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13. ABSTRACT (Maximum 200 words)  
The thrust of the work completed is an investigation on the effect of an electric field on the synthesis and densification of complex materials. Experimental investigations were made on the field effect in the synthesis of (a) solid solution precursors for nanoscale modulated composites, (b) a high temperature ceramic with relatively high fracture toughness, (c) macro-alloyed high temperature silicides, and (d) hard materials of boride composites with highly oriented precipitates. Modeling studies on the effect of the electric field (current) on synthesis reactions were also made. In addition, an important new direction in the completed work was the investigation of the simultaneous synthesis and densification of nanometric materials. The latter work has led to the issuance of a US Patent and a pending application for an International Patent. The work was facilitated by the use of the Spark Plasma Synthesis (SPS) apparatus, the only one of its kind in the US.

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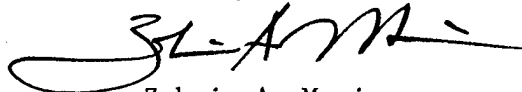
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Sincerely,



Zuhair A. Munir  
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## **Final Progress Report**

### **1. Forward:**

The thrust of the work completed is an investigation on the effect of an electric field on the synthesis and densification of complex materials. Experimental investigations were made on the field effect in the synthesis of (a) solid solution precursors for nanoscale modulated composites, (b) a high temperature ceramic with relatively high fracture toughness, (c) macro-alloyed high temperature silicides, and (d) hard materials of boride composites with highly oriented precipitates. Modeling studies on the effect of the electric field (current) on synthesis reactions were also made. In addition, an important new direction in the completed work was the investigation of the simultaneous synthesis and densification of nanometric materials. The latter work has led to the issuance of a US Patent and a pending application for an International Patent. The work was facilitated by the use of the Spark Plasma Synthesis (SPS) apparatus, the only one of its kind in the US.

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### 3. STATEMENT OF THE PROBLEM STUDIED:

The imposition of an electromagnetic field (or a current) has been shown to have a marked influence on a variety of materials processes, including crystal growth, defect mobility, microstructure formation, phase transformations, and others [1]. The goal of our work has been the investigation of the effect of an electric field on the synthesis and consolidation of complex materials, including hard materials and nanocrystalline materials. In this regard, the availability of the Spark Plasma Synthesis (SPS) apparatus (obtained by funds from ARO) has made possible the accomplishment we have achieved. As indicated before, our SPS unit is the only such facility in the US. Under the general umbrella of field effect studies, we have conducted investigations on several aspect of this topic, as detailed in the next section along with a summary of the most important results.

### 4. SUMMARY OF THE MOST IMPORTANT RESULTS:

#### (a) Investigations on the Synthesis and Stability of AlN-SiC Composites and Solid Solutions:

Motivated by a desire to increase the fracture toughness of AlN, the feasibility of adding SiC to form a solid solution or a composite has been investigated. Above about 1960°C AlN and the 2H (hexagonal) polytype of SiC form extensive solid solutions [2], which decompose spinodally when annealed below this temperature. The resulting product, which is a composite modulated at the nanoscale, is reported to possess improved fracture toughness [3]. The common method of synthesis of the solid solutions is to heat mixtures of AlN and SiC ( $\alpha$  or  $\beta$ ) to higher than about 2100°C for up to up to 16 hrs. With field-activation, solid solutions can be synthesized in seconds [4,5]. When forming composites, the composition of the phases depended on the magnitude of the applied field, and when forming solid solutions, the homogeneity (elemental distribution) was influenced by the strength of the field.

The recent accomplishments in this area include investigations on the formation of AlN-SiC solid solutions by direct nitridation and by *induction* field activation. The reactions of Al +  $\beta$ -SiC and Al + Si + C with gaseous nitrogen were used to synthesize the solid solutions. For the first case, the role of  $P_{N_2}$  and powder compact relative density was investigated [6]. Solid solutions could be formed at  $P_{N_2} = 6.0$  MPa. It was also shown from quenched reactions that SiC decomposes during the reaction and that the solid solution forms from the solidification of a transient liquid phase. The homogeneity of the solid solutions (as evaluated from FWHM measurements) was shown to have a dependence on the relative density of the reactant compacts and on the nitrogen gas pressure,  $P_{N_2}$ . The most homogeneous solid solutions were obtained with low-density compacts ( $\approx 25\%$ ), but the variation of the FWHM with relative density depended on the gas pressure. For the case of nitridation of elemental reactants (Al + Si + C), the feasibility of solid solution formation was also demonstrated [7]. A model of

dissolution-precipitation for the synthesis process was proposed to explain the results. *A most interesting observation was that of modulated AlN/SiC structures, implying a spinodal decomposition during the cooling down of the product.* Such a decomposition was previously reported to take about 100 hrs at temperatures below the miscibility gap [8].

