



Review on Cold Spray Process and Technology: Part I—Intellectual Property

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The number of research papers as well as of patents and patent applications on cold spray and cold spray related technologies has grown exponentially in the current decade. This rapid growth of activity brought a tremendous amount of information on this technology in a short period of time. The main motivation for this review is to summarize the rapidly expanding common knowledge on cold spray to help researchers and engineers already or soon to be involved for their future endeavors with this new technology. Cold spray is one of the various names for describing an all-solid-state coating process that uses a high-speed gas jet to accelerate powder particles toward a substrate where they plastically deform and consolidate upon impact. Cold gas dynamic spray, cold spray, kinetic spray, supersonic particle deposition, dynamic metallization or kinetic metallization are all terminologies found in the literature that designate the above-defined coating process. This review on cold spray technology is divided into two parts. In this article, Part I, patents and patent applications related to this process are reviewed, starting from the first few mentions of the idea at the beginning of the 20th century to its practical discovery in Russia in the 1980s and its subsequent occidental development and commercialization. The patent review encompasses Russian and USA patents and patent applications. Part II will review the scientific literature giving a general perspective of the current understanding and capability of this process.

Keywords cold gas dynamic spraying, cold gas dynamic spraying of nanopowders, TS process reference information

1. Introduction

In recent years, thermal spray technologies have evolved from fairly crude processes that were relatively difficult to control into increasingly precise tools for which the process is tailored to take into account the properties of both the deposited material and the required coatings. For instance, the development of the HVOF process has enabled the wide usage of carbide and metal-based coatings for demanding applications. Plasma spray systems have been redesigned, and the use of new diagnostic tools has resulted in process reliability not previously achievable. Nowadays, thermal spray technology is well implanted in industry. Coatings are produced for numerous applications such as thermal barrier, corrosion protection, wear protection, or biomedical implants to name a few. Fundamentally, thermal spray processes require the

melting or partial melting of the feedstock powder to produce a coating, splat by splat, into a lamellar structure. For some materials, the use of high processing temperature causes issues. For oxygen-sensitive materials for instance, it is often required to produce coatings in an expensive vacuum chamber, thus limiting broader penetration of thermal spray for some commercial applications. For temperature-sensitive materials, there are sometimes no solutions. These limitations seem to be overcome for some materials by the newest thermal spray process—cold spray. Cold spray is an all-solid-state process, thus making it suitable for the deposition of oxygen-sensitive materials such as aluminum, copper, or titanium or for temperature-sensitive materials such as nanostructured and amorphous powders. This specificity enables the development of new markets that, up to now, were not accessible to thermal spray technologies. Furthermore, cold spray is known to present other characteristics that offer unique advantages compared to existing spray technology: (i) the coatings can exhibit wrought-like microstructures with near theoretical density values; (ii) the spray trace is small (typically 1–25 mm²) and well defined allowing for precise control on the area of deposition; (iii) the coatings can be produced with compressive stresses, thus ultra thick (5–50 mm) coatings can be built-up without adhesion failure (Ref 1) and three-dimensional free-standing structures can be built at high deposition rates, which make cold spray extremely promising for spray forming and repairs; and (iv) coatings can be deposited on temperature-sensitive materials such as glass or polymers.

Although the cold spray process has been known for more than 20 years, its commercial development started

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only in the early 2000s. Since that time, the number of publications on this subject has grown exponentially, reaching a critical value for which a literature review would be helpful to scientists, engineers, and management staffs who are currently using this coating technology or who are examining the possibility of implementing it into their current facilities. Moreover, it appears that there is a clear need by many scientists and industrialists to clarify the patent history of cold spray technology. It was noticed that there has been a trend in the last few years of patenting every idea that can use cold spray, leading to some confusion in the community regarding the potential commercial usage of the technology.

This review of the cold spray technology is divided in two parts. In Part I, patents and patent applications related to this process are reviewed, starting from the first few mentions of the idea at the beginning of the 20th century to its practical discovery in Russia in the 1980s and its subsequent occidental development and commercialization. The patent review encompasses Russian and USA patents and patent applications as most of the new inventions were protected in these two countries. It is worth mentioning that these patents are summarized and reviewed in this article based on the information given in the official patent documents without further extensive critical review. In some cases, the patented inventions seem difficult to put onto practice. In Part II, the scientific literature is reviewed, giving a general perspective of the current understanding and capability of this process. Fundamentals of gas dynamics in cold spray, coating build-up, and the influence of process parameters on coating properties are summarized and presented in the second part of the article.

1.1 Historical Perspective on Cold Spray Technology

Even though cold spray is the newest member of the thermal spray family, mention of this process can be found one century ago, before thermal spray itself. The following section relates some patent precursors to this technology, giving an historical perspective to cold spray.

In 1900, Thurston (Ref 2) filed a patent for a method of applying a metal upon another. In this method, metal particles are thrown upon or against a metal plate by a blast of pressurized gas with such force as to cause the particles to become embedded in the surface of the metal article and to form a permanent coating. The schematic of this invention is shown in Fig. 1. It is composed of a chamber (D) into which both the air supply and metal particles enter from the air pipe (B) and hopper (C). The particles are propelled through the nozzle by the action of the gas flow.

