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ANALYTICAL AND EXPERIMENTAL STUDIES FOR THERMAL PLASMA PROCESSING OF MATERIALS

DOE-FG02-85ER-13433
PROGRESS REPORT FOR THE PERIOD 9/1/88 TO 5/31/1990

DOE/ER/13433--T1

DE91 000599

I. SUMMARY OF PROGRESS

A. EXPERIMENTAL STUDIES

1. Powder Synthesis

Ceramic powders of carbides, aluminum nitride, oxides, solid solutions, magnetic and non-magnetic spinels, superconductors, and composites have been successfully synthesized in a Triple DC Torch Plasma Jet Reactor (TTPR) and in a single DC Plasma Jet Reactor. All the ceramic powders with the exception of AlN were synthesized using a novel liquid injection method developed to overcome the problems associated with solid injection, in particular for the single DC plasma jet reactor, and to realize the benefits of gas phase reactions.

The TTPR consists of three identical plasma torches. The plasma jets from these torches form a converging large plasma volume into which the starting material, i.e. Al powder for AlN, is fed. In this injection mode the feed material is totally engulfed by the plasma flame which provides maximum heating for the materials. Aluminum nitride collected in a quartz tube within the reactor chamber shows a single phase of hexagonal AlN. Individual particulates measure approximately 0.3 μm while the agglomerated particles average about 2μm. ZrC and $MgAl_2O_4$ were also prepared with the TTPR using liquid precursors as reactants. Liquid precursors are injected into the coalesced part of the plasma just as in the case of powder injection. ZrC reaction makes use of liquid phase zirconium alkoxide as the precursor while a mixture of Ar and CO_2 serves as the reactive atomizing gas. Since the alkoxide has a very high C/Zr ratio the concentration of CO_2 is varied to control the precipitation of free carbon in the reaction. In the $MgAL_2O_4$ reaction, aqueous solution of the soluble metal acid salts were used as precursors and the powder was synthesized in a manner similar to the ZrC.

Equilibrium calculations based on the standard technique of minimization of the system total Gibbs free energy are not adequate for predicting the yield and the proper composition of the products from thermal plasma systems. This is due to domination by nucleation kinetics, a non-equilibrium effect. Therefore, total Gibbs free energy minimization calculations using a quasi-equilibrium modification have been applied to, for example, AlN, ZrC and $MgAl_2O_4$ reactions. The modelling results agree well with experimental data in terms of product yield and composition. Figures 1a and 1b show the experimental and modelling results of the effects of CO_2 on the ZrC reaction.