Solid solution synthesis was also accomplished using a solid as well as a gas as a source of nitrogen ( $\text{Si}_3\text{N}_4 + \text{C} + \text{Al} + \text{N}_2$ ) [9]. In contrast to the case in which the nitrogen source is gaseous, the use of  $\text{Si}_3\text{N}_4$  made possible the formation of solid solutions at ambient nitrogen pressure. Furthermore, and again in contrast to the case where nitrogen comes from a gaseous source only, the degree of homogeneity of the solid solutions decreased with increasing nitrogen pressure. Activation by an inductive field was also investigated in the synthesis of AlN-SiC solid solutions under pseudo-isostatic pressing [10].

In addition we have also investigated the reported stabilizing influence of AlN on the structure (polytype) of SiC in AlN-SiC composites and the thermal stability of SiC-AlN solid solutions [11]. The presence of AlN with Si + C reactants did not enhance the formation of the 2H polytype of SiC, in contrast to the reported stabilizing effect of the hexagonal AlN. The product was the cubic 3C-SiC polytype. The thermal stability of solid solutions formed by field activation was investigated. The end product of heating a solid solution or a composite in vacuum at 1700°C is 3C-SiC. This implies that after the initial loss of AlN (due to decomposition) SiC transformed from the 2H to the 3C polytype. *These results indicate that the presence of AlN is crucial in the stability of the 2H structure but not in the formation of this polytype.*

#### **(b) Synthesis of Complex Phases by Field-Activation**

The ternary ceramic compound  $\text{Ti}_3\text{SiC}_2$  is reported to possess an unusual combination of attractive properties: good electrical and thermal conductivities, high ductility and fracture toughness, and good oxidation resistance [12]. It has a relatively low ratio of hardness to Young's modulus which has led some authors to refer to it as a "ductile ceramic", although this is subject to debate. Its synthesis is rather complex, however, requiring relatively long times at high temperatures in a hot press. Starting with elemental reactants, we have been able to synthesize nearly fully-dense samples using electric field activation [13]. *The products of this method were purer than those obtained by SHS and had a smaller average grain size than those obtained by hot pressing.* The lack of dependence of microhardness on the applied force is viewed as indication of the small grain size. The thermal stability and oxidation resistance of this 312 compound was also investigated. Vacuum annealing at temperature in the range 1600-2000°C resulted in the formation of a TiC surface layer while annealing in air at 1000°C resulted, expectedly, in a  $\text{TiO}_2$  surface layer. TGA studies provided two substantially different dependences of the rate constant on temperature over low and high

temperature ranges. The surface layer contained two oxides ( $\text{TiO}_2$  and  $\text{SiO}_2$ ) at low temperatures and only  $\text{TiO}_2$  at high temperatures. In light of EPMA results, a two-step oxidation process was proposed and discussed in terms of thermodynamic calculations.

Another investigation was focused on the preparation and characterization of materials in the  $\text{TiB}_2$ - $\text{WB}_2$ - $\text{CrB}_2$  system. Regions of extensive solid solubilities exist for these borides, and when such solid solutions are annealed at lower temperatures, a second phase (*W-rich*) precipitates in platelet-like form giving the potential for enhanced mechanical properties similar to the case of fiber-reinforced composites. The common synthesis approach of the solid solutions involves long time (8hr) annealing at high temperatures ( $2100^\circ\text{C}$ ) [14]. Even at these conditions the product uniformity is not high. In our investigation, we have demonstrated the feasibility of synthesizing relatively pure solid solutions using the SPS method at  $1900^\circ\text{C}$  [15]. With annealing, we observe the spinodal-like precipitate of  $(\text{W},\text{Ti},\text{Cr})\text{B}_2$  and the  $\beta$ - $\text{WB}$  precipitates in the form of thin (0.4-0.7 nm thick) layers. A dependence of phase composition, density, and microhardness on the temperature of synthesis was observed. The density varied from 78 to 94% over the temperature range  $1400$ - $1900^\circ\text{C}$  and the microhardness varied from 7.0 to 22.7 GPa over the same range.

Silicides of transition metals have been identified as the next generation high-temperature structural materials, particularly in such applications as gas turbines [16]. Among these,  $\text{MoSi}_2$  has received considerable attention and is currently used in electric furnace heating elements. There are two problems associated with the potential application of this material: the temperature limitation related to the melting of the  $\text{SiO}_2$  surface oxide layer, and the ductile-brittle transition temperature ( $1200^\circ\text{C}$ ), below which its fracture toughness drops to an unacceptable level ( $2$ - $3 \text{ MPa}\cdot\text{m}^{1/2}$ ). Our recent investigation on  $\text{MoSi}_2$  has focused on the first problem. Our approach to increase the working temperature in an oxidizing environment is to alloy  $\text{MoSi}_2$  with Al. We have been successful in synthesizing dense (99%)  $\text{MoSi}_{2-x}\text{Al}_x$  with  $0.4 \leq x \leq 1.0$  by electric field activation using the SPS. Oxidation studies were conducted on this C40 structured material as well as one with  $x=0.7$ . The temperature dependence of the parabolic rate constants for the oxidation of  $\text{MoSi}_{1.6}\text{Al}_{0.4}$  and  $\text{MoSi}_{1.3}\text{Al}_{0.7}$  was determined for the range  $1470$ - $1725\text{K}$ .