With such a method, the velocity of the propelling air gas is limited and consequently the maximum particle velocity is expected to be less than 350 m/s for room temperature deposition. According to today's knowledge and within this maximum expected particle velocity, the variety of metals that can be used to coat an article must have been limited. In a concomitant patent, Thurston (Ref 3) disclosed an

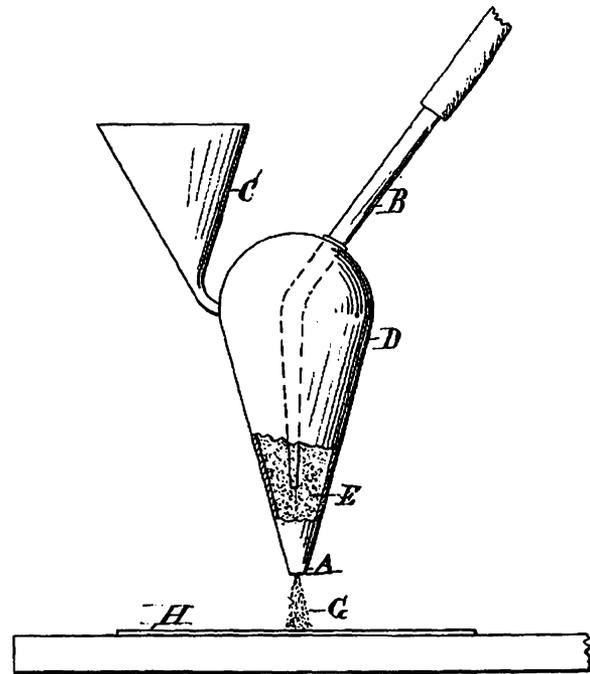
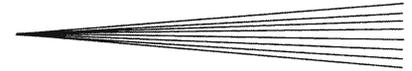


Fig. 1 Schematics of Thurston's invention patented in 1902 (Ref 2)

improvement to this method by heating up the metal to be coated. Even though the heating of the substrate should facilitate the deposition of metal particles, it is foreseen that Thurston's invention must have had limited coating capabilities.

Despite the fact that supersonic nozzles were already known in the 19th century, it took more than 50 years after Thurston's patents to find a report on the use of a supersonic gas flow to propel powder particles at higher velocities in order to apply a coating to an article. Indeed, in 1958, Rocheville (Ref 4) filed a patent to protect a device that essentially uses the method patented by Thurston but using a DeLaval type nozzle with high pressure air to propel the fine powder particles at higher velocity in order to form a coating. The inventor explains that powder particles are propelled by the supersonic blast of air directed against a workpiece and as a result the powder adheres to the surface where it is firmly retained. He mentioned that a thin layer is formed which is uniform over the entire surface, the coating being built up only over the surface of the part but not upon itself. It was believed that the adherence to the part was to some extent from the entry of the micron-size particles into the pores of the surface of the parts and in some cases when lower melting temperature materials were used, fusing of the metallic powder particles may have taken place because the friction of these particles passing through the nozzle may have raised the particle temperature significantly. It appears that even with the use of a supersonic nozzle the device proposed by Rocheville could not propel the powder particles to velocities high enough to produce thick coatings on a part. The nozzle and powder feeder



designs are important factors that may have been difficult to control at that time, resulting in non-optimized spray conditions.

In the 1980s, a group of scientists from the Institute of Theoretical and Applied Mechanics of the Siberian Branch of the Russian Academy of Sciences (ITAM of RAS) in Novosibirsk, Russia, conducted experimental and theoretical work on the interaction of a two-phase flow with the surface of immersed bodies. They used new gas dynamics diagnostic tools to study two-phase flow around bodies, which resulted in the discovery of what they called the “cold spray” phenomenon (Ref 5). One outcome of their work has been the invention of a method (Ref 6) and a device (Ref 7) for accelerating powder particles by a high-pressure gas at temperatures significantly below their melting points in order to apply to a work piece a dense thick highly bonded coating. This coating process, which they called the cold gas dynamic spray method, has since successfully permitted the deposition of a large variety of materials such as metals, alloys, polymers, or mixtures.

Almost a century after Thurston’s invention, a new generation of scientists, helped with modern technology, has brought this old idea to a breakthrough in the coating industry.

1.2 Search Strategy

1.2.1 Overview. This technical review of patents and patent applications, referred to as intellectual property (IP), on cold spray covers exclusively the Russian patents and the USA patents and patent applications. As most of the patent applications were filed in these two countries, it is believed that this review offers an extensive overview of the IP on cold spray technologies. Cold spray designates an all-solid-state coating process using a high-speed gas jet to propel powder particles toward an article where they plastically deform and consolidate upon impact. Other designations of processes that fit this definition are found in the literature such as cold gas dynamic spray (CGDS), cold spray (CS), kinetic spray (KS), supersonic particle deposition (SPD), dynamic metallization (DYMET) or kinetic metallization (KM). For simplicity, the designation cold spray or CS will be exclusively used for this review and refers to all the processes that correspond to the above definition, though a consensus still needs to be made across the scientific community for choosing a unique terminology for this technology.

1.2.2 Statistics. A search was performed using the invention database FAMPAT (Ref 8) containing patent publications from 78 patent authorities. The search returned 116 granted inventions and 174 published patent applications relevant to cold spray. All these patents were separated into two categories: the first one, called inclusive, refers to patents that include the cold spray technology as one of the many coating methods that can be employed for the purpose of the invention. The second category, called exclusive, refers to patents that protect an idea that uses exclusively cold spray as part of the invention. The technical IP review reported in this article will include only inventions that are in the latter category.

A total of 82 invention disclosures were found to be exclusive to the cold spray technology with 55 written in English and 27 in other languages. Since no critical review was done on patent applications, those were treated independently and are covered in a separate section of this article. Out of the 55 English-written inventions, 49 patents have the USA as priority country and 53 have been patented in the USA. It is expected that some inventions were not found because no abstract was provided in English, the searching language used. However, it is believed that this is unlikely the case for broadly patented inventions and is limited to inventions patented in one country in which the language is not English. It is expected that, due to the large market and high research activities in cold spray, the USA patents should include the most important part of the world intellectual property on this subject.

However, since cold spray was first developed in Russia in the 1980s and because no USA patents obtained by Russian inventors or Russian organizations could be found until the late 1990s, it is expected that a significant number of early patents in cold spray have been published only in Russian during the 1985-2000 period. Consequently, a separate search through three databases, namely RUPAT, RUPAT_OLD, and RUABEN, available at the Federal Institute of Industrial Property (FIPS) of ROSPATENT (RUSSIA) (Ref 9), was conducted, covering the 1924-2007 period. A total of 36 relevant patents exclusive to cold spray were found in these databases.

