further processing very difficult.[1,2] However, while the particles are within the plasma they carry a charge, and tend to repel each other, thus inhibiting agglomeration. The harmful agglomeration takes place primarily after the particles exit the plasma.

Colloidal plasma processing is a term coined to describe a potential technique of dispersing a powder in a plasma and depositing it on a suitable substrate or mandrel such that the green compact is formed without separate collection and compaction procedures. It thus would circumvent the agglomeration problem.

The process can be divided into three stages. Stage I is the powder generation stage in which the ultrafine ceramic powders are produced. Stage II is the colloidal plasma stage in which the particles are charged and suspended in a plasma. Stage III is the deposition stage. Here the particles are deposited onto a substrate in such a manner as to produce a bulk ceramic body with or without simultaneous densification. The main focus of this work will be the colloidal plasma stage and its feasibility.

A colloidal plasma is the gas phase equivalent of a colloidal suspension in a liquid, and many similarities can be expected to be found.

An evaluation of the pertinent literature was conducted to explore the feasibility of this method of processing.

BACKGROUND

Ultrafine Particles.

There are well recognized advantages to using small particles in ceramic processing. The instantaneous densification rate is inversely proportional to the particle size to the third or fourth power for volume or grain boundary diffusion, respectively. Thus, small particles sinter significantly more rapidly than large ones. However, inherent difficulties limit the usefulness of extremely small particles. Van der Waals forces become significant, resulting in agglomeration. This agglomeration often is persistent during subsequent processing with resulting particle packing inhomogeneities and residual porosity. The elimination of agglomerates results in a dramatic reduction in sintering temperature, as has been demonstrated by liquid colloidal processing.[3,4]

Another major disadvantage of ultrafine powders is their high surface reactivity. Although beneficial for sintering, this characteristic also sets limitations on the environment in which the powders can be processed. In particular, surface adsorption of water vapor on oxide powders or oxygen on non-oxide powders can have large effects on sintering. The presence of an oxide film on small particle size non-oxides, even though that film may be very thin, may result in a deleteriously large oxygen content of the final material.

Another disadvantage of fine particles related to their high surface area is their flow and packing characteristics. Agglomeration has already been mentioned as a result of Van der Waals forces. In addition, these forces inhibit particle sliding and rearrangement during compaction, which has serious effects on the green density of compacted powders.

Liquid colloidal processing has been utilized successfully to overcome the above limitations of small oxide particles. Agglomeration is prevented by additives to the slurry which adsorb to the surface of the particles, imparting either a surface charge or steric hindrance, both of which minimize agglomeration. Filtration or electrophoresis then can be utilized to form compacts free of the agglomerates that would result if the powder were dried and dry-pressed.

Colloidal Plasma.

A plasma consists of four main species: positive and negative ions, neutral atoms, and electrons. A colloidal plasma, in addition, contains a suspension of particles. The study of colloidal plasmas has been primarily in the field of astrophysics, since most of the mass of the universe exists as colloidal plasma.

It is thought that the electrons, which have a much higher average energy and mobility than the ions, will charge the surfaces of the particles because of their greater impingement flux. Once charge builds up on an isolated object in a plasma, a sheath layer develops in which ions of the opposite sign to the surface charge surround the object. The interaction of sheath layers is what is thought to cause the repulsion between particles suspended in a plasma. If the repulsion is sufficiently strong to overcome the Van der Waals attraction, the particles will remain isolated. There should be a similar layer on the walls of the chamber if it is made up of an insulator. This wall sheath layer will inhibit particles from sticking to the surface of the chamber.

Much information is needed to facilitate proper equipment and process design. For instance, the plasma must exist throughout the processing chamber and impart sufficient charge to the surface of each particle to enable the particles to remain isolated until they are deposited. Major topics include the effects of plasma properties, gas properties and flow dynamics, and powder characteristics on particle agglomeration behavior. For example, the type of plasma used (equilibrium versus nonequilibrium, glow discharge, corona discharge, RF or microwave discharge, etc.) and the electron concentration in the plasma are important. The efficiency of particle charging and agglomeration are dependent on these plasma characteristics. The size, shape, and initial charge of the powders also may be important in the charging and agglomeration process.