### (c) Simultaneous Synthesis and Densification of Nanometric Materials

The product of most methods of preparation of nanomaterials is in powdered form and thus requires an additional processing step to obtain dense bodies. Typically the nanopowders are hot-pressed or sintered at relatively high temperatures. While there are cases where exposure to such high temperatures does not lead to grain growth because of kinetic constraints [17-20], in many other cases grain growth remains a serious concern. The difficulty in obtaining dense nanomaterials has been given as a reason for the paucity of data on

mechanical properties [21], as was pointed out before. *We have recently developed a method in which the simultaneous synthesis and densification can be achieved. The preliminary results have led to the issuance of a US Patent [22] and an application for an International Patent (covering Europe, Canada, and Japan) has been filed.* We have demonstrated the feasibility of this method with preliminary results on the preparation of dense nanometric intermetallics (FeAl [23], Al<sub>3</sub>Nb [24]), ceramics (MoSi<sub>2</sub> [23,25]), and composites (TiN/TiB<sub>2</sub> [26]). The process involves the co-milling of reactants in a planetary mill to achieve intermixing and crystallite size reduction, but to avoid formation of a significant amount of a reaction product. The appropriate milling conditions (ball/powder ratio, rpm, and milling time) are determined to produce the smallest crystallite size for the reactant components. The milled nanocrystalline materials are then cold-pressed and introduced into the SPS apparatus. They are then subjected to pulsed high DC current while under a uniaxial pressure. Real-time measurements of temperature, pressure, current, and sample volume displacement (shrinkage) are made during the synthesis and densification process.

The initiation of reactions among the nanocrystalline powders occurred at markedly lower temperatures (lower by several hundreds of degrees) than in microcrystalline powders, in agreement with observations reported by others [27]. In most cases, the reaction and densification is complete within a few minutes, as indicated by the abrupt volume change. In the case of FeAl formation, the process took 2-3 min and the reaction between Fe and Al was complete. A local phase analysis (EDAX) showed the composition of the FeAl phase to be 51.5 at% Fe. The density of the product was found to be in the range 98-99%. Using a Williamson-Hall analysis on the line broadening of the XRD results, the crystallite size of the FeAl was determined to be in the range 35-65 nm. Using the same approach, dense nanocrystalline MoSi<sub>2</sub> was synthesized with a crystallite size in the range 30-60 nm. Results on the TiN/TiB<sub>2</sub> composite showed the product to be nanostructured in both phases with the crystallite size ranges for TiN and TiB<sub>2</sub> to be 48-53 nm and 46-63 nm, respectively.

#### **(d) Modeling of Current-Induced SPS Synthesis Reactions**

To provide an understanding for the role of the current in the SPS synthesis, we have carried out a simulation analysis on the assumption that a major contribution of the current is thermal, i.e., Joule heating. As indicated above, there is strong evidence that other contributions can arise from the application of the current [28,29-35], but thermal effects are significant, nevertheless. Due to resistive heating, the passage of a current raises the temperature of the sample up to the "ignition temperature". After ignition the rise in temperature is due to both electrical and chemical energy inputs. The implication of this is that the reaction takes place everywhere at once, in a manner referred to as "volume" or "simultaneous" combustion (as opposed to "wave combustion"). It is anticipated that the temperature profiles in these two cases will be markedly different, with significant implications on phase and microstructural

developments during synthesis. Steep temperature gradients can lead to non-equilibrium phase quenching and to reduced grain growth.

The model was based on the following Fourier relationship in cylindrical coordinates:

$$\rho r C_p(T, \gamma_c) \frac{\partial T}{\partial t} = \frac{\partial}{\partial r} \left( \kappa(T, \gamma_c) r \frac{\partial T}{\partial r} \right) + \frac{\partial}{\partial z} \left( \kappa(T, \gamma_c) r \frac{\partial T}{\partial z} \right) + \frac{Qr}{c} \frac{\partial \gamma_c}{\partial t} + \sigma(T, \gamma_c) r |\nabla \phi|^2$$

where  $\rho$  is the density,  $C_p$  is the heat capacity,  $\kappa$  is the thermal conductivity,  $\sigma$  is the electrical conductivity,  $\phi$  is the electrostatic potential,  $r$  is the sample radius,  $T$  is temperature,  $t$  is time,  $Q$  is the enthalpy of the chemical reaction,  $c$  is the molar coefficient ( $aA + bB = cC$ ), and  $\gamma_c$  is the molar fraction per unit volume of the product. Furthermore, the model was designed to account for heat loss at the surfaces of the cylindrical sample according to boundary condition criteria [36]. The results of this simulation showed, contrary to expectations of volume combustion, that the mode of combustion depended on the size (radius) of the sample for the cases of SiC and MoSi<sub>2</sub>. With the increase in radius from 1 to 2 cm, the combustion process in SiC changes from a primarily volume mode to a wave mode. Such a transition was found to be materials-system dependent. In the case of MoSi<sub>2</sub> synthesis, mode transition takes place as the radius increases from 2 to 3 cm.