The technical review on cold spray patents presented in this section is divided in two parts. As the early IP on cold spray was developed in Russia, the Russian patent review is presented first, followed by the USA patent review. Finally, a brief review of USA patent applications exclusive to cold spray technology is presented despite the fact that no critical review of these documents has been done. This latter section gives an indication of the trends in the IP related to cold spray today.

2. Russian Patents Review

2.1 General Overview

In Russia, three groups of researchers have significantly contributed to the early development of the cold spray technology. The discovery of the cold gas dynamic spray process and the original experimental and theoretical work occurred in the 1980s at the Institute of Theoretical and Applied Mechanics of the Siberian Branch of the Russian Academy of Sciences (ITAM of RAS), now called Khristianovich Institute of Theoretical and Applied Mechanics. The main inventors from this organization are A.P. Alkhimov, V.F. Kosarev, and A.N. Papyrin. In the 1990s, the Obninsk Center for Powder Spraying (OCPS) brought noteworthy developments to the cold spray technology and it became a leading Russian company producing, selling, and supporting DYMET® gas-dynamic coating equipment. The main inventors associated with the OCPS are A.I. Kashirin, O.F. Kljuev, A.V. Shkodkin, and T.V. Buzdygar. Researchers from the Moscow

Aviation Institute (State University of Aerospace Technologies) have also participated significantly in the development of the cold spray technology during the 1990s, with the main inventors being J.V. Dikun, P.V. Nikitin, and A.G. Smolin. Figure 2 shows the number of inventions granted to the main Russian inventors. Overall, these three groups of researchers have patented 35 out of the 36 Russian cold spray inventions found in the review.

Figure 3 presents the number of Russian inventions as a function of their priority year. Of the 36 Russian patent families, 34 have Russia as priority country and 2 have the USA. Twenty-four inventions have a priority year before 2000 with five of these patented outside Russia. These

results confirm that a tremendous amount of work has been done on cold spray in Russia many years before this technology was exported and commercialized in the USA, and most of this IP were not spread outside of Russia. Due to both the language issue and the small coverage of these inventions, it was not surprising to find some of those protected ideas in some of today's USA patent applications.

2.2 Technical Review

Unless specified otherwise, the inventions described in this section were patented only in Russia or in the former USSR.

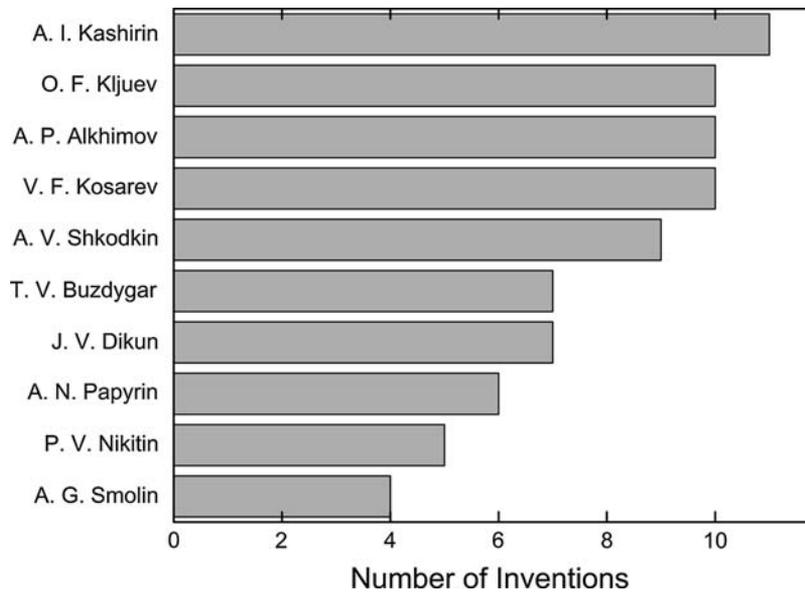


Fig. 2 Number of inventions patented by the main Russian inventors

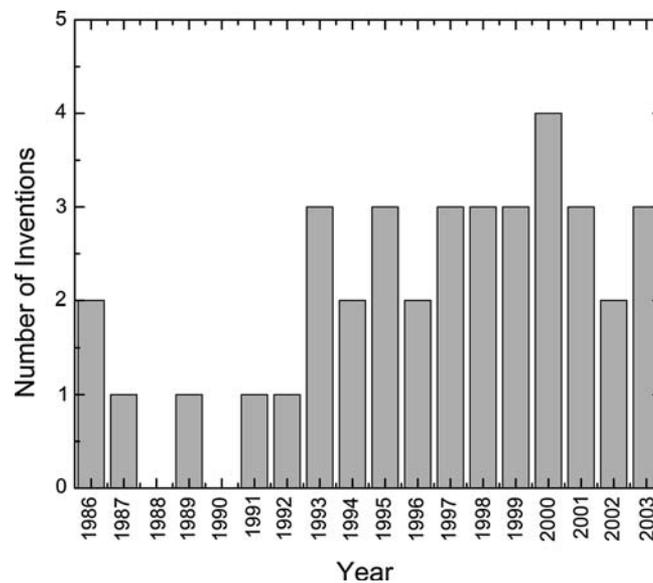


Fig. 3 Yearly number of Russian inventions against their priority year

2.2.1 Early Cold Spray Inventions. Alkhimov et al. developed the early cold spray inventions in the 1980s. They filed in 1986 the first two cold spray patents that were issued in 1991 in the Soviet Union. The first patent claims a method for applying a coating to an article that consists of the acceleration (650-1200 m/s) of powder particles (1-200 μm) by an unheated gas stream (Ref 6). The second patent (Ref 7) claims a device for applying a coating using the previous method consisting of a mixing chamber (3) with an intermediate nozzle (4), a powder feeder fabricated as a crenellated roll (9), and a supersonic rectangular nozzle (2) as shown schematically in Fig. 4.

