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Plasma synthesis of ceramic powders

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Abstract - Production of high quality ceramic powders for high technology ceramics is becoming one of the most urgent issues in the ceramic industries. In particular, the development of fine ceramic powders with unusual and superior properties will be of great interest. Thermal plasmas with their unique processing capabilities will play an important role in these developments. High temperature gas-phase chemistry within thermal plasma environments provides an attractive and chemically unspecific route for powder synthesis. Furthermore, the supersaturation of vapor species which provides the driving force for particle condensation can be very large, leading to the production of ultrafine particles by homogeneous nucleation. Ceramic powders such as carbides, nitrides, oxides and solid solutions have been successfully synthesized in thermal plasma reactors based on high intensity arcs, plasma jets and rf inductively coupled discharges. Starting materials are either in the form of gases, liquids or solids. However, the availability of gas phase precursors for metals is severely limited. Therefore, the most commonly used reactants for plasma synthesis are solids. In this case the injection process is not trivial; in fact it is almost an insurmountable problem because of the high viscosity of the plasma. Recently, a liquid injection method has been developed to overcome the problems associated with solid injection and to realize the benefits of gaseous reactants. This paper will present an overview of recent advances in plasma synthesis of ceramic powders including liquid injection plasma synthesis.

INTRODUCTION

Over the last decade, there has been a growing interest in the production and processing of fine particles, especially of high-tech ceramic materials. The principal driving force is essentially one of technical and economical advantage that can be achieved through the use of these new materials in a wide range of applications, varying from improved diesel engines made with ceramic components, gas turbine engines for automotive and stationary power generation, advanced electronic and magnetic materials, fiber optics and more recently ceramic superconductors. The process used for generating particles determines the degree of sintering ability of the powder since the process controls the particle morphologies, the purity and its size distribution. Among the different techniques commonly used for preparation of these materials, thermal plasmas which provide high temperatures and steep temperature gradients offer an attractive and chemically unspecific route for synthesizing fine refractory powders. Today, this technology is known as "Thermal Plasma Synthesis" where thermal plasmas serve as the processing medium. Thermal plasmas suitable for synthesis are primarily produced by means of high intensity ac or dc arcs, high frequency discharges, dc-rf hybrid plasmas, and by a reactive submerged arc (RSA). Depending on the process, either the discharge itself or the plasma flame downstream of the discharge may be used for synthesizing the powders. In thermal plasma synthesis the reactants may be gases, liquids or solids before injection into the plasma.

PLASMA GENERATION AND POWDER SYNTHESIS

Plasma generation

High intensity arcs Generally, there are two types of high intensity arcs, i.e., ac or dc arcs. In the case of dc arcs, both nontransferred and transferred arcs have been used to promote chemical reactions. The nontransferred arcs (Fig. 1) can be operated in the low voltage (20-150 V dc) mode and are characterized by their ability to sustain at relatively low flows and high exit gas enthalpies. Typically, the flow through the device is mildly turbulent, and the gas flow has a minimum swirl content. The low flow condition in the low voltage mode is ideal for materials synthesis. But there is one disadvantage with the low voltage mode for high power operation, because the device will operate at higher currents thus leading to significant electrode erosion. The high voltage mode uses longer anode nozzles and has a significant amount of swirl gas. The more intense the swirl, the longer the arc and the higher the voltage. Typical voltages for this type of device range between 150 and 1000 V. The advantages are operation at lower amperages, minimizing electrode erosion at high power levels. The transferred arc operation can be divided into two arc modes: either transfer to the work piece to be heated or to an intermediate electrode. In the first case, the arc is transferred from the cathode

directly to a work piece to be heated. In the second case, the transferred arc is terminated on a secondary electrode and the device produces a nontransferred *Free Burning Arc* which is shown in Fig. 2.