Direct current arcs, induction coupling, and microwave excitation have all been utilized to generate plasmas for synthesis of fine powders. Any of these might be utilized in colloidal plasma processing provided a reduced pressure is used so that the plasma expands to fill the processing chamber and allow for particle deposition. The electrodeless RF and microwave plasmas have the advantage of minimizing contamination from evaporation and sputtering of electrode materials.

Plasmas can be grouped into two categories: thermal (hot or equilibrium plasmas) and cold (non-equilibrium plasmas).[5] The distinction is in the temperatures of the electrons and heavy particles (ions and neutrals). In a thermal or equilibrium plasma, the temperatures of heavy particles and electrons are approximately equal; therefore these particles possess the same average energy. Examples of plasmas of this type are high intensity arcs, plasma torches, and RF and microwave discharges above about 0.5 atm. Non-equilibrium plasmas are characterized by large differences in electron and heavy particle temperatures and, therefore, energies. Heavy particle temperatures can be as low as a few hundred K, while electron temperatures are measured in tens of thousands of degrees[6]. This difference is due to the low mass of the electron which allows it to gain a large amount of energy from the electric field. Electrons do not gain as much energy from the field in a thermal plasma because of their more frequent collisions with neutral gas atoms. The sensible heat of the plasma is governed by the temperature of the heavy particles, since the electrons, although they may have very high temperature, do not possess high enthalpy.

Particle Charging.

The charging of fine particles in gaseous media has been studied for many years by a variety of researchers[7-10]. Almost all naturally occurring and man-made aerosols are charged to some degree. The charging of aerosols such as rain and dust clouds in the atmosphere has been well documented.[11] Flue gases and other industrial exhausts are found to contain many highly charged fine particles which can be removed by electrostatic precipitation.

Small particles in gaseous media can be classified into four different (increasing) size regimes: free molecule, transition, slip flow, and continuum.[12] The size regimes are classified by a non-dimensional number called the Knudsen number, Kn, and the particle size. The Knudsen number is defined as

$$Kn = \frac{2\lambda_g}{d} \qquad (1)$$

where λ_g is the mean free path of the gas, and d is the mean particle diameter. The various size regimes for aerosol particles in air at 1.0 atm is shown in Table I.

TABLE I

Size Regimes of Aerosol Particles in Air at 1.0 atm[12]

	Size Regimes			
	Free Molecule	Transition	Slip Flow (Cunningham)	Continuum (Stokes)
Kn	> 10	10–0.3	< 0.3	< 0.1
d,μm	< 0.01	0.01–0.4	> 0.4	> 1.3

In the continuum regime, Stokes' law is satisfied. In the slip flow region there are insufficient collisions between gas molecules and particles, and the particles "slip-through" the gas molecules and obtain a higher terminal velocity under a force field than predicted by continuum theory (Stokes' law). In the free molecule regime, $d \ll \lambda_g$, there are few particle-gas molecule collisions. The particles in the process under consideration are in the transition regime which, unfortunately, is the one which is the least well modeled.