Improvements to this original device with preheated gas chamber permitting particle velocity control were patented in 1987 and 1989. In the 1987 patent, the method of using a preheated gas-powder mixture is proposed (Ref 10) and in the 1989 one, a device that has two separate ducts, one for the preheated gas and one for the gas-powder mixture, is disclosed (Fig. 5) (Ref 11).

These four inventions were at the basis of the first USA cold spray patent issued to Anatoly Payrin in 1994

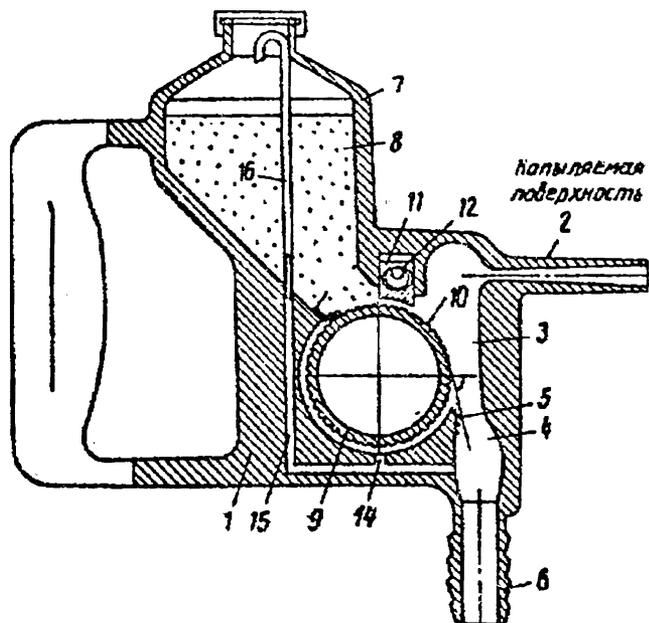


Fig. 4 First device for applying a coating by cold spray patented in 1986 in Russia (Ref 7)

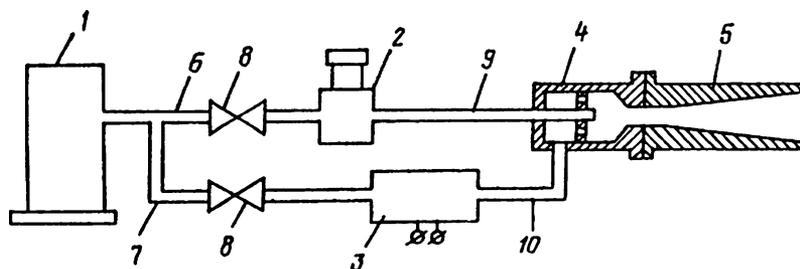


Fig. 5 Cold spray apparatus with separated ducts for preheated propelling gas and for gas-powder mixture (Ref 11)

(priority year 1990), which is described later in the high-pressure cold spray method section of the USA patent review (Ref 12).

2.2.2 Powder Injection in the Supersonic Region of the Nozzle. In 1996, Kashirin et al. (Ref 13) proposed a modified device for the injection of powder particles. The main feature of this device is that the powder material from the feeder-dispenser is fed through a separate line into the diverging part of the nozzle. It is claimed that this design reduces the apparatus weight and heat loss, and that increased operational safety is obtained since the pressure at the injection location is reduced. This invention is patented in the USA (Ref 14) and is described in more detail in the low-pressure cold spray system section.

Shkodkin developed a method where preheated powder is injected in the diverging portion of the nozzle and a heat exchanger is used to remove heat from the nozzle walls. It is claimed that this provides enhanced operational reliability and reduction of particle adhesion on the nozzle walls (clogging) (Ref 15).

2.2.3 Transportable and Portable Cold Spray. The first portable cold spray apparatus was patented by Nikitin et al. (Ref 16) in 2004. The invention filed in 1999 consists of a device that contains a pistol-type body with a DeLaval nozzle, powder and working gas feeding pipes, control button and gas-powder mixing chamber that is linked with the powder and working gas feeding pipes (Fig. 6).

Improvement of the original cold spray apparatus was made in the early 2000s by Alkhimov et al. The device comprises two units interconnected by means of flexible pneumatic and electrical lines. The spraying unit is made in the form of a portable remotely operated hand tool, which includes a converging-diverging nozzle rigidly connected with a preheating unit and a control and monitoring unit having electronic systems for presetting and automatic maintenance of the temperature of the working gas (Ref 17).

A portable apparatus also with a hand-held spraying unit (Fig. 7) was invented by Kosarev et al. (Ref 18). The novelty of this invention resides in the deposition unit that has a DeLaval nozzle and a gas heater rigidly connected with it. It is claimed to have enlarged manufacturing possibilities, simplified design, lowered mass, improved capability for repairing works, and enhanced operational efficiency. (This invention was also patented in China.)

Kashirin et al. (Ref 19) also filed a patent in 2003 describing a portable cold spray apparatus that comprises

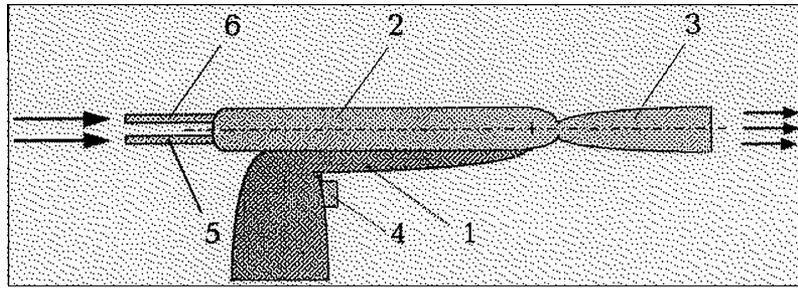


Fig. 6 First portable cold spray gun patented by Nikitin et al. (Ref 16)