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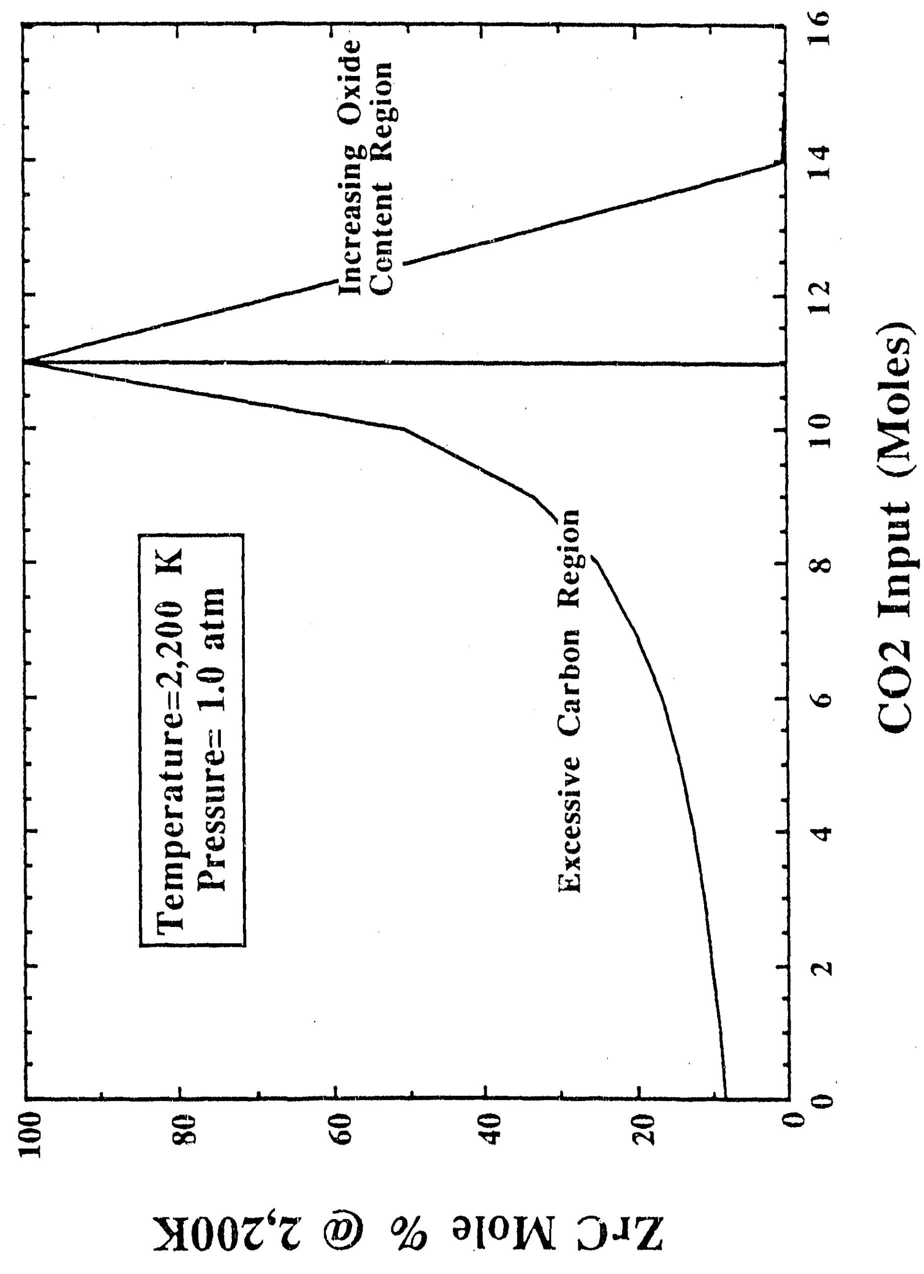


