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# (54) Title: REACTIVE GAS SHROUD OR FLAME SHEATH FOR SUSPENSION PLASMA SPRAY PROCESSES

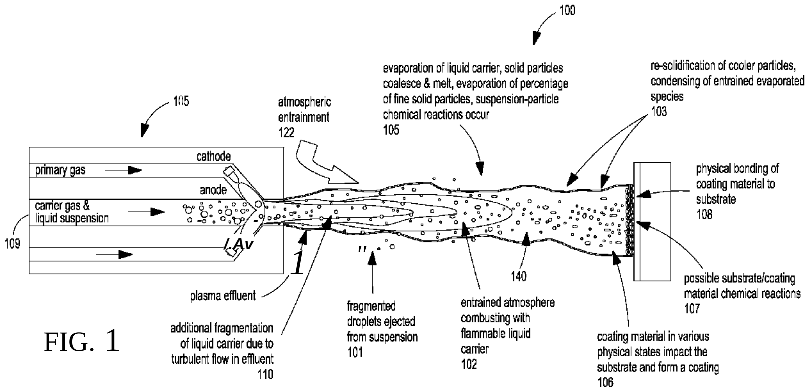


FIG. 1

**(57) Abstract: A** system and method for producing thermal spray coatings on a substrate from a liquid suspension is disclosed. The disclosed system and method include a thermal spray torch for generating a plasma and a liquid suspension delivery subsystem for delivering a flow of liquid suspension with sub-micron particles to the plasma to produce a plasma effluent. The liquid suspension delivery subsystem comprises an injector or nozzle which can produce a reactive gas shroud surrounding the plasma effluent. **A** flame envelope can also be used to isolate injection of the liquid suspension. The shroud or flame envelope can retain the sub-micron particles entrained within the plasma effluent and substantially prevent entrainment of ambient gases into the plasma effluent. The liquid suspension delivery subsystem can be arranged as an axial injection system, a radial internal injection system or an external radial injection system.

# Reactive Gas Shroud or Flame Sheath for Suspension Plasma Spray Processes

## Field of Invention

**[0001]** The present invention relates to suspension plasma sprays, and more particularly to methods and systems for the shrouding of suspension plasma spray effluents and/or sheathing the injection of liquid suspensions using a reactive gas and/or flame envelope to facilitate and control the effluent and suspension interactions.

## Background

**[0002]** Conventional plasma spray technology primarily uses powder feeders to deliver powdered coating material into a plasma jet of a plasma spray gun. However, this technology is typically limited to the use of particles of at least +350 mesh (i.e., a median particle size of approximately of 45 microns in which 50 percent of particles are smaller than the median size and the other 50 percent of the particles are larger than the median size) or larger. As particle size decreases below +325mesh, introducing powdered coating material directly into the plasma jet becomes progressively more difficult. Fine particles tend to pack tightly and agglomerate, increasing the likelihood of clogging in conventional powder feed systems.

**[0003]** In addition to clogging, conventional plasma spray technology is also ill-suited to the use of fine particles for other reasons. Because of the low mass of fine particles, combined with the extreme velocities of the plasma jet, fine particles tend to be deflected away from a boundary layer of the plasma jet without penetrating the boundary layer during radial injection. The velocity necessary for penetration of the fine coating particles is too large to physically be accomplished without disturbing the effluent itself. Practical limitations exist to increase velocity to this degree.

**[0004]** The need for coating finer particles is desired for use in thermal barrier coatings. The finer particles typically result in denser coatings and finer microstructural features, including for example, smaller lamellar splats and grains. The finer particles also tend to produce coated parts with improved microstructure. Fine particles are also easier to melt because of its large surface area relative to its small mass.

[0005] Suspension plasma spray (SPS) has emerged as a means for depositing finer particles. SPS is a relatively new advancement in plasma spray techniques which utilizes a liquid suspension of sub-micron size particles of the coating constituents or particulates materials, rather than a dry powder, as the coating media. The liquid serves as a carrier for the sub-micron size particles that would otherwise tend to agglomerate restricting or eliminating powder flow to the torch. The liquid also has been shown to function as a thermally activated solution that precipitates solids or reacts with suspended particles. Due primarily to the use of very small particles suspended in the liquid carrier, the suspension plasma spray process has demonstrated the ability to create unique coating microstructures with distinctive properties. The liquid droplets also provide the additional mass to impart the momentum necessary for entrainment by radial injection.

[0006] Notwithstanding the improvements of SPS over conventional plasma spray technology, current SPS systems and processes continue to suffer from a variety of drawbacks. For instance, conventional SPS typically produce coatings having uncontrolled microstructure grain size and/or lack of directional orientation growth, both of which can result in poor coating properties. To further compound the microstructural problem, adverse chemical reactions can occur between the substrate and the deposited coating materials.

[0007] Further, longer stand-off distances between the nozzle location and the deposition point may be required to adequately coat complicated geometries such as turbine blades. However, the longer stand-off distances may provide the coating constituents excessive dwell or residence time, thereby causing cooling and resolidifcation of coating constituents prior to reaching the substrate. Reducing the stand-off distance can cause insufficient heating such that the particulates are never able to absorb enough heat and fully melt. In both cases, the end result is lack of particulate adhesion to the substrate, thereby reducing deposition efficiency of the material. The finer particulate size of the coating constituents have increased surface areas that can rapidly heat up and cool down at faster rates than typically encountered in standard plasma technology. Accordingly, the increased surface area of the finer particulates creates unprecedented challenges to optimizing the correct stand-off distance.

[0008] Still further, turbulent flow of the plasma gas effluent emerges from the nozzle of the torch. The turbulent interaction of the plasma effluent with the atmosphere imparts rapid decreases in effluent temperature and rapid directional flow changes that result in the ejection of the coating particulates from the flow path directed to the substrate. As a result, the ejected particulates result in decreased deposition efficiency.

**[0009]** The above problems are only a few examples of the types of new challenges posed by the utilization of SPS systems and processes to deposit ever increasingly finer coating media constituents. In view on the on-going challenges, there is a need to improve upon the current suspension plasma spray processes and systems.

## Summary of Invention

**[00010]** As described in more detail below, the present embodiments of the invention addresses some of the disadvantages and provides techniques to control the aforementioned interactions through use of a reactive gas shroud surrounding the plasma effluent stream and liquid suspension contained therein (collectively, referred to as "effluent," "effluent stream," "plasma," or "plasma effluent," or "plasma effluent stream" herein and throughout the specification). The present invention uniquely combines a reactive gas shroud with a plasma spray process using submicron particles delivered via liquid suspension to improve current suspension plasma spray capabilities and create new coating microstructure possibilities through controlling the suspension injection and fragmentation as well as the interactions between the effluent and suspensions.

**[00011]** The invention may include any of the following aspects in various combinations and may also include any other aspect described below in the written description or in the attached drawings.

**[00012]** The present invention may be characterized as a thermal spray system for producing coatings on a substrate from a liquid suspension comprising: a thermal spray torch for generating a plasma; a liquid suspension delivery subsystem for delivering a flow of the liquid suspension with sub-micron particles; and a nozzle assembly for delivering the plasma from the thermal spray torch to the liquid suspension to produce a plasma effluent, the nozzle assembly adapted for producing a reactive gas shroud substantially surrounding said plasma effluent; the reactive gas shroud configured to substantially retain entrainment of the sub-micron particles in the plasma effluent and substantially inhibit gases from entering and reacting with the plasma effluent; wherein the reactive gas shroud reacts with the plasma effluent to enhance fragmentation of the suspension droplets and create evaporative species of the sub-micron particles within the plasma effluent.

**[00013]** The present invention may also be characterized as a method of producing coatings on a substrate using a liquid suspension with sub-micron particles dispersed therein, the method comprising the steps of: generating a plasma from a thermal spray torch; delivering a flow of liquid suspension with sub-micron particles dispersed therein to the plasma or in close proximity thereto to produce a plasma effluent stream; surrounding the plasma effluent with a reactive gas shroud to keep the sub-micron particles entrained within the plasma effluent and substantially prevent entrainment of ambient gases into the plasma effluent; reacting the shroud gas with the plasma effluent to enhance fragmentation of the suspension droplets and create evaporative species of the sub-micron particles within the plasma effluent; and directing the shrouded plasma effluent with the sub-micron particles contained therein towards the substrate to coat the substrate.

## Brief Description of the Drawings

**[00014]** The above and other aspects, features, and advantages of the present invention will be more apparent from the following, more detailed description thereof, presented in conjunction with the following drawings, wherein:

**[00015]** Fig. 1 is a schematic illustration of a prior art suspension plasma spray process employing an axial injection of the liquid suspension;

**[00016]** Fig. 2 is a schematic illustration of a prior art suspension plasma spray process employing an internal radial injection of the liquid suspension;

**[00017]** Fig. 3 is a schematic illustration of a prior art suspension plasma spray process employing an external radial injection of the liquid suspension;

**[00018]** Fig. 4 is a schematic illustration of a reactive gas shroud of a suspension plasma spray process employing an axial injection of the liquid suspension in accordance with an embodiment of the present invention;

**[00019]** Fig. 5 is a schematic illustration of a reactive gas shroud of a suspension plasma spray process employing an internal radial injection of the liquid suspension in accordance with another embodiment of the present invention;

**[00020]** Fig. 6 is a schematic illustration of a reactive gas shroud of a suspension plasma spray process employing an external radial injection of the liquid suspension in accordance with yet another embodiment of the present invention;

**[00021]** Fig. 7 shows yet another embodiment of the present invention employing a dual gas shroud consisting of an inner reactive gas layer and an outer inert gas shield surrounding a suspension plasma spray process;

**[00022]** Fig. 8 shows yet another embodiment of the present invention employing a dual gas shroud consisting of a first reactive gas layer and a second reactive gas layer surrounding a suspension plasma spray process;

**[00023]** Fig. 9 is a schematic illustration of an suspension plasma spray process employing a gas shrouded or gas sheathed axial injection of the liquid suspension in accordance with an embodiment of the present invention;

**[00024]** Fig. 10 is a schematic illustration of a suspension plasma spray process employing a gas shrouded or gas sheathed internal radial injection of the liquid suspension in accordance with another embodiment of the present invention; and

**[00025]** Fig. 11 is a schematic illustration of a suspension plasma spray process employing a gas shrouded or gas sheathed external radial injection of the liquid suspension in accordance with yet another embodiment of the present invention.

