COMBUSTION SYNTHESIS OF CERAMIC AND METAL-MATRIX COMPOSITES

N93-20203

John J. Moore, Heng J. Feng, and Kevin J. Hunter
Department of Metallurgical and Materials Engineering
Colorado School of Mines
Golden, Colorado 80401

and

David G. Wirth
Coors Ceramics Company
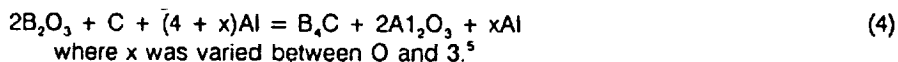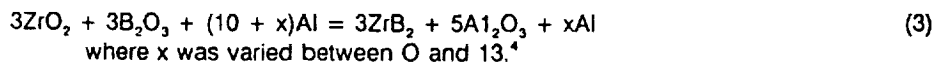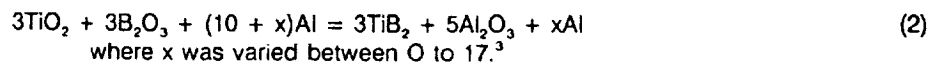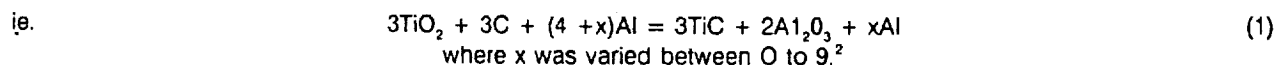Golden, Colorado 80401

Introduction

Combustion synthesis or self-propagating high temperature synthesis (SHS) is effected by heating a reactant mixture, to above the ignition temperature (Tig) whereupon an exothermic reaction is initiated which produces a maximum or combustion temperature, Tc. These SHS reactions are being used to produce ceramics, intermetallics, and composite materials.[1] One of the major limitations of this process is that relatively high levels of porosity, e.g., 50%, remain in the product. Conducting these SHS reactions under adiabatic conditions, the maximum temperature is the adiabatic temperature, Tad, and ΔH (Tad) = 0, Tad = Tc. If the reactants or products go through a phase change, the latent heat of transformation needs to be taken into account,

$$\text{i.e.} \quad \Delta H(Tad) = \Delta H(To) - \int_{To}^{Ttrans} CpdT \pm \Delta H(trans) + \int_{Ttrans}^{Tad} Cpdt = 0 \qquad (6)$$

where To is the initial or starting temperature, eg. 298 K. Ttrans is the phase transition point of a reactant $-\Delta H$(trans) or a product $+\Delta H$(trans) and ΔH(trans) is the corresponding heat of transformation. Tad can be determined from equation (6) or graphically as indicated in Figure 1.

Experimental Reaction Systems

Several model composite systems have been investigated in which an excess amount of Al is used both as a reductant in the reaction and as the metal component of the ceramic-metal composite.[3-6]

ie.

$$3TiO_2 + 3C + (4 + x)Al = 3TiC + 2Al_2O_3 + xAl \qquad (1)$$
where x was varied between O to 9.[2]

$$3TiO_2 + 3B_2O_3 + (10 + x)Al = 3TiB_2 + 5Al_2O_3 + xAl \qquad (2)$$
where x was varied between O to 17.[3]

$$3ZrO_2 + 3B_2O_3 + (10 + x)Al = 3ZrB_2 + 5Al_2O_3 + xAl \qquad (3)$$
where x was varied between O and 13.[4]

$$2B_2O_3 + C + (4 + x)Al = B_4C + 2Al_2O_3 + xAl \qquad (4)$$
where x was varied between O and 3.[5]

The excess amount of liquid Al, created by the combustion synthesis reaction, is allowed to simultaneously infiltrate the pores produced in the ceramic composite thereby taking advantage of this major limitation in the SHS process, and hence improve the relative density of the composite produced. Incorporating a ductile metal into a brittle ceramic composite matrix has considerable potential for substantial improvements in fracture toughness. A variation of reaction (1) is given in reaction (5) in which the excess Al is used to reduce TiO_2 and generate an excess amount of Ti.[6]

$$(3 + x)TiO_2 + 3C + (4 + 4/3x)Al = 3TiC + (2 + 2/3x)Al_2O_3 + xTi \qquad (5)$$
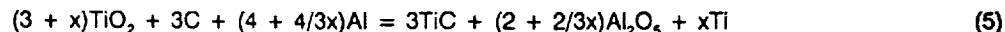
The enthalpy-temperature plots for these five reaction systems have been examined and that for reaction (1) is given in Figure 1 in which Xr and Xp refer to the respective reactant and product H-T plots associated with the corresponding excess amount of aluminum used in the reaction. The corresponding melting and boiling points of reactants and products are indicated in Figure 1 and Table I.

