Thermal Plasma Processing of Materials: A Review

PATRICK R. TAYLOR* AND SHAHID A. PIRZADA

Dept. of Metallurgical Engineering, College of Mines, University of Idaho, Moscow, ID 83843

Abstract. The use of thermal plasma in materials processing industries is becoming an increasingly active and attractive field for the development of new technology. The potential applications of thermal plasma processing technology cover a wide range of activities, such as: the extraction of metals, the refining/alloying of metals/alloys, the synthesis of fine ceramic powders, spray coatings, and the consolidation and destruction of hazardous wastes. A review of thermal plasma applications in materials processing is presented.

Keywords: thermal plasma, plasma processing, materials processing, ceramic powders

Introduction

Thermal plasma processing is a diversified field which has a broad range of applications ranging from spray coating to the destruction of toxic wastes. Plasma based spray coating technology has become nearly a billion dollar industry [1]. The potential use of plasma based processes in extraction and process metallurgy also covers a broad range of activities [2–4]. The generation of value added material is an area of research where plasma processing appears to have a large potential for growth. Over the last several years, many new plasma technology based processes have been demonstrated on the laboratory scale [5–10] to generate value added materials (metals, ceramics, composites etc.). The destruction of hazardous waste, using plasma technology, has also become an area of active research and development [11]. Plasma based technology, for hazardous waste reduction and destruction has become commercially available. In general, thermal plasma processing may be categorized into the following general topics:

- 1. Extractive Metallurgy—The beneficiation, extraction and processing of metals from ores, scrap and wastes.
- 2. Process Metallurgy—The remelting and refining of metals/alloys and the provision of heat augmentation to casting operation.
- 3. Advanced Materials Synthesis—The generation of value added materials (metals, ceramics, nanophase materials, composites).
- 4. Plasma Spray Coatings—The formation of coating for wear, thermal barriers, and novel materials (including plasma assisted CVD and reactive spray forming).
- 5. Toxic and Hazardous Waste Treatment—The volume reduction or destruction of waste materials, including: liquid organic wastes, radioactive wastes etc.

^{*}To whom correspondence should be addressed. Address: College of Mines, University of Idaho, Moscow, ID 83843, (208)885-6769, Fax: (208)885-5724.

6. Plasma welding/cutting is a well established field.

Each of these categories may include a broad range of endeavors and could be the topic of separate reviews. In this paper, an overview of thermal plasma processing with an emphasis on metals/materials processing is presented.

Background

Plasma processing may be characterized by the ability to generate a high temperature gas (concentrated enthalpy) and reactive chemical species. In thermal plasma generating devices, electrical energy is converted to thermal energy. Plasma is an ionized form of gas. When an electric arc is established between two electrodes in the presence of a gas, the gas partially ionizes and becomes electrically conductive. In general, a plasma gas consists of electrons, ions and neutral species. Negative and positive charges compensate each other and the overall plasma is electrically neutral. There are several methods that are employed to produce plasmas, such as; passing current through the gas, high frequency discharge, high energy particle beam, etc. Plasma that is produced by electrical discharge can be classified into two categories. First is the equilibrium or thermal plasma. In this type of plasma, the temperatures of the electrons and heavy particles are about the same and reach local thermodynamic equilibrium [12]. The second type of plasma produced by electrical discharge is the non-equilibrium or cold plasma. In these, the electron temperature is much higher than the heavy particle temperature. An example of this type of plasma would be a glow discharge.

There may be several classifications of plasma torches depending upon the geometry and configuration. One common classification is based upon the position of the electrodes i.e non-transferred or transferred arc mode. In the non-transferred arc mode (Figure 1), both the anode and the cathode are located in the torch and the arc is established between these electrodes. These are sometimes also called plasma arc heaters. Most plasma spray guns are also operated as non-transferred arcs. In the transferred arc mode (Figure 2), one electrode is located outside the torch (which may be the work piece or the material to be heated). The arc is established between the torch and the work piece. In this mode, more energy is dissipated to the work piece than in the non-transferred arc mode. In radio frequency (RF)



Figure 1. Sketch of non-transferred arc plasma torch.



Figure 2. Sketch of transferred arc plasma torch.