FIG. 1A EFFECTS OF CO_2 ON THE SYNTHESIS OF ZrC

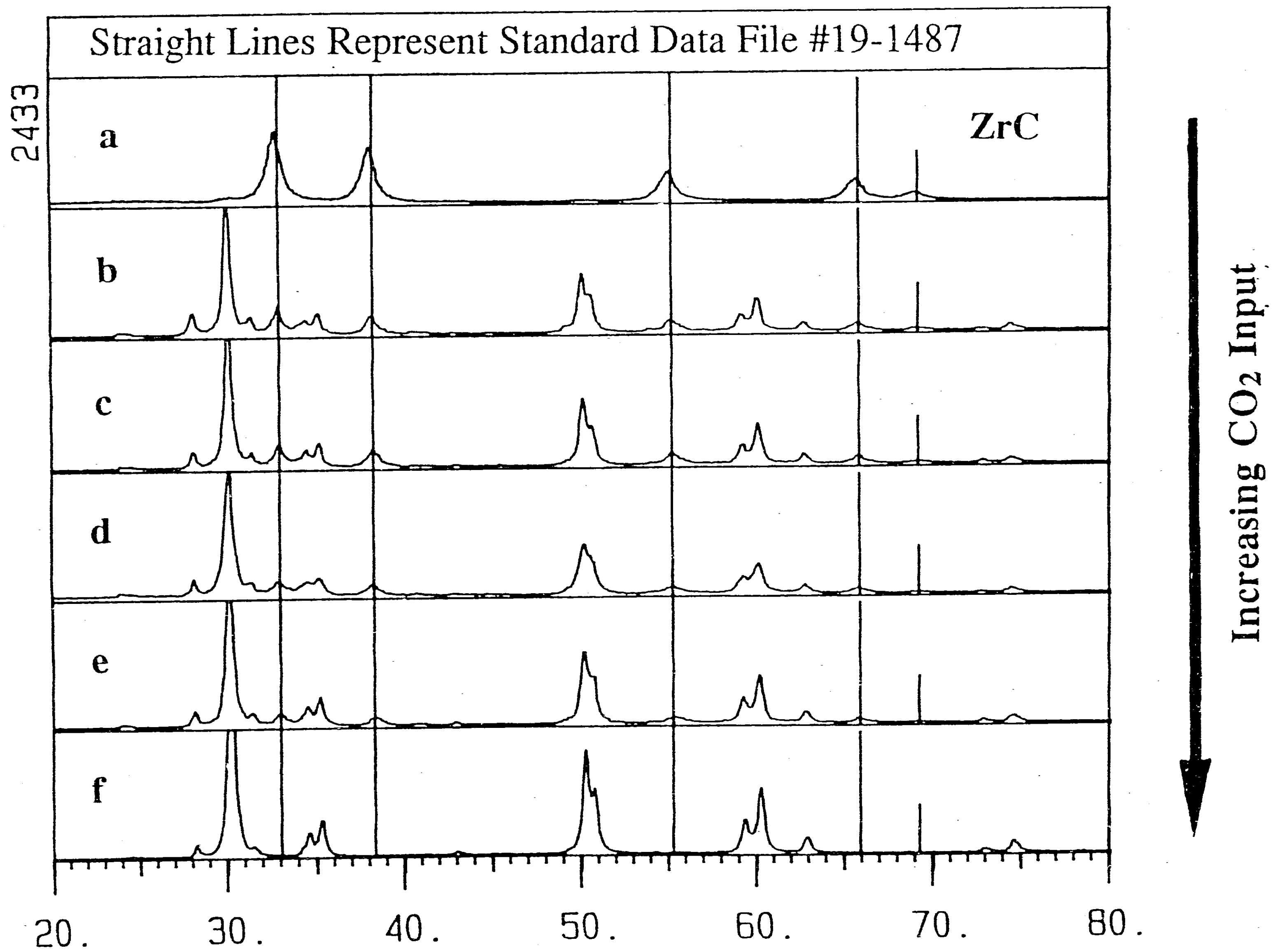


FIG. 1B EFFECTS OF CO_2 ON THE SYNTHESIS OF ZrC

Figure 2 shows the quasi-equilibrium composition for the $MgAl_2O_4$ reaction.

In parallel to the TTRP experiments, plasma synthesis has been performed in a single torch plasm jet reactor using a recently developed novel injection method. This method uses fluid dynamic effects to modify both flow and temperature fields inside the plasma reactor. This novel development is designated as **Counter-Flow Liquid Injection Plasma Synthesis (CF-LIPS)**. In this counter-flow liquid injection plasma reactor, the temperature field is rather uniform and extends much further downstream in the reaction chamber. Large recirculation zones developed above and below the stagnation region of the two flows. This recirculation increases the residence time and mixing of the reactants in the plasma. Modelling results indicate that the residence time of materials in a 25 cm long reaction chamber is more than 120 ms which is two orders of magnitude higher than the conventional parallel injection. Figures 3a and 3b show the modelling results of temperature and flow fields and the particle trajectories inside the reaction chamber. A large variety of ceramic powders has been synthesized by this method. The powders produced are uniform, single phased, spherical and non-agglomerating particles. Consistently, more than 70% of the powders by volume is within 1-2 μm. The results are highly reproducible and agree well with our modelling predictions. Table 1 is a summary of the materials produced by this CF-LIPS.

Table 1. SUMMARY OF DC PLASMA COUNTER-FLOW LIPS.

CARBIDES	B_4C, SiC and ZrC
OXIDES	Al_2O_3, MgO, NiO, CoO, ZrO_2, Y_2O_3, and CeO_2
SOLID SOLUTIONS	Y_2O_3 & CeO_2:Y_2O_3 stabilized ZrO_2
	Co, Mg, Ni, and Zn aluminates
SPINELS	Co, Mg, Ni, Cu, and Zn ferrites
	Co, Mg, Ni, and Cu chromites
SUPERCONDUCTORS	$YBa_2Cu_3O_{7-x}$, Bi-Sr-Ca-Cu-O_X (2212 and 2223 phases)
COMPOSITES	$[ZrC]_x$:$[ZrO_2]_y$

2. Diamond Coating Deposition

Initial experiments have been performed for the deposition of diamond coatings on Si wafers using the TTPR with methane as the carbon source. The wafer surface was treated with diamond paste or beta SiC seed particles. The methane concentration varied from 3.5% to 6.5% with the balance being hydrogen. Well faceted diamond crystallites were deposited on the surface of the wafers, forming a continuous one particle thick coating. Nearly all crystallites showed {111} growth planes with {h00} growth planes also observed. The formation of diamond has been confirmed with X-ray diffraction and further confirmation will make use of Raman spectroscopy. At higher methane content (6.5%), crystallite sizes decreased and <h00> growth became more prominent. To our knowledge, well faceted diamond crystals formed at such a high methane content at one atmosphere have not been observed before. More detailed studies of diamond formation will follow. Figure 4 shows typical diamond crystals produced by this method.