Experimental Procedure

The reactant powders (Table 1) were thoroughly mixed using porcelain ball milling for a minimum of six hours, and pressed to various green densities with varying values of x, into cylindrical compacts of 0.5 inches (12.7mm) in diameter and 1 inch (25.4mm) in length. These pellets were dried for 1 hour at 110°C in an oven and were subsequently ignited in the propagating mode using a heated tungsten wire in an argon atmosphere as described in an earlier publication.[2] The ignition temperatures, Tig, were determined using a Pt-Pt/10%Rh thermocouple and the combustion temperatures, Tc, were determined using an Ircon Mirage Two Wavelength Infrared Pyrometer. A video camera was used to record the propagation of the combustion front. In this way, it was possible to assess the stability of the combustion wave and also its rate of propagation. The ceramic-metal composites produced were examined using optical and scanning electron microscopy (SEM) interfaced with an energy dispersive spectroscopy (EDS) facility and also by x-ray diffraction (XRD). The density of the products was determined using an immersion in water technique.

Results and Discussion

A maximum of 75% theoretical density could be achieved in the composites produced in reactions (1), (2) and (3) while an expanded or foamed ceramic-metal composite was produced in reaction (4). Reaction (3) also produced a large volume of Al_2O_3 whiskers while reaction (2) produced a small amount of Al_2O_3 whiskers present in the pores of the composite. SHS reaction stability diagrams were constructed for each of the reactions (1)-(5) as shown in Figure 2-5. A stable combustion front was observed for each level of excess Al used in reaction (4), i.e. x = 0, 1, 2 and 3. Increasing excess Al and green density eventually resulted in decreased stability of the combustion front and possible quenching out. This is almost certainly the result of increased heat losses from the SHS reaction on account of increased thermal conductivity (increased green density) and latent heat of fusion (increased excess Al). There is a slight increase in thermal conductivity of the green pellet on increasing the excess amount of Al or Ti and increasing the green density.[2-6] This increased thermal conductivity could have two opposing effects: (i) the heat from the reaction front is more efficiently transferred to the reactants ahead of the reaction front and (ii) the heat lost from the reactants ahead of the reaction front is increased. Even though the velocity of the reaction front is considered to be high [typically 0.2cm s^{-1} for reaction (1),[2] and (5)[6] and 2cm s^{-1} for reaction (2),[3] 7cm s^{-1} for reaction (3)[4] and 5cm s^{-1} for reaction (4)],[5] it is more likely that (ii) will prevail in the small reactant pellet systems used. In each reaction system studied, except reaction (4), the aluminum becomes liquid (melting point 660°C) before the ignition temperature is reached, ie. Tig for reaction (1) >900°C,[3] for reaction (2) >850°C,[4] for reaction (3) >900°C,[5] for reaction (4) >600°C.[6] for reaction (5) of >950°C. The typical values of Tc achieved in each system were 1600-2000°C for reaction (1),[2] 1550-2300°C for reaction (2),[3] 2000-2400°C for reaction (3),[4] 1850-2050°C for reaction (4),[5] and 2000-2300° for reaction (5).[6]