## 5. PUBLICATIONS, AND PRESENTATIONS BASED ON RESULTS SUPPORTED BY GRANT

### (a) Publications

#### 1. Papers in Refereed Journals and Volumes

- Z. A. Munir, "Electrically-Stimulated SHS," *Int. J. SHS*, **6**: 165-185 (1997).
- I. J. Shon and Z. A. Munir, "Electric field-Activated Combustion Synthesis of Ti<sub>5</sub>Si<sub>3</sub>-xNb and Ti<sub>5</sub>Si<sub>3</sub>-ZrO<sub>2</sub> Composites," *J. Mater. Sci.*, **32**:5805-5810 (1997).
- Z. A. Munir, "Field Effects in Self-Propagating Solid State Reactions," *Zeit. Physik. Chem.*, **207**: 39-57 (1998). **Invited Paper.**
- S. Gedevanishvili and Z. A. Munir, "An Investigation of the Combustion Synthesis of MoSi<sub>2</sub>-βSiC Composites through Electric Field Activation," *Mater. Sci. Eng.*, **A242**: 1-6 (1998).
- Z. A. Munir, "Field-Activated Combustion Synthesis of Composites," *Silicate Indust.*, **63**: 45-50 (1998). **Invited Paper.**
- S. Gedevanishvili and Z. A. Munir, "The Synthesis of TiB<sub>2</sub>-TiAl<sub>3</sub> Composites by Field-Activated Combustion," *Mater. Sci. Eng.*, **A246**: 81-85 (1998).
- I.J. Shon and Z. A. Munir, "Synthesis of TiC and TiC-Cu Composites and TiC-Cu Functionally-Graded Materials by Electrothermal Combustion," *J. Amer. Ceram. Soc.*, **81**: 3243-3248 (1998).

- Z. A. Munir and U. Anselmi-Tamburini, "Self-Propagating High-Temperature Synthesis of Hard Materials," in *Handbook of Ceramic Hard Materials*, R. Riedel, Ed., Wiley-VCH, Weinheim, Germany, 2000, pp. 322-373. **Invited Chapter.**
- H. Xue, K. Vandersall, E. Carrillo-Heian, N. N. Thadhani, and Z. A. Munir, "Initiation of Self-Propagating Combustion Waves in Dense Mo + 2Si Reactants through Field-Activation," *J. Amer. Ceram. Soc.*, **82**: 1441-1446 (1999).
- A. Feng, T. Orling, and Z. A. Munir, "Field-Activated Pressure-Assisted Combustion Synthesis of Polycrystalline Ti<sub>3</sub>SiC<sub>2</sub>," *J. Mater. Res.*, **14**: 925-939 (1999).
- I.J. Shon, H. C. Kim, D. H. Rho, and Z. A. Munir, "Simultaneous Synthesis and Densification of Ti<sub>5</sub>Si<sub>3</sub> and Ti<sub>5</sub>Si<sub>3</sub>-20vol% ZrO<sub>2</sub> Composites by Field Activated Pressure Assisted Combustion," *Mater. Sci. Eng.*, **A269**:129-135 (1999).
- N. Balandina, M. Ohyanagi, and Z. A. Munir, "Formation of AlN-SiC Solution by Combustion Nitridation of Al with SiC," *Key Eng. Mater.*, **161-163**: 91-94 (1999).
- T. D. Xia, Z. A. Munir, Y. L. Yang, W. J. Zhao, and T. M. Wang, "Structure Formation in the Combustion Synthesis of Al<sub>2</sub>O<sub>3</sub>-TiC Composites," *J. Amer. Ceram. Soc.*, **83**: 507-512 (2000).
- H. B. Lee, S. J. Kim, Y. H. Han, J. E. Garay, and Z. A. Munir, "Synthesis and Characterization of Dense Ti<sub>0.5</sub>Zr<sub>0.5</sub>B<sub>2</sub>Solid Solutions by Electrically-Stimulated Combustion," *Korean J. Ceram.*, **6**: 172-176 (2000).
- Z. A. Munir, "The Effect of External Electric Field on the Nature and Properties of Materials Synthesized by Self-Propagating Combustion," *Mater.Sci. Eng. A*, **A287**, 125-137 (2000). **Invited Contribution**
- D. Kata, M. Ohyanagi, and Z. A. Munir, "Formation Mechanism of AlN-SiC Solid Solution by Combustion Nitridation in the Si<sub>3</sub>N<sub>4</sub>-Si-Al-C System," *J. Amer. Ceram. Soc.*, in press, 2001.
- Z. A. Munir, "Synthesis by Self-Propagating Combustion," in *The Encyclopedia of Materials: Science and Technology*, Elsevier Science, Oxford, 2001. **Invited Contribution**
- M. Ohyanagi and Z. A. Munir, "Covalently-Bonded Solid Solutions Formed by Combustion Synthesis," *Korean J. Ceram.*, **6**: 250-257 (2000). **Invited Paper.**
- M. Ohyanagi, K. Shirai, N. Balandina, M. Hisa, and Z. A. Munir, "Synthesis of AlN-SiC Solid Solutions by Combustion Nitridation," *J. Amer. Ceram. Soc.*, **83**: 1103-1107 (2000).
- D. Kata, M. Ohyanagi, and Z. A. Munir, "Induction Field Activated self-Propagating High Temperature Synthesis of AlN-SiC Solid Solutions in the Si<sub>3</sub>N<sub>4</sub>-Al-C System," *J Mater. Res.*, **15**: 2514-2525 (2000).
- E. M. Carrillo-Heian, H. Xue, M. Ohyanagi, and Z. A. Munir, "Reactive Synthesis and Phase Stability in the AlN-SiC System," *J. Amer. Ceram. Soc.*, **83**: 1103-1107 (2000).
- F. Charlot, E. Gaffet, F. Bernard, and Z. A. Munir, "One-Step Synthesis and Consolidation of Nanophase Iron Aluminide," *J. Amer. Ceram. Soc.*, in press, 2001.
- H. Kaga, E. M. Carrillo-Heian, Z. A. Munir, C. Schmalzried, and R. Telle, "Synthesis of Hard Materials by Field Activation: The Synthesis of Solid