High frequency discharges There are two types of plasmas which can be sustained by high frequency discharges. The first one is the rf inductively coupled plasma, ICP, (Fig. 3) and the second is the microwave produced plasma. Usually the frequency ranges from kHz to MHz for rf and GHz for microwave plasmas. These types of plasmas are referred to as electrodeless discharges. Both ICP and MWP produce ultraclean, high temperature, large diameter and low velocity plasmas which are particularly suitable for chemical reactions. Since ICP and MWP are electrodeless plasmas the reactor is insensitive to the type of gas used. Therefore, this type of reactor is ideal for producing reactive plasmas for chemically specific reactions. Microwave plasmas (MWP) differ significantly from dc arc plasmas and ICPs by higher electron densities and higher reactivities at lower input power levels. However, the operating pressure range for MWP is very narrow and the plasma volume is rather small at high pressures. This difficulty arises from the dimensional restriction of MWP generation in a resonant cavity. Mitsuda et al [1] solved this problem by coupling a rectangular waveguide to a tapered coaxial waveguide which also acts as electrodes for igniting a high reactivity, low power and large volume MWP jet (Fig. 4) at 1 atmosphere. Under their operating conditions for the MWP it would be impossible to sustain either a dc arc plasma or an ICP.

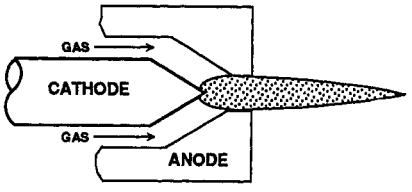

Fig. 1. Non transfer arc.

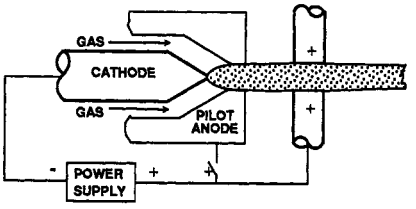

Fig. 2. Free burning arc.

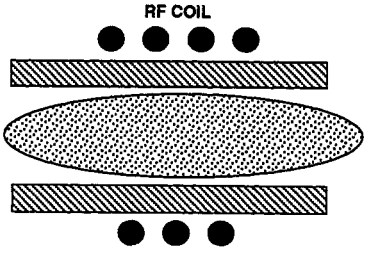

Fig. 3. RF induction coupled plasma.

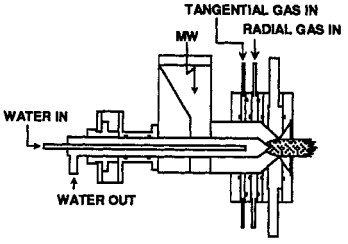

Fig. 4. Microwave plasma jet.

Hybrid plasmas It is possible to operate the ICP in tandem with a dc or another ICP discharge as shown in Fig. 5. In contrast to dc arc discharges, which exhibit maximum temperatures in the core of the plasma, the ICP shows an off-axis temperature maximum. In general, the core of the ICPs is rather cold and the maximum temperature is lower than that of a dc plasma. The superimposed dc plasma or ICP acts as an ignition source, and the second ICP adds auxiliary heat downstream to maintain a high temperature level. Hybrid plasmas increase the volume of the combined plasma and alter the temperature profiles as shown in Fig. 6. It is also possible to superimpose successive ICPs beyond the first one to produce a longer hot reaction zone with uniform temperature.

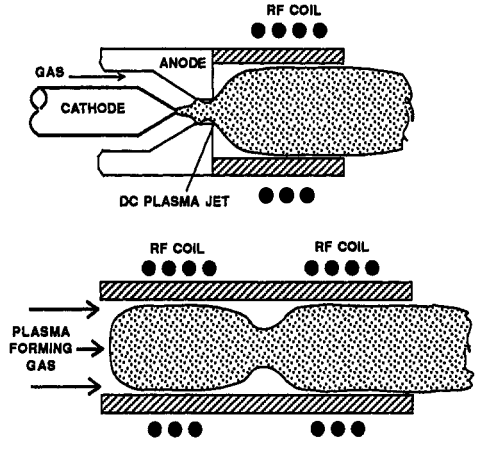

Fig. 5. DC/ICP and ICP/ICP hybrid plasmas.

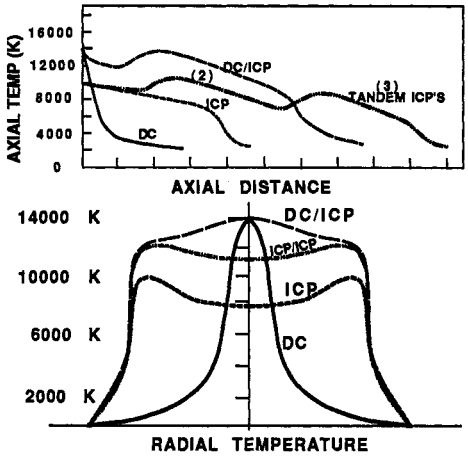

Fig. 6. Hybrid plasma temperature profiles.