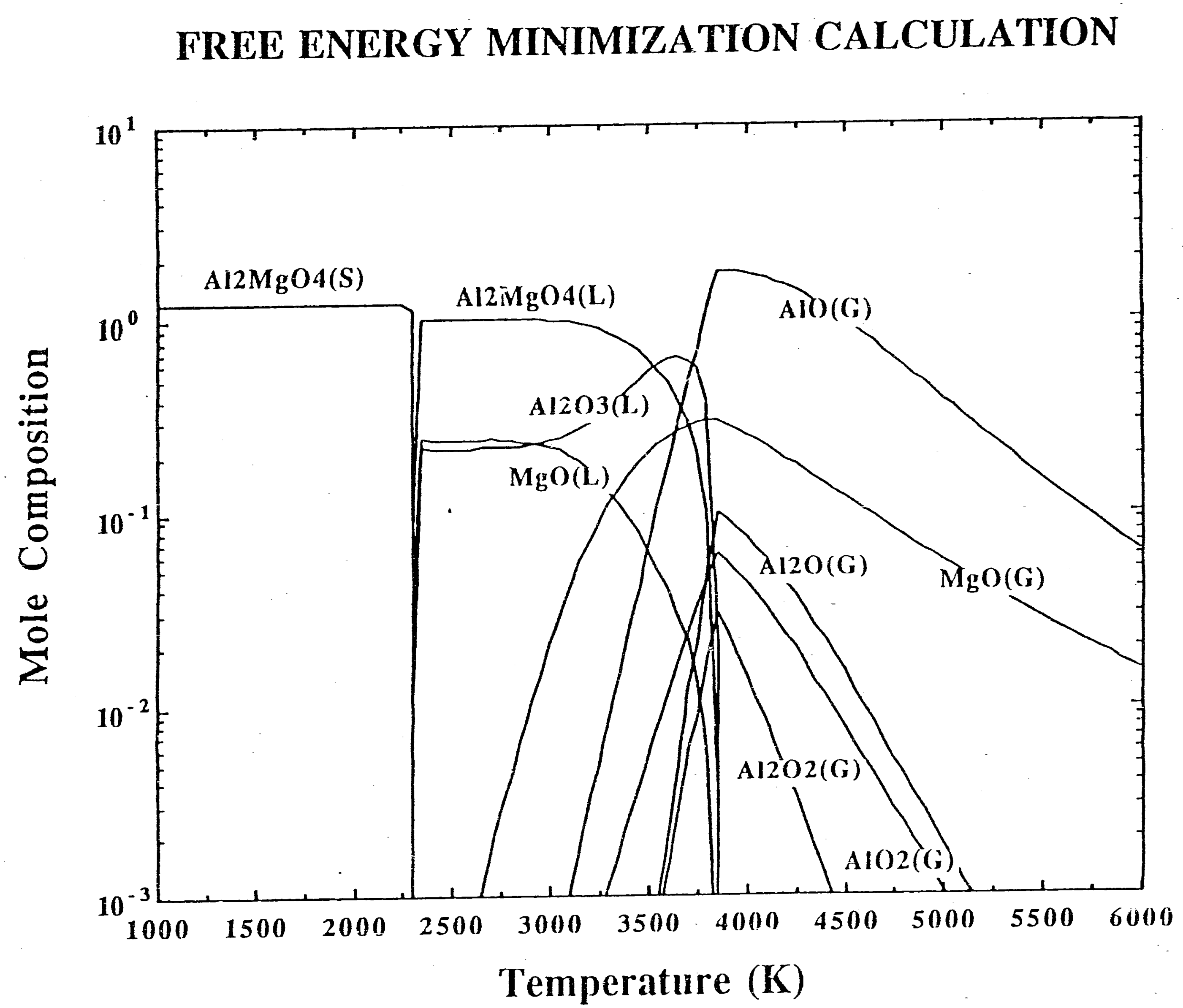
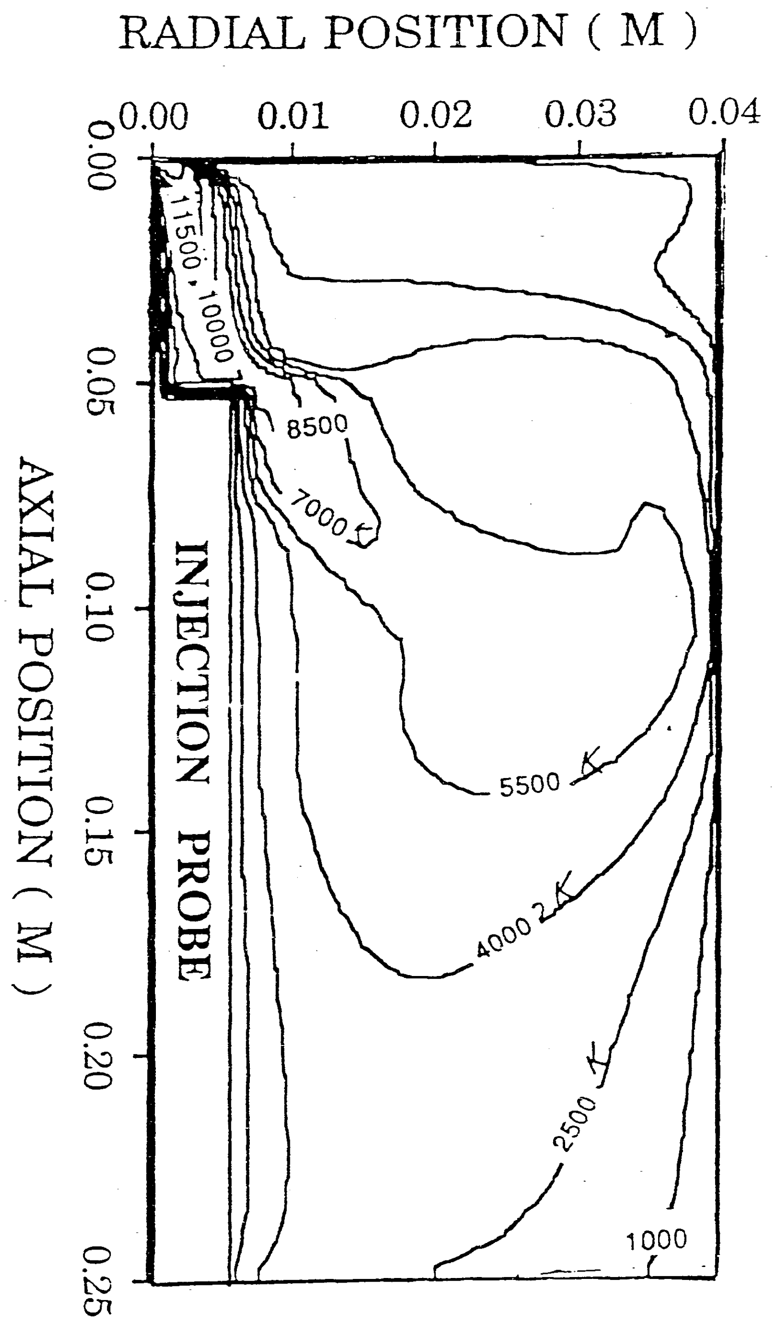