Solutions and Composites in the TiB<sub>2</sub>-WB<sub>2</sub>- CrB<sub>2</sub> System," *J. Amer. Ceram. Soc.*, in press, 2001.

- R. Orru, J. Woolman, G. Cao, and Z. A. Munir , "Synthesis of Dense Nanometric MoSi<sub>2</sub> through Mechanical and Field Activation," *J. Mater. Res.*, in press, 2001.
- Z. A. Munir , "Synthesis and Densification Of Nanomaterials by Mechanical and Field Activation," *J. Mater. Synth. Process.*, in press, 2001. **Invited Conference Paper.**

**(b) Papers in Proceedings of Conferences and Symposia:**

- M. Ohyanagi, N. Balandina, K. Shirai, M. Koizumi, and Z. A. Munir, "Synthesis of AlN-SiC Solid Solutions by Combustion Nitridation," *Proceedings of Symposium on Innovative Processing and Synthesis of Ceramics, Glasses, and Composites II*, Amer. Ceram. Soc., Weaverville, OH, 1999, pp.3-12.
- Z. A. Munir, "The Synthesis of MoSi<sub>2</sub> and MoSi<sub>2</sub>-Composites by Field Activated Combustion," in *Molybdenum and Molybdenum Alloys*, A. Crowson, E. S. Chen, J. A. Shields, P. R. Subramanian, Eds., TMS, Warrendale, PA, 1999, pp. 49-60. **Invited Paper.**
- Z. A. Munir, "Simultaneous Synthesis and Densification of Ceramics, Composites, and FGMs by Field activation," *Proceedings of NEDO International Symposium on Functionally-Graded Materials*, Tokyo, October, 1999, pp. 107-113. **Invited Paper**
- M. Ohyanagi and Z. A. Munir, "Covalently-Bonded Solid Solutions Formed by Combustion Synthesis," *Proceedings of the Third International Meeting of Pacific Rim Ceramic Societies (Pac Rim 3)*, Kyongju, Korea, September 20-23, 1998, **Invited Paper.**
- Z. A. Munir , "Synthesis and Densification Of Nanomaterials by Mechanical and Field Activation," *Proceedings of 3<sup>rd</sup> International Conference on Mechanochemistry and Mechanical Alloying*, Prague, September 4-8, 2000. (Invited Paper)

**(c) Presentations:**

- Z.A.Munir, "Synthesis and Processing of Ceramics, Composites, and Intermetallics by Field Activated Combustion," *Symposium on Advances in Synthesis and Processing of Metal and Ceramic Matrix Composites*, TMS Annual Meeting, Orlando, FL, Feb. 9-13, 1997. **Invited Paper**
- Z. A. Munir, "The Synthesis of Ceramics, Composites, and Solid Solutions by Field-Activated Combustion," *Ninth International Conference on High Temperature Materials Chemistry*, Pennsylvania State University, State College, PA, May 19-23, 1997
- Z. A. Munir, "The Influence of an Electric Field on Self-Propagating High-Temperature Solid-Solid Synthesis Reactions," *Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Nagoya, Japan*, July 1, 1997. **Invited Seminar**

