N96- 15577

COMBUSTION SYNTHESIS OF CERAMIC-METAL COMPOSITE MATERIALS IN MICROGRAVITY

John Moore, Colorado School of Mines
Grants: NCC3-215, (8/1/91 to 18/1/95), and
NAG3-1698, (1/19/95 to 1/18/98)

Introduction:

Combustion synthesis[1-3], self-propagating high temperature synthesis (SHS) or reactive synthesis provides an attractive alternative to conventional methods of producing advanced materials since this technology is based on the ability of highly exothermic reactions to be self sustaining and, therefore, energetically efficient. The exothermic SHS reaction is initiated at the ignition temperature, T_{ig}, and generates heat which is manifested in a maximum or combustion temperature, T_c, which can exceed 3000K. Such high combustion temperatures are capable of melting and/or volatilizing reactant and product species and, therefore, present an opportunity for producing structure and property modification and control through liquid-solid, vapor-liquid-solid, and vapor-solid transformations

Experimental Reaction Systems

Several model ceramic-metal composite SHS reaction systems have been investigated in which an excess amount of metal, e.g., (xAl), is used both as a reductant in the SHS reaction and as the metal component of the ceramic-metal composite.[4] These model reaction systems are given below:

$$3TiO_2 + 3C + (4+x)Al = 3TiC + 2Al_2O_3 + xAl \quad (1)$$

$$3TiO_2 + 3B_2O_3 + (10+x)Al = 3TiB_2 + 5Al_2O_3 + xAl \quad (2)$$

$$3ZrO_2 + 3B_2O_3 + (10+x)Al = 3ZrB_2 + 5Al_2O_3 + xAl \quad (3)$$

$$2B_2O_3 + C + (4+x)Al = B_4C + 2Al_2O_3 + xAl \quad (4)$$

$$(3+x)TiO_2 + 3C + (2+4/3x)Al = 3TiC + (2+2/3x)Al_2O_3 + xTi \quad (5)$$

These reaction systems were selected on the basis of generating a liquid (e.g. Al) and/or a gas (e.g., B_2O_3 gas) at, and ahead of, the reaction front. The main focus of this research is to investigate the effect of gravity on these reactant species and on the resultant composite microstructure and properties.

The research concerned with conducting these reactions in the propagating mode was presented at the Second International Microgravity Combustion Workshop. Therefore, this paper will provide the main conclusions and observations of the research work conducted over the past two years.

Reaction systems (1) and (4) were examined in more detail under 1g, microgravity (±0.2g) and 2g (in the NASA Lear Jet) under the propagating mode of combustion synthesis. A modification of reaction (1) was also investigated using the combined simultaneous combustion plus pressing (SC-HP) process under 1g conditions in order to establish the criteria for producing dense ceramic-metal composites[5] in which Al_2O_3 is used as a diluent to control T_c and therefore, product microstructure,

i.e.,
$$3TiO_2 + 3C + (4+x)al + yAl_2O_3 = 3TiC + 2Al_2O_3 + xAl + yAl_2O_3 \quad (6)$$

Applying a consolidating load of 33 MPa as soon as the exotherm was recorded on the thermocouple in the die, and maintained for ten minutes at 1600°C, resulted in significantly improved densities compared with those produced in the propagating mode without pressing (Figure 1). The compressive strengths achieved in these composites are given in Figure 2 for reaction (6) as a function of x when y = 0 and as a function of y when x = 0 respectively, and the corresponding microstructures are presented in Figure 3.