Reaction systems (1), (2) and (5) produced considerable increases in product density with increased excess Al as expected, eg. from 45% (x = 0) to 75% (x = 9) relative densities. However, unlike reaction (1), the maximum density in the ceramic-metal product for reactions (2) and (3) were obtained at low to intermediate green densities, while reaction (4) expanded 400% in length producing a maximum density of 35%. This is most likely due to the high volatility of B_2O_3 used in these reactions. The calculated vapor pressures of the reactant and product species in reactions (1) to (5) (presented in Figure 3) indicate that the combustion temperatures produced in reaction (3) resulted in considerable volumes of both B_2O_3 and Al gases which resulted in Al_2O_3 whisker formation from a vapor-liquid-solid mode of synthesis (Figure 4). Al_2O_3 whiskers were also produced in pores in the TiB_2-Al_2O_3-Al composite produced by reaction (2). However, these whiskers were far less numerous than those produced by reaction (3). Since the Tc achieved in reaction (2) produces a high vapor pressure (eg. > 1 at) of B_2O_3 vapor and only a moderate vapor pressure of Al gas (ie. from 10^{-5} to 10^{-1} at). Both these reaction systems (2) and (3) resulted in improved product densities with excess Al provided that lower green densities were maintained, i.e., using a compaction pressure of 1.6 x 10^7 kg/m^2 or below. The lower Tc value in reaction (4) would result in a low vapor pressure of Al ie. typically 10^{-3} to 10^{-2} at., but the large vapor pressure of B_2O_3 produced by this Tc (ie. > 1 at) and the larger reaction mass of B_2O_3 in reaction (4) compared with those in reactions (2) and (3) has resulted in a large volume of B_2O_3 at 1 atmosphere pressure or higher. This high pressure, high volume B_2O_3 gas is able to push or expand the reactant materials ahead of the combustion

front in the vertical direction, thereby producing an expanded or foamed ceramic-metal composite which exhibited ≥65% uniform porosity (Figure 5) and an expansion of up to 400%. The more readily predicted behavior of product densities in reactions (1) and (5), ie. increased product densities with increased green density and excess Al, is readily explained in the absence of any major volatile species. However, reaction (5) was able to produce a semi stable combustion front up to at least a value of x = 50 due to the fact that the exothermicity of reaction (5) increases with xTi. The effect of density-driven fluid flow of liquid Al was also evident in these products (Figure 6).

Conclusions

Although reaction systems (1) to (5) use the same concept of synthesizing ceramic-metal composites, the different physical properties of the reactants and products, eg melting and boiling points, thermal conductivity, and combustion temperatures achieved in each system result in different product formations, morphologies, microstructures and relative densities. The presence and extent of liquid and gaseous species appear to have a significant influence over these product microstructures and densities. Incorporating an excess amount of metal within the combustion synthesis reaction in which no significant gaseous phases are generated increased the composite relative density from 45% to 75% without the application of pressure. The prospect of synthesizing reinforcing whiskers in-situ from gaseous species generated within the combustion synthesis reaction to produce a ceramic-metal composite without the problem of handling these hazardous materials iś extremely attractive. The concept of producing stability diagrams has been introduced for these ceramic-metal combustion synthesis reactions that indicate how the process parameters can produce stable propagating reaction fronts. Also the effect of green density and excess Al on the composite product density is dependent on the character and extent of the liquid and gaseous species present at the reaction front. The concept of producing expanded or foamed ceramic and ceramic-metal composites by utilizing a high volume of a volatile specie at the reaction front has been introduced. These materials could find considerable applications varying from catalyst support systems to filters to ultra light weight structural materials. The effect of gravity on density driven fluid flow and vapor transport is likely to be significant in producing tough, dense ceramic-metal composites with uniform microstructures and properties.

Acknowledgements

References
1.   Z. A. Munir, Ceramic Bulletin, 67(2) (1988) 342.
2.   H.J. Feng, J.J. Moore, D.G. Wirth, "The Combustion Synthesis of Ceramic-Metal Composites: The TiC-Al₂O₃-Al System", accepted for publication in Met. Trans.
3.   H.J. Feng, J.J. Moore, D.G. Wirth, "Combustion Synthesis of TiB₂-Al₂O₃-Al Composite Materials" published in proceedings of Symposium on Developments in Ceramic and Metal Matrix Composites, TMS Annual Meeting, San Diego, March 1-5, 1992. Pub by TMS, pp 219-239.
4.   H.J. Feng, J.J. Moore, D.G. Wirth, "Combustion Synthesis of Ceramic Metal Composite Materials: The ZrB₂-A₂O₅-Al System" to be published in proceedings of the International Symposium on Self-Propagating High Temperature Synthesis (SHS), Alma-Ata, USSR, Sept 23-28, 1991; pub by Soviet Academy of Sciences.
5.   H.J. Feng, J.J. Moore, D.G. Wirth, "The Combustion Synthesis of B₄C-Al₂O₃-Al Composite Materials" to be published in proceedings of Symposium on Synthesis and Processing of Ceramics: Scientific Issues, MRS Fall Meeting, Boston Dec 2-6 1991; pub by MRS.
6.   K. J. Hunter, J. J. Moore, D. G. Wirth, Proceedings of 6th International Titanium conference, San Diego, CA, June 28- Aug. 2, 1992, pub. by TMS.