## Detailed Description

**[00026]** The present disclosure relates to a novel SPS system and process for the deposition of coating material. The SPS system and process of the present invention is particularly suitable for deposition of sub-micron particles. The disclosure is set out herein in various embodiments and with reference to various aspects and features of the invention.

**[00027]** The relationship and functioning of the various elements of this invention are better understood by the following detailed description. The detailed description contemplates the features, aspects and embodiments in various permutations and combinations, as being within the scope of the disclosure. The disclosure may therefore be specified as comprising, consisting or consisting essentially of, any of such combinations and permutations of these specific features, aspects, and embodiments, or a selected one or ones thereof.

**[00028]** The present invention recognizes the shortcomings of current SPS systems and processes. These shortcomings can be better identified by referring to Figures 1-3. Figs. 1-3 show several schematic illustrations of prior art suspension plasma spray systems and processes 100, 200 and 300 employing an axial injection of the liquid suspension; internal radial injection of the liquid suspension and external radial injection of the liquid suspension, respectively. In each of these prior art systems, numerous physical and chemical interactions are occurring, many of which are uncontrolled. For example, Figures 1 and 2 show fragmentation of the liquid carrier occurs at regions 110 and 201 in an undesirable random-like manner due to the turbulent flow in the effluent. The fragmentation occurs soon after the plasma effluent and liquid suspension are in contact. As used herein, the term "effluent" and "plasma effluent" will be used interchangeably and are intended to refer to any combination of the plasma gas, coating constituents or particles and liquid carrier, each of which is flowing from the outlet of a torch nozzle. For example, at the immediate outlet of each of nozzles 105, 205 and 305 of their respective torches, the effluent 140, 240 and 340 will more than likely consist of plasma (i.e., hot primary torch gas ionized by virtue of being exposed to an arc generated between the cathode and anode) and droplets of liquid carrier containing coating particles (i.e., liquid suspension 109, 209 and 309). However, within the vicinity of the substrate 108, 208 and 308, the effluent 140, 240 and 340 will primarily consist of the coating particulates and a potentially significantly cooler effluent 140, 240 and 340, as substantially all of the liquid carrier has evaporated by this stage of the SPS coating process 100, 200 and 300.

**[00029]** Figures 1 and 2 also show that a portion of the fragmented droplets of the liquid suspension 109 and 209 are ejected from the effluent 140 and 240 at regions 110 and 210, respectively.

**[00030]** Figures 1-3 further show atmospheric entrainment 122, 222 and 322 into the plasma effluent 140, 240 and 340 in a region that is in close proximity to the outlet of the torch nozzle 105, 205 and 305. The infiltration of atmospheric gases, including oxygen, results in accelerated combustion of the entrained atmosphere with flammable liquid carriers (e.g., ethanol). In addition, Figure 1 shows there is evaporation of the liquid carrier, as shown by representative region 105, causing many of the sub-micron solid particles to coalesce and melt. Where ideal thermal conditions within the effluent 140, 240 and 340 exist, a percentage of the sub-micron or very fine particles transform into an evaporative species, thereby resulting in lowered deposition efficiency and inadequate coating of the substrate 108, 208 and 308.

**[00031]** These fragmented droplets, melted particles and evaporated species of the suspension 109, 209 and 309 along with the combustion by-products resulting from atmospheric entrainment are carried along the effluent stream 140, 240 and 340 towards the substrate 108, 208 and 308, during which time additional suspension-particle chemical reactions occur including unwanted reactions such as particle oxidation, as depicted at regions 105, 205 and 305. Also during the transit of the effluent 140, 240 and 340, many fragmented droplets and particles continue to be ejected from the suspension 109, 209 and 309, thereby further lowering deposition efficiency.

**[00032]** Figures 1-3 further show that as the effluent stream 140, 240 and 340 approaches the substrate 108, 208 and 308 to be coated, the temperature profile within the effluent stream 140, 240 and 340 changes resulting in some re-solidification of cooler particles and condensing of entrained evaporated species. Upon reaching the substratel08, 208 and 308, the coating material in the various physical states impact the substrate and form a coating 106, 206 and 306, including the physical bonding of coating material to the substrate. Adverse chemical reactions between the substrate 108, 208 and 308 and the coating materials can occur.

**[00033]** Current suspension plasma spray systems suffer from the disadvantage of not adequately controlling these physical and chemical interactions during the three key phases of the suspension plasma spray process, namely: (i) suspension injection and fragmentation; (ii) effluent and suspension interactions; and (iii) substrate interactions with effluent and coating buildup.

**[00034]** As will be discussed in Figures 4-1 1, the present embodiments of the invention address many of the aforementioned disadvantages shown in Figures 1-3. The present invention provides techniques to control the aforementioned adverse interactions through use of a reactive gas shroud and/or sheath surrounding the effluent stream and/or injection location for liquid suspension.

**[00035]** Turning now to Figs. 4 through 6, there are shown schematic illustrations of different embodiments of the present invention, namely depictions of suspension plasma spray systems and processes 400, 500 and 600, respectively. SPS system and process 400 employs an axial injection of the liquid suspension 409 with an extended reacted gas shroud 401 surrounding the effluent 440 (i.e., plasma and liquid suspension 409). Any suitable reactive gas may be used to create the reacted gas shroud 401, such as, for example, oxygen, hydrogen carbon dioxide; hydrocarbon fuels and in some instances nitrogen or combinations thereof. Through use of reactive gas shroud 401, the effluent440 and suspension 409 interaction can be more precisely controlled to create new coating microstructure possibilities as a result of the chemical reactions occurring between the suspension 409 and the reactive gas shroud 401 .

**[00036]** Figure 4 shows that the shroud 401 is created by flowing reacted gas at a predetermined flow rate through an outer nozzle that surrounds an inner nozzle through which the liquid suspension 409 and primary torch gas 416 can sequentially or co-flow relative to each other. The shroud 401 is oriented around the flow of effluent 402, thereby forming a protective envelope of reactive gas that surrounds the effluent 440. Figure 4 shows that the shroud 40 1 extends continuously from within the nozzle 405 of the torch to the substrate surface 408 to create a completed envelope of the effluent 440 contained therein.

**[00037]** Prior to the liquid suspension 409 emerging from the outlet of nozzle 405, a plasma 419 is created as primary torch gas 416 flows between a cathode 412 and anode 413 into a region where an arc is generated. The carrier gas transports the liquid suspension 409 and is shown flowing with the liquid suspension 409 through the center of the nozzle 405. An arc is generated between the cathode 412 and anode 413. The primary torch gas 416 passes through the arc region and ionizes into a hot plasma 419 of gaseous ions and/or radicals within the nozzle 405. The plasma 419 provides the thermal energy source required to evaporate the liquid carrier and melt the coating constituents 415 of liquid suspension 409 as the effluent 440 flows towards the substrate surface 408. The plasma 419 also provides the energy source to provide sufficient momentum to accelerate the coating constituents or particles 415 towards the substrate surface 408.

**[00038]** After the plasma 419 is created, the liquid suspension 409 (i.e., liquid carrier droplets with coating constituents 415 contained therein) and plasma 419 emerge from the outlet of the nozzle 405 as an effluent 440. The shrouded gas 401 converges within a throat section of the nozzle 405 and thereafter emerges from the nozzle 405. It should be understood that the terms "shroud" and "shrouded gas" have the same meaning and will be used herein and throughout the specification interchangeably.

**[00039]** In a preferred embodiment, the reactive gas shroud 401 is an oxygen-containing gas, such as, for example, oxygen gas or an oxygen diluted mixture of gases. The oxygen-containing reactive gas shroud 401 can be used to control or increase the degree of mixing and spatial location of the mixing of the reactive gas 401 with the effluent 440, thus more precisely controlling the degree and location of the combustion with the effluent 440 and resulting thermal energy profile. Enhanced combustion or other thermal reactions also can improve the fragmentation of the droplets of the liquid suspension 409 as well as evaporation of the sub-micron coating particles 415 within the suspension 409. The oxygen-containing reactive gas shroud 401 can be used with a fuel based liquid carrier to produce more complete combustion which can be initiated or effected further upstream or closer to generation of the plasma source 419 than would occur with a non-shrouded spray process or traditional inert gas shroud around the plasma spray effluent. The embodiment of Figure 4 demonstrates that advancing the combustion process further upstream toward the plasma source 419 would enable use of lower power plasma torches to both melt and evaporate the sub-micron particles 415 within the liquid carrier through more efficient use of the plasma stream's thermal energy.

**[00040]** The reactive gas shroud 401 is configured to flow at a sufficient flow rate relative to that of the effluent 440 so as to form a continuous envelope about the effluent 440. The effluent 440 is characterized as having a trajectory or flow path of the liquid suspension 409 defined, at least in part, from the outlet of the nozzle 405 to the substrate surface 408, whereby the flow path is partially or fully enveloped by the reactive shroud 401 . As shown in the embodiment of Figure 4, the length of the reactive shroud 401 extends from the outlet of the nozzle 405 to the substrate surface 408 to fully surround the effluent 440. The continuous envelope of the shroud 401 creates a thermal envelope that acts as an effective insulator to retain heat in the effluent stream 440 across longer flow path distances from the outlet of the nozzle 405 to the surface of the substrate 408. The controlled temperature from the outlet of the torch 405 to the substrate 408 enables evaporation of the liquid carrier of the liquid suspension 409. After evaporation of the liquid carrier, the heat used to evaporate the liquid carrier is now realized by the coating constituents 415 generally contained within the droplets of the liquid suspension 409, which are now free floating and travelling towards the substrate surface 408. The coating constituents 415 partially or substantially melt without undergoing significant cool down as they flow towards the surface of the substrate 408. The molten coating constituents 415 impact the substrate surface 408 to deposit as a coating 403. In this manner, the improved thermal envelope therefore improves deposition efficiency. Further, the retention of heat within the effluent 440 creates improved uniformity in temperature distribution that can decrease stand-off working sensitivity. As such, the present invention as shown in the embodiment of Figure 4 allows a unique SPS system and process 400 for coating complicated geometries at father stand-off distances than previously attainable with conventional SPS, without incurring substantial solidification of the coating constituents 415 as they impact the substrate surface 408.

