RF PLASMA: from R&D to commercial applications

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Abstract: In this paper we overview and describe the characteristics of various types of RF plasma system, which are used for different applications such as: powder processing; plasma sintering; plasma sterilization; waste treatment; element separation and nano-powder synthesis.

Keywords: RF plasma, applications, parameters

1. 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 12 000 K. The advantages of ICP torches are well known and described elsewhere. 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.

2. 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. RF plasma was successfully employed for a large number of materials and a wide range of particle size.

1.1. RF-plasma treatment (RFPT) of spray materials

The potential for this market is based on exploiting the demonstrated advantages of RFPT. 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. RFPT is based on RF inductive power used to create plasma at atmospheric pressure. Advanced schemes have been developed to increase the heat transfer from the plasma stream to particles by up to 35%. Some of the materials processed include: ZrO_2, W_2C, WC and WC-Co combinations. Full or partial spheroidization of powders can be achieved by the process. RFPT improves the working characteristics of cermet and coatings such as: hardness, density, bond strength, and wear and corrosion resistance. A typical layout of a basic RFPT installation include: the RF generator, RF plasma torch consisting of quartz or water cooled metallic chamber. The following gases having rates G_p ranging from 0.2 to 5 m^3/Hr has been employed: Ar, O_2, Air, Ar + H_2, N_2 + H_2. Initial materials are introduced through the powder feeder by the carrier gas G_c and a water cooled probe. Powder injection locations include: the center of the plasma streams, the exit of the plasma chamber, or counter flow to the plasma stream. An important factor for the thermal treatment of materials is the coefficient of the heat transfer. For instance, due to high heat transfer, W_2C powder can be spheroidized by RFPT for powder size of 400 µm and higher. A 10 kW RF plasma unit produces dense W_2C/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 of spherical, dense powder. It is operated 20 hours per day, 6 days per week.

1.2. Effect of modulated RF plasma for powder treatment

One of the important factors to increase the heat transfer between plasma and particles is the modulation of plasma parameters. The modulation of plasma parameters is realized by modulation of the plasma current. RF modulated plasma has been successfully applied to the spheroidization and densification of molybdenum and tungsten. Efficiency of the plasma system was a major subject of research. Frequency and amplitude modulations were optimized for the plasma process. The efficiency of the heating process with modulated plasma is 30% higher.

1.3. RF plasma technology for densification of palladium powder

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 starting material enters the plasma zone, where the particles are heated. 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 µm; 0.93 ± 0.17 µm; 0.95 ± 0.15 µm; 1.04 ± 0.3 µm; some samples included particles greater than 2 µm. XRD crystalline size is more than 4 000 Å. The dynamics of oxidation when heating in air is an important parameter for Pd powder. Oxidation starts at low temperature (around 250 - 300 °C) and the Pd starts to transform into PdO. Above 800 °C the PdO dissociates back to Pd metal. The RFPT decreases the TGA by about 36%.

1.4. Nano-powder production

Using conventional thermal or milling methods to produce nano-powders is technically difficult and economically unattractive. Arc plasma technology due to the erosion of the electrodes results in unacceptable level of impurities. High purity powders with a narrow PSD in the nano-size range are produced by RFP technology.

1.5. Synthesis of nano-crystalline materials

The synthesis of high purity oxides (SiO_2, TiO_2) and nitrides (Si_3N_4, 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 Si_3N_4 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 contaminations are most evident at the filter and packaging stages. The most common impurity is carbon. 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 m^2/g. X-ray diffraction shows that TiO_2 is produced in two phases: anatase (30%) and rutile (70%). It is worth noting that only harmless gases are generated in the process, which results in an environmentally clean process.

1.6. Plasma processing of aluminium nanofuel

Ultrafine aluminum powder with the size range of 300 to 15 000 Å may be produced by electrical explosion of aluminum wire in the hydrogen and argon containing media. However, the electrical explosion procedure of Al powder is not applicable for industrial production of such powder. The powder produced by using RF plasma process has a similar size range, but narrower particle size distribution. Plasma processed aluminum powder can contain approximately 2.2 times more hydrogen than chemically obtained AlH_3. Oxidation of this hypothetical substance is as follows: $2(AlH_{6.7}) + 4.85O_2 = Al_2O_3 + 6.7\ H_2O$. 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. A hydrogen saturated aluminum powder with the formula of ($AlH_{6.7}$), has a theoretical Specific Calorific Power (SCP) more than 20 000 kcal/kg. 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 g) and incombustible (0.36 g) components in 1 gram of sample. SCP for all combustible components for this sample (assuming the atomic state of hydrogen) is about 21 888 BTU/lb. In order to produce Al particles saturated with hydrogen and interrupt the increase of particle size (i.e., to fix the particle in its meta-stable form) the quenching procedure is required. The A-type samples were obtained as a consequence of quenching of Al powder on a cooled surface. The B-type samples were obtained by volume liquid argon quenching of Al particles. Rapid solidification can be achieved by imposing a high cooling rate (10^3 - 10^9 °C/sec) for the layer thickness not more than 10 µm. The average quantity of captured hydrogen was about 1 % to 3.2%.