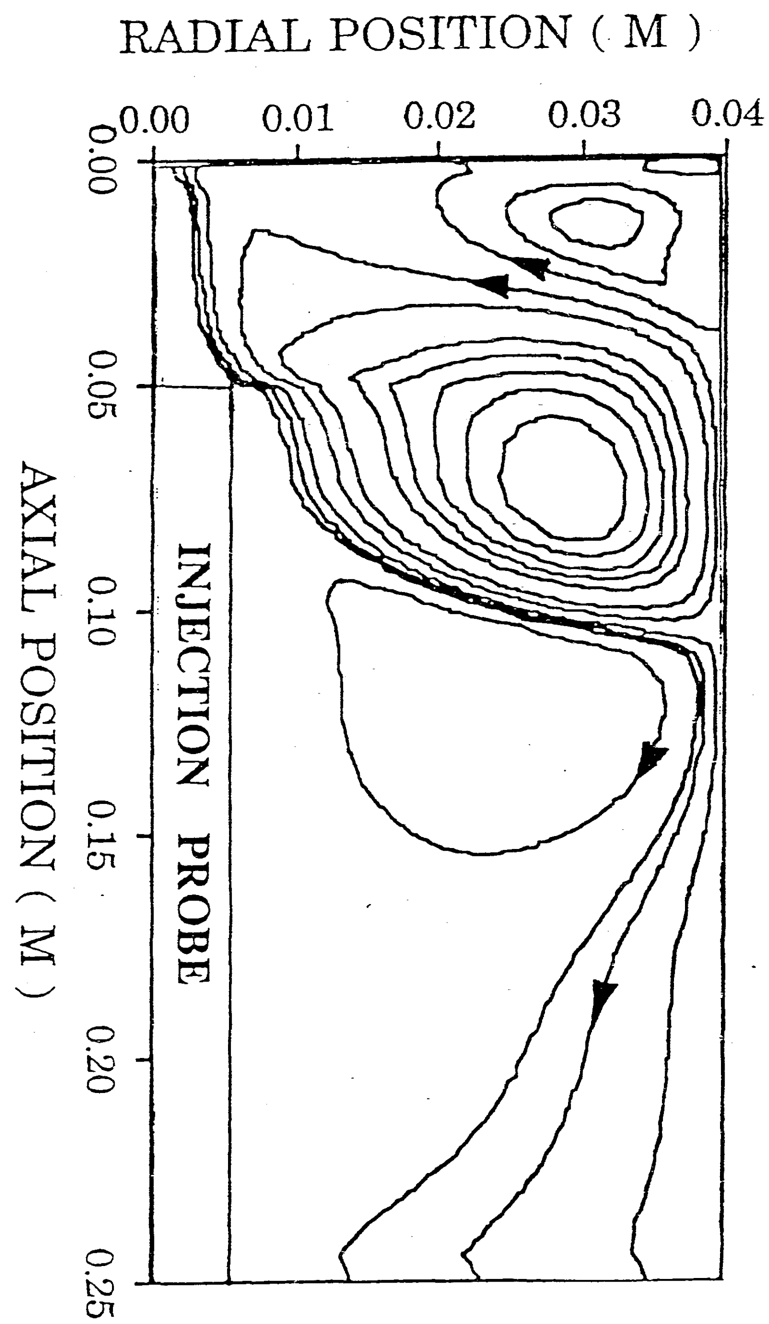