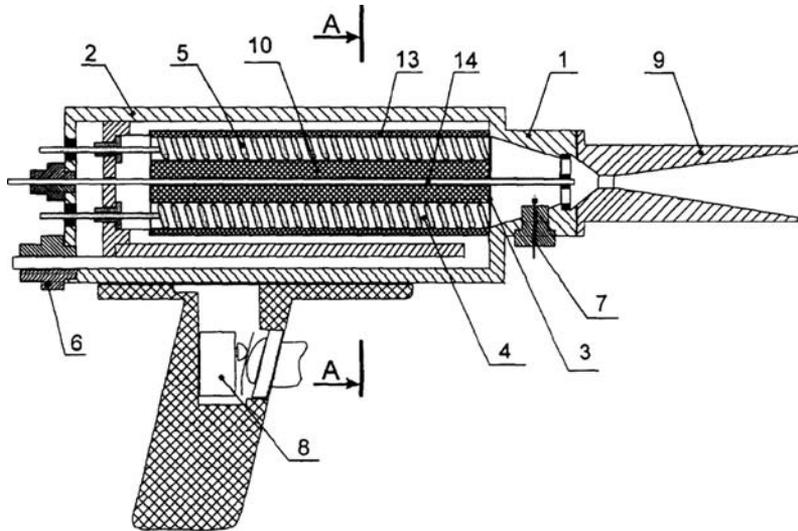


Fig. 7 Spraying unit remotely operated hand tool (Ref 18). The novelty of this invention resides in the capacity of heating the working gas in the spray unit for improved performance

a hand tool spraying unit composed of an electric heater of compressed gas and a DeLaval nozzle. As opposed to the other portable systems, the powder is fed into the diverging portion of the DeLaval nozzle at an inclination angle relative to its axis. The inventors claim that this configuration results in an enhanced spraying efficiency due to the uniform distribution injection of the powder along the nozzle.

2.2.4 Nozzle Design. Numerous nozzle shapes and designs have been proposed throughout the years but few of them have demonstrated major improvements over the original nozzle design. They are nevertheless briefly reported here.

A novel nozzle design, proposed by Alkhimov et al. (Ref 20), is claimed to increase the operating capability by increasing the spray area while limiting the angle of divergence to keep a steady gas flow. The nozzle is in the form of a few pneumatic channels with individual gas-powdered mixture feed channels and with a common pre-chamber (Fig. 8).

In the invention of Dikun (Ref 21) filed in 1998, the powder is subjected to preliminary acceleration by inert gas and then introduced in the core of the accelerating flow of the working gas. Furthermore, it is claimed that

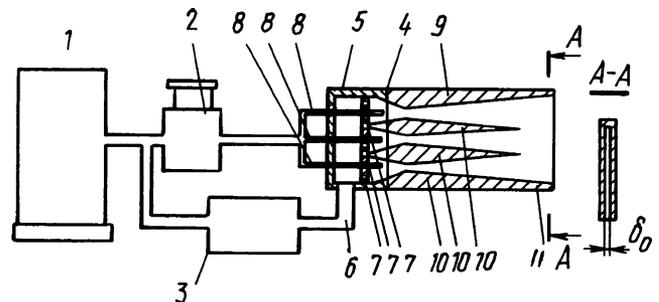


Fig. 8 A multi gas-powder mixture channels nozzle patented in 1994 for increasing the spray area while limiting the angle of divergence of the supersonic sections to ensure a steady flow (Ref 20)

powder particles are separated from the gas by diverting the supersonic flow from its direction using a curvilinear surface. (This invention was also patented in Canada and in Europe.)

Krysa et al. (Ref 22) patented a nozzle in which the converging section is divided into an upper and a lower part, as shown schematically in Fig. 9. The gas-carrier flow

is mixed with the powder and passes through the upper part of the section while the heated gas-carrier flow passes through the lower part. Both flows are accelerated and superimposed in the subsequent region and the cumulative jet is directed to an article. It is claimed that the advantage of such a design is the small apparatus size required. (This invention was also patented in the USA and is described in more detail later in the USA section (Ref 23).)

Kashirin et al. patented a method in which the novelty resides in the deceleration of the gas flow into the long constant cross-sectional portion of the nozzle (part 7 of Fig. 10) to subsonic speed due to wall friction. It is claimed that this design provides an increased deposition efficiency due to the significant temperature increase of the particles (Ref 24). The heated particles remain in the solid state but

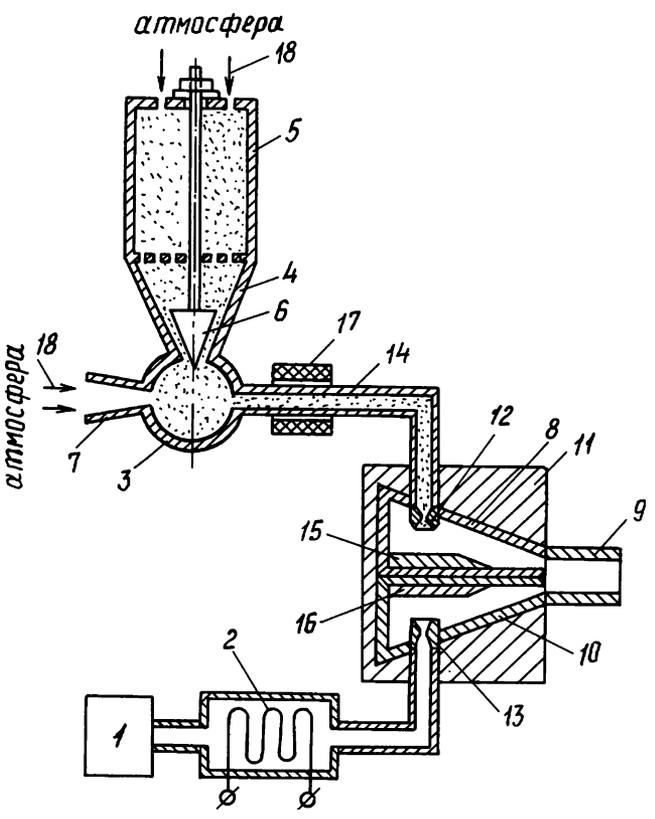


Fig. 9 Small size nozzle composed of an upper and a lower part generating two flows that are accelerated and superimposed to form a steady flow with particles (Ref 22)