Table I. Physical Properties of Reactants and Products in Reactions (1)-(5)

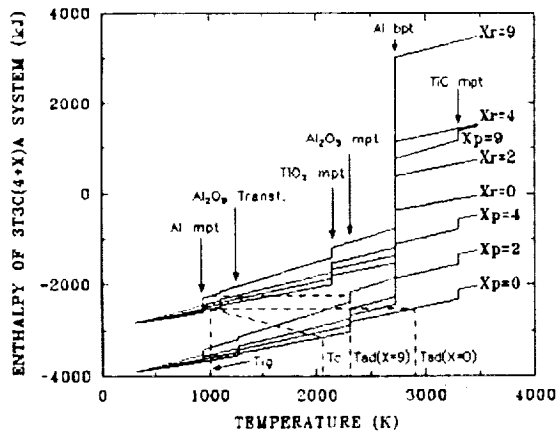| Material	TiO₂	C	Al	TiC	Al₂O	B₂O₃	TiB₂	ZrO₂	ZrB₂	B₄C	Ti
Mpt°C	1830		660	3140	2050	450	2900	2715	3000	2450	1660
Bpt°C	3000		2467	4820	2980	1860		5000		3500	3287
SG*	4.26	2.25	2.70	4.93	3.97	2.46	4.50	5.60	6.09	2.52	4.54
Size (μm)	-44	-44	-44			-75		-44			

*Specific Gravity

Figure 1 Enthalpy-temperature plots for reactants (Xr) and products (Xp) for various amounts of excess Al for Reaction (1)
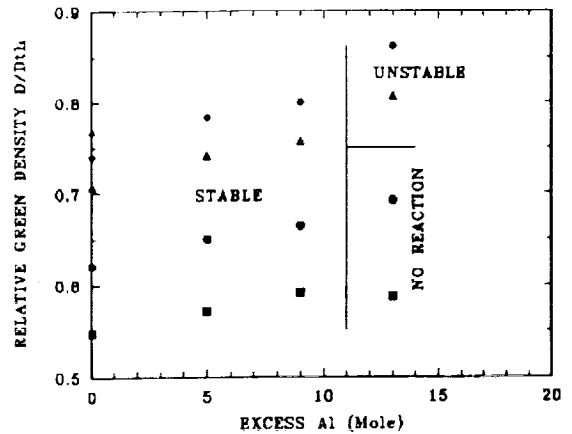

Figure 2 Effect of excess Al and relative green density on the stability of the propagating combustion wave for Reaction (1).
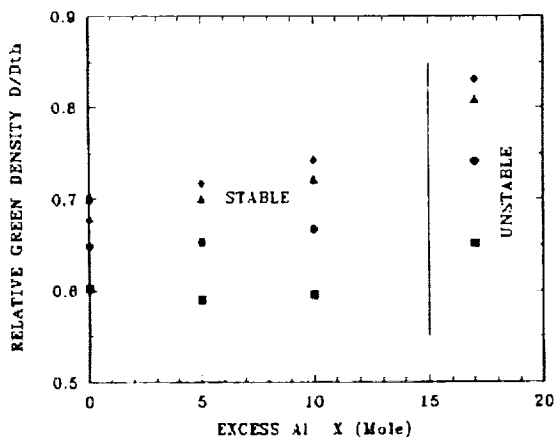

Figure 3 Effect of excess Al and relative green density on the stability of the porpagating combustion wave for Reaction (2).
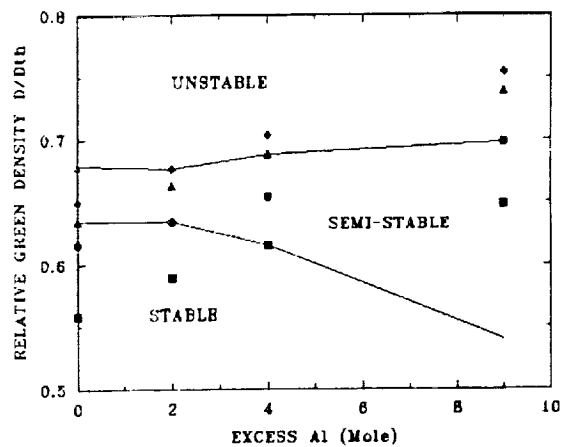

Figure 4 Effect of excess Al and relative green density on the stability of the propagating combustion wave for Reaction (3).

