

Background: The high vapor pressures of americium (Am) and americium nitride (AmN) are cause for concern in producing nitride ceramic nuclear fuel that contains Am. Along with the problem of Am retention during the sintering phases of current processing methods, are additional concerns of producing a consistent product of desirable homogeneity, density and porosity. Similar difficulties have been experienced during the laboratory scale process development stage of producing metal alloys containing Am wherein compact powder sintering methods had to be abandoned. Therefore, there is an urgent need to develop a low-temperature or low-heat fuel fabrication process for the synthesis of Am-containing ceramic fuels. Self-propagating high temperature synthesis (SHS), also called combustion synthesis, offers such an alternative process for the synthesis of Am nitride fuels.

Although SHS takes thermodynamic advantage of the high combustion temperatures of these exothermic SHS reactions to synthesize the required compounds, the very fast heating, reaction and cooling rates can kinetically generate extremely fast reaction rates and facilitate the retention of volatile species within the rapidly propagating SHS reaction front. The initial objective of the research program is to use Mn as the surrogate for Am to synthesize a reproducible, dense, high quality Zr-Mn-N ceramic compound. Having determined the fundamental SHS reaction parameters and optimized SHS processing steps using Mn as the surrogate for Am, the technology will be transferred to Idaho National Laboratory to successfully synthesize a high quality Zr-Am-N ceramic fuel.

STATUS

AICS: The reaction parameters of auto-ignition combustion synthesis (AICS) and their effects on the production of metal oxide, carbide and nitride powders for use in nuclear fuel applications have been examined. Although it was initially thought that the AICS reaction occurs in one step, it has been determined that there are two distinct reaction steps that make up the total reaction. The first is the formation of an intermediate reactant complex from the initial decomposition of the starting reactants. The second step is further decomposition of this complex that initiates an exothermic combustion reaction and thus the formation of the final product.

The reactants used in an AICS reaction are nitrate salts mixed with an organic fuel in specific ratios as determined by propellant chemistry. Both reactants melt and decompose at low temperatures which helps make AICS reactions energy efficient. Metal nitrate salts are an ideal reactant for AICS since they easily decompose into a metal oxide that is relatively unstable (thermodynamically) and dissociates during the combustion reaction. The type of organic fuel used to react with the metal nitrate salt affects the intermediate reactant complex that is

formed but not the overall reaction since the off gases produced during the combustion reaction are the same for each fuel. However, the type of fuel does not seem to affect the products formed, only the amount of those products formed. This is due to the difference in decomposition products, but not the overall combustion products.

The salt to fuel ratio controls the type of compounds that are formed in the final product. This is primarily indicated by the difference in the color of the powders when the salt to fuel ratio is changed. It has been determined that samples reacted with lower amounts of fuel have more oxide in the product. Furthermore, higher salt to fuel ratios produce more nitride in the sample due to the increase of nitrogen in the reactant complex.

The reaction environment does not have an effect on the decomposition of the individual reactants or the formation of the intermediate complex, but it does react with the intermediate reactant complex during the second reaction step to form the desired product. Nitrogen-rich environments aid in the formation of nitride powders due to a nitriding reaction that takes place during the combustion reaction. Inert environments do not provide any extra reactants to the combustion reaction and therefore oxides are more likely to be produced.

The activation energy for the first and second decomposition reactions as well as the combustion reaction was calculated to be 4.66, 7.04 and 2.14 eV respectively. These values indicate that the first reaction step, the formation of the intermediate reactant complex, is the slowest step in the overall AICS reaction and the combustion reaction is the most rapid. In addition, higher heating rates lead to a more defined exothermic combustion reaction which affects the product conversion.

Two additives were considered in this project to aid in the formation of nitride powders. Sodium azide is a solid source of nitrogen since the compound does not dissociate until the combustion reaction occurs. Ammonium nitrate dissociates into gaseous by-products when heated, therefore adding more nitrogen to the reaction environment that is available to react with the reactant complex during the combustion reaction. Both additives have shown to produce more nitride in the final power product.

This project has demonstrated the feasibility of producing ceramic powders by igniting a mixture of a metal nitrate salt and a suitable organic fuel. The reaction parameters of an AICS reaction have been defined and researched in order to form pure oxide, nitride, or carbide powders that can be further processed into nuclear fuel pellets. This is an excellent method to reprocess nuclear waste since the waste stream can be easily transformed into metal

nitrate salts and reacted using AICS to produce powders that can be processed into recycled nuclear fuel pellets. Currently, however, the levels of impurities in these as produced powders are too high to be used in any nuclear application and further research should address methods to purify the powders.

Pellet Production: The investigation of nitride pellet production is an ongoing project, however the progress of the project is stated below. Initially, using manganese as a surrogate for the high vapor pressure transuranics, manganese nitride and zirconium powders were mixed, pressed and reacted. This system provided some valuable information in that the manganese retention was upward of 90%, as compared to upward of 20% for conventional synthesis methods. However, the nitride phases of manganese are not representative of the nitride phases of the transuranics. In addition, the intermetallic formed in the manganese-zirconium system is neither representative of the final system, nor is it thermodynamically favorable. With this in mind, new surrogates were found.