Reactive submerged arc (RSA) The RSA (Fig. 7) is a rather new technique for synthesizing fine powders. In this process an arc is struck between two electrodes which are submerged in a dielectric liquid. Electrode materials are vaporized and quenched in the liquid to form desired products.

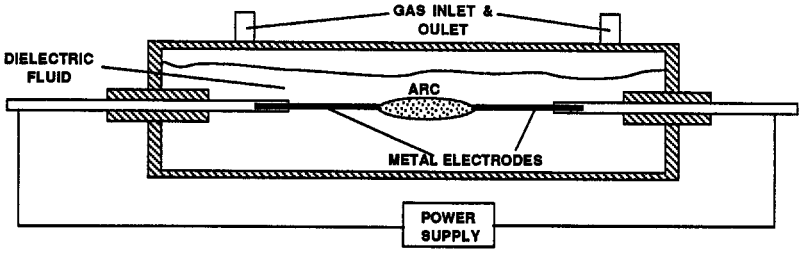

Fig. 7. Reactive submerged arc (RSA).

Powder synthesis

Over the past years, thermal plasma synthesis of ultrafine and ultra-pure powders has been attracting increasing interest, especially in the area of ceramic materials. Since the temperatures in a thermal plasma are extremely high (>10^4K), chemical reactions are much more energetic than those encountered in conventional processes. Also the quench rates of the product powders are very rapid which is necessary to avoid decomposition of the products in particular for metastable compounds. Fast reaction and quench rates result in very short overall processing times which may be as short as milliseconds.

Thermal plasma synthesis of powders may proceed from gaseous, liquid or solid reactants. A literature survey indicates that the majority of thermal plasma synthesis involve solid reactants and metal halides. Table 1 is a summary of plasma chemical reactions in the synthesis of ceramics.

TABLE 1. Plasma Chemical Reactions

Compounds	Precursors	Plasma	Phase	Ref
	Carbides			
SiC	CH_3SiCl_3	rf, arc	*l*	2-4
SiC	SiO_x, CH_4	arc	*s*	5-11
SiC	SiH_4, CH_4	rf, arc	*g*	12
SiC	$SiCl_4$, CH_4, CHX	rf, arc	*l*	2-4,13,14
SiC	SiH_4, B_2H_6, CH_4	arc, *TT*	*g*	15,16
SiC	organosilicon	arc	*l*	17,18
WC	C/W, W, CH_4	arc	*s*	19-21
WC_{1-x}	W_3O, CH_4	arc	*s*	22
WC_{1-x}, MoC_{1-x}	oxides, C	arc	*s*	23
TiC	$TiCl_4$, CH_4, H_2	arc	*l*	24
TaC	Ta, CH_4	rf	*s*	25,26
TaC	$TaCl_3$, CH_4, H_2	arc	*s*	24
B_4C	BCl_3, CH_4, H_2	rf	*g*	27
B_4C	organoboron	arc	*l*	17,18
	Oxides			
Al_2O_3	Al, O_2	arc	*s*	28
Al_2O_3/Cr_2O_3	AlX_3, CrO_2Cl_2, O_2	rf	*s*	29
Fe_2O_3	metal salt solutions	rf	*l*	30
SiO_2/Al_2O_3	Si, Al, O_2	rf	*s*	31
TiO_2, TiO_2 /Cr_2O_3	$TiCl_4$, CrO_2Cl_2, O_2	rf	*s*	29,32
SiO_2, MgO	oxides	arc	*s*	10
MgO, NiO,	metal nitrate solution	rf, arc	*l*	33,34,17
ZrO_2, Al_2O_3	metal nitrate solution	rf, arc	*l*	33-35,17
ZrO_2/Al_2O_3	metal nitrate solution	rf	*l*	36
CoO, Co_2O_3, Co_3O_4	metal nitrate solution	arc	*l*	17,18
Y_2O_3, CeO_2	metal nitrate solution	arc	*l*	17,18
9%Y_2O_3:ZrO_2	metal nitrate solution	rf, arc	*l*	35,17,18
1%CeO_2:9%Y_2O_3:ZrO_2	metal nitrate solution	arc	*l*	17,18
Co, Mg, Ni, Zn : $Al_2O_4^{2-}$	metal nitrate solution	arc	*l*	17,18
Al, Zr, Ti, Fe, Cr oxides	corresponding metals	RSA	?	37