206

Figure 5 (left graph):

GREEN DENSITY (%)

70
65
60
55
50

Stable | Semi-Stable (significant cracking)

EXCESS Ti (mole)

0 10 20 30 40 50

Figure 6 (right graph):

To range for reaction (5)
To range for reaction (4)
To range for reaction (3)
To range for reaction (2)
To range for reaction (1)

VAPOR PRESSURE (atm. in Log Scale)

5
0
-5
-10
-15

B_2O_3 Al TiO_2 Ti

Al   Ti Al_2O_3
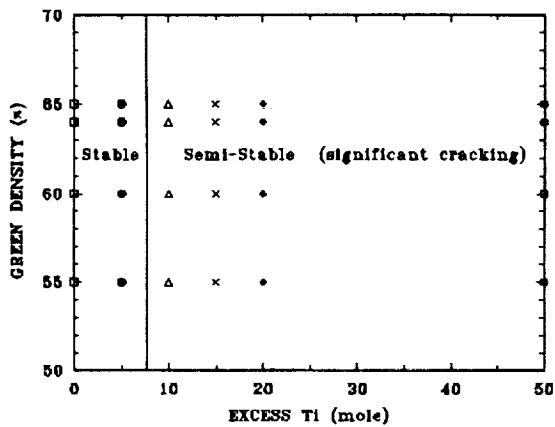
B_2O_3

TEMPERATURE (K)

500 1500 2500 3500

Figure 5 Effect of excess Ti and relative green density on the stability of the propagating combustion wave for Reaction (5).
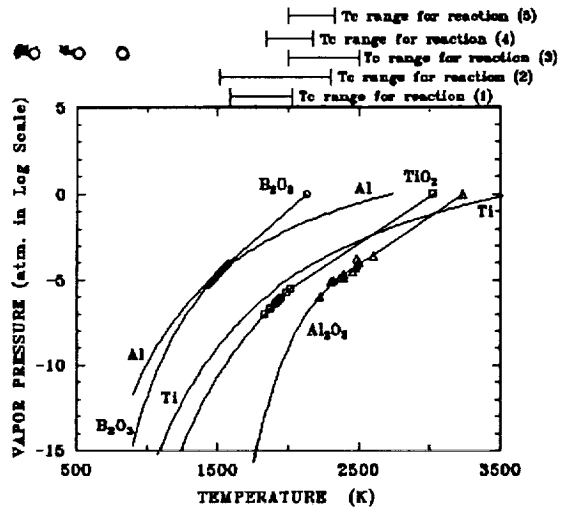
Figure 6 The effect of temperature on the calculated vapor pressues of species present in Reaction (1) to (4).
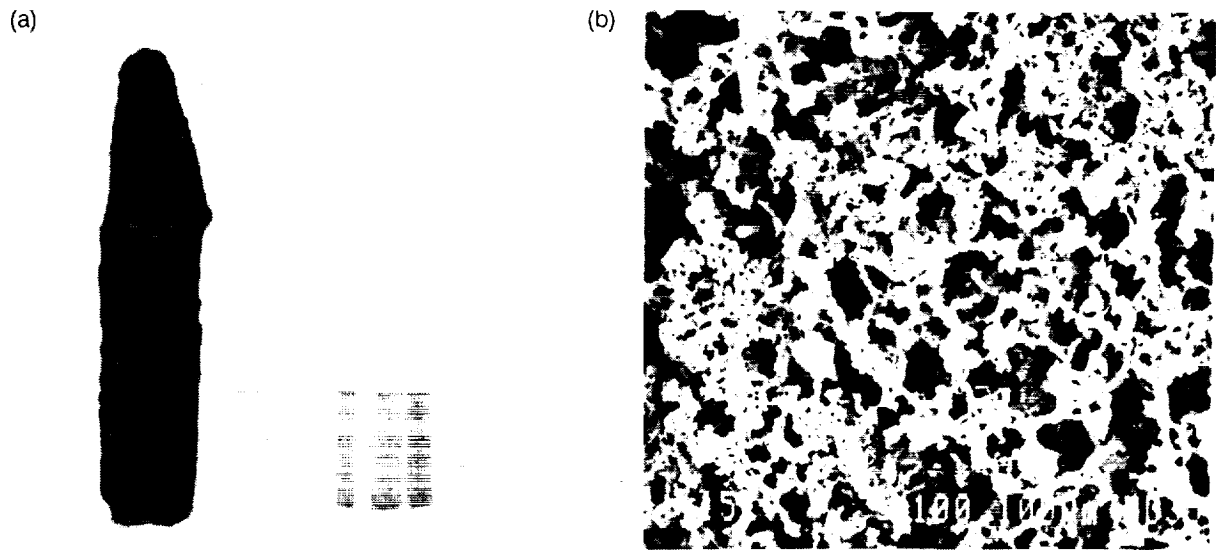
Figure 7 Al_2O_3 whisker formation during Reaction (3).