Fine particles which are immersed in an ionized gas and subjected to an applied electric field can receive charge through two different processes, namely field and diffusional charging. During field charging, the electrons and ions present in the gas are accelerated under the influence of the electric field and collide with the particles, causing charging to take place. Diffusional charging is caused by the random motion of both charged species and particles, which results in collision and subsequent charging. Field and diffusional charging are found to be the most dominant mechanism for large and small particles, respectively.[10,12]

Once a particle obtains a charge it repels like charges, thereby reducing the probability of further charging. This introduces the concept of a saturation charge to be obtained by a particle when it is in equilibrium with the incoming flux of the surrounding charged species. This charge can be defined as the maximum obtainable surface charge for a particle.[12] These matters are discussed in detail in Fletcher's M.S. thesis.[13]

The characteristics of an optimal method of applying charge to the particle surfaces are as follows. First, a sufficient amount of charge must be deposited onto the particle surfaces to prevent agglomeration. The charging should be unipolar in nature, i.e., utilize electrons or ions of one polarity. The charging plasma should not cause significant changes in particle structure, morphology, or composition. A plasma of this type must be a low temperature, non-equilibrium plasma. Three types of plasmas fill these qualifications, the hollow cathode discharge, the negative corona discharge, and the low pressure capacitively or inductively coupled RF discharge. It is probable that a low pressure microwave discharge would also be satisfactory.

Fine Particle Agglomeration.

The agglomeration (or coagulation) of fine particles in aerosols has been studied extensively by reseachers in the field of air pollution control. This agglomeration can be thought of in terms of the frequency of collisions between particles.[14] If one assumes that the probability of two particles remaining attached (sticking probability) after collision is unity, then the rate of coagulation is proportional to the collision rate. During coagulation, the number of particles in the aerosol is reduced and the average size of the agglomerates is increased.

The mechanisms by which particles collide include Brownian motion, gravitational sedimentation, coulombic attraction, and bulk fluid flow. Each of these mechanisms will have a different collision frequency function.

Once a mechanism is assumed, the time for an aerosol concentration to be reduced to some fraction of its initial value can be calculated using the collision frequency function for the mechanism under consideration. The collision frequency will, of course, be a function of any charge that exists on the particles. Electrostatic repulsion will tend to reduce agglomeration, but at the same time may force particles towards the wall unless the wall is similarly charged (which can be so if the wall is an insulator). It has been shown that for uni-polar diffusional charging the ratio between the loss of particles due to space charge repulsion and that due to coagulation was over three.[15]

The term "aerosol aging" is used to describe the process by which the number of particles per unit volume in an aerosol changes with time. Much work has been reported on the aging of aerosols in the air pollution and meteorology literature.[16-20] The basic aging equation is

$$\frac{dn}{dt} = -(kn^2 + \beta n) \qquad (2)$$

where k is the coagulation rate constant, β is the surface loss rate constant, and n is the number of particles per unit volume.

The coagulation rate constant is a function of particle size, and therefore changes with time as the particles coagulate and become larger. The greater mobility of smaller particles give rise to a larger coagulation rate constant than for larger particles.[19,20] Because coagulation is proportional to the square of the particle concentration, it dominates the aerosol behavior during the initial stages of aging when the concentration is the highest.

It has been found that turbulence has little effect on the coagulation constant but does increase the surface loss rate constant.

The coagulation of charged particles smaller than 2 μm and larger than the mean free path of the gas has been studied.[21] For aerosols in which all particles have carried charges of the same sign, the coagulation rate was reduced approximately 60% from the value calculated for uncharged aerosols.

Particle Deposition.

Particle deposition onto a substrate can be accomplished using several different techniques. If the particles are large, i.e., several micrometers in diameter, gravitational and inertial methods can be used. For smaller particles, phoretic forces such as electrophoresis and thermophoresis can be employed.

Electrophoresis is the action of an electrostatic field on charged particles. Particles that are charged oppositely to the substrate will be drawn towards the substrate by coulombic attraction. The deposition force must overcome any force on the particles due to fluid motion. The motion of large particles will tend to be controlled more by fluid motion than by electrostatic forces. Particles which are very small cannot obtain very large charges, and therefore the coulombic force on these particles is also small. However, the ratio of electrostatic forces to bulk fluid forces is greater for very fine particles than for large particles, allowing electrostatic forces to be useful in depositing small particles.