The large plate of Al_2O_3 observed in Figure 3(a) indicates that the combustion temperature, when x = 0, exceeded the melting point of Al_2O_3 (2050°C). The excellent distribution of a fine Al network between the fine TiC and Al_2O_3 particles [Figure 3(b)] is clearly evident in the 3TiC-2Al_2O_3-4Al (x = 4, y=0) ceramic-metal composite. Increasing xAl has decreased T_{ad} to below 2050°C producing fine 1μm~3 μm Al_2O_3 particles. Increasing the relative density of the composite from 83% to 96% produced a considerable increase in compressive strength and decrease in scatter of the data (Figure 2), even though the volume fraction of the soft ductile aluminum has increased. The terraced appearance of the fractured surface of the samples tested in the compression tests [Figure 3(c)] indicates a potential for increased toughness. A K_{1c} fracture toughness value of 9MPa m^{-2} and a modulus of ruture (MOR) of 320 Mpa have recently been acieved in these TiC-Al_2O_3 ceramic composites. A more detailed examination of this SC-HP approach for producing ceramic-matrix composites has been provided elsewhere.[5]

Conducting reactions (1) and (6) under microgravity conditions produced a much more uniform distribution of porosity and excess Al, (Figure 4).[8]

The compressive strengths of the $3Ti\text{-}2Al_2O_3\text{-}xTi$ for reaction (5) were found to increase with increase in excess Ti (xTi), (Figure 4).

Another variation of the same approach is presented by reaction (4) in which the combustion temperature (1500-1900°C) was sufficient to generate a large volume of high pressure (>1 atm.) B_2O_3 gas, but very little, if any Al gas. 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 and an expansion of 230% (x = 0 Al) and 210% (x = 3Al) (Figure 5). Conducting these reactions under microgravity in the NASA Lear Jet resulted in expansion of over 300% while an expansion of only 150% was achieved at 2g, (Figure 5).

In a separate investigation, reaction (2) was investigated using the propagating mode under 1g and microgravity and also the elemental SHS reaction system:

$$Ti + 2B = TiB_2 \tag{7}$$

In each of these reaction systems, a higher T_c and, therefore, larger product grains sizes were obtained under microgravity conditions compared with 1g. The minimization of heat losses when conducting SHS reactions under microgravity conditions is thought to be the cause for these higher T_c values.

Summary and Conclusions

This research has clearly demonstrated that gravity can substantially influence combustion synthesis (SHS) reactions with respect to the control of the micro- and macrostructure, and therefore, the properties of the combustion synthesized materials. This conclusion has been particularly strengthened when liquid and/or gaseous species are generated at, and/or ahead of, the propagating SHS reaction front. Some examples that have recently been observed of the effect of gravity on the control of SHS reactions are given below.

Subjecting a liquid phase, generated by the SHS reaction, to gravity-driven fluid flow has been clearly shown to result in severe segregation of the product phases. Conducting the same reaction in a microgravity environment, i.e., NASA Lear Jet, has resulted in a minimization of segregation of the liquid phase and a more uniform distribution of the synthesized product phases. This will be particularly important in the combustion synthesis of metal-matrix composites in which a slurry, consisting of fine, solid, ceramic particles, is generated in a large volume of liquid metal.

The minimization of heat losses, when conducting SHS reactions under microgravity environments, has resulted in a maximum combustion temperature, T_c, that is much closer to that predicted by adiabatic conditions than when conducting the reaction under normal 1g conditions. The higher T_c has resulted in an increased grain size of the synthesized materials. Therefore, variation of gravity may provide a means by which product grain size can be controlled in SHS reactions.

The generation of a large volume of gaseous specie(s) at, and/or ahead of, the reaction front has resulted in the formation of expanded or foamed ceramic materials. This expansion has been found to increase when a highly fluid liquid is simultaneously generated together with the gas, so the gas can be readily transported through the fluid liquid, establishing a highly porous network. Conducting the SHS reaction in the propagating mode of combustion generally results in an expansion of the material in the vertical direction, e.g., 250-300%, with very little expansion in the lateral direction. However, conducting the SHS reaction in the simultaneous combustion (or thermal explosion) mode has resulted in near equal three dimensional expansion of the product material. Conducting these SHS reactions under microgravity conditions in the propagating mode has resulted in increased expansions, e.g., 350-400%, in the vertical direction, while an expansion of only 150% was achieved when conducting the same SHS reaction under 2g conditions in the NASA Lear Jet. Therefore, variation of gravitational forces may provide a practical means of controlling porosity, surface area, and expansion in this type of SHS reaction.