207

Figure 8 (a) Expanded or foamed ceramic and ceramic-metal composites produced by reaction (4) comparison of reacter (left) with unreacted (right) green pellet; (b) scanning electron photomicrograph of (a) for x = 0.
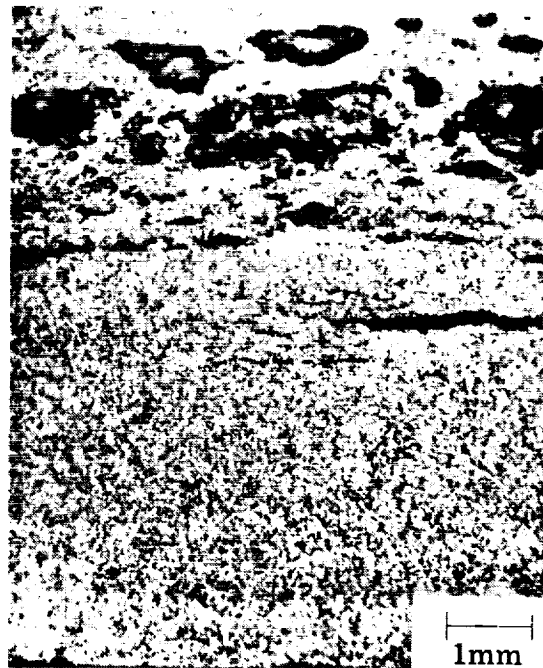

Figure 9 Optical photomicrograph of $TiC-Al_2O_3-9Al$ composite, indicating gravity-driven fluid flow of the liquid Al to the bottom half of the coposite.

COMMENTS

Question (Prof. Bernard J. Matkowsky, Northwestern University): You referred to experiments in the former Soviet Union, in which the sample produced by S.H.S. is significantly expanded (i.e., its porosity is significantly increased). I presume you are referring to the experiments of A. Shteinberg. First, in his experiments the increase in porosity was due to gas being liberated, rather than consumed, in the reaction. Was this true in your experiments as well? Second, he observed that the degree of increase in porosity was different if the sample was arranged (1) horizontally or (2) vertically in normal gravity, and (3) in microgravity. I understand that you have not yet done the experiments in microgravity, but did you observe similar differences between horizontal and vertical arrangements in normal gravity.

Finally, you described the propagation of the combustion wave as being either (1) stable, by which you mean that it propagated with a planar front with a constant velocity, or (2) unstable, by which you mean that propagation ceased. However, in addition to the stable mode of propagation, there have been observations of pulsating propagation, in which a planar front propagates with an oscillatory velocity, and spinning propagation, in which a hot spot (or spots) moves in a helical fashion. Did you observe either of these modes of propagation?

Answer: The increase in porosity was due to gaseous species both liberated and consumed. For example, in combustion synthesis reactions involving B_2O_3, which has a boiling point slightly in excess of 1800 degrees C, the combustion temperature was well above this point, and, therefore, generated B_2O_3 gas of 1 atmosphere pressure. At the same time, the B_2O_3 gas was also consumed in the reaction to produce compounds such as TiB_2 with $TiBO_2$ reactant or B_4C with graphite as the reactant. In certain combustion synthesis reactions that we studied, the combustion temperature was sufficient to produce a significant volatility (i.e., partial pressure of aluminum gas). In this respect, the aluminum gas and the B_2O_3 gas reacted to produce Al_2O_3 whiskers. In our experiments, the very large levels of porosity (e.g., greater than or equal to 75%) were produced when there was only one major gaseous species produced (i.e., B_2O_3 gas).

Yes, I was referring to Professor Alex Shteinberg's work in Russia. Most of our experiments were conducted in which the pellet was ignited at the bottom of the cylindrical pellet and the major expansion occurred in the vertical direction against gravity.