3. Environmental applications

2.1. Dissociation of the hydrogen chloride in the RF plasma

The dissociation of HCl in the RF plasma discharge with the temperature above 6 000 K has thermodynamic character. 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 in cooperation with Kurchatov Science Center 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 3 to 5 MW with optimal conversion level of hydrogen sulphide about 50 - 70% at a pressure of 1 – 10 atm, and an energy consumption of ~1.2 - 1.5 $kWh/nm^3\ H_2$.

2.2. RF plasma system for medical waste treatment

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 atmosphere and reduces to carbon residue. The off gas is directed to the oxidizer and scrubbed before being discharged. The system works as a continuous batch. Processing rate is 1 ton/day. Total power required = 160 kW.

2.3. Plasma processing of used tires

This system is used to study the process of recycling waste tires. Defined regimes where typical products are distinguished during the tire recycling process, such as: Synthesis Gas, Liquid Fraction and Carbon. In some experiments we observed only Synthesis Gas and Carbon Black (without Liquid Fraction). Particle size of carbon black is within nano-size range. Process parameters vary considerably and are dependent of the process temperature and energy used. The module is equipped with RF ICP torch and RF generator (2 MHz frequency at power level of 100 kW). Additional to the plasma part, the reactor contents low-frequency (LF) induction heater. LF frequency heating generators are in 20 - 40 kHz frequency range at 15 kW power level. Modular construction of the installation allows different connection combinations of process equipment and the establishment of technological regimes depending on tasks. For example, the process system could use RF plasma torch or LF induction heater only or combined treatment (HF + LF). This principle provides the flexibility of the equipment by transforming internal and external structure of a plant depending on its purpose. Temperature processes can be adjusted from 500 to 5 000 °C.

4. Plasma system for element separation

The separation of metallic elements and isotopes in fully ionized metal plasma has been studied since 1966. In this paper we describe the characteristics of a system in which metallic elements: copper and gold are separated by using ionized plasma in a strong magnetic field. Copper/gold alloy was sputtered in microwave plasmas, ionized and accelerated by RF antenna in an axial magnetic field. The uniformity of plasma was controlled by optimizing plasma parameters and the axial magnetic field. Control of the plasma profile has been carried out by using microwave ICRH and special RF antenna configuration. The sputter plate (copper Dore bar) was biased by negative DC voltages in the range of -100 to 1000 Volts. The RF antenna was tuned to the ion-cyclotron frequency and sharp resonances were observed for collected material. The purity of the product (gold) depends on the configuration of the collector and substrate’s material.

5. Plasma sintering

Our interest is especially focused to zirconia nano-crystalline structure modification. It is shown that RF plasma technology is capable to process (sinter) partially and fully stabilized Zirconia in flight without grain growth and binders. Plasma processed Zirconia has a nearly 100% theoretical density. Pre-existing oxidation and contaminates are evaporated during plasma process. Atmospheric and low pressure plasma systems are presented. The process of producing of pure zirconia powder from Zircon ($ZrSiO_4$) also is presented in this paper.

6. Plasma sterilization of dispersed material

Current methods of decontamination must weigh the level of microbial reduction with the amount of acceptable product degradation. Some current methods affect detriment upon the substrate. For instance, substances with heat-labile active ingredients are prone to degradation when exposed to high heat; the active element in dry and steam is heat treatments. Oxidizing agents, such as, ethylene oxide or sodium hypochlorite can either be reactive toward or be absorbed into the processed material. Cold, low pressure RF plasma (CLPP) was modeled for decontamination of powdered botanicals, such as: hydrilla, stinging nettle leaf, organic wheat grass powder and saw palmetto. Chia seeds were tested as a coarse-material out-group.

7. Conclusion

The following conclusion is related only to the areas, which have been described in this overview. A few issues 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.