There is likely to be an increased demand in the future for such expanded or foamed ceramic and composite materials in such applications as filters, catalyst support materials, precursors for ceramic-metal composites, and ultra lightweight structural materials. The latter material may find particular applications as future space station materials. The mechanical and physical properties of these foamed materials are essentially unknown and may provide interesting new combinations of material properties, especially if the distribution and morphology of the porosity, micro- and macrostructures can be controlled.

Future Research Program

Although the limited research work conducted to date on the effect of gravity on SHS reactions has indicated some interesting trends, a more fundamental, multidisciplinary, and interactive research program is needed in order to clearly identify the controlling mechanisms by which gravitational forces can be used to advantage in the control of combustion synthesis reactions that could be used in the production of new advanced materials. Such a program is currently being planned at CSM.

There are two combustion synthesis research programs currently funded by NASA at CSM. One of these programs (CSM^1) is funded through the Microgravity-Combustion Science Program with Dr. J.J. Moore as the Principal Investigator and Dr. Suleyman Gokoglu (NASA Lewis Research Center) as the NASA Program Manager. This research program is concerned with developing a fundamental understanding of the role of gravity in synthesizing (a) uniformly porous ceramic composites and (b) dense metal-matrix composites. The second program (CSM^2) is funded through the Microgravity-Materials Science Program with Dr. J.J. Moore and Dr. D.W. Readey as Co-Principal Investigators and Mr. Tom Glasgow (NASA Lewis Research Center) as the NASA Program Manager. This research program is concerned with developing a fundamental understanding of the role of gravity on SHS reactions conducted in inert and reactive gas conditions, the effect of gas pressure and the effect of the density of small amounts of liquids generated at, and/or ahead of, the propagating SHS reaction front.

A joint **NASA-CSM-ISMAN** (Russia) research proposal has been submitted in the recent NASA-RSA initiative and is aimed at pooling the existing expertise and resources from these three sources to establish a fundamental research program. The overall combustion synthesis research program will, therefore, couple the two NASA Microgravity Sciences research programs at CSM with those proposed by ISMAN in the NASA-RSA proposal.

Also, a joint research program between CSM and Guigne International Ltd. (GIL) in Newfoundland has recently been established on the NASA-Microgravity-Combustion Science Program (CSM^1) in which the containerless processing facilities of GIL and the SHS facilities and expertise of CSM have been coupled to investigate containerless microgravity combustion synthesis reactions. GIL, under the direction of their president, Dr. Jacques Guigne, has recently developed a new, unique acoustic levitation system capable of levitating 80 gram, golf ball size, samples. Therefore, the joint interaction and cooperation between NASA-CSM-ISMAN-GIL will provide considerable leveraging of the total research program

A further interaction on these NASA research programs has also been established between the CSM group and that of Professor Matkowsky's NASA funded group at Northwestern University. Dr. Matkowsky's research group will use CSM's data in the development of their mathematical models. In addition, Dr. Mark Linne, a professor at CSM with an expertise in heat transfer modeling, will be part of the CSM team that will establish heat transfer experiments and modeling of selected SHS reactions under 1g, low and high gravity conditions.

