**RF PLASMA SOURCES AND APPLICATIONS**

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**INTRODUCTION**

Over the past decades RF plasma technology has been used in many areas, such as material science, electronics, basic physics, etc. Typically, the RF plasma system includes power supply (RF generator and matching network), plasma torch and reactor. Depending on the applications two different RF plasma sources are used: inductive and capacitive. Most thermal plasma processes are based on inductively coupled plasma (ICP), which generates equilibrium plasma in the temperature range of 8000 to 12000 K. The advantages of ICP torches are well known and described elsewhere [1-3]. Non-equilibrium plasma is mostly used in the semiconductor industry and for some special applications, such as plasma synthesis of fine powder and bio-material surface treatment. We will focus on the present situation in this field by discussing the commercial and R&D efforts. In this overview an attempt is made to present existing and future research and development related to RF plasma technology. In particular, the following area will be covered: powder processing (spheroidization, densification and purification); synthesis of ultra-fine and nano-size materials; environmental applications.

**A. POWDER PROCESSING**

This technology refers primarily to the densification, spheroidization and purification of metal, ceramic and inter-metallic powders. The process of powder treatment contains a few stages: in-flight melting of the material, quenching and collection.

1. RF-Plasma treatment (RFPT) of spray materials [4].

The potential for this market is based on exploiting the demonstrated advantages of RFPT [1-3]. Powders injected into the plasma change the shape, morphology, chemical composition, and crystal structure. These changes occur with the plasma exposure time measured in tens of milliseconds. The efficiency and flexibility of RFPT provide the opportunity for the economically viable production of powders with the high degree of densification, spheroidization and purity. Advanced schemes have been developed to increase the heat transfer from the plasma stream to particles by up to 35%. For instance, due to high heat transfer, W2C powder can be spheroidized by RFPT for powder size of 400 microns and higher. On the other hand, RFPT processing of carbides (WC, W2C) typically results in de-carbonization (from 4.95% to 4.8%) of the powder. RFPT treatment of WC/12%Co, increased W component from 76% to 80% and increased Co to 15%. The content Fe and other impurities were decreased to 0.01%. An important distinction is that no lines of pure W were found which confirms that no complete de-carbonization took place. A 10 kW RF plasma unit produces dense W2C/12%Co at a rate of about 50 lbs per hour. In 2007 we built the first RF Plasma Powder Processing plant, which has four industrial 300 kW RF Plasma units. Each system produces more than 150 lbs/hr spherical, dense powder continuously 20 Hr/day, 6 days per week. One of the important factors to increase the heat transfer between plasma and particles is the modulation of plasma parameters. RF modulated plasma has been successfully applied to the spheroidization and densification of molybdenum and tungsten [5]. The velocity of the plasma jet is changed in accordance with the current modulation frequency. When the particle velocity reaches the velocity of the plasma, the coefficient of heat exchange has a minimum value. Because the inertia of plasma is lower than particle, the modulation changes the plasma velocity relative to the particles. Thus, the coefficient of heat exchange is substantially increased. Theoretical results were obtained for N2/H2 plasma gas applied to Mo. For instance, the following parameters were used for treatment of Mo (dm= 44 m): Iiomax = 250 Amps, GMo = 0.7 gr./sec; Gpl.(N2/H2) = 0.7/0.01. Current vs time dependence could be described by the following formula: Iiom (t) = 137(1 + 0.84 sin (t)). Discharge power varied during the oscillation period (fm = 100 Hz) from 17 kW to 2.1 kW, respectively. The average plasma discharge temperature varied from 6,000 K to 8,000 K during the same period. The efficiency of the heating process with modulated plasma is higher than 30%. Based on theoretical and experimental results, pilot plasma installation was designed.