**[00041]** While enhanced combustion resulting from use of the oxygen containing gas and a fuel based liquid carrier is one embodiment of the present system and method, other chemical reactions may be facilitated with the use of a reactive shroud gas that will react with various elements or compounds in the liquid medium resulting in a chemical reaction that occurs spontaneously or occurs due to the thermal energy of the plasma effluent. Such chemical reactions can be designed and controlled to yield improvements in the coating chemical composition, physical property or microstructure, including for example the formation of oxides, carbides or nitrides of the particles.

**[00042]** Advantageously, the use of the reactive gas shroud 401 around the plasma effluent 440 operates to create and/or retain more heat in the effluent 440 providing a larger operation envelope for the coating process. The larger operational envelope translates to longer working distances between torch nozzle 405 and substrate 408 as well as better thermal treatment of the sub-micron particles 415. In other words, the sub-micron particles 415 along its flow path trajectory are maintained at the prescribed operating temperatures for longer residence times resulting in improved melting and an increase in the evaporative species of the particles within the plasma effluent 440. Use of reactive gas shroud 401 also facilitates control of the environment and temperatures near the substrate surface 408.

**[00043]** The use of a reactive gas shroud 401 surrounding a suspension plasma spray effluent 440 opens up numerous possibilities to develop new liquid carriers for such sub-micron particle containing suspensions 409 or solutions.

**[00044]** In each of the embodiments of the present invention, the reactive gas shroud can be configured in a controlled manner. The most likely means of control involve adjusting or manipulating the flow characteristics of the reactive gas shrouds, including the volumetric flow rate and/or velocity of the gas shroud as well as concentrations of the reactive elements in the reactive gas shrouds. In addition, the turbulence and dispersion characteristics of the reactive gas shroud may also be controlled. Many of these flow characteristics are dictated by the geometry and configuration of the nozzle or nozzles used to form the reactive gas shrouds as well as the reactive shroud gas supply pressures and temperatures.

**[00045]** The embodiment of Figure 4 shows that the shrouded gas 401 is configured to flow in a laminar flow rate regime. The controlled and lowered velocity of the laminar flowing shroud 401 can enable the fragmentation phenomena of the droplets of the liquid suspension 409 across the shroud 401 to occur in a more controlled manner compared to conventional SPS systems and processes 100, 200 and 300 of Figs. 1-3. The fragmented droplets of liquid suspension 409 therefore attain an improved uniformity in size distribution. As a result, the coating constituents 415 deposit on the substrate surface 408 to form a coating 403 having a more controlled particle size distribution.

**[00046]** The shroud 401 also counteracts any tendency for droplets of the liquid suspension 409 to eject from the effluent 440. Generally speaking, in the absence of the shroud 401, the effluent 440 is in a turbulent flow regime which may be sufficient to break up liquid droplets into smaller droplets, and in the process of doing so, undesirably impart excessive momentum to at least some of the droplets to eject them from the effluent stream 440. Employing the shroud 401 can facilitate the retention of the droplets of the liquid suspension 409 and coating constituents 415 within the effluent 440. As a result, increased utilization of the coating constituents 415 is attained.

**[00047]** The combination of the aforementioned process benefits can produce a coating 403 deposited onto the substrate surface 408 having a microstructure with grain orientation and sufficiently small particle size distribution. The favorable microstructural possibilities are controllable and reproducible by virtue of the innovative SPS system and process 400.

**[00048]** In accordance with another embodiment of the present invention, Figure 5 shows an SPS system and process 500 in which the liquid suspension 509 is internally injected within the torch nozzle 505. The internal injection of the liquid suspension 509 can occur in a substantially radial direction at an orthogonal orientation with respect to the axis of the plasma 519 that is generated within the nozzle 505 between the cathode 512 and anode 513. It should be understood that the angle of injection of the liquid suspension 509 relative to the plasma 519 may be varied.

**[00049]** Figure 5 shows that the primary torch gas 516 passes through the arc region and ionizes into a hot plasma state 519 of gaseous ions within the nozzle 505. The liquid suspension 509 is internally injected into the plasma region 519 It should be understood that injection of suspension 509 can occur downstream of the plasma 519 within the anode, which may represent a region where the torch gas 516 has cooled down from the plasma state to a superheated gas. The turbulent flow of the plasma 519 fragments and/or atomizes the liquid carrier droplets of suspension 509 within the nozzle 505 and also at the outlet of the nozzle 505.

**[00050]** As shown in the embodiment of Figure 5, the length of the reactive shroud 501 extends in a continuous manner from the outlet of the nozzle 505 to the substrate surface 508. The shroud 501 provides heat retention to create a continuous thermal envelope and also prevents ejection of the droplets of suspension 509 from the effluent 540. The embodiment of Figure 5 shows that the shrouded reactive gas 501 is configured to flow in a laminar flow rate regime. The controlled and lowered velocity of the laminar flowing shroud 501 can enable the fragmentation phenomena of the droplets of the liquid suspension 509 across the shroud 501 to occur in a more controlled manner compared to conventional SPS systems and processes 100, 200 and 300 of Figs. 1-3. The fragmented droplets of liquid suspension 509 therefore attain an improved uniformity in size distribution. As a result, the coating constituents 515 deposit on the substrate surface 508 to form a coating 503 having a more controlled particle size distribution. It should be understood that certain coating applications may not require substantial fragmentation of the droplets of liquid suspension 509. As such, in another embodiment of the present invention, the shroud 501 can be configured to not fragment the droplets yet still achieve the other benefits of utilizing a shroud 501 that have been mentioned above.

**[00051]** Other injection locations of the liquid suspension are contemplated in accordance with the principles of the present invention. For instance, Figure 6 shows an SPS system and process 600 in which the liquid suspension 609 is injected externally to the torch nozzle 605. The external injection of the liquid suspension 609 can occur in a substantially radial direction at an orthogonal orientation with respect to the axis of the plasma effluent 640. It should be understood that the angle of injection of the liquid suspension 609 relative to the plasma effluent 640 may be varied. Similar to Figure 5, the reactive shrouded gas 601 is configured to flow in a laminar flow rate regime to produce more uniform fragmentation of the droplets of the liquid suspension 609.

**[00052]** Other variations for the reactive gas shroud are contemplated by the present invention. For example, Fig. 7 is a schematic illustration of another embodiment of the present invention employing a dual gas shroud consisting of an inner reactive gas shroud layer 701 and an outer inert gas shield 702 surrounding a suspension plasma spray process 700. The inner reactive gas shroud layer 701 is preferably laminar flowing, as shown in Figure 7. Use of the dual shroud in this specific arrangement may further improve heat retention within the region that the effluent 740 flows within, particle fragmentation of the droplets and temperature uniformity along the substrate 708. The dual shroud also can improve confinement of the coating particulates 715 within the effluent 740 along the flow path, thereby substantially reducing or eliminating coating particulate 715 ejection from the effluent 740. As a result, increased deposition efficiency on the substrate 708 is attained.

**[00053]** In yet another design variation of the reactive gas shroud, Fig. 8 shows a dual reactive gas shroud consisting of a first inner reactive gas shroud layer 802 and a second outer reactive gas shroud layer 801 surrounding a suspension plasma spray process 800. The first inner reactive gas shroud layer 802 is preferably laminar flowing, as shown in Figure 8. Unlike Figure 7, the dual reactive gas shroud has two reactive shrouds. Each of the reactive gas shrouds 801 and 802 is independently controlled (e.g., the flow rates are independently controlled). The gases used for the reactive gas shrouds 801 and 802 may be the same or different. The presence of two reactive shrouds or shields that are independently controlled can help improve combustion reactions along the flow path of the effluent 840. In addition to enhanced combustion resulting from use of a dual reactive gas shroud system and process 800, other chemical reactions may be facilitated with the use of a dual reactive shroud gas in which each of the reactive gas shrouds 801 and 802 preferentially react with specific elements or compounds in the liquid suspension 809 resulting in a chemical reaction that occurs spontaneously or occurs due to the thermal energy of the plasma effluent 840. Such chemical reactions can be designed and controlled to yield improvements in the chemical composition, physical property or microstructure of the deposited coating 803.

**[00054]** Where dual layer shrouds or mixed shrouds are employed using both reactive gases and inert gases, the inert gases typically include argon, nitrogen, and helium or combinations thereof.

**[00055]** Other variations of the reactive gas shroud can be employed. In one example, two or more reactive gas shrouds can be configured, preferably independent of each other, to surround an effluent. In another example, two or more reactive gas shrouds in combination with an inert gas shroud can be employed. The inert gas shroud can be configured between the reactive gas shrouds. Alternatively, the inert gas shroud can be arranged so as to surround all of the reactive gas shrouds. Still, as a further design variation, the inert gas shroud or shield can be positioned within each of the reactive gas shrouds. In another embodiment, a reactive gas shroud may also be selectively configured so as to only surround only a portion of the effluent along its flow path towards the substrate.

**[00056]** The process benefits, some of which have been mentioned above, can translate into more controlled microstructures of deposited coatings. The present invention recognizes that parameters which determine the microstructure and properties of the coatings include the temperature, size and velocity of the coating constituents or particles and the extent to which the particles have reacted with or exposed to the surrounding environment during deposition. In the present invention, the reactive gas shroud can retain heat and create a more uniform temperature and controlled temperature distribution as the coating particles impact the substrate surface. Additionally, the laminar flow reactive gas shrouds can help create more uniformly fragmented coating particles. The shrouded effluent therefore creates an improved microstructure.