References

1. Z.A. Munir and U. Anselmi-Tamburini, "Self-Propagating Exothermic Reactions: The Synthesis of High-Temperature Materials by Combustion", Mater, Sci. Report 3 (1989), 227-365.
2. H.C. Yi and J.J. Moore, "Self-Propagating, High Temperature (Combustion) Synthesis (SHS) of Powder Compacted Materials", J. Mater, Sci., 25 (1990), 1159.
3. J.J. Moore, "An Examination of the Thermochemistry of Combustion Synthesis Reactions", Processing and Fabrication of Advanced Materials. III. (Tms. Warrendale, PA. 1994) Ed. V.A. Ravi, T.S. Srivatsan and J.J. Moore, 813-817.
4. H.J. Feng, K.R. Hunter and J.J. Moore, "Combustion Synthesis of Ceramic and Metal-Matrix Composites", J. Mat, Synth. Proc., 2-2 (1994), 71-86.
5. H.J. Feng and J.J. Moore, "In-Situ Combustion Synthesis of Dense Ceramic and Ceramic-Metal Interpenetrating Phase Composites", Submitted to Met. and Mat. Trans.
6. H.J. Feng, J.J. Moore and D.G. Wirth, "Combustion Synthesis of Ceramic-Metal Composite Materials: The ZrB_2-Al_2O_3-Al System", Int. J. Self Prop. High Temp. Synth. 1, 2 (1992), 228-283.
7. N.R. Perkins, J.J. Moore and D.W. Readey, "Synergistic Effects of Coupled Combustion Synthesis and Vapor Phase Transport in the Synthesis of Advanced Materials:, Advanced Synthesis of Engineered Structural Materials, (ASM Int. Materials, Park, OH, 1992), Ed. J.J. moore, E.J. Lavernia, F.H. Froes, 7-23.
8. K.R. Hunter and J.J. Moore, "The Effect of Gravity on the Combustion Synthesis of Ceramic and Ceramic-Metal-Composites", Accepted for publication in J. Mat. Synth. and Proc.

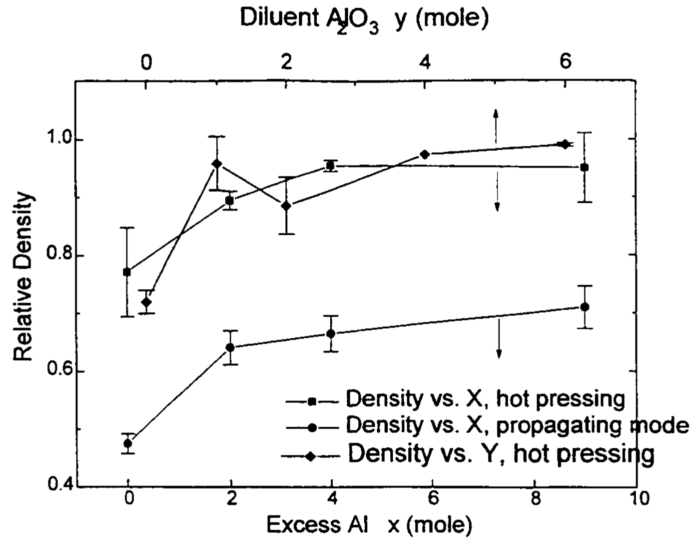


Figure 1 - The effect of excess Al (xAl) with no Al_2O_3 diluent (y = 0), (■), and Al_2O_3 diluent (yAl_2O_3) with no excess Al (x = 0), (◆), on the relative density of the TiC-Al_2O_3-Al ceramic-metal composite using the simultaneous combustion mode and a pressure of 24.8 MPa (3600 psi) applied to the reaction system (6) in a graphite die for ten minutes and maintained at 1600°C once the SHS reaction had been initiated. These data are compared with similar data obtained for the SHS reaction (1) conducted in the propagating mode without pressure, (●).