Compounds	Precursors	Plasma	Phase	Ref
	Oxide Superconductors			
$YBa_2Cu_3O_x$	metal nitrate solution	rf, arc	*l*	17,38,39
$YBa_2Cu_3O_x$	Y and Cu oxides, $BaCO_3$	rf	*s*	40
$Bi_2Sr_2CaCu_2O_x$	metal nitrate solution	arc	*l*	39
$Bi_2Sr_2Ca_2Cu_3O_x$	metal nitrate solution	arc	*l*	39
$BaPb_{1-x}Bi_xO_3$	metal nitrate solution	rf	*l*	41
	Nitrides			
Si_3N_4	$SiCl_4$, NH_3, H_2	rf, arc	*l*	42-45
Si_3N_4	SiH_4, NH_3	rf	*g*	12,42,44
Si_3N_4	Si, N_2, H_2	rf, arc	*s*	46,4
AlN	Al, NH_3, N_2	rf	*s*	4,47
AlN	Al, N_2, NH_3	arc, *TT*	*s*	48,49
AlN	Al, N_2	arc	*s*	50
TiN	$TiCl_4$, N_2, H_2	arc	*l*	28
TiN	Ti, N_2	rf, arc	*s*	51,20
TaN	Ta, N_2	arc	*s*	20
NbN	Nb, N_2	arc	*s*	20
VN	V, N_2	arc	*s*	20
BN	B, N_2	arc	*s*	52
	Borides and Diamond			
C	CH_4, H_2	arc, MW	*g*	1
TiB_2	$TiCl_3$, BCl_3, H_2	arc	*g*	15

Legend : *s* = solid, *l* = liquid, *g* = gas, *TT* = triple torch

This survey indicates that the majority of the plasma chemical reactions make use of at least one solid reactant as the starting material. Particle injection into a thermal plasma is not trivial. In fact, it can be a very serious problem due to the high viscosity of the plasma. Precursor powders are usually entrained into carrier gases for injection into a thermal plasma. The carrier gas is either inert or reactive. On the other hand, gas phase reactants involved in thermal plasma chemical reactions are rather limited. Consequently, plasma chemical reactions largely depend on solid reactants. Over the past 6 years, liquid reactants have been introduced for plasma synthesis. A survey of plasma synthesis including liquid reactants has been given in the table above. Kagawa et al pursued research in this area over the past 6 years using rf plasmas (see table 1 for listing of references). Recently, this laboratory applied a counter-flow injection technique for the synthesis of various ceramic powders in DC plasma jets [17, 18]. Most recently, the synthesis of the yttrium barium cuprate superconductors in a rf plasma has been reported [38] using an injection method similar to that of Kagawa. There are two broad classes of liquid reactants, the aqueous and the nonaqueous liquids, which can be used for plasma synthesis. Aqueous solutions find their applications only for oxide synthesis while the nonaqueous solutions may be used for both nonoxides as well as oxides.

Particulates, whether they are liquid or solids, injected into a thermal plasma may undergo physical as well as chemical changes. In the physical change process, the heat transfer is particularly important and is much more complex than in an ordinary gas, due to the presence of charged and dissociated species. The chemical changes are even more complex because, in addition to the physical changes, there are competing chemical reactions induced on or within the particle itself or in the gas phase after evaporation. The chemical kinetics of the competing reactions is still poorly understood. Guidelines for the chemistry taking place in a plasma may be obtained from chemical equilibrium calculations [7-9]. However, the actual situation is far more complex due to non-equilibrium effects. In fact, kinetic factors are more important than chemical equilibrium considerations.

After the desired chemical reactions are completed, a fast quench is necessary to preserve the product. In thermal plasmas, the fast quench rates ($> 10^6$ K/s) will lead to high degrees of supersaturation of the vapor species which provide the driving force for homogeneous nucleation, resulting in ultrafine particles with sizes down to 10 nm. If heterogeneous processes prevail in a chemical reaction, larger particles ($>> 10^2$ nm) may be formed.

The new plasma synthesis process, using a reactive submerged arc, deserves some discussion. This process is capable of making fine oxide powders in the range from 10 to 1000 nm. It is based on striking an arc between two metallic electrodes submerged in a dielectric liquid, typically water. By controlling the process

parameters such as current, voltage and the composition of the liquids, one can produce dispersable anhydrous fine oxide powders. It is conceivable that by exercising control over the composition of the dielectric liquids, this technique could be extended to the synthesis of nonoxides.