- Z. A. Munir, "Synthesis and Densification by Field-Activated SHS," Department of Materials Chemistry, Ryukoku University, Otsu, Japan, July 2, 1997. *Invited Seminar*
- Z. A. Munir, Electric Field Activation of Self-Propagating Combustion Synthesis Reactions Dipartimento di Chimica Fisica, Università di Pavia, Pavia, Italy, September 10, 1997. *Invited Seminar*
- Z. A. Munir, "The Influence of an Electric Field on Materials Synthesis by Self-Propagating Combustion," Department of Chemical Engineering, University of Cagliari, Cagliari, Italy, September 12, 1997. *Invited Seminar*
- Z. A. Munir, "Electrically-Stimulated SHS," Fourth International Symposium on Self-Propagating High-Temperature Synthesis, Toledo, Spain, October 6-10, 1997. *Invited Plenary Lecture*
- Z. A. Munir, "Field-Activated Combustion Synthesis of Composites," Fourth International Conference on Ceramic-Ceramic Composites, Mons, Belgium, November 18-20, 1997. *Invited Keynote Paper*
- Z. A. Munir, "The Synthesis of High Temperature Materials by Field-Activated Self-Sustaining Combustion," Institut für Gesteinshüttenkunde, Rheinische-Westfälische Technische Hochschule, Aachen, Germany, November 21, 1997. *Invited Seminar*
- Z. A. Munir, "The Synthesis of  $\text{MoSi}_2$  and  $\text{MoSi}_2$ -Composites by Field-Activated Combustion," Symposium on Molybdenum and Molybdenum Alloys, TMS Annual Meeting, San Antonio, TX, February 16-18, 1998. *Invited Paper*
- Z. A. Munir, "Field-Activated Combustion Synthesis," Symposium on Innovative Processing and Synthesis of Ceramics, Glasses, and Composites, Annual Meeting of the American Ceramic Society, Cincinnati, OH, May 4, 1998. *Invited Paper*
- M. Ohyanagi and Z. A. Munir, "Covalently-Bonded Solid Solutions Formed by Combustion Synthesis," Presentation at Third International Meeting of Pacific Rim Ceramic Societies (Pac Rim 3), Kyungju, Korea, September 20-23, 1998. *Invited Paper*
- Z. A. Munir, "Mechanistic Effects of Field Application in Combustion Synthesis," Laboratoire de Chimie du Solide Minéral, Université Henri Poincaré, Nancy, France, June 8, 1998. *Invited Seminar*
- Z. A. Munir, "Synthesis and Densification of High Temperature Materials by Field-Activated Combustion," Laboratoire de Physicochimie de la Matière Condensée, Université Montpellier, France, June 12, 1998. *Invited Seminar*
- Z. A. Munir, "The Effect of Electric Fields on the Combustion Synthesis and Processing of Composite Materials," Ninth World Ceramic Congress and Forum on New Materials (CIMTEC'98), Florence, Italy, June 16, 1998. *Invited Presentation*
- Z. A. Munir, "Electric Field Effects in Self-Propagating Synthesis Reactions," Institut für Physikalische und Theoretische Chemie, Technische Universität Braunschweig, Braunschweig, Germany, September 17, 1998. *Invited Seminar*
- Z. A. Munir, "Electrically-Stimulated Self-Propagating Synthesis Reactions," Solid State Chemistry and Materials Science Meeting, Deutsche Chemiker Gesellschaft (German Chemical Society), Saarbrücken, Germany, September 24, 1998. *Invited Main Lecture*

- Z. A. Munir and M. Ohyanagi, "Covalently-Bonded Solid Solutions Formed by Combustion Synthesis," Third International Meeting of Pacific Rim Ceramic Societies (Pac Rim 3), Kyungju, Korea, September 20-23, 1998. *Invited Paper*
- Z. A. Munir, "Modeling and Experimental Studies on Electrically-Stimulated Self-Propagating Combustion Synthesis," Materials Science and Engineering Department, The Johns Hopkins University, Baltimore, MD, February 17, 1999. *Invited Seminar*
- Z. A. Munir, "Recent Advances in Self-Propagating High-Temperature Synthesis," Department of Materials Engineering, Federal University of São Carlo, São Carlos, Brazil, March 15, 1999. *Invited Seminar*
- Z. A. Munir, "The Use of an Electric Field as a Processing Parameter in the Combustion Synthesis of Ceramic, Metallic, and Composite Materials," The Korea Institute for Science and Technology (KIST), Seoul, Korea, April 21, 1999. *Invited Seminar*
- Z. A. Munir, "Electric Field Activated Combustion Synthesis," Workshop on "Enhanced Synthesis, Processing, and Properties of Materials with Electric and Magnetic Fields," sponsored by US Army Research Office, Johns Island, SC, May 16-19, 1999. *Invited Presentation*
- Z. A. Munir, "Activation of Self-Propagating Combustion Synthesis by Electric Fields," Department of Materials Science, Gansu University of Technology, Lanzhou, China, September 8, 1999. *Invited Seminar*
- Z. A. Munir, "Simultaneous Synthesis and Densification by Field Activation," NEDO International Symposium on FGMs, sponsored by the New energy and Industrial Technology Development Organization (NEDO), Ministry of International Trade and Industry (MITI), Tokyo, Japan, October 21-22, 1999. *Invited Presentation*
- Z. A. Munir, "One-Step Synthesis and Densification of Monolithic and FGM Materials by Electric Field Activation," Workshop on "Functionally Graded Materials in the 21<sup>st</sup> Century: Trends and Forecasts", Tsukuba City, Japan, March 26-28, 2000. *Invited Presentation*
- Z. A. Munir, "Modeling and Experimental Studies on the Effect of Thermophysical Properties on Field-Activated Combustion Synthesis Reactions," Tenth International Conference on High-Temperature Materials Chemistry, Jülich, Germany, April 10-14, 2000. *Invited Keynote Paper*