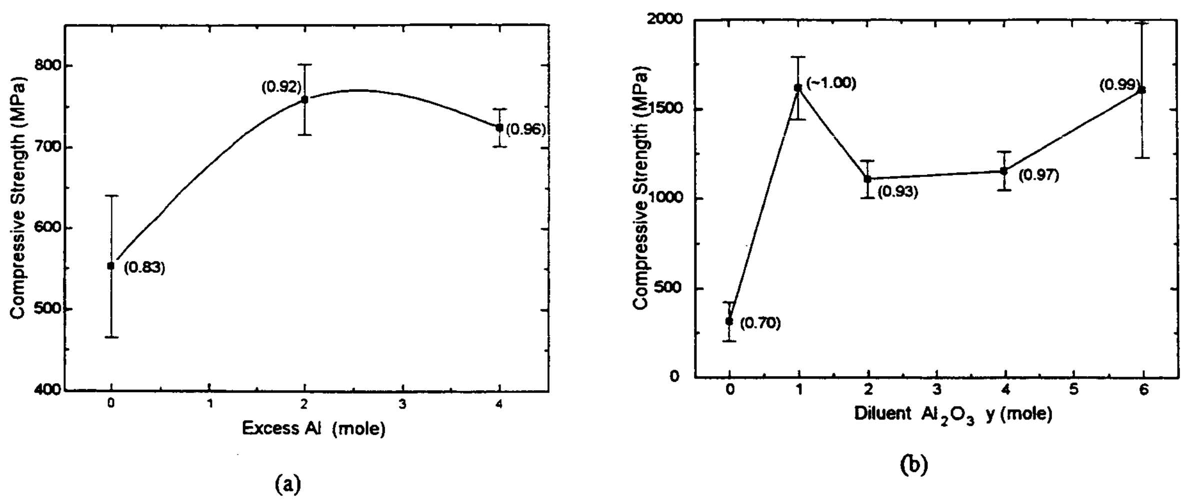


Figure 2 - (a) The Effect of excess Al on compressive strength for TiC-Al_2O_3-Al ceramic-metal composites produced by simultaneous combustion synthesis and pressing in a graphite die, for reaction (6) for y = 0. (b) The effect of excess Al_2O_3 (diluent) in reaction system (6) when x = 0, (no excess Al) on the compressive strength for TiC-Al_2O_3 composites produced by simultaneous combustion synthesis and pressing in a graphite die. The figures in parentheses indicate the relative density of the samples tested.