In order to build up a deposited layer, the charge must be conducted away from the depositing particles. One could speak of an initial charge, the charge of the particles while they are suspended in the gas, and an induced charge, the charge induced onto the deposited particles by the substrate.[22] The particles must reverse the sign of their charge after they reach the substrate in order for further deposition to occur.

The important factor controlling this process is the resistance of the deposited layer.[22-26] This resistance is controlled by several material properties such as the resistivity and surface chemistry of the particles as well as the particle packing arrangement. It is anticipated that at somewhat elevated temperatures there will be sufficient electronic conductivity in most ceramic materials to bleed away the charge arriving via depositing particles.

Fine aerosol particles also can be deposited by the presence of temperature gradients through a process known as thermophoresis. This process is utilized in devices called thermo precipitators in the same manner than electrophoresis is used in electrostatic precipitators. There are two main mechanisms by which thermophoresis is believed to occur, depending upon the gas pressure. At low pressures, the high mean speed of the molecules on the hotter side of the particle impart more momentum to the particle, thereby driving it in the direction of decreasing temperature.[27] A model based on radiometry theory has been proposed for higher pressures.[28] In this theory desorbed molecules from the particle have a higher velocity component away from the hotter side of the particle, which causes the particle to be driven in the direction of decreasing temperature. A model for intermediate pressures uses the molecular bombardment concept.[29]

PROCESS FEASIBILITY

The feasibility of the colloidal plasma process depends on whether the agglomeration of fine ceramic powders can be prevented by charging the surfaces of the particles while they are suspended in a gas plasma. Three different, though related, characteristics are important, namely an optimum charging medium, the amount of charge on the particle surface, and the particle material.

The characteristics of an optimum charging medium are as follows. First a sufficient charge must be deposited onto the particle surfaces to prevent agglomeration. Secondly, the charging should be unipolar in nature, utilizing electrons or ions of one polarity. The charging media should not cause a significant change in particle structure, morphology, or composition.

The optimum amount of charge deposited on a particle surface must fulfill the following requirements. First and most importantly, the amount of charge should be sufficient to prevent agglomeration of the particles while they are suspended in a charging medium. A competing requirement is that the amount of charge on each particle is not sufficiently high to cause electrical dispersion and loss to the wall; this may be circumvented if the wall is similarly charged.

The optimum particulate materials should have the following characteristics. A high value of the material work function will allow maximum negative charge to be required in the low temperature plasma. Here the high barrier to thermionic emission would allow the maximum amount of electron absorption to occur. The particulate material must have a relatively high value of electrical resistivity. If the resistivity is too low the plasma may be extinguished by the incorporation of the particles into the plasma. This requirement is contradictory to the low resistivity requirement for bleeding off the particle charge during deposition. Empirical studies are needed to determine the optimum property combinations. High thermal conductivity is also important for particle deposition by thermophoresis.

An actual colloidal plasma process is different from the optimum process in many important ways. First, the amount of charge deposited on a particle surface is a function of particle size. Second, the charging media are not always unipolar. Thirdly, materials properties probably will be a compromise. However, the requirement for a high work function is met by most ceramic materials, with the exception of some semiconductors. These effects will now be discussed.

Particle size.

The size of particles that can be processed in the colloidal plasma will be limited by the amount of charge needed to keep the particles from agglomerating. From the literature that has been reviewed, it appears that particles smaller than approximately 35 nm will not acquire the needed charge. On the other hand, particles which are too large might acquire such a large amount of charge that electrical dispersion will become a significant problem. It is therefore possible that the desired particle size might lie in the range from 100–1000 nm.

Process Capacity.

The overall process capacity will be limited by a number of factors including gas flow conditions, particle generation method, particle deposition rate, and the effect that the particle concentration has on the plasma stability. Each of these effects are related, and the overall process capacity must be determined empirically.

The optimum gas flow conditions for particle deposition would be nearly laminar flow. Since the particles are held onto the substrate surface by relatively weak Van der Waals and surface adhesion forces, re-entrainment of deposited particles could result in turbulent flow conditions.