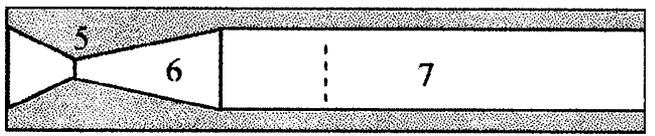


Fig. 10 Long cross section nozzle patented by Kashirin et al. (Ref 24) in 2004 for reducing gas velocity due to wall friction and increasing particle temperature for improved deposition efficiency

become more ductile, which favors their deformation upon impact and thus favors their adhesion.

2.2.5 Other Apparatus and Methods. In 1999, Dikun and Kapbasov (Ref 25) patented the method of pulsed cold spray coatings in which the heated gas is pulsed to 2-50 Hz. It is claimed that instead of a stable shock wave near the target (bow shock), the pulsations will result in a moving shock wave so that the size of the high-pressure zone near the target will vary, allowing for higher deposition efficiency and enhanced coating properties.

Nesterovich et al. suggested the use of a superheated steam, in particular water steam, to accelerate the powder particles. They claimed that using steam instead of gas increases the spray efficiency (Ref 26).

2.2.6 Coating of the Inner Surfaces of Holes and Surfaces of Long Articles. Dikun (Ref 27) patented an equipment for applying coatings to the inner walls of dead and through openings of elongated objects. It provides a supersonic powder-gas flow mixture in a predetermined direction with required thermal and gas-dynamic parameters to form coatings of required thickness on the inner surfaces of elongated objects of different configuration without rotating the objects, as well as on surfaces of dead and through openings. A schematic of this device is shown in Fig. 11. It is claimed that the particles and the flow change their direction into the curved nozzle.

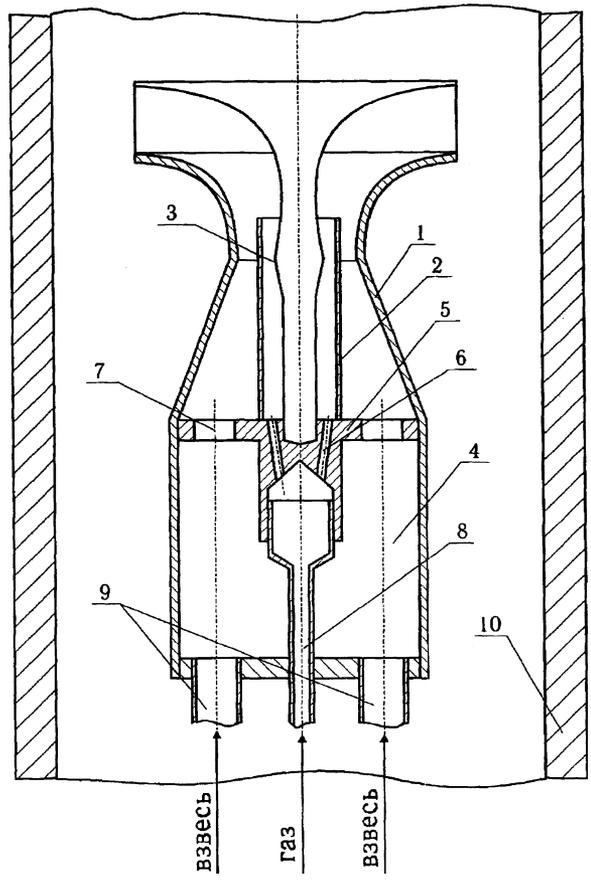


Fig. 11 Apparatus for applying coating to inner walls of dead and through openings of elongated objects (Ref 27)

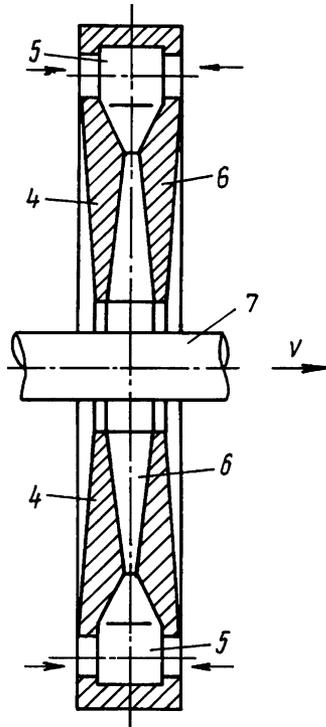


Fig. 12 Device for applying a coating on the outer part of long circular objects (Ref 28)

Nikitin et al. have patented a few inventions for applying coatings onto the inner and outer surfaces of long articles such as rolling mills. The device for application onto the outer surface offers a spraying head that consists of an annular prechamber and a supersonic circular nozzle (Ref 28). The cross-sectional drawing of this device is shown in Fig. 12. During the process, the article is moved across the circular nozzle and thus is simultaneously coated all around its surface without the need to be rotated.

Nikitin et al. patented two other designs based on the previous device for deposition of coatings on the external (Ref 29) and internal (Ref 30) surfaces of items.

Alkhimov et al. addressed the issue of coating the inner surface of pipes with a set-up made of a spraying unit mounted in movable hollow bars. Gripping and turning mechanisms connect the pipe to be coated with an isolating chamber and a suction system that forms a dust isolating channel allowing collection and reprocessing of powder (Ref 31).