**[00057]** Additional factors impacting the microstructure and properties of the deposited coatings include the rate of deposition, angle of impact, and substrate properties, each of which can be controlled to a greater degree, by virtue of the shroud. Since the coating constituents or particles are heated and accelerated by the gaseous effluent of the plasma, the temperature and velocity of the coating particles are a function of the physical and thermal characteristics of the effluent stream and the standoff distance between the exit of the plasma spray device and the substrate. By controlling the properties of the effluent stream by use of the shroud, the temperature and velocity of the coating particles can be controlled with greater precision to improve coating adhesion and coating microstructure.

**[00058]** A specific type of reactive gas shroud which can be employed in the present invention is a flame envelope surrounding the liquid suspension at or near the injection point. Turning now to Figs. 9 through 11 there are shown schematic illustrations of different embodiments of the configuration of a flame envelope, namely depictions of suspension plasma spray systems and processes employing a flame envelope shrouding the axial injection of the liquid suspension; a flame envelope shrouding an internal radial injection of the liquid suspension; and a flame envelope shrouding an external radial injection of the liquid suspension, respectively. The term "flame envelope" as used herein and throughout the specification means a combusting flow formed by the combustion of a fuel and an oxidant which extends along the axis of the injected suspension stream.

**[00059]** Fig. 9 shows a suspension plasma spray system and process 900 employing a flame envelope 910 shrouding the axial injection of the liquid suspension 909. The flame envelope 910 extends from the distal end of the injection nozzle 905 or nozzle face up to a point where the plasma 919 is generated between the cathode 912 and the anode 913. It should be understood that the flame envelope 910 can extend the entire length of the suspension stream being injected from out of the nozzle 905(i.e., extends from the nozzle face to the entry point in the plasma effluent). The flame envelope 910 can provide sufficient thermal energy to evaporate the liquid droplets prior to exiting nozzle 905. As such, dry sub-micron coating particulates 915 can be introduced as the effluent 940 without agglomeration and without clogging in the injector. The flame envelope 910 can also provide sufficient kinetic energy to improve fragmentation of the droplets of the suspension 909 and coating particle 915 size distribution.

**[00060]** Fig. 10 shows an alternative suspension plasma spray system and process 1000 employing a flame envelope 1010 shrouding the radial injection of the liquid suspension 1009. The flame envelope 1010 extends along the injector of the liquid suspension 1009 and can evaporate the liquid droplets prior to being introduced into the effluent 1040. The flame envelope 1010 can also impart sufficient kinetic energy to the droplets of suspension 1009, thereby improving fragmentation and coating particle 1015 size distribution.

**[00061]** The flame envelope may also be configured external of the nozzle as shown in Figure 11. Figure 11 shows a suspension plasma spray system and process 1100 employing a flame envelope 1110 shrouding the radial injection of the liquid suspension 1109. The flame envelope 1110 extends along the injector of the liquid suspension 1109 and can evaporate the liquid droplets prior to being introduced into the plasma effluent 1119. The flame envelope 1110 can also impart sufficient kinetic energy to the droplets of suspension 1109, thereby improving fragmentation and coating particle 1015 size distribution.

**[00062]** As shown in the illustrated embodiments of Figs. 9-1 1, the flame envelope 910, 1010 and 1110 serves several functions. For example, the flame envelope 910, 1010 and 1110 can function as a shroud for the liquid suspension 909, 1009 and 1109 that prevents the entrainment of ambient gases into the injected suspension stream 909, 1009 and 1109 and thereby inhibits unwanted physical and chemical reactions such as oxidation of the sub-micron particles contained within the suspension 909, 1009 and 1109. Preventing entrainment of ambient gases also inhibits velocity decay of the suspension injection and allows the liquid suspension 909, 1009 and 1109 with the sub-micron particles contained therein to penetrate into the plasma 919, 1019 and 1119 with substantial retention of the injection velocity.

**[00063]** Furthermore, the flame envelope 910, 1010 and 1110 also functions as a reactive shroud or partially reactive shroud that, when properly controlled, can initiate desired reactions within their respective liquid suspensions 909, 1009 and 1109 or between the suspension 909, 1009 and 1109 and the shroud gases at or near the point of injection. For example, where the liquid carrier is a fuel, such as ethanol, the flame envelope initiates the combustion reaction of the liquid carrier which increases both the thermal and kinetic energy of the injection event proximate the entry to the plasma effluent. This additional thermal and kinetic energy causes improved fragmentation of the droplets as well as enhanced melting or evaporation of the sub-micron particles in the suspension before they reach the plasma effluent. In applications where the liquid carrier is not a fuel, the flame envelope provides an energy source to evaporate the liquid carrier and melt, partially melt or even evaporate the suspended particles prior to entrainment into the plasma effluent.

**[00064]** Generally speaking, by shrouding the liquid suspension in the flame envelope as it is directed towards the plasma effluent, the process characteristics of the overall suspension plasma spray (SPS) system are radically altered. In short, use of the flame envelop or similar reactive shroud surrounding the injection stream effectively separates the control of the delivery of the sub-micron coating particles to the SPS system, which is accomplished via suspension from a supply vessel, from the control of the entrainment of the sub-micron coating particles into the plasma, which can be in suspension or non-suspension form.

**[00065]** For example, using the disclosed flame envelope surrounding the suspension injection stream enables an SPS system employing delivery of a suspension but entrainment or injection of a dry submicron particle into the plasma effluent similar to APS powder injection, but at the sub-micron particle size. Alternatively, the flame envelope surrounding the suspension injection stream enables an SPS system employing delivery of a suspension but entrainment or injection of melted sub-micron particles into the plasma effluent, the injection of evaporated species of the sub-micron particles into the plasma effluent. Still further, the disclosed flame envelope surrounding the suspension injection stream enables an SPS system employing delivery of a liquid suspension with entrainment or injection of highly fragmented suspension droplets into the plasma effluent. Finally, if properly designed and controlled, the disclosed flame envelope or reactive shroud surrounding the injection stream enables delivery of a liquid suspension wherein the sub-micron particles are reacted in-situ to form the desired ceramic or cermet coating materials which are entrained into the plasma effluent.

[00066] In addition, each of the above-described delivery, injection and entrainment techniques allows more precise control of the average particle size and particle size distribution injected or entrained into the effluent and subsequently impacting the substrate to provide the desired coating microstructures. The use of a flame envelope or reactive shroud surrounding the suspension injection enables new choices or design options for the composition of the SPS liquid suspensions, including make-up of the liquid carriers and particle characteristics.

[00067] Finally, since the flame envelope or reactive sheath/shroud surrounding the liquid suspension injection in reference to the Figures has the potential to provide additional thermal and kinetic energy to the SPS spray process, the present system and method would enable use of lower power plasma torches in an SPS process and a more efficient use of the thermal energy in the plasma stream. Also, the use of the presently disclosed flame envelope or reactive sheath/shroud surrounding the liquid suspension injection provides opportunities to further control and enhance the entire SPS process including: delivery or handling of the suspension; creating of the plasma jet; injection or entraining the coating materials into the plasma jet; and delivery/impact of the coating materials onto the substrate to be coated.

[00068] Through the use of the present flame envelope or reactive sheath/shroud and the additional kinetic energy associated therewith, the injection of the coating materials into the plasma jet is preferably controlled so as to reach the optimized location within the effluent and with reduced interaction by effluent flow at the point of injection. For example, a portion of effluent at or near the point of suspension injection can be deflected to allow the sub-micron particles in either dry powder for, partially melted form, melted form and/or evaporative form to extend further into the effluent stream in a controlled and uniform manner

**[00069]** Alternatively, where the flame envelope or sheath/shroud is employed as part of the SPS process merely to inhibit entrainment of ambient gases into the injected suspension and to allow the liquid suspension to penetrate deeply into the plasma effluent stream, the sheath/shroud is likely to promote further fragmentation of the suspension into droplets in controlled manner and location. By fragmenting the droplets, the flame envelope or reactive gas shroud aids in the control of the droplet size and droplet size distribution of the suspension being injected into the plasma effluent. In this manner, there is less fragmentation occurring in the plasma effluent and droplet size and droplet size distribution will be generally independent of spatial and temporal changes occurring as the plasma effluent moves toward the substrate to be coated. In other words, the droplet size and droplet size distribution is more precisely controlled resulting in improved plasma spray process control and improved coating microstructures Fig. 9 shows another embodiment of the present invention employing a combustion flame shroud surrounding a suspension plasma spray process.

**[00070]** It should be appreciated that the use of dual gas shrouds depicted in Fig. 7 and Fig. 8 as well as the use of a combustion flame shroud surrounding the effluent depicted in Fig. 9 can be equally applied to suspension plasma spray systems utilizing internal radial injection configurations, external radial injection configurations and axial injection configurations.

**[00071]** As indicated above, the typical reactive gases used for the reactive gas shroud include oxygen, hydrogen, carbon dioxide; hydrocarbon fuels, and nitrogen or combinations or combinations thereof.

**[00072]** It is to be noted that the present invention is capable of depositing a wide array of fine particulate sizes in the sub-micron range, previously not possible by coating technologies, including that of conventional plasma spraying. For example, in one embodiment, the SPS system and process of the present invention can deposit coating particulates below 100 nm. In another embodiment, the present invention can deposit coating particulates IOμηι or lower, without incurring undesirable agglomeration of the fine particulates as typically encountered in conventional spray systems and processes.

**[00073]** Advantageously, the SPS system described herein can be prepared utilizing suitable torch and nozzle assemblies that are commercially available, thus enabling and simplifying the overall fabrication process. Aspects of plasma generation can be carried out using standard techniques or equipment.

[00074] Any suitable liquid suspension delivery subsystem can be employed for delivering a flow of the liquid suspension with sub-micron particles dispersed therein to the plasma. The liquid suspension source is a dispenser for the liquid suspension. The source typically includes a reservoir, transport conduit (e.g., tubing, valving, and the like), and an injection piece (e.g., nozzle, atomizer and the like). In addition, the liquid suspension delivery subsystem may contain measurement feedback of the process (e.g., flow rate, density, temperature) and control methods such as, for example, pumps and actuators that can work in conjunction or independently from one another. The system may also contain additional flushing or cleaning systems, mixing and agitation systems, heating or cooling systems as known in the art.