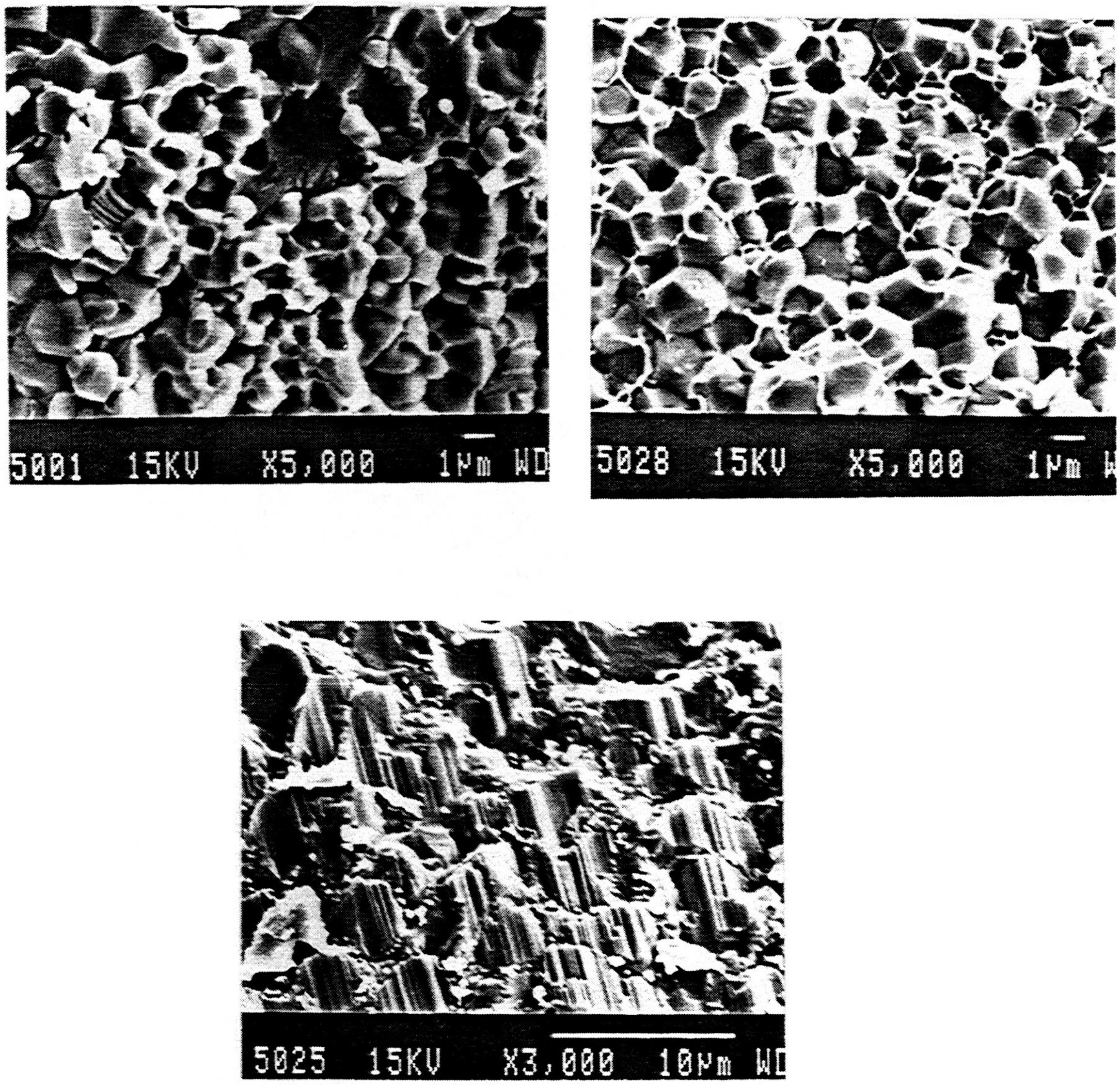


Figure 3 - SEM photomicrograph of (a) $3TiC\text{-}2Al_2O_3$ (x = 0, y = 0). Note the large plate of Al_2O_3 at top center, (b) $3TiC\text{-}2Al_2O_3\text{-}4Al$ (x = 4, y = 0), (c) fractured surface of $3TiC\text{-}2Al_2O_3\text{-}4Al$ (x = 4, y = 0) samples tested in compression test.

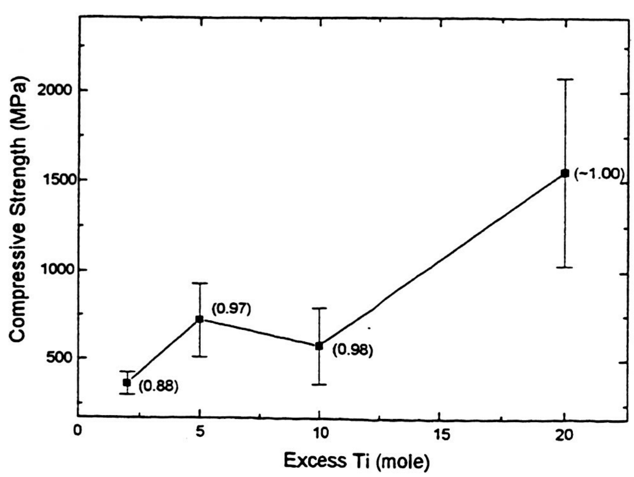


Figure 4 - Effect of excess Ti (xTi) and relative composite densities (figures in parenthesis) on compressive strengths of composites produced from reaction (5).