The deposition rate will have obvious effects on the overall process capacity. The quality of the deposited layer will depend on the deposition rate. If the rate is too slow, one might expect a thin layer which would limit process capacity. Conversely, if the deposition rate is too fast, a poorly consolidated porous layer would result. If the flux of particles reaching the substrate surface is too high there will not be sufficient time for the particles to arrange themselves into a compact layer, and fractal type growth will result.

The process capacity will also be dictated by the maximum amount of particles that can be dispersed in a plasma before the plasma is extinguished. This amount must be determined empirically.

If electrophoresis is used as a deposition method, the effect of substrate charge on plasma stability must also be considered. The potential applied to the substrate may perturb the plasma enough to alter the charging conditions. One way of alleviating this problem is to use the substrate as one of the plasma electrodes as is done in electrostatic precipitators. Here, however, the deposited layer must have a relatively high electrical conductivity.

The operating temperature of the colloidal plasma will have a large effect on its efficiency. The operating temperature will be governed by the pressure, primarily, although the initial temperature will be governed by the particle synthesis technique.

The particle generation method will dictate the particle temperature as it enters the colloidal plasma dispersion. This temperature may change as the particle passes through the system. If the particle starts out of the temperature sufficiently high that thermionic emission is greater than electron absorption, the particle will become positively charged. As the particle cools, the electron absorption may become the dominating charging mechanism and the particles become negatively charged. If this process occurs, substantial (undesirable) agglomeration probably will occur due to the presence of both positively and negatively charged particles. This effect may outweigh all other factors in terms of the design of the colloidal plasma processing system.

The deposition method used will also affect the operating temperature of the system. If thermophoresis is employed as the depositing mechanism a temperature gradient must exist in the system. This gradient must be large enough to generate sufficient thermal forces to deposit a particle onto the substrate. This may be facilitated by a high temperature particle generation method which would produce a temperature gradient in the system if the substrate is cooled.

Particulate Material Properties.

The material properties that are important for the colloidal plasma are the work function, electrical resistivity, and thermal conductivity. Since these properties are hard to modify for a given material type, the limitations of the process may dictate the type of material that can be processed in a colloidal plasma system.

The work function will affect the amount of thermionic emission that occurs from the particles at a given temperature. One would like the amount of thermionic emission to be as small as possible in order to avoid a change of particle charging regimes discussed previously. If the work function is large, the particles can be heated to a higher temperature without switching from the electron absorption regime to the electron emission regime. This may be very important because the particles may be at a very high temperature when they reach the colloidal plasma suspension.

The electrical resistivity of the particles has two effects on the colloidal plasma process. One effect is the absorption of electrons from the plasma and its effect on plasma stability. If the resistivity is too low the particles may absorb too many electrons and extinguish the plasma. The other effect is electrical resistivity of the deposited layer that was discussed earlier. The trade-off between the requirements will have to be determined experimentally, and should depend upon the plasma used in the system.

Thermal conductivity will affect the process in two ways. First a high thermal conductivity is desired for thermophoretic deposition for the same reasons that a high electrical conductivity is desired for electrophoretic deposition. If the deposited layer has a low thermal conductivity the heat from the incoming particles will not be removed and the sufficiently rapidly and the deposition rate decreased. The second reason for having a high thermal conductivity is the cooling rate of the particles as they emerge from the generation stage. The higher the thermal conductivity the faster the cooling rate will be. This would reduce the amount of thermionic emission for the particles as well as the propensity for viscous glass to be present on the particle surfaces.

Unfortunately most ceramics have low thermal conductivities. The thermal conductivity requirement must be accounted for in the design of the system as well as in the choice of materials which are appropriate for colloidal plasma processing.