In the following, some of the most recent results of plasma synthesis experiments will be reported using two liquid injection techniques, the counter-flow and the parallel flow liquid injection plasma synthesis (**LIPS**). **LIPS** has a number of advantages when compared to solid injections. (1) The time required for complete evaporation of liquid droplets is relatively short when compared to solids. (2) Complete control of the molar concentrations of liquid reactants is feasible, resulting in products with precise chemical composition. (3) The reaction is essentially gas phase, fast and complete. Therefore, products should be free of impurities. (4) It is possible to manipulate the reaction process to produce a powder with a desired particle size distribution, particle morphology and phase composition. (5) The availability of liquid precursors for ceramics is extensive.

Parallel-flow injection into rf plasmas for powder synthesis is not a new approach and has been studied by Kagawa and by this author. Recently, yttrium barium cuprate has been successful synthesized in a rf plasma using a parallel-flow injection. The reaction involved is a two step process. The liquid precursors, mixed nitrate solutions, are atomized in the plasma core and then pyrolyzed into a dark brown powder. This precursor powder transforms to the $YBa_2Cu_3O_{7-x}$ superconducting powder upon annealing in oxygen. Critical temperature measurement shows a zero resistance at 84 K with a transition width of 2 K (Fig. 8).

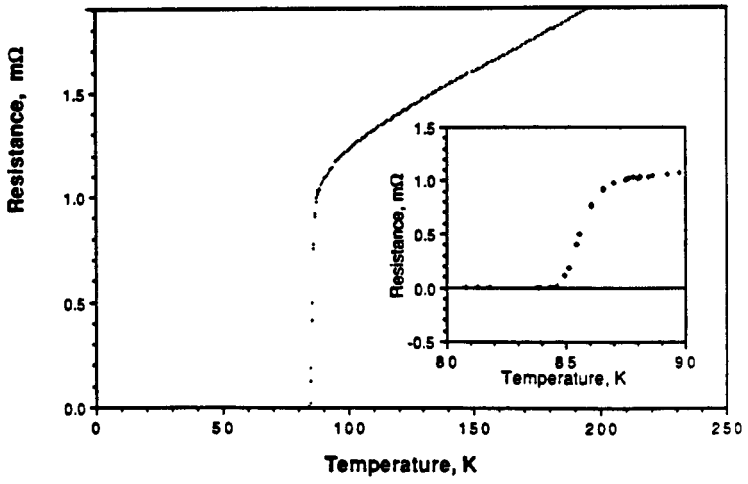

Fig. 8. T_c measurement for the $YBa_2Cu_3O_{7-x}$ superconductor produced by paralle-flow RF **LIPS**.

Another method, the counter-flow injection, has been used extensively in the synthesis of ceramic powders. In this method the liquids are atomized and injected against a dc plasma jet (Fig. 9).

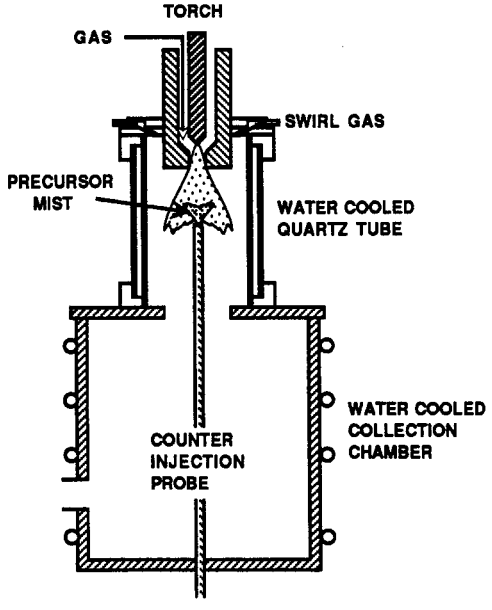

Fig. 9. Schematic for the counter-flow **LIPS**.