Figure 3. Sketch of radio frequency (RF) plasma torch.

plasma torches (Figure 3), there are no electrodes. The energy transfer in this system can be by inductive or capacitive coupling. An induction coupled discharge is maintained by a time varying magnetic field [13]. The discharge is usually maintained in a quartz tube surrounded by a few turns of a RF coil to couple energy into the plasma. There are some examples of hybrid plasma where both RF and DC plasma are maintained in series in one system [8].

There is a substantial amount of information available, in the literature, regarding the fundamental aspects of plasma processing. Several investigators, such as Pfender [12], Dembovsky [14], Fauchais [15], Boulos [16], Szekely [17], and others [18, 19], have conducted very thorough investigations concerning different fundamental aspects of plasma technology.

The main advantages of plasma processing are:

 Generation of very high temperatures (>5000 K) and the formation of chemically reactive species which leads to: tremendous acceleration of reaction rates, the formation of vapor phases from solid feed materials, and the ability to quench from high temperatures leading to the formation of fine particles and metastable phases.

- Pure and controlled atmosphere that may lead to minimum contamination and the ability to adjust the reactor atmosphere to be inert, oxidizing or reducing.
- Ability to use fine particulate feed directly.
- Improved environmental aspects relative to the use of fossil fuels and much smaller reactors for a given throughput.
- As thermal plasma reactors are electricity based they may be easier to instrument and control compared to conventional fossil fuel based processes.

There are a variety of drawbacks associated with plasma technology. Many of these may be eliminated with proper engineering and research. Some of the disadvantages are:

- Lower thermal efficiency of the process (as compared to the fossil fuel based processes). The recovery of thermal energy from the reactor and the gases may lead to more efficient processes.
- Electricity based technology. The economics of plasma processes are directly related to the cost of electricity.
- Electrode wear is important. The lifetime of the plasma electrodes is limited and increases operating costs due to the need for fairly frequent changes. This disadvantage may be obviated through research on the wear mechanisms and through the study of alternative electrode materials.
- Lack of knowledge in the area of process chemistry at temperatures prevalent in plasma reactors. This requires additional research on the fundamental behavior of plasma reactors, particularly in the area of very high temperature chemistry and transport phenomena.
- Short residence time for the particulate material and difficulty in the injection of feed into the arc. The need for the feed material to penetrate the very viscous hot zone of the plasma and for prolonged residence times in the reactor has led to the identification of new types of reactors to overcome these problems.
- New unknown technology! As the plasma processing of materials is typically only demonstrated using very small scale laboratory experiments, further research is needed for design and engineering and to confirm the value of the reactor systems.

A review of plasma processing is presented with an emphasis on the synthesis of value added materials. Applications, such as, plasma remelting/refining and spraying are briefly discussed.

Melting/remelting & refining

Plasma melting and refining of metals/alloys have been used successfully in industry, specifically with regard to refractory metals and alloys. The main advantages of using plasma furnaces in this area are: high melting rates, inert atmosphere, minimum contamination of the products, low noise levels, and stable power conditions. Mostly transferred arc systems are used for melting/refining. In plasma melting, the Linde DC transferred arc furnace [18] was one of the first to be used for steel melting. In this furnace an induction coil was used for stirring the molten bath to achieve homogeneity of the metal. There are several other examples of plasma furnaces, including a hybrid plasma furnace (DC and induction), were developed by Daido Steel [18] for melting/refining specialty alloys, a plasma furnace (with four transferred arc plasma torches each of 4.0 MW power) was used at Freital in Germany [19] for melting iron and nickel based alloys, and Tetronics [20] developed a DC transferred arc plasma system which was used for melting waste dusts, direct steelmaking etc.

Plasma arc remelting (PAR) is an attractive route for metal refining. A plasma arc remelting furnace was developed at Paton Institute, Kiev. In this process, consumable electrodes are remelted using plasma torches [21]. The ingot is solidified in a water cooled copper mold that is fitted with a continuously withdrawn bottom plate. Controlled plasma heating and a cold mold produces a flat and shallow metal pool. Metal loss through evaporation is negligible during plasma arc remelting. Plasma arc remelting is also used to produce ingots of refractory metals/alloys directly from the lump sponge.