RECOMMENDED CERAMIC MATERIAL

Most ceramics have a high electrical resistivity, with the exception of semiconductors such as NiO and SiC. The electrical resistivity of ceramics is a function of the environment, temperature, and impurity content. Controlling these parameters is an attractive means to decrease the electrical resistivity of ceramics without altering their mechanical properties significantly.

Most ceramics have large work function because the energy barrier to remove electrons from the solid is combined with the energy barrier to excite electrons into the conduction band. Barium oxide is an exception and has a low work function because of its defect chemistry. Barium oxide is used as a coating for cathodes such as Ni to increase the thermionic emission current.[30] Reducing elements in the cathode react with some of the oxygen in the BaO, thus creating oxygen vacancies. The oxygen vacancies act as electron donors which makes BaO an n-type semiconductor. Similar phenomena occur in many ceramics by the incorporation of impurities which create acceptor or donor levels in the band gap of these materials. The carbides also have a somewhat lower work function than most ceramics. This is due to the band structure in these materials which results in a lower energy barrier electron emission. Most ceramics also have low thermal conductivities.

The desired material properties for colloidal plasma processing are a high work function, low electrical resistivity and high thermal conductivity. In general, semiconductors have lower electrical resistivities and lower work functions than insulators. Although the low electrical resistivity is desirable, a high value for the work function is the most important material property for colloidal plasma processing. Therefore, insulating ceramics, oxides in particular, are good candidates for colloidal plasma processing because of their high work functions. Carbides have a relatively low work function also and therefore would not be as good a candidate for colloidal plasma processing as oxides.

CONCLUSIONS AND RECOMMENDATIONS

Ultrafine ceramic powders have many advantages over coarse ceramic powders. The higher sintering rates and lower sintering temperatures of ultrafine powders, compared to coarse ceramic powders, allow materials to be sintered that otherwise could not be densified. However, ultrafine ceramic powders to possess some disadvantages which severely limit their use in ceramic processing. The high degree of agglomeration which occurs immediately after generation in these powders is the main disadvantage. These agglomerates cause processing defects during pressing and sintering. Another major disadvantage of ultrafine powders is the tendency to adsorb large amounts of impurities onto the powder surfaces. The very high surface areas of ultrafine powders, 75-120 m^2/gram, results in a large amount of impurity adsorption if the environment is not controlled during the entire body formation process.

In an effort to alleviate some of the difficulties in processing ultrafine ceramic powders, a process has been proposed in which the agglomeration and impurity problems can be controlled. In this process, the agglomeration that occurs in ultrafine powders will be reduced by charging the particles in an ionized gas. Agglomeration can be reduced if a repelling force is produced between the particles as soon as they are formed. Such a repelling force is produced if the particles become similarly charged. Charging of this nature can be facilitated by immersing the particles in an ionized gas.

Many parameters will affect the capacity and efficiency of the proposed colloidal plasma process. The particle size, material properties, and gas flow conditions all determine the efficiency of the colloidal plasma process. The particle size is important because a sufficient charge must be placed on the particle surface in order to inhibit agglomeration. The lower limit in the size of the particles that can be processed in a colloidal plasma system is estimated at 35 nm. The material properties that affect the performance of the colloidal plasma process are the material work function, thermal conductivity, electrical resistivity, and composition (glass content). Ideally, one would like a high work function, high thermal conductivity and low electrical resistivity. The gas flow conditions are also important. Slightly turbulent conditions for particle charging and nearly laminar conditions for particle deposition should be optimal.

The temperature of the plasma and particles is also important and will dictate the charge on the particle surfaces. The method of particle generation is an important parameter in determining the particle temperature. The particle temperature is also determined to a large degree by the type of plasma used to charge the particle surfaces.

In conclusion, it is the authors' opinion that colloidal plasma processing is feasible. To what scale this process can be effective is not known. The applicability of colloidal plasma processing must be determined empirically for each set of particle generation, material type, and particle deposition systems. Only time will tell if the colloidal plasma process is a useful one in the ceramic industry.

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