3. RF Plasma technology for densification of Palladium powder [6].

Significant quantities of palladium are consumed in the form of dispersed powder used for the manufacture of conducting or resistive paste for electronics. RF plasma is used to convert a regular palladium powder into a new product with reduced grain boundaries and increased resistance to oxidation. The power required to densify Pd powder is 2850 Watts for a production rate of GPd = 1 g/sec. The Pd powder was introduced in different places: along the axis of discharge, along the axis of plasma jet, and perpendicular to the plasma stream. After quenching with liquid argon, the treated powder was collected under the reactor on the surface of the metal-ceramic filter. Sixty particles were analyzed to provide statistically significant measurement. The average particle size for four different samples are: 0.92+/- 0.25 m; 0.93+/- 0.17 m; 0.95+/- 0.15 m; 1.04+/- 0.3 m; some samples included particles greater than 2 m. Research grade argon having moisture content of less than 0.001% must be employed as a carrier and fluidized gas to prevent the agglomeration of particles. Plasma stream temperature uniformity reduced the formation of ‘debris’ and fines to provide a specific surface area range of 0.5 to 1.0 m2/g. XRD crystalline size is more than 4000 Angstroms. Oxidation starts at low temperature (around 250-300 oC) and the Pd starts to transform into PdO. Above 800 oC the PdO dissociates back to Pd metal. The RFPT decreases the TGA by about 36%.

**B. RFP TECHNOLOGY FOR POWDER SYNTHESIS**

Using conventional thermal or milling methods to produce nano-powders is technically difficult and economically unattractive. Arc plasma technology (APT) utilizes a very high temperature (10,000 K), which can produce fine powder. However, in APT erosion of the arc electrodes results in unacceptable level of impurities. This combined with an inability to control particle size distribution (PSD) make APT poor choice for producing fine, high purity powders. High purity powders with a narrow PSD in the nano-size range can be produced by RFP technology. Oxides and nitride powders can be synthesized by introducing powders or solutions of the metal salts into RF plasma.

1. Synthesis of nano-crystalline materials [7].

The synthesis of high purity oxides (SiO2, TiO2) and nitrides (Si3N4, TiN) is done by using tetraethyl orthosilicate (TEOS) and tetrabutoxititanium (TBT) as an initial material. The plasma gases used were air, ammonia, oxygen or nitrogen. To synthesize TN and Si3N4 powders of Ti and Si are used as the raw material. The process is based on the interaction of vaporized Ti or Si with the ionized nitrogen plasma gas. The purity of the initial materials and the RFP are assured by the content of admixtures less than 10-5 %. The most common impurity is carbon. Elemental carbon may result from dissociation reaction: C2H\* 🡪2C + H. Ammonia (NH3) is employed as inhibitor. An ammonia content of 19%wt. inhibits agglomeration and limits carbon content to 0.001%. The TEM results showed the shape of the 70 to 200 nm powder is spherical. The specific surface area (measured by BET) is in the range of 15 to 45 m2/g. X-ray diffraction shows that TiO2 is produced in two phases: anatase (30%) and rutile (70%). The ratio of rutile and anatase can be controlled by adjusting reaction time and temperature. The X-ray diffraction spectrum does not present a peak for SiO2, which indicates the SiO2 is amorphous. It is worth noting that only harmless gases are generated in the process, which results in an environmentally clean process.