Plasma technology is being used in cold hearth melting of titanium alloys [22]. According to the aircraft industry requirement, titanium should be free of impurities such as high density inclusions (HDI), e.g. tungsten carbide, and high interstitial defects(HID). In cold hearth melting of titanium, the occurrence of these impurities is prevented. In this process, the feed material which might be titanium sponge or recycled scrap is fed into a copper hearth where it is melted by a plasma heat source. The molten metal goes to the refining hearth and finally to the withdrawal crucible. Each section has a plasma torch as a heat source. A skull is formed between the molten pool and the water cooled hearth. High density inclusions and many other high interstitial defects sink to the bottom and are trapped in the skull. If the inclusions are less dense than the molten metal, they are carried along with the flow and are dissolved before reaching the ingot. As a result, a titanium ingot of high quality is produced which may fulfill the demand of defect free titanium for the aircraft industry.

Plasma chemical synthesis

One of the most promising areas of research in plasma processing is the production of fine (submicron sized) powders of high value materials (such as oxides, carbides, nitrides and borides). The gas phase synthesis, conducted in a pure and controlled atmosphere, gives the produced powder properties such as: high sphericity, small average size, and narrow size distributions. These properties may be essential for the subsequent fabrication of advanced materials through powder metallurgical processing.

Production of good quality powders is one of the pre-requisites for the development of advanced structural materials. The particle size and purity of the powder is very important in determining the final properties of the sintered material. Fine particles may be more reactive and may enhance the densification process. Materials made of fine particles may have smaller flaw sizes which may enhance mechanical properties such as strength and fracture toughness. Strength, fracture toughness and mechanical reliability in the sintered product requires as fully dense a ceramic body as possible. Fracture toughness declines drastically with increasing size of pores, particularly at or near the surface of the sintered body. Particles below one micron may lead to high fired densities. It is also important to eliminate even a few large grains (larger than one micron) because they may tend to lead to similar size pores, which become initiators for crack propagation and failure at low stress. Various new processing techniques have been developed, such as sol-gel technologies and chemical vapor deposition, to generate fine ceramic powders with a minimum of oversize particles. The high temperatures available in plasma reactors can vaporize almost any material and may enhance the reaction kinetics by several orders of magnitude. The steep temperature gradient available in plasma reactors provide for the possibility of generating fine sized particles. Also, if the factors which contribute to the growth mechanism of the particles are well understood, it is possible to have some control over the particle size of the desired product. There have been several excellent studies related to the formation of fine ceramic powders in plasma reactors [5-10].

Plasma processing is being used to generate fine ceramic powders. Up to the present time, this activity is mainly on the laboratory or pilot plant scale. Several unique and novel plasma based reactor systems have been developed for the generation of fine ceramic powders. There is a long list of these powders synthesized on the laboratory scale. Both D.C. arc and R.F. plasma systems have been used for this purpose. A list of some of these processes for the generation of ceramic powders is given in Table 1 & Table 2.

In the plasma processing laboratory at the University of Idaho [57], there is an ongoing research project regarding the synthesis of ceramic powders (such as carbides, nitrides, and borides) using a thermal plasma system. Fine ceramic powders $(0.2-0.4\mu)$ of SiC, TiC, B₄C, TiB₂, and Si₃N₄ have been produced in this reactor setup using solid precursors. Presently fine titanium diboride (TiB₂) is being synthesized using TiO₂, B₂O₃, and CH₄ as precursors. The experimental system is shown in Figure 4. The central component of the system is a refractory lined, water cooled stainless steel tubular reactor. A non-transferred arc plasma torch is attached to the one side of it. A quench section is attached to the other end. Particulate feed is injected into the plasma flame through various configurations. Having an extended hot reaction zone eliminates the problem of short residence time for the particulate material in the hot zone. Powders produced are chemically treated, hot pressed and sintered and compared by mechanical testing with powders commercially available and produced by other processing routes.

The processes mentioned in Tables 1 & 2 can be classified into two categories: Processes using solid feed and non-solid (gaseous and liquid precursors). Gaseous or liquid feed materials are easily vaporized and good product conversion is obtained. At the same time, liquid precursors (such as chlorides) are difficult to handle due to their corrosiveness. Contamination of the product and the corrosiveness of the system can be a substantial problem

Table	1.