2.2.7 Mixtures of Powders in Cold Spray. A patent describing the method of producing a coating using cold spray with a mixture of ductile and brittle particles as feedstock powder was granted to Buzdygar et al. (Ref 32) in 1995. According to this patent, at least two components have to be used: ductile metals or their alloys and materials whose hardness exceeds that of ductile metals, such as ceramics. The hard particles are included in the sprayed powder for the so-called hammer effect. The shocks of the impinging hard particles deform the deposited ductile particles, thus reducing the porosity of the coating and

increasing its hardness. These inventors also protected an application of this method for manufacturing filter elements by deposition onto grids (Ref 33). A variant of this coating method consisting in the deposition of a mixture of powders of two metallic components and hard spherical particles of at least 30 μm diameter on average (Ref 34) was patented by Kashirin et al. in 1998.

In 2001, Buzdygar et al. (Ref 35) filed a patent application for a cold spray method where two different inorganic powder materials are fed simultaneously: one generally made of metal, into the converging section of the nozzle, and the other made of hard particles such as ceramics, in the diverging part. It is claimed that this increases the deposition efficiency without deteriorating the surface of the throat, thus ensuring a longer life of the nozzle.

Dikun et al. (Ref 36) proposed a method in which the carrier gas is preheated up to temperatures where chemical reaction initiation can be attained with selected materials. This results in composite material coatings. In their patent issued in 1997, an example is given for Cu (40%) and Zn (60%) powders resulting in the α , β , γ , and ϵ phases of brass in the coating. This method of reaction spraying is of practical interest since it enables the formation of high hardness coatings due to the high hardness of the γ phase without the problems associated with its brittleness.

Dikun (Ref 37) has patented a method of producing composite material coatings. Each powder component is fed individually in separated carrier gas flows, which are then intensively mixed and accelerated in an elongated portion of the nozzle throat section. During the transit time from the nozzle to the substrate, chemical interaction of the powder mixture is initiated by gas dynamic action; as a result, composite material is obtained.

The method proposed by Vladimirov et al. in 2002 involves sequentially building a three-layer coating for the fabrication of a self-propagated high-temperature synthesis (SHS) reaction layer. The first layer providing cohesion of the coating is deposited using finely dispersed particles of metal like aluminum, nickel, or a mixture thereof forming a 50-700 μm thick layer. The second layer, 200-1000 μm thick, is made of a low-activity aluminothermic mixture while the third layer is deposited by introducing an exothermic mixture and a modification admixture in the form of high-melting point oxides and oxygen-free compounds. The final step is the initiation of exothermic reactions by SHS with an infrared heater (Ref 38). This procedure allows for the low-cost production of a broad range of composite coatings having unique physicochemical and thermophysical properties.

Kashirin et al. patented a method in which two powders are used alternatively: first the abrasive powder material with a particle size of from 30 to 300 μm is supplied into the supersonic air flow and then the powder material meant for forming the coating is added. The beneficial effect is achieved by the fact that the stage of surface preparation and that of coating application are practically not separated in time, which ensures cleanliness of the surface to be coated (Ref 39).

2.2.8 Cold Spray Coatings and Repairs. The potential of cold spraying for manufacturing and/or repairing parts has been recognized by many inventors. A method for reconditioning defective metallic surfaces of machine parts was patented by Nedajvoda et al. (Ref 40) in 2001. The method includes the application by cold spray of an aluminum and silicon carbide mixture to an amount up to 20-40 wt.% of SiC. According to the inventors, the method provides the possibility of reconditioning articles of any shape without use of special complicated equipment and considerable reduction of heat transfer to the article.

Another method was invented by Kashirin et al. (Ref 41). Their invention aims at creating metallic coatings on surfaces of articles, in particular when manufacturing and repairing articles requiring impermeability, elevated corrosion resistance, or heat resistance. The powder feedstock is a mechanical mixture of ceramic powder and powder of at least one metal, of which zinc powder represents 20-60% in the total weight of the powder.

A method for metallic coating of ceramics under soldering was proposed by Kashirin and Shkodkin (Ref 42) in 2002. The method involves the application of a two-layer coating: the first 5-200 μm thick layer is deposited from a mixture of ceramic and metal or alloy powders; the second layer is deposited from another powder material that contains components enabling soldering. This method provides strength cohesion of the first layer with a ceramic surface and the soldering of the second layer provides strength cohesion of the second layer with the first one. This method can be used for soldering ceramic articles used in electrical engineering, electronics, and the instrument-making industry.

A few other patents are related to coatings and repairs, for example, in the field of electrical engineering where connecting articles have clamping and tail parts. The contact surfaces of such articles are made of cold sprayed conducting material on all-metal bases as patented by Alkhimov et al. (Ref 43). Also, Buznik et al. (Ref 44) filed a patent providing a method for cold spraying antifriction coatings. This invention describes a method in which a cold spray coating provides lowered friction coefficient with no loss in mechanical strength and heat conduction to a part. The coating is produced using a formulation consisting of different-hardness powder components, one of them being a polymer with particle size not exceeding 10 μm .

3. USA Patents Review

3.1 General Overview

As described previously, the patents and patent applications found in the USA patent review were classified into two categories: inclusive and exclusive. Figure 13 shows the yearly number of patents and patent applications inclusive and exclusive to cold spray, thus giving a general trend of the IP activity on CS in the USA. It can be seen that the total patent activity has increased without