Counter-flow **LIPS** is a new approach which provides additional significant advantages over the parallel-flow method. (1) In counter-flow **LIPS** the heat transfer between the plasma and the liquid droplets is substantially higher due to the higher relative velocities between droplets and the plasma. (2) The residence time for the liquid droplets in the plasma is longer. This ensures complete evaporation of the liquid precursors, i.e. a gas phase reaction in the plasma. The feasibility of producing ceramic powders by this counter-flow **LIPS** has been demonstrated by the synthesis of carbides, binary oxides, oxide solid solutions, spinels and the ceramic superconductors. A summary of the advanced ceramics synthesized by the counter-flow **LIPS**, based on their chemical composition, is shown in table 2.

TABLE 2. Summary of Counter-flow DC **LIPS.**

CARBIDES	B_4C and SiC
OXIDES	Al_2O_3, MgO, NiO, CoO, Co_2O_3, Co_3O_4, ZrO_2, Y_2O_3, CeO_2
OXIDE SOLID SOLUTIONS	Y_2O_3 or CeO_2:Y_2O_3 stabilized ZrO_2
SPINELS	Co, Mg, Ni, and Zn aluminates
SUPERCONDUCTORS	$YBa_2Cu_3O_{7-x}$, Bi-Sr-Ca-Cu-O_X (2212 and 2223 phases)

X-ray diffraction profiles of cobalt aluminate, SiC, ceria, and yttria are shown in Fig. 10. X-ray line width at half maximum indicates that the powders produced have similar average particle size. In the SiC reaction, beta SiC formed as the major product with a minor phase of alpha SiC. A small amount of SiO was also observed. The SiO impurity could be suppressed by adjusting the Si:O:C:H ratios in the reaction. Ceria and yttria formed single phase product from their corresponding reactions. In the cobalt and aluminium reaction, cobalt aluminate formed as the major product with a small amount of the spinel cobalt oxide coprecipitated from the reaction. The resulting cobalt aluminate powder is weakly magnetic.

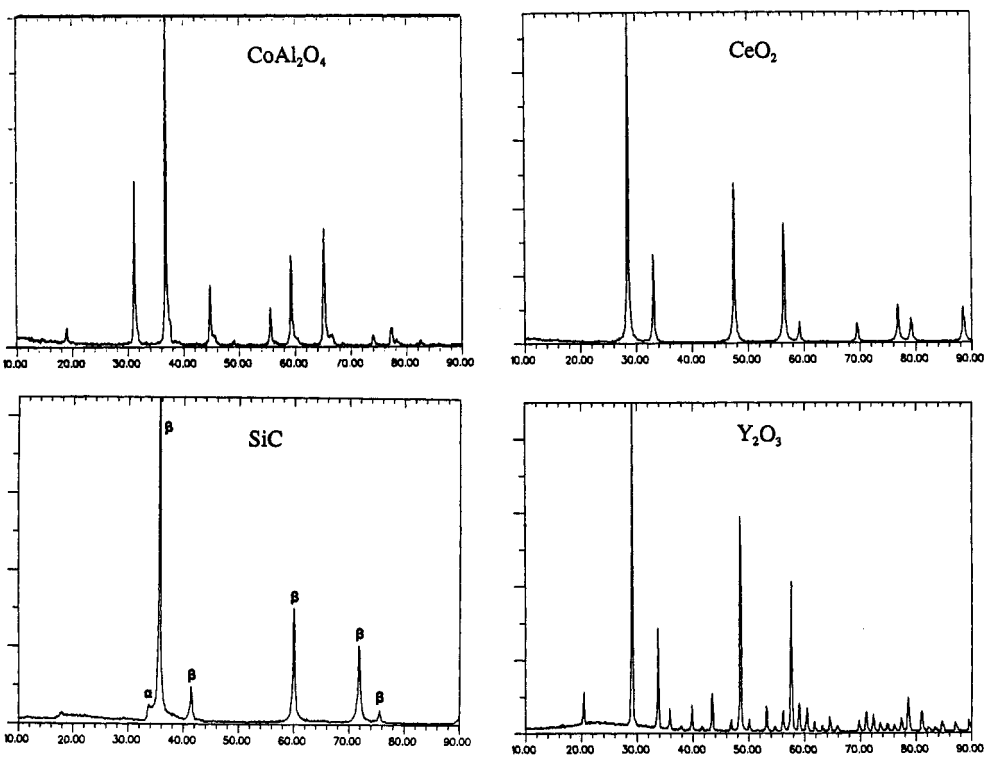

Fig. 10. X-ray diffraction traces for the ceramic powders produced by counter-flow **LIPS.**