Reactants	Prod	Gas	Туре	KW	Size	Ref.
$SiO_2 + CH_4$	SiC	Ar	RF	10	μ size	23
MeSiCl ₃	SiC	$Ar + H_2$	RF	50	$< 1.0 \ \mu$	24
$SiH_4 + CH_4 + H_2$	SiC	Ar	RF	50	7.5 nm	25
$SiO + CH_4$	SiC	Ar	DC		31 nm	26
$SiCl_4 + CH_4$	SiC	H_2	DC	60	$.12 \mu$	27
$SiO + CH_4$	SiC	Ar	DC	22.5	2-40 nm	28
Si + C	SiC	Ar	DC	_	1060 nm	29
$SiO_2 + CH_4$	SiC	Ar	RF	3.5	10-30 nm	30
$SiO_2 + CH_4$	SiC	Ar + He	DC	30	$.23 \mu$	31
$SiCl_4 + CH_4$	SiC	$Ar + H_2$	DC	100	50 nm	32
$SiCl_4 + CH_4$	SiC	Ar	DC		.4–.6µ	33
$BCl_3 + CH_4 + H_2$	B ₄ C	Ar	RF	28	20–30 nm	34
$B_2O_3 + C_3H_8$	B ₄ C	Ar, N_2, H_2	DC		_	35
$B_2O_3 + CH_4$	B ₄ C	Ar, He	DC	30	$.23 \mu$	36
$TiCl_4 + CH_4$	TiC	Ar, H_2	DC	11.4	$.01 \mu$	37
$TiCl_4 + CH_4$	TiC	H_2	DC	30	10–40 nm	27
$Ti + CH_4$	TiC	Ar	DC	10.5	5–20 nm	38
$TiCl_4 + CH_4$	TiC	H_2	DC	45	_	39
$TiO_2 + CH_4$	TiC	Ar, He	DC	35	.2–.3µ	40
$WCl_6 + CH_4$	W_2C	Ar, H ₂	DC	11.5	$.02\mu$	37
$W + CH_4$	WC	Ar, H_2	DC		10 nm	41
$WCl_6 + CH_4$	WC	H_2	DC	30	${\sim}10~{ m nm}$	38
$\frac{\operatorname{Zr}(\operatorname{C}_4\operatorname{H}_9\operatorname{O})_4 + \operatorname{CO}_2}{$	ZrC	Ar	DC	30		42

Table 2.

Reactants	Prod	Gas	Туре	KW	Size	Ref
SiCl ₄ + NH ₃	Si ₃ N ₄	Ar, H ₂	DC	10	3060 nm	43
Si + NH3	Si ₃ N ₄	Ar	DC	9	50–90 nm	44
$SiCl_4 + NH_3$	Si_3N_4	Ar, H_2	RF	25	30nm	45
SiCl ₃ +NH ₃	Si_3N_4	Ar	RF	40	300 nm	46
Si + NH ₃	Si_3N_4	Ar	RF	4-8	$.5\mu$	47
SiCl ₄ +NH ₃					$.01\mu$	
SiCl ₄ + NH ₃	Si_3N_4	Ar, H_2	DC + RF	26	10–30 nm	48
$SiH_4 + NH_3$	Si_3N_4	Ar	RF	35	_	49
$Al + N_2$	AlN	Ar	RF	20	30 nm	50
Al	AIN	N_2	DC	2	30 nm	51
Al +NH ₃	AlN	Ar, N_2	RF	25	50–70 nm	52
Al	AIN	N_2	DC	6		53
$Ti + N_2$	TiN	Ār	RF	30	10 nm	54
$TiCl_4 + NH_3 + H_2$	TiN	Ar, N_2	RF	30	$.011 \mu$	55
$TiCl_4 + BCl_3 + H_2$	TiB ₂	Ār	DC	75	.1–.5 μ	9
$TiO_2 + B_2O_3 + CH_4$	TiB ₂	Ar	DC	30	.2–.4 µ	56



Figure 4. Schematic of the plasma system to synthesize ceramic powders. (1-Power supply, 2- Plasma gases, 3-Carrier gases, 4-Gas flow meters, 5-Reactor, 6-Plasma torch, 7-Quench chamber, 8-Powder feeder, 9-Water tank, 10-Water pump, 11-Water flow meters, 12-Filter, 13-Burner, 14-Pyrometer, 15-Data acquisition, 16-Computer.)

when scaling up the process. Using solid feed may be a reasonable choice in the plasma processing of ceramic materials. Using the solid feed has its own challenges, such as: injection into the plasma plume to provide a residence time sufficient for complete vaporization. But this may be the route which can make this technology economically competitive.