[00075] From the foregoing, it should be appreciated that the present invention thus provides a system and method for reactive gas shrouding of suspension plasma sprays and/or flame sheathing of liquid suspensions. While the invention herein disclosed has been described by means of specific embodiments and processes associated therewith, numerous modifications and variations can be made thereto by those skilled in the art without departing from the scope of the invention as set forth in the claims or sacrificing all of its features and advantages.

## Claims

What is claimed is:

1. A thermal spray system for producing coatings on a substrate from a liquid suspension comprising:

a thermal spray torch for generating a plasma;

a liquid suspension delivery subsystem for delivering a flow of the liquid suspension with sub-micron particles; and

a nozzle assembly for delivering the plasma from the thermal spray torch to the liquid suspension to produce a plasma effluent, the nozzle assembly adapted for producing a reactive gas shroud substantially surrounding said plasma effluent;

the reactive gas shroud configured to substantially retain entrainment of the sub-micron particles in the plasma effluent and substantially inhibit gases from entering and reacting with the plasma effluent;

wherein the reactive gas shroud reacts with the plasma effluent to enhance fragmentation of the suspension droplets and create evaporative species of the sub-micron particles within the plasma effluent.

2. The thermal spray system of claim 1, wherein the shroud extends from the substrate surface to the nozzle assembly.

3. The thermal spray system of claim 1, wherein the shroud is a laminar flowing shield.

4. The thermal spray system of claim 1, wherein the shroud has an axial distance less than a distance from the nozzle to the substrate surface.

5. The thermal spray system of claim 1, further comprising an inert gas shroud disposed about the reactive gas shroud.

6. The thermal spray system of claim 1, further comprising a first reactive gas shroud and a second reactive gas shroud.

7. The thermal spray system of claim 1, further comprising an injector adapted to produce a flame envelope surrounding the flow of the liquid suspension.

8. The thermal spray system of claim 1, wherein the liquid suspension system is configured internal to the nozzle.

10. The thermal spray system of claim 1, wherein the liquid suspension system is configured internal to the nozzle so as to deliver an axial flow of the liquid suspension.

11. The thermal spray system of claim 1, wherein the liquid suspension system is configured external to the nozzle.

12. A method of producing coatings on a substrate using a liquid suspension with sub-micron particles dispersed therein, the method comprising the steps of:

generating a plasma from a thermal spray torch;

delivering a flow of liquid suspension with sub-micron particles dispersed therein to the plasma or in close proximity thereto to produce a plasma effluent stream;

surrounding the plasma effluent with a reactive gas shroud to keep the sub-micron particles entrained within the plasma effluent and substantially prevent entrainment of ambient gases into the plasma effluent;

reacting the shroud gas with the plasma effluent to enhance fragmentation of the suspension droplets and create evaporative species of the sub-micron particles within the plasma effluent; and

directing the shrouded plasma effluent with the sub-micron particles contained therein towards the substrate to coat the substrate.

13. The method of claim 12, further comprising the step of-substantially preventing entrainment of gases into the shrouded effluent.

14. The method of claim 12, further comprising the step of fragmenting droplets of the liquid suspension across the reactive shroud.

15. The method of claim 12, further comprising the step of introducing an inert gas shroud substantially surrounding the effluent.

16. The method of claim 12, further comprising the step of introducing a second reactive shroud gas substantially surrounding the effluent.

17. The method of claim 12, further comprising the step of introducing a flame envelope surrounding the liquid suspension.