We defined a stable combustion front as one which propagated a steady rate down through the pellet, wherein an unstable combustion front was one which eventually quenched out. Our definition of a semi-stable combustion front was one that slowed down, almost extinguished, and then picked up speed again, probably going through two or three of these cycles. In one or two occasions we did observe a spinning mode of propagation, which we defined as semi-stable front.
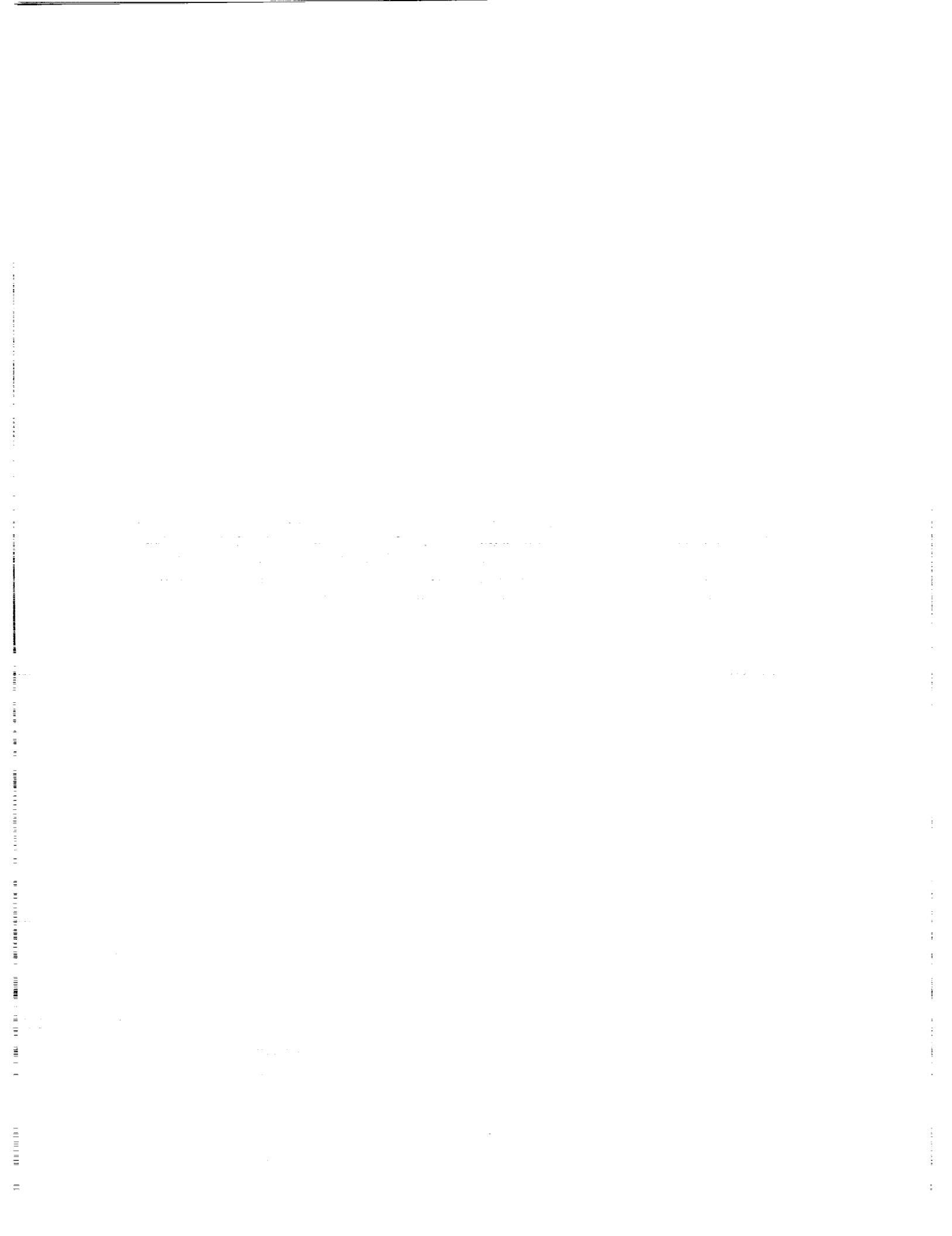
SESSION E - PLENARY DINNER

(Chair, Robert Rhome)