In these synthesis processes, in many instances the produced powder contain some undesirable compounds formed during the process. Purifying these powders (by physical or chemical means) is an area which requires more attention.

Thermodynamic analysis, performed on the proposed reaction systems, gives very helpful guidelines concerning the expected reactions and species formation at different temperatures. There are several computer packages, such as CSIRO [58], SOLGASMIX [59], Outokumpu [60] etc., available for thermodynamic analysis. An example of the use of thermodynamic analysis is shown in Figure 5. This diagram presents the results of a free energy minimization plot in terms of moles versus temperature. This figure shows the region of stability for titanium diboride (TiB₂) when a mixture of titanium oxide (TiO₂), boron oxide (B₂O₃) and methane (CH₄) is used as input in the system with a molar ratio of 1:1:5 at atmospheric pressure. Plasma gas (Ar) is also taken into account but is not shown in the plot.



Figure 5. Free energy minimization plot for the system TiO₂:B₂O₃:CH₄ with a molar ratio of 1:1:5.

Due to kinetic effects in the plasma reactors there might be some misleading results in free energy minimization calculations. Kinetic factors are the most important aspect in predicting the reaction product or to formulate the reaction mechanism of a particulate process. Kinetic analysis would include the prediction of rates of vaporization of the feed material, kinetics of the nucleation and growth of the product and the reactor heat, mass and momentum transfer.

Most of the processes mentioned in Tables 1 & 2 are laboratory scale efforts. Though powders produced on the laboratory scale have very attractive properties which are prerequisite for the development of advanced structural materials, there is still a lack of activity on the industrial scale for the production of ceramic powders using plasma processing routes.

The fundamentals of these types of processes have been studied extensively. There have been several excellent investigations into various fundamental aspects, such as: heat and mass transfer in plasma reactors; plasma-particle interaction; nucleation and growth kinetics; high temperature thermodynamic studies; non-equilibrium effects, etc. There is a lack of information concerning the engineering and design aspects of plasma chemical synthesis and this might be one of the primary reasons for the slow adaptation of this technology to the industrial production level. Problems such as: process thermal efficiency, powder injection into the plume, recycling of plasma gases, electrode life and short residence times need further research. There are several research groups that are investigating these

problems and it appears that the industrial use of plasma reactors for ceramic powder generation will be developed in the near future.

Nanophase materials

Plasma processing has the potential to produce ultrafine (in the order of nanometers) powders which can be insitu consolidated into nanophase or nanocrystalline materials. Nanophase (or nanocrystalline) metals or materials are solids with a grain size of a few nanometers (1–50 nm) [61]. Nanophase materials can be metals, ceramics or composites. Due to their extremely small grain size, these materials are comprised of two structural components. Crystallites with long-range order and a disordered interfacial component with a variety of interatomic spacings. Due to very fine grain size and a substantial interfacial component, these nanophase materials show enhanced physical and mechanical properties [62]. There are several ways to generate or synthesize nanophase materials, such as: gas condensation method, mechanical alloying, rapid solidification from the liquid state, chemical vapor deposition, etc. There have been several successful laboratory attempts to produce nanosize materials in plasma reactors.

The highly concentrated enthalpy available in the plasma arc has the ability to vaporize virtually any material, provided the reactant is properly injected into the plasma arc and has sufficient residence time in the hot zone. The steep temperature gradients available in plasma reactors may lead to homogeneous nucleation which can result in the generation of nanosize materials. Girardin and Maurer [63] produced nanosize metallic powders of several transition metals in a plasma reactor. The mean diameter of the produced metal powders was 10nm. Uda [64] generated nanosize metallic powders using a DC plasma arc furnace. Kikukawa et al. [65] used an RF plasma reactor to generate nanosize Ni particles with a typical diameter of 12 nm. Girshick et al. [66] synthesized iron powder (20–70 nm sized) in an atmospheric pressure RF plasma reactor. Research is also underway at the University of Idaho to generate nanosize materials using a transferred arc thermal plasma reactor [67]. Many other examples can be found in Tables 1 & 2, where the produced ceramic powders were in the nanosize range.