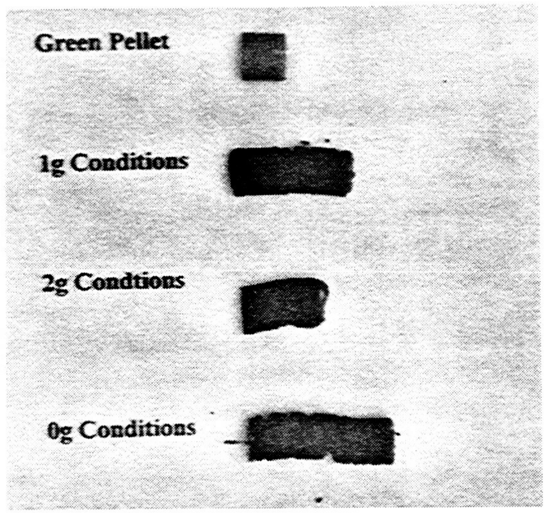
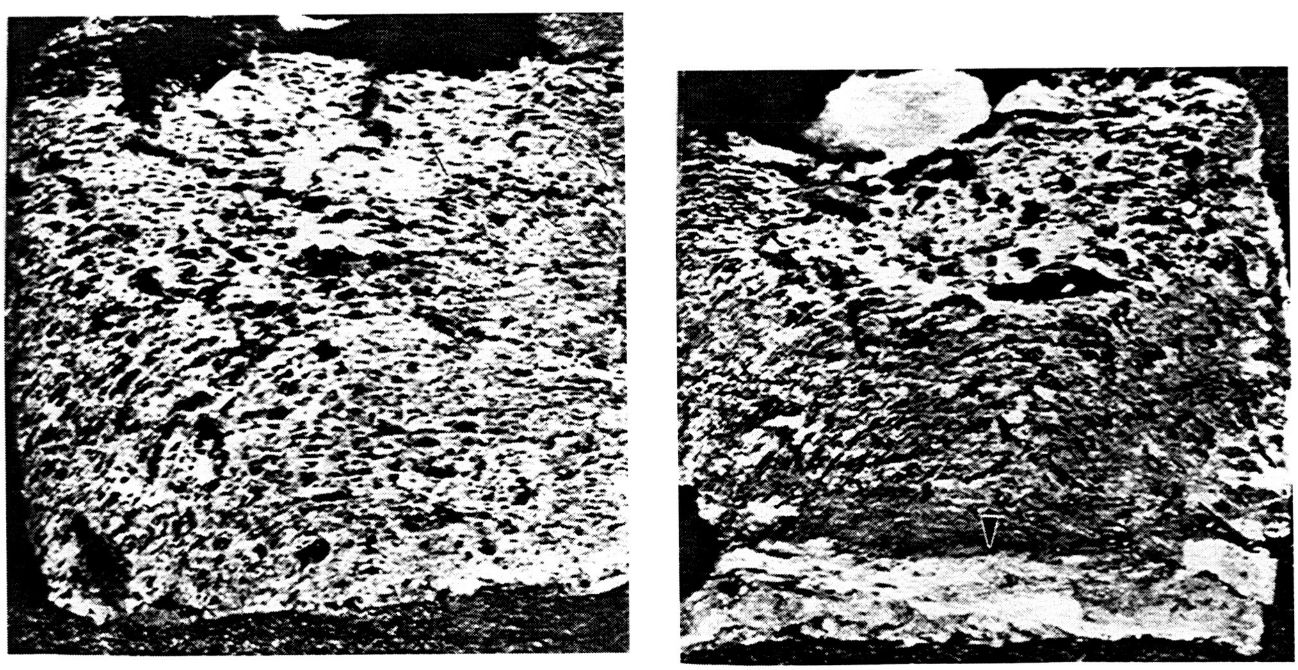


Figure 5 - Photographs of green pellet for reaction (4) with reaction stoichiometry x = 0, and reacted samples of this same green pellet conducted under microgravity (0.01g), normal gravity (1g) and elivated gravity (2g) conditions.



(a) (b)

Figure 6 - Microstructures of products for reaction (1) for a reaction stoichiometry x = 9Al: (a) reacted in propagating mode under microgravity conditions; (b) reacted under propagating mode under normal gravity conditions. Note the increased Al segregation at bottom of Figure 6(b), indicated by arrow.