18. The method of claim 12, further comprising injecting the liquid suspension external to the nozzle.

19. The method of claim 12, further comprising injecting the liquid suspension internal to the nozzle.

20. A coating deposited on the substrate prepared according to the process of claim 12.

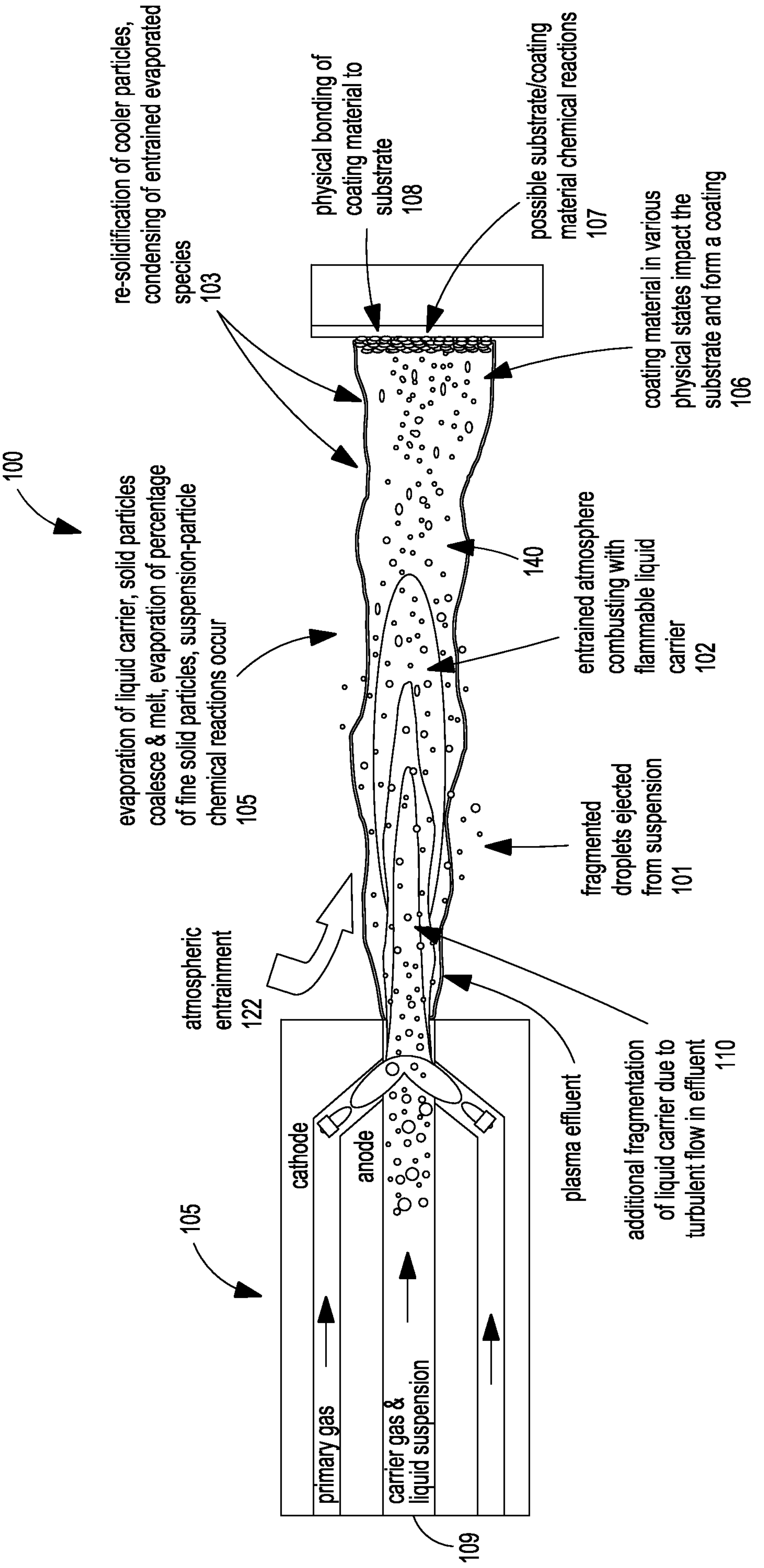


FIG. 1
PRIOR ART

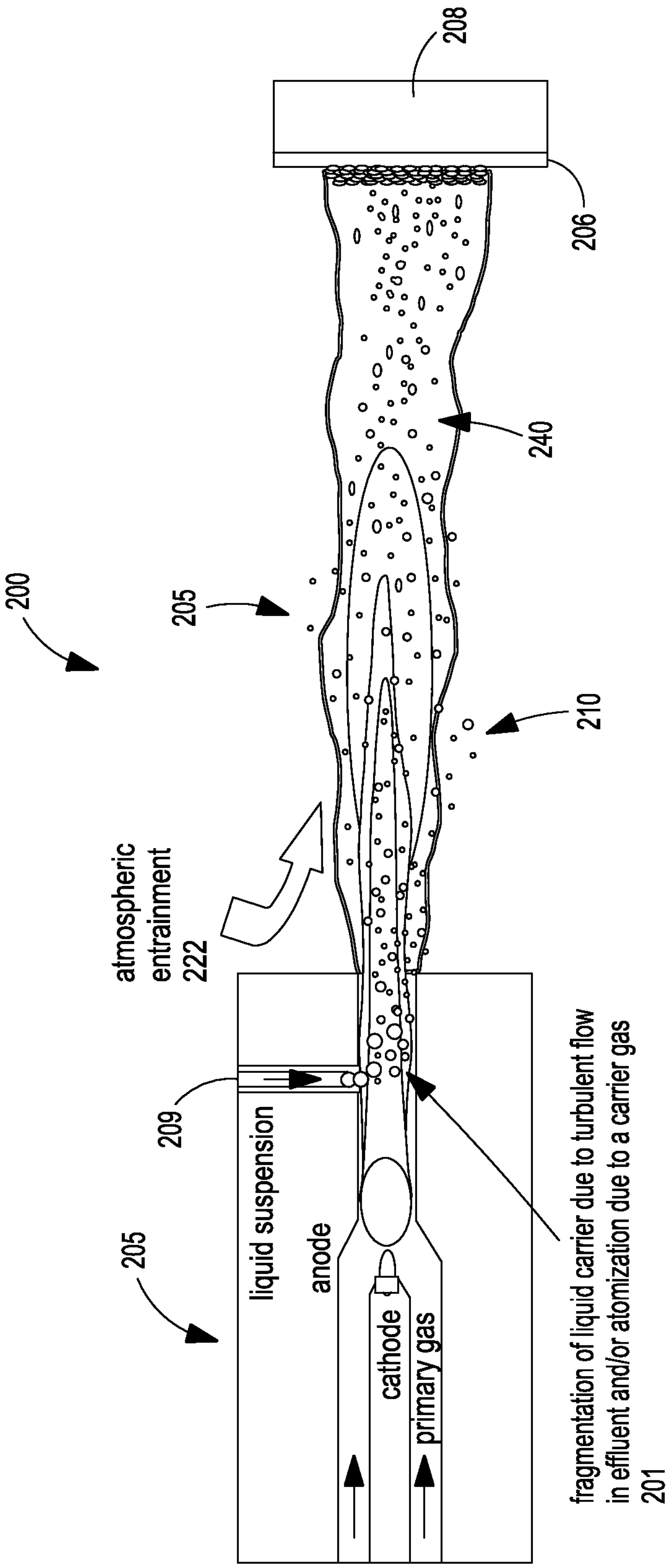


FIG. 2
PRIOR ART

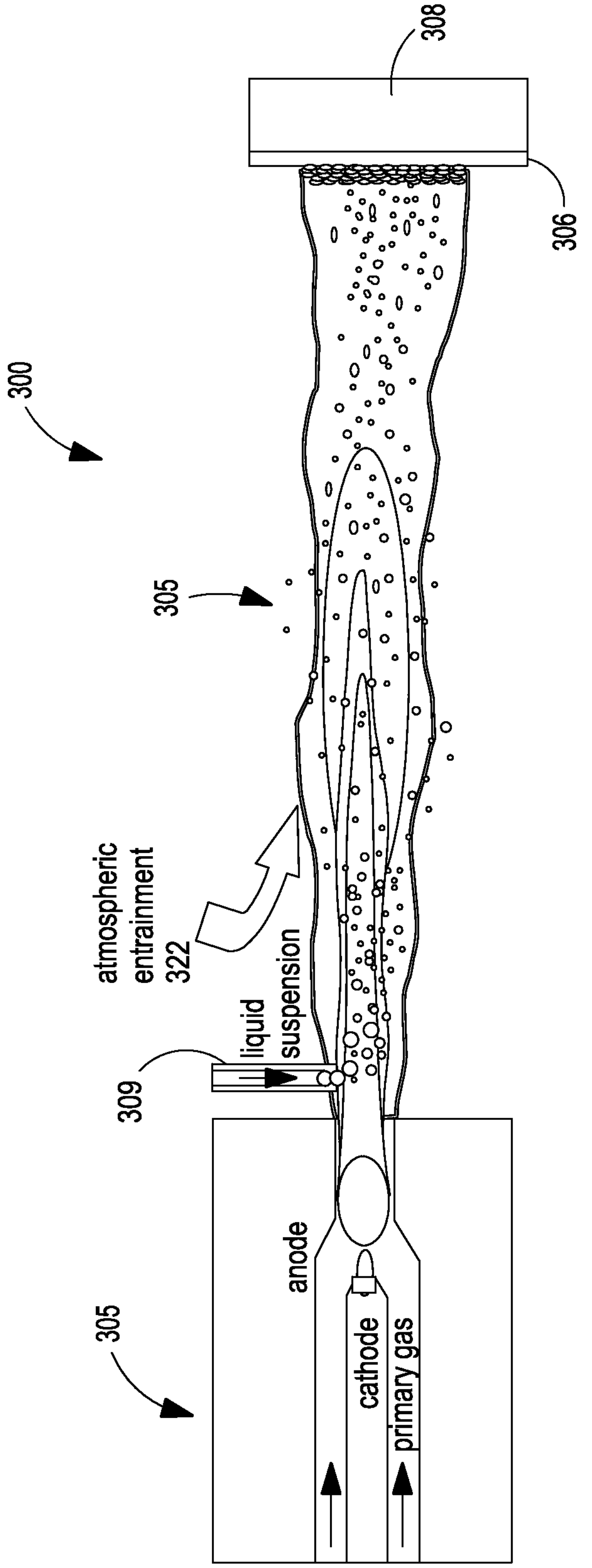


FIG. 3
PRIOR ART

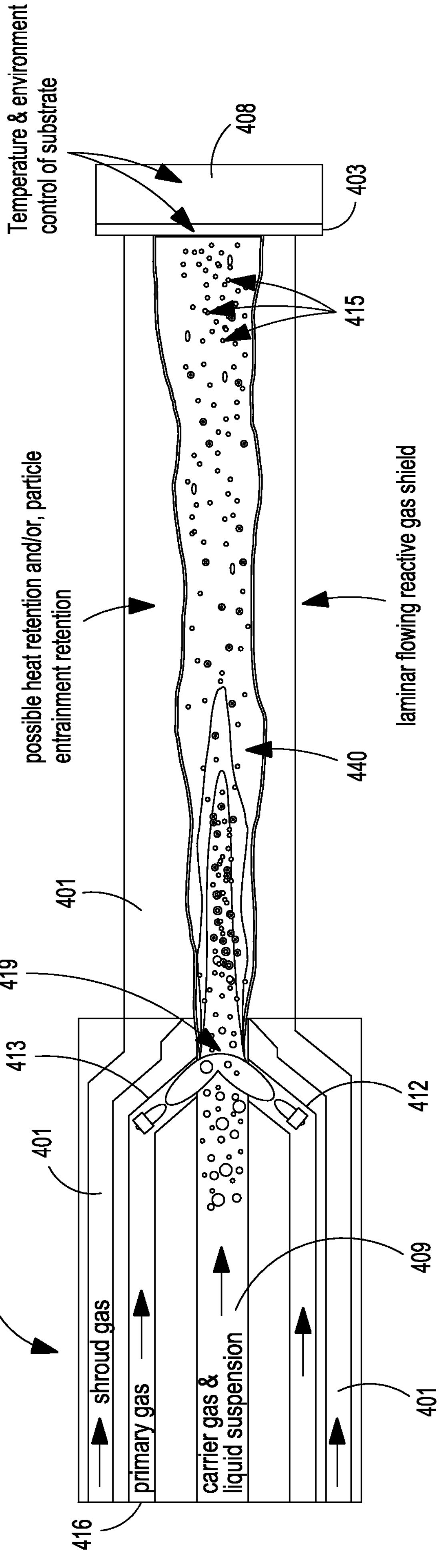
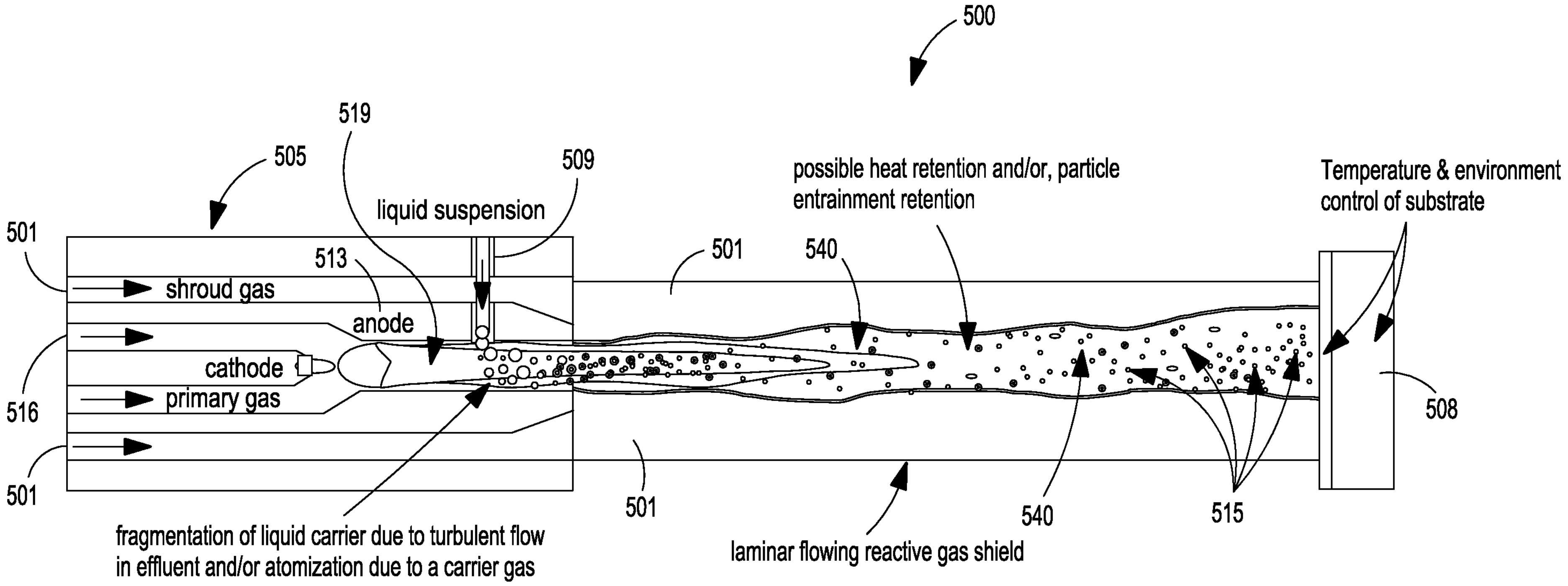

Temperature & environment control of substrate
408
403
415
400
possible heat retention and/or, particle entrainment retention
laminar flowing reactive gas shield
440
401
419
413
412
401
405
shroud gas
primary gas
carrier gas & liquid suspension
409
401
416

FIG. 4


500
505
519
509
liquid suspension
501
513
shroud gas
anode
516
cathode
primary gas
501
fragmentation of liquid carrier due to turbulent flow in effluent and/or atomization due to a carrier gas
501
540
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Temperature & environment control of substrate
501
laminar flowing reactive gas shield
540
515
508