FIG. 2 EQUILIBRIUM COMPOSITIONS FOR $MgAl_2O_4$



TEMPERATURE FIELD

FIG. 3A



FLOW FIELD

FIG. 3B

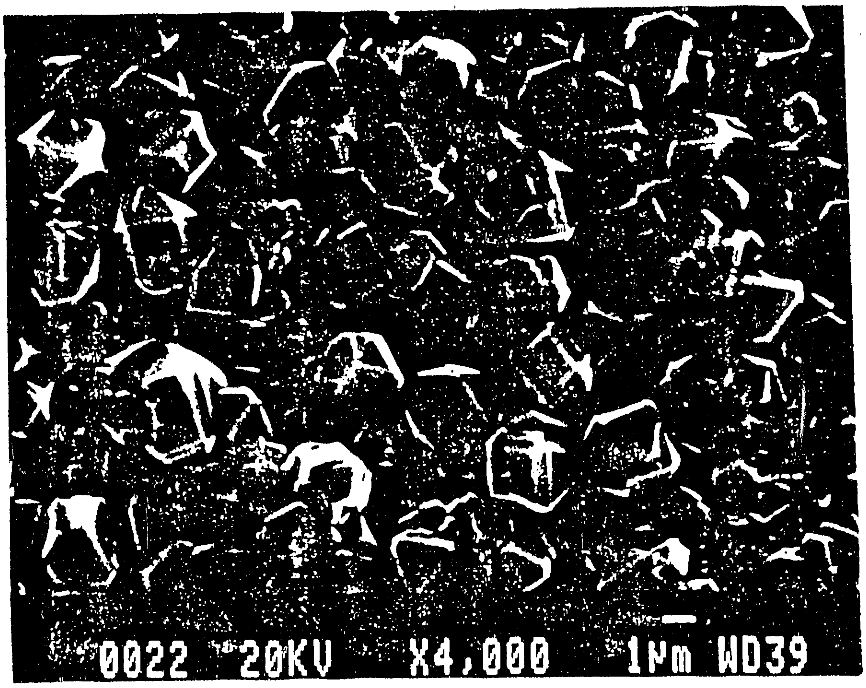


Fig. 4 Diamond crystallites

3. Enthalpy Probe Measurements

For measuring temperature and velocity fields in plasma systems, enthalpy probes have been developed and tested in this laboratory. The validity of measured enthalpy and velocity profiles has been checked by performing energy and mass flux balances in an argon plasma jet operated in argon atmosphere. More details of this work are reported in Ref. 12 of the publication list.