## 6. Scientific Personnel

The following individuals were involved in some aspect of the research summarized above:

Z. A. Munir, Principal Investigator, Professor of Materials Science and Dean of the College of Engineering

J. W. Lee, Postdoctoral Fellow

E. M. Corrillo-Heian, PhD Student

J. Woolman, PhD Student

M. Manshi, Professor, Riyukoku University, Japan, collaborator

G. Cao, Professor, University of Cagliari, Italy, collaborator

R. Orru, Professor, University of Cagliari, Italy, collaborator

## 7. Patents

Z. A. Munir, F. Charlot, F. Bernard, and E. Gaffet, "One-Step Synthesis and Consolidation of Nanophase Materials":

- *US Patent* No.6,200,515; issued March 13, 2001..
- *International Patent Application* (Europe, Canada, and Japan), filed May 5, 2000.

## 8. Bibliography:

1. Z. A. Munir and H. Schmalzried, "The Effect of External Fields on Mass-Transport and Defect-Related Phenomena," *J. Mater. Synth. Process.*, **1**: 3-16 (1993).
2. A. Zangvil and R. Ruh, "Phase Relationships in the Silicon Carbide-Aluminum Nitride System," *J. Amer. Ceram. Soc.*, **71**: 884-890 (1988).
3. M. Landon and F. Thevenot, "The SiC-AlN System: Influence of Elaboration Routes on the Solid Solution Formation and Its Mechanical Properties," *Ceram. Int.*, **17**: 97-110 (1991).
4. H. Xue and Z. A. Munir, "The Synthesis of Composites and Solid Solutions of  $\alpha$ -SiC/AlN by Field-Activated Combustion," *Scripta Metall. Mater.*, **35**: 979-982 (1996).
5. H. Xue and Z. A. Munir, "Synthesis of AlN-SiC Composites and Solid Solutions by Field-Activated Self-Propagating Combustion," *J. Euro. Ceram. Soc.*, **17**: 1787-1792 (1997).
6. M. Ohyanagi and Z. A. Munir, "Covalently-Bonded Solid Solutions Formed by Combustion Synthesis," Presentation at Third International Meeting of Pacific Rim Ceramic Societies (Pac Rim 3), Kyungju, Korea, September 20-23, 1998. *Kor. J. Ceram.*, **6**: 250-257 (2000).
7. M. Ohyanagi, K. Shirai, N. Balandina,, M. Hisa, and Z. A. Munir, "Synthesis of AlN-SiC Solid Solutions by Combustion Nitridation," *J. Amer. Ceram. Soc.*, **83**: 1103-1107 (2000).
8. S. Y. Kuo and A. V. Virkar, "Modulated Structures in SiC-AlN Ceramics," *J. Amer. Ceram. Soc.*, **70**: 125-128 (1978).
9. D. Kata, M. Ohyanagi, and Z. A. Munir, "Formation Mechanism of AlN-SiC Solid Solutions by Combustion Nitridation in the  $\text{Si}_3\text{N}_4 + \text{Si} + \text{Al} + \text{C}$  System," *J. Amer. Ceram. Soc.*, in press, 2001.
10. D. Kata, M. Ohyanagi, and Z. A. Munir, "Induction Field Activated self-Propagating High Temperature Synthesis of AlN-SiC Solid Solutions in the  $\text{Si}_3\text{N}_4$ -Al-C System," *J Mater. Res.*, **15**: 2514-2525 (2000).
11. E. M. Carrillo-Heian, H. Xue, M. Ohyanagi, and Z. A. Munir, "Reactive Synthesis and Phase Stability in the AlN-SiC System," *J. Amer. Ceram. Soc.*, **83**: 1103-1107 (2000).