FIG. 5

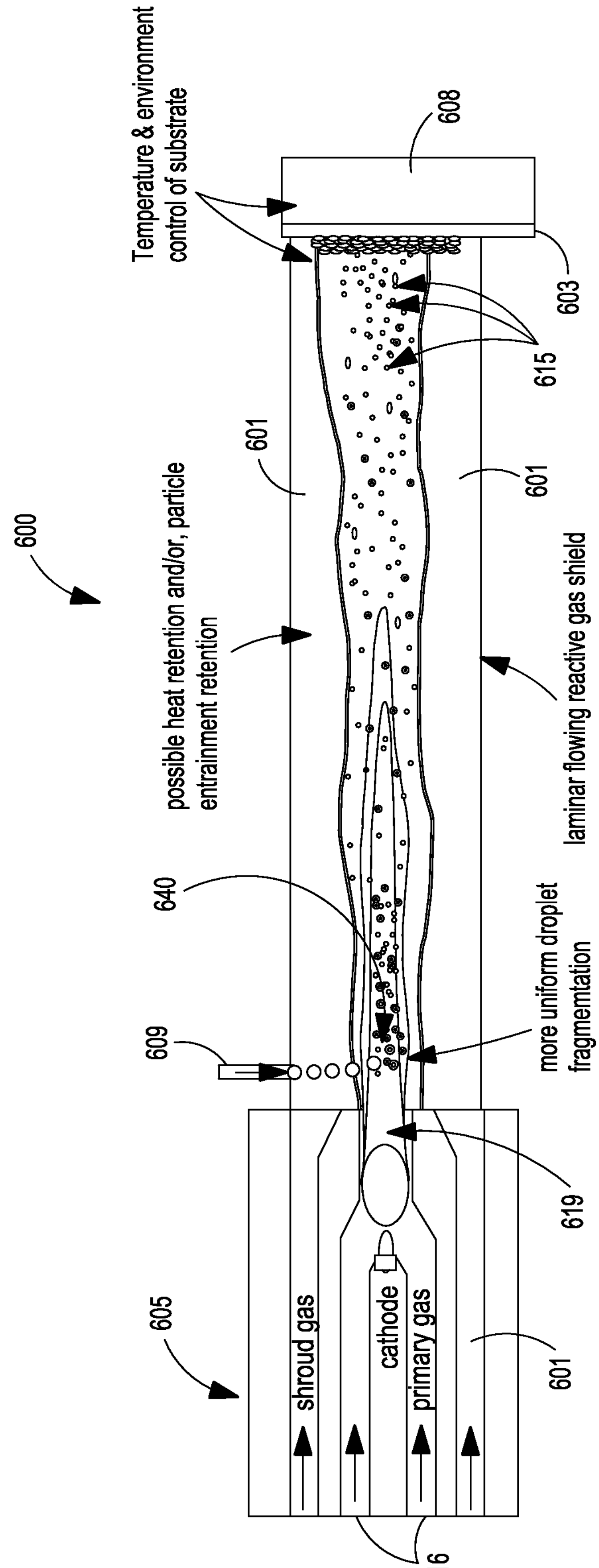

600
608
Temperature & environment control of substrate
603
615
601
601
601
possible heat retention and/or, particle entrainment retention
laminar flowing reactive gas shield
640
609
more uniform droplet fragmemtation
619
605
shroud gas
cathode
primary gas
616

FIG. 6

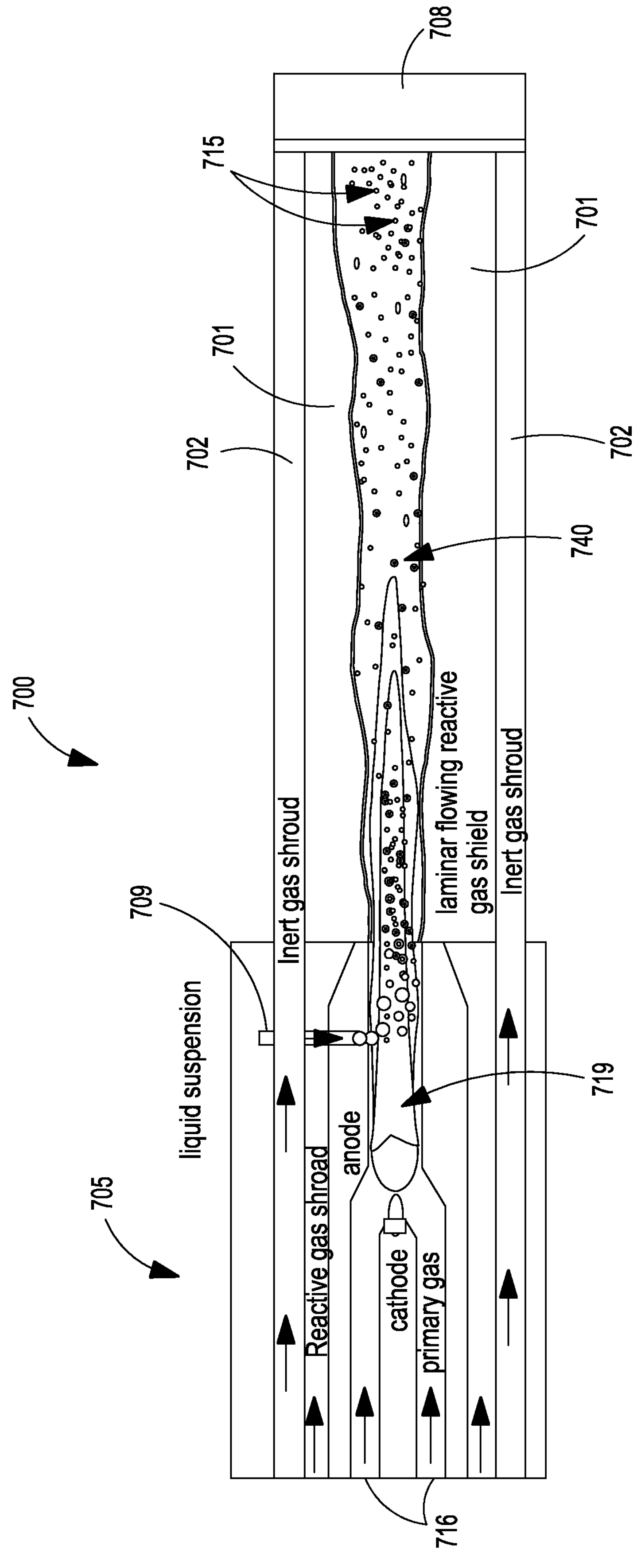
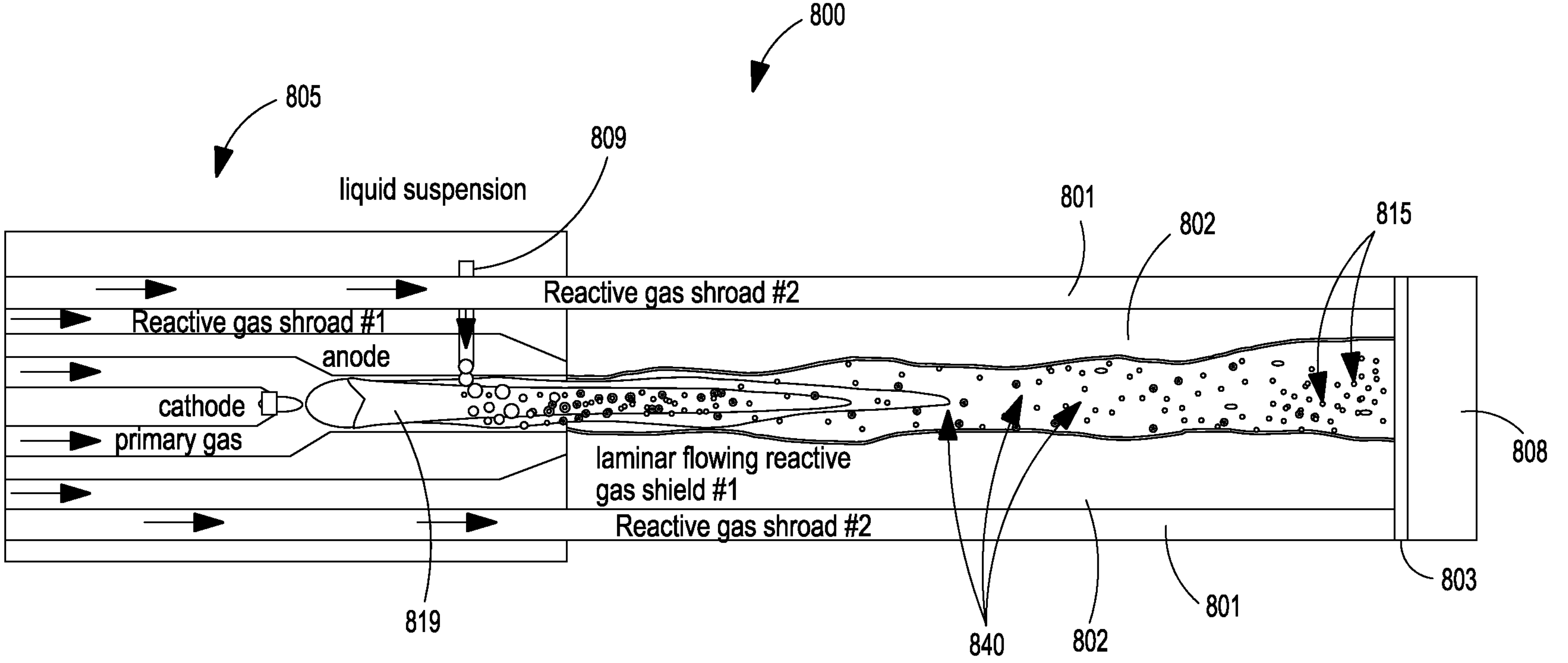

708
715
701
701
702
702
740
700
709
Inert gas shroud
laminar flowing reactive gas shield
Inert gas shroud
liquid suspension
Reactive gas shroad
anode
719
705
cathode
primary gas
716

FIG. 7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805
809
liquid suspension
801
802
815
Reactive gas shroad #2
Reactive gas shroad #1
anode
cathode
primary gas
laminar flowing reactive
gas shield #1
Reactive gas shroad #2
808
803
819
840
802
801