One aspect that may be important in using plasma reactors for the generation of nanosize materials is the possibility of producing substantial quantities of these types of materials in a very clean atmosphere. Moreover highly concentrated enthalpy available in the plasma arc has the ability to vaporize any refractory material, providing the possibility of producing nanophase structures of refractory materials.

Novel spray coatings

Plasma sprayed coatings on different types of substrates have been used for the last three decades for applications such as wear and corrosion resistance, thermal barrier, thermal shock resistance, electrical and magnetic parts, etc. These coatings can be of metals, alloys, ceramics, composites, etc., and there is a long list of materials which have been plasma sprayed for various applications [68–71]. These numerous applications of these coating



Figure 6. Plasma spraying.

range from the textile industry to the aircraft industry. Plasma spraying has become a billion dollar industry. The main advantages of plasma spraying is very high temperature and high particle velocity. Almost any material can be melted in the plasma torch. Both DC and RF plasma torches are used for spray coatings. A schematic of a plasma spraying system is shown in Figure 6. In recent years there has been a substantial effort in the area of reactive spray coatings and plasma assisted chemical vapor deposition of novel materials (such as metal-matrix composites, diamond films, superconducting films and more recently carbon nitride C_3N_4) on different substrates.

Diamond is an exceptional material due to its extreme hardness, high thermal conductivity and electrical resistivity and chemical inertness. Eversole at Union Carbide was the first to grow diamond successfully at low pressures [72]. Derjaguin et al. synthesized diamond film by chemical vapor deposition (CVD) using excess hydrogen. In the last decade there has been a dramatic increase in the area of research on diamond deposition on different substrates by plasma CVD. Both RF and DC plasma CVD systems are being employed to grow diamond films by using a mixture of hydrocarbon and excess hydrogen. Using excess hydrogen is important because it etches the graphite which competes with the diamond deposition. Matsumuto et al. [73] prepared diamond films by CVD in a RF plasma reactor. Silicon wafers and molybdenum plate were placed on a water cooled holder. Argon was used as plasma gas and a mixture of CH_4/H_2 with different molar ratios was used as reactant. The substrate temperature was 973–1473 K. A deposition rate of 1 μ m/min was achieved. The structure of the deposit was characterized by XRD and Raman Spectroscopy. Kurihara et al. [74] synthesized diamond by DC plasma jet CVD. A non-transferred arc plasma torch was used and the plasma was formed by a mixture of CH₄ and H₂. Silicon was used as a substrate at temperatures 1000–1450 K. A growth rate of 200 μ m/hr was achieved.



Figure 7. Schematic of the ICP system for diamond deposition.

It was shown that the morphology of the diamond film is affected strongly by the CH_4 concentration and the spacing between the torch and substrate. Several other investigators [75–79] have demonstrated excellent results in depositing diamond films using RF or DC plasma CVD and the mechanism of growth under plasma conditions is being investigated.

An investigation is in progress in the plasma processing laboratory at the University of Idaho [80] regarding plasma CVD of diamond film on a silicon substrate. The schematic of the system is shown in Figure 7. An inductively coupled RF plasma torch is used in this setup. Argon is used as the plasma gas. The substrate (silicon) is held on a moveable water cooled holder to adjust the substrate position. A mixture of C_2H_2/H_2 is used as reactant and fed into the plasma through a water cooled probe. Oxygen is also added to the reactants to etch graphite. One of the objectives is to understand the mechanism of diamond film growth under the conditions of plasma CVD.

Superconducting Y-Ba-CuO films have been deposited by thermal plasma CVD by several researchers [81–83]. Terashima et al. [81] prepared Y-Ba-CuO superconducting film by a reactive plasma evaporation method. Powders such as Y_2O_3 , BaCO₃, CuO are injected into a RF plasma reactor (Ar + O₂ plasma gas) where they are evaporated and the ternary composition controlled high temperature metallic vapors were deposited on a substrate. The deposition rate was 10 μ m/min.

Deposition of carbon nitride films using a non-equilibrium plasma is an other example of potential use of plasma processing in the field of novel materials coatings [84].

Conclusions

An overview of the use of plasma processing of materials is given. There are a large number of past and current laboratory investigations that have demonstrated the possibility of using plasma technology to generate a number of important engineering materials as fine powders.

There is a substantial amount of fundamental information on the behavior of plasma reactors available in the literature but there is still a need for engineering and design work to be performed to improve our understanding of the utility of these types of reactor systems.

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