Figure 11 shows the electron micrographs of some of the powders formed. The particles are ultrafine, ranging from 0.1 to 0.25 μm. Factors such as precursor solution concentration, atomizing gas to liquid flow ratios, injection probe position relative to the plasma jet and the quenching of the reaction show a certain effect on the final product size distribution. Similar to the spray-ICP case, the formation of the yttrium barium cuprate and the bismuth calcium strontium cuprates require a two step process. The precursor powders formed require oxygen post treatment at moderate temperatures. The bismuth calcium strontium cuprate always form a mixed product of 2212 and 2223 phases regardless of the starting solution compositions. Resistivity measurement of the sintered powder compact shows a broad temperature transition with an onset of T_c at 110 K (Fig. 12) which indicates the presence of the higher temperature 2223 phase in the product.

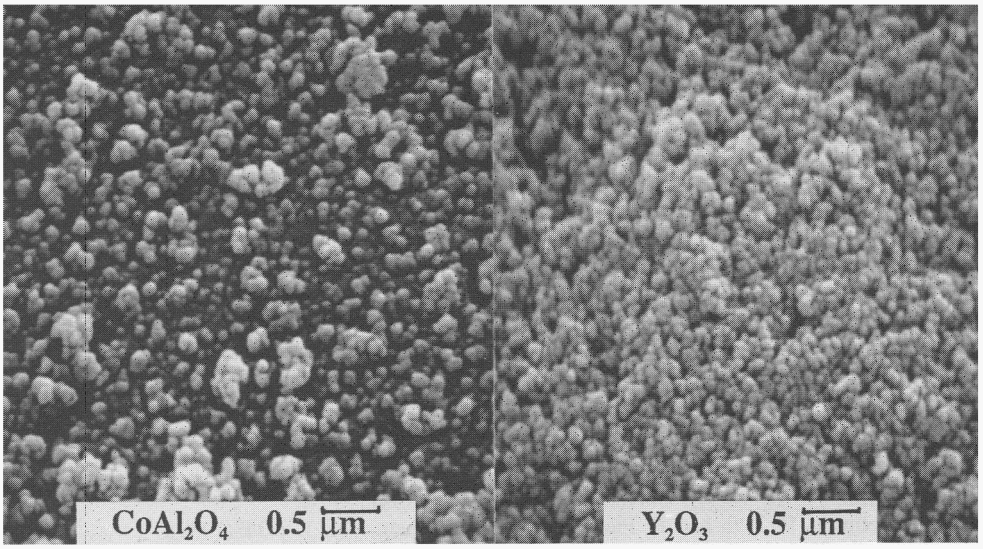

Fig. 11. SEM micrographs of ceramic powders produced by Counter-flow **LIPS.**

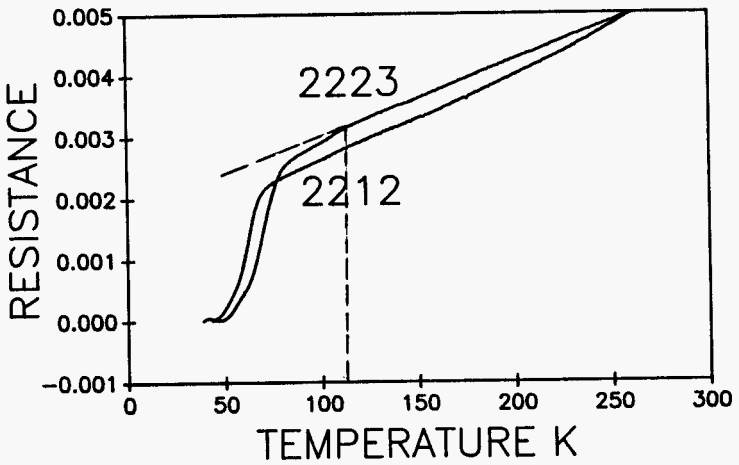

Fig. 12. T_c measurements for the $BiSrCaCuO_x$ (2212 & 2223) superconductors.

SUMMARY

A general survey on plasma generation devices and powder synthesis methods has been given. Electrode and electrodeless plasmas are suitable media for fine and pure powder generations. Particle injection into plasmas remains a severe problem which will hinder large scale application of this technology. Liquid injection and reactive submerged arc plasma synthesis offer attractive alternatives for powder production.
Recent results of the former are included in this paper.

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