2. Plasma processing of aluminum nano-fuel [8].

Ultrafine aluminum powder with the size range of 300 to 15000 Angstrom may be produced by electrical explosion of aluminum wire in the hydrogen and argon containing media. Mass Spectroscopy and thermal desorption analytical methods of powder produced from wires showed that aluminum powder consisted of spherical particles with a distorted crystal lattice, and contained amorphous phase, surface gases, and gases inside of particle volume of about 5 to 7% mass. Those results are in agreement with our results. However, the electrical explosion procedure of Al powder is not applicable for industrial production of such powder. Plasma processed aluminum powder can contain approximately 2.2 times more hydrogen than chemically obtained AlH3. Oxidation of this hypothetical substance has the thermal effect about 1435 kcal/mol. Molecular hydrogen is absorbed on the surface of the melted aluminum particles. The hydrogen then dissociates into atoms and diffuses into the depth of the metal. The atomic nature of hydrogen diffusion in metals was experimentally verified during the research of hydrogen diffusion in a deuterium mixture. Having diffused into the metal, the gas is distributed among atoms of metal. The absorption of hydrogen by aluminum is endothermic. This is why the amount of absorbed hydrogen increases with the increase of temperature and reaches a peak at 2000 to 3000 K. The technology is based on direct vaporization of powdered aluminum in a RF hydrogen plasma discharge at atmospheric pressure. The resulting matrix is rapidly quenched into ultra-fine aluminum powder. Typical plasma sample content: Al = 51.4%; total Al = 69.5%; free carbon = 2.15%. SCP presents the total calorific value for both combustible (0.64 gr.) and incombustible (0.36 gr.) components in 1 gram of sample. The gross formula for produced combustible components is Al\*5.5H2\*0.08C. SCP for all combustible components for this sample (assuming the atomic state of hydrogen) is: 6,962: 0.5725 = 12,160 cal/g = 21,888 BTU/lb. Rapid solidification is achieved by imposing a high cooling rate (103 – 109 oC/sec) for the layer thickness not more than 10 microns. The average quantity of captured hydrogen was about 1 % to 3.2%.

1. **ENVIRONMENTAL APPLICATIONS**

1. Dissociation of the hydrogen chloride in the RF plasma [9].

The dissociation of HCl in the RF plasma discharge with the temperature above 6000K has thermodynamic character. The processing time was around 3x10-3 sec. According to our theoretical calculations for processing time 3x10-3 sec at T = 6000K, we could achieve 95% conversion. Argon was chosen for two reasons: a) the ignition and stabilization of RF discharge at atmospheric pressure are not difficult b) argon is an inert gas and could be recycled. The full dissociation of HCl to hydrogen and chlorine is achieved at the following conditions: plasma gas consisting of the mixture of Ar and HCl at ratio 1:1; plasma gas rate = 1 liter per second; discharge power = 10 kW. These results are confirmed by gas analysis of the product before and after the quenching device. The analysis of the gas mixture in the reactor shows that they contain argon, chlorine and hydrogen in molecular form. A similar RF plasma system was developed for plasmachemical decomposition of hydrogen sulphide. The efficiency of the process was demonstrated by using a 100 kW plasma torch. The pilot unit, having 600 kW power level was designed and tested at a gas refinery plant. An industrial plasma chemical reactor will be based on a RF plasma system at a power level of 1 MW with optimal conversion level of hydrogen sulfide about 50-70% at a pressure of 1-10 atm,with an energy consumption of ~ 1.2 – 1.5 kWh/nm3 H2.

2. RF Plasma system for medical waste treatment [10].

This work is focused on the studies of RF plasma discharge with respect to use on bio-hazardous medical waste. The system includes: liquid nitrogen crushing unit, plasma reactor, high temperature oxidizer and emission control system. The medical waste is processed in the plasma reactor under nitrogen at atmospheric pressure and reduces to carbon residue. The off gas is directed to the oxidizer and scrubbed before being discharged. Processing rate is 1 ton/day. Total power required – 160 kW.

**CONCLUSION**

The following conclusion is related only to the areas, which have been described in this overview. A few problems still exist and require future investigation and development, such as ignition of RF plasma discharge at atmospheric pressure, precise control of the plasma parameters and efficiency of RF power supplies. Solid state RF generators, having efficiency of 90% and higher, are successfully used for low pressure and low power plasma torches. High power (>25 kW) solid state RF generators are in the development stage. For the last decade a big progress was made by introducing RF plasma to some of bio-medical, water treatment and waste-to-energy applications. Efficiency of plasma processes is one of the critical factors for existing and new plasma systems.

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