12. M. W. Barsoum and T. El-Raghy, "A Progress Report on  $Ti_3SiC_2$ ,  $Ti_3GeC_2$ , and the H-Phases,  $M_2BX$ ," *J. Mater. Synth. Process.*, **5**: 197-216 (1997).
13. A. Feng, T. Orling, and Z. A. Munir, "Field-Activated Pressure-Assisted Combustion Synthesis of Polycrystalline  $Ti_3SiC_2$ ," *J. Mater. Res.*, **14**: 925-939 (1999).
14. I. Mitra and R. Telle, "Phase Formation during Anneal of Supersaturated  $TiB_2$ - $CrB_2$ - $WB_2$  Solid Solutions," *J. Solid State Chem.*, **133**: 25-30 (1997).
15. H. Kaga, E. M. Carrillo-Heian, Z. A. Munir, C. Schmalzried, and R. Telle, "Synthesis of Hard Materials by Field Activation: The synthesis of Solid Solutions and Composites in the  $TiB_2$ - $WB_2$ - $CrB_2$  System," *J. Amer. Ceram. Soc.*, in press, 2001.
16. J. J. Petrovic, "High Temperature Structural Silicides," *Ceram. Engin. Sci. Proceedings*, **18**: 3-17 (1997).
17. C. E. Krill, R. Klein, S. Janes, and R. Birringer, "Thermodynamic Stabilization of Grain Boundaries in Nanocrystalline Alloys," *Mater. Sci. Forum*, **179-181**: 443-448 (1995).
18. P. Knauth, A. Charai, C. Bergman, and P. Gas, "Calorimetric Analysis of Thin Film Reactions: Experiments and Modeling in the Nickel/Silicon System," *J. Appl. Phys.*, **76**: 5195-5201 (1994).
19. H. J. Hofler and R. S. Averback, "Grain Growth in Nanocrystalline  $TiO_2$  and its Relation to Vickers Hardness and Fracture Toughness," *Scripta Metall. Mater.*, **24**: 2401-2406 (1990).
20. C. Bansal, Z. Q. Gao, and B. Fultz, "Grain Growth and Chemical Ordering in  $(Fe,Mn)_3Si$ ," *Nanostruct. Mater.*, **5**: 327-336 (1995).
21. H. Hahn and K. A. Padmanabhan, "A Model for the Deformation of Nanocrystalline Materials," *Phil. Mag.B*, **76**: 559-571 (1997).
22. Z. A. Munir, F. Charlot, F. Bernard, and E. Gaffet, "One-Step Synthesis and Consolidation of Nanophase Materials," US Patent No.6,200,515; issued March 13, 2001.
23. F. Charlot, E. Gaffet, F. Bernard, and Z. A. Munir, "One-Step Synthesis and Consolidation of Nanophase Iron Aluminide," *J. Amer. Ceram. Soc.*, in press, 2001.
24. V. Gauthier, J. P. Larpin, and Z. A. Munir, unpublished results.
25. R. Orru, J. Woolman, G. Cao, and Z. A. Munir, "Synthesis of Dense Nanometric  $MoSi_2$  through Mechanical and Field Activation," *J. Mater. Res.*, in press, 2001.
26. J. A. Lee and Z. A. Munir, M. Shibuya, and M. Ohyabagi "Synthesis of Dense  $TiB_2$ - $TiN$  Nanocrystalline Composites through Mechanical and Field Activation," *J. Amer. Ceram. Soc.*, in press, 2001.
27. C. Gras, F. Charlot, E. Gaffet, F. Bernard, and J. C. Niepce, "In Situ Synchrotron Characterization of Mechanically-Activated Self-Propagating High-Temperature Synthesis Applied in Mo-Si System," *Acta Mater.*, **47**: 2113-2123 (1999).
28. M. Tokita, "Trends in Advanced SPS Systems and FGM Technology," *Proceedings of NEDO International Symposium on Functionally Graded Materials*, Tokyo, Japan, October 21-22 (1999), pp. 23-33.

29. P. S. Ho and T. Kwok, "Electromigration in Metals," *Rep. Prog. Phys.*, **52**: 301-348 (1989).
30. L. Klinger and L. Levin, "Interface Instability in an Electric Field," *J. Appl. Phys.*, **78**: 1669-1672 (1995).
31. J. P. Barnak, A. F. Sprecher, and H. Conrad, "Colony (Grain) Size Reduction in Eutectic Pb-Sn Castings by Electropulsing," *Scripta Metall. Mater.*, **32**: 879-884 (1995).
32. A. K. Misra, "A Novel Solidification Technique of Metals and Alloys under the Influence of Applied Potential," *Metall. Trans.* **16A**: 1354-1355 (1985).
33. O. A. Kobelev, A. I. Sotnikov, and A. V. Kobelev, "New Experimental Method for the Determination of the Electrocapillary Curves in Copper/Boron + Aluminum Oxide Melt," *J. Electroanal. Chem.*, **427**: 43 (1997).
34. Y. Nakamura, K. Kamada, Y. Katoh, and A. Watanabe, "Studies on Secondary Electrocapillary Effects: I. The Confirmation of the Young-Dupre Equation," *J. Coll. Interface. Sci.*, **44**: 517-524 (1973).
35. N. Ivosevic, V. Zutic, and J. Tomaic, "Wetting Equilibria of Hydrocarbon Droplets at an Electrified Interface," *Langmuir*, **15**: 7063 (1999).
36. O. Graeve, E. M. Corriillo-Heian, A. Feng, and Z. A. Munir, "Modeling of Wave Configuration during Electrically-Ignited Combustion Synthesis," *J. Mater. Res.*, **16**: 93-100 (2001).