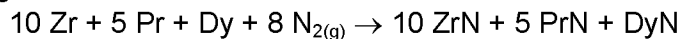
First, surrogates meeting the high-vapor pressure characteristics as well as forming similar compounds were required. Zirconium (Zr) is an acceptable surrogate for Uranium (U); praseodymium (Pr) has similar vapor pressures and thermodynamic considerations as plutonium (Pu) for this study. Dysprosium (Dy) is similarly an acceptable surrogate for americium (Am). The second step was to find a reaction system that was suitable for forming a nitride since all of the transuranics and their surrogates only form mononitride compounds. The reaction systems being considered involved two nitrogen sources, the first was a higher uranium nitride (U_2N_3) reacted with U, Pu, and Am powders. This system provided difficulty because the surrogate material, Zr, does not form a higher nitride. This system can still be analyzed, using depleted uranium (DU) as a surrogate for U, in the future. The second system involved mixing U, Pu, and Am elemental powders and pressing them into a compact then reacting the powders with a nitrogen source, either a nitrogen atmosphere or sodium azide (NaN_3) as a solid source mixed in with the elemental powders. This system's issues are much simpler and more fundamental than the other system.

The difficulties presented by the second system are detailed as follows. The first scenario, of a solid nitrogen source, would require a powder that decomposes at a low temperature. NaN_3 decomposes at $200^{\circ}C$ which is favorable for nitrogen supply, but unfavorable due to the fact that the ignition temperature of the reaction is between 400 and $800^{\circ}C$. In addition, the significant off-gassing of the decomposition reaction results in a physical instability of the pellet causing it to disintegrate. The second reaction system, using nitrogen gas, is much more preferable,

however, getting the nitrogen gas to penetrate the full depth of the sample is the challenge.

By using samples that are 12.7 mm in diameter, a system can be developed so as to ensure that the entire sample of 6-8 mm in diameter can be reacted. The first study involved Zr powder reacted with nitrogen. Low pressures of nitrogen (up to 72 psi) were utilized to make sure that the process could be duplicated in current production facilities with minor adjustments. The penetration of the nitride formation reached a maximum depth of 3 mm from the surface. This was due to melting of Zr powder from the high temperatures achieved by the reaction. In order to minimize this effect, zirconium nitride (ZrN) powder was included in the initial pellet to act as a diluent, or heat sink, to reduce melting. At 20 wt. % ZrN, 80 wt. % Zr, the penetration increased to approximately 5 mm, and at 40 wt. % ZrN, the reaction was complete.

The next step was to include transuranic surrogates into the initial powder. The reaction chemistry that is currently being investigated is:



This is a “worst case scenario” fuel chemistry provided by Idaho National Laboratory due to the fact that the driving force of the reaction, the ZrN formation is diluted by the PrN and DyN formation reactions. Results of this system are currently being compiled.

There are two further steps to this system. The first is to replace the Zr with DU in the next phase of reactions. This is to be done in a glove box at Colorado School of Mines. Finally, using either the Zr or DU systems, a densification process will be evaluated using a Gleeble 1500 thermo-mechanical testing apparatus.

Plans for Future Work:

- DU-Nitriding depth study
- DU/Pr/Dy-Nitriding depth study
- Lanthanide retention study
- Initiation of lanthanide and DU surrogate experiments for forming densified nitrides

Patents:

“Method for Production of Metal Nitride and Oxide Powders Using an Auto-Ignition Combustion Synthesis Reaction.” (72-06P)

The patent has been filed but is pending proof of concept.

Publications/Presentations:

A paper entitled "Nitride Nuclear Fuel Production Using Combustion Synthesis" was presented at the American Nuclear Society (ANS) meeting in Boston, June 24-28, 2007.

A paper entitled "Production of Oxide and Nitride Powders Employing Auto-Ignition Combustion Synthesis (AICS)" was presented at the annual International Symposium of Self-Propagating High Temperature Synthesis in Dijon, France in July 2007.

A paper entitled "Application of Combustion Synthesis to the Production of Actinide Bearing Nitride Ceramic Nuclear Fuels" was presented at the annual PCRM-6 conference in Korea, November, 2007.

A paper entitled "SHS Production of Nitride Nuclear Fuels Using Surrogate Materials" was presented at the American Nuclear Society (ANS) winter meeting in Reno, NV, November 2008.

Milestone Status Table:

ID Number	Task / Milestone Description	Planned Completion	Actual Completion	Comments
	Synthesis of Porous Mn-N	10/31/08	11/30/08	Completed
	DTA of Mn+N ₂ SHS Reactions	4/30/06	6/30/06	Completed
	Optimization of SHS of Mn-N	5/31/07	1/31/09	Completed
	SHS-consolidation of Dense Zr-Mn-N compounds	10/31/06	1/15/08	Completed
	DTA of SHS formation of Zr-Mn-N compounds	4/30/07	3/31/06	Completed
	Combined SHS-consolidation of dense Zr-Mn-N compounds	10/31/07	1/15/08	Completed
	Optimization of SHS of Zr-N	5/31/08	2/15/09	Completed
	Optimization of DU-N SHS systems	9/30/08		Ongoing
	Optimization of SHS-consolidation of dense DU-N compounds	11/30/08		Ongoing
	Optimization of SHS-consolidation of DU-La*-N compounds	11/30/08		Ongoing
	Final Report	12/31/08	3/31/09	Submitted

Research into these areas is still being conducted.