FIG. 8

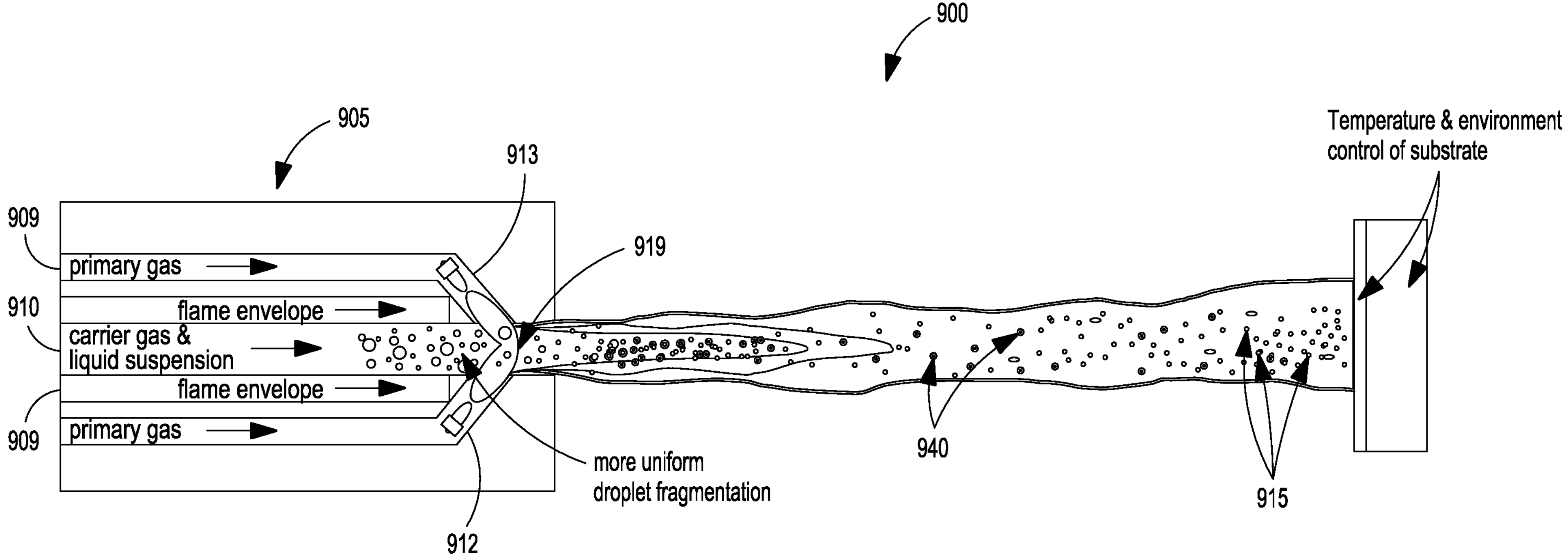
900
905
913
919
Temperature & environment
control of substrate
909
primary gas
910
flame envelope
carrier gas &
liquid suspension
flame envelope
909
primary gas
912
more uniform
droplet fragmentation
940
915

FIG. 9

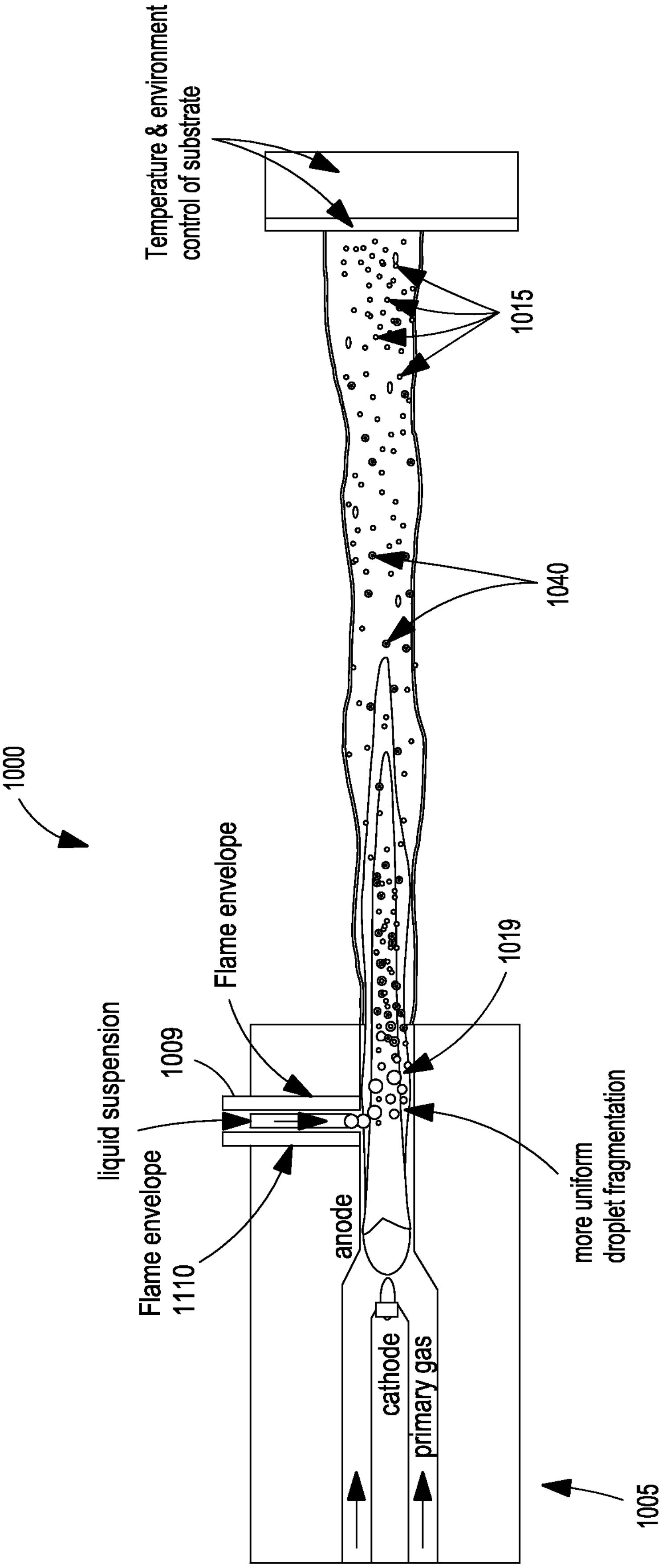
Temperature & environment control of substrate
1015
1040
1000
Flame envelope
1019
liquid suspension
1009
Flame envelope 1110
anode
more uniform droplet fragmentation
cathode
primary gas
1005

FIG. 10

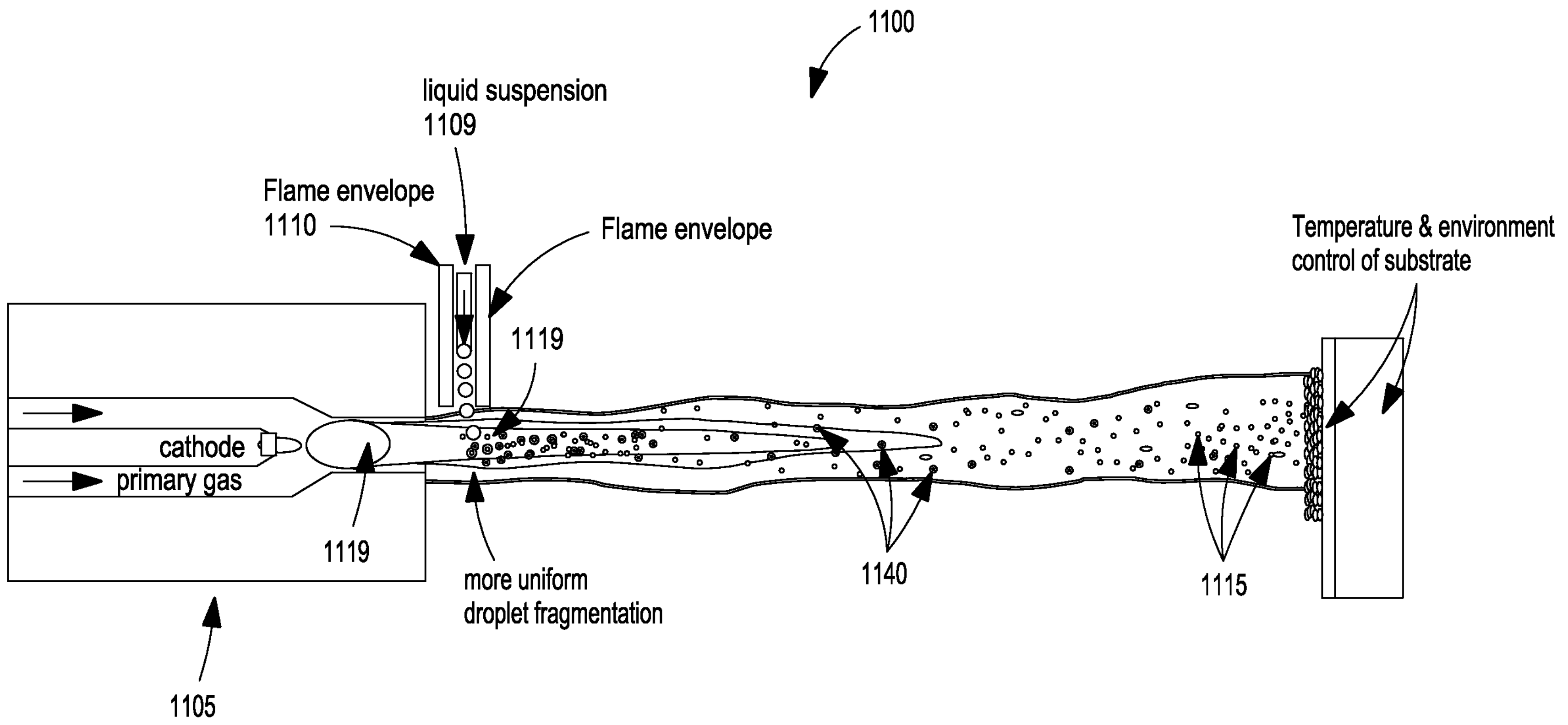
1100
liquid suspension
1109
Flame envelope
1110
Flame envelope
1119
cathode
primary gas
1119
more uniform
droplet fragmentation
1105
1140
1115
Temperature & environment
control of substrate

FIG. 11