B. MODELLING STUDIES

Total Gibbs free energy minimization calculations using a quasi-equilibrium modification have been applied to simulate several chemical reactions. The modelling results agree well with experimental data in terms of product yield and composition.

Plasma reactor modelling has been performed for the counter-flow liquid injection plasma synthesis experiment. Results indicate that temperature fields and flow fields are greatly modified. Temperature fields are much more uniform and extend further downstream in the reactor. Large recirculation regions developed in the reaction chamber enhance mixing, heating, and residence time (>120 ms) for the materials. Future modelling will include turbulence in the reactor.

C. DIAGNOSTICS

Plasma diagnostics has been initiated to determine the pressure gradient in the coalesced part of the plasma jet. The pressure gradient drives the diffusion of chemical species which ultimately controls the chemical reactions.

Plans have been initiated to perform diagnostics on the counter-flow reactor in particular the stagnation region of the two flows.

II. PUBLICATIONS

1. P. C. Kong and E. Pfender, " Plasma Synthesis of Fine Powders by Counter-Flow Liquid Injection ", invited lecture, published in <u>*Combustion and Plasma Synthesis of High Temperature Materials*</u>, (peer reviewed) edited by Z. A. Munir and J. B. Holt, VCH Publishers, 1990.
2. Z. P. Lu, T. W. Or, L. Stachowicz, P. Kong and E. Pfender, " Synthesis of Zirconium Carbide in a Triple Torch Plasma Reactor Using Liquid Organometallic Zirconium Precursors ", presented at the 1990 MRS Spring Meeting, accepted for publication in the Proceedings, (peer reviewed).
3. Z. P. Lu and E. Pfender, " DC Plasma Synthesis of Aluminum Nitride Ceramic Powders ", presented at the 1990 MRS Spring Meeting, accepted for publication in the Proceedings, (peer reviewed).
4. P. Kong, T. W. Or, L. Stachowicz and E. Pfender, " Plasma Synthesis of Fine Ceramic Powders by A Novel Counter-Flow Liquid Injection Method ", presented at the 1990 MRS Spring Meeting, accepted for publication in the Proceedings, (peer reviewed).
5. T. W. Or, Z. P. Lu, L. Stachowicz, P. Kong and E. Pfender, " Counter-Flow Liquid Injection Plasma Synthesis (**CF-LIPS**) of Spinel Fine Powders ", presented at the 1990 MRS Spring Meeting, accepted for publication in the Proceedings, (peer reviewed).
6. S. H. Paik, Xi Chen, P. Kong and E. Pfender, " Modelling of a Counter-Flow Plasma Reactor ", accepted for publication in the *J. Plasma Chem and Plasma Processing*, 1990.
7. R. Spores and E. Pfender, " Flow Structure of a Turbulent Thermal Plasma Jet ", Surface and Coatings Technology, Vol. 37, 251 (1989).
8. Y. P. Chyou and E. Pfender, " Behaviorof Particulates in Thermal plasma Flows ", Plasma Chem. and Plasma Processing, Vol.9 (1), 45 (1989).
9. Yl Chang, P. Kong and E. Pfender, " Characterization of Silicon Nitride Particles Synthesized in an Atmospheric-Pressure Convection-Stabilized Arc ", Plasma Chem and plasma Processing., Vol. 9 (1), 73 (1989).
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12. A. Capetti and E. Pfender, " Probe Measurements in Argon Plasma Jets operated in Ambient Argon ", Plasma Chem. and Plasma Processing, Vol. 9 (2), 329 (1989).
13. Z. P. Lu and E. Pfender, " Synthesis of AlN Powder in a Triple Torch plasma Reactor ", Proc. of the 9th Int. Symp. on Plasma Chem., Pugnochiuso, Italy, Vol. 2, 675 (1989).
14. R. M. Young and E. Pfender, " A Novel Approach for Introducing Particulate matter into Thermal Plasmas; The Triple-Cathode Arc ", Plasma Chem. and Plasma Processing, Vol. 9 (4), 465 (1989).

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