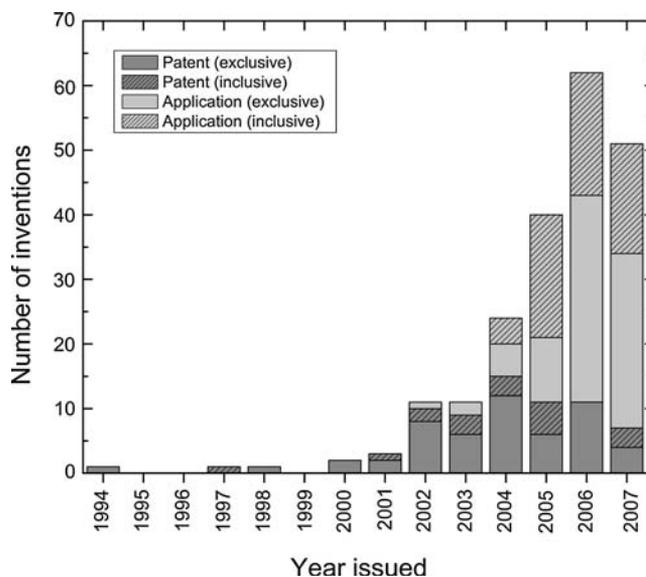


Fig. 13 Number of US patents and patent applications inclusive and exclusive to cold spray technology as a function of issued year. An inclusive patent refers to a patent that includes cold spraying as one of many coating technologies while an exclusive patent refers to a patent that protects an idea that uses exclusively cold spray as part of the invention (statistics for 2007 covers the first 10 months only)

interruption from 2000 to the present time. One can note that this trend cannot be seen for granted patents, which may indicate a reduction of the industrial R&D activity and mark the end of the first stage of cold spray development. However, 51 and 44 patent applications were published in 2006 and for the first 10 months of 2007, respectively, confirming the real surge of enthusiasm for the cold spray technology.

The number of patents and applications per assignee are shown in Fig. 14. In this figure, the numbers are given only for patents/applications that have been categorized as exclusive to the cold spray technology.

The automotive and aerospace industries were the first to show interest in the cold spray technology. A few years after the 1994 patent by Alkhimov et al. was issued, a cooperative research project initiated by a consortium formed under the name of the National Center for Manufacturing Sciences (NCMS) started to work on the development of this technology. The members of the NCMS were Flame Spray Industries, Ford Motor Company, General Electric – Aircraft Engines, General Motors Corporation, the Naval Aviation Depot, TubalCain Company, and the Pratt and Whitney Division of United Technologies Corporation (Ref 45).

In 2000, a second consortium funded Sandia National Lab to execute a Cooperative Research and Development Agreement (CRADA) on the cold spray technology (Cold Spray CRADA, Project Task Statement No. 1589.01, Sandia National Lab., Albuquerque, 2000-2003). The funding members were Alcoa, ASB Industries, Ford Motor, K-Tech, Pratt & Whitney, and Siemens Westinghouse. Many cold spray patents were assigned to these

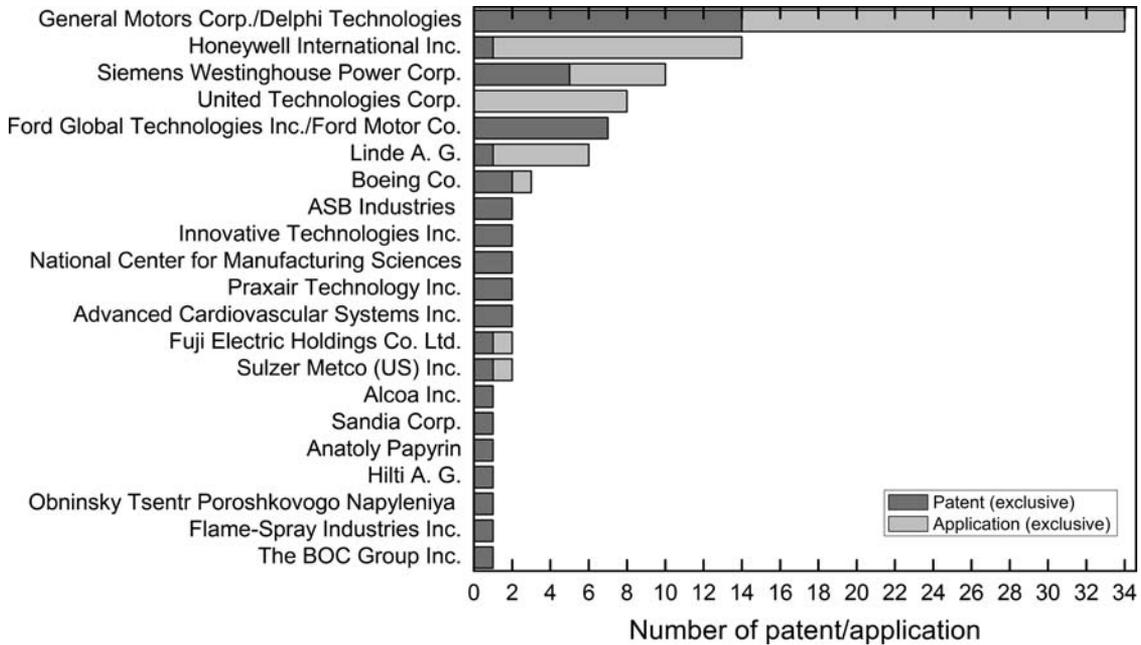


Fig. 14 Number of US patents and US patent applications issued/published for each assignee for the period ending November 1, 2007

companies. ASB Industries and K-Tech have worked on the development of cold spray apparatus and nozzles and have performed research project with the aerospace industries to develop coatings for aerospace and gas turbine industries.

Linde, Innovative technology, and OCPS have developed their own commercial cold spray apparatus. Praxair and BOC group have developed helium recovery systems.

The aerospace industry is now more visibly involved in cold spray development, at least in terms of IP. Honeywell International Inc. and United Technologies Corp. have been undeniably very active players in patenting cold spray applications recently.

Finally, the electronic industry is among the latest groups involved in cold spray.

3.2 Technical Review

The technical review of USA patents is divided into three sections: patents related to apparatus and methods, patents related to cold spray coatings and repairs, and patents related to free forms and devices.

3.2.1 Patents Related to Apparatus and Methods. *High-Pressure Cold Spray Apparatus and Methods:* The method based on the two-phase flow work conducted at the ITAM of RAS during the 1980s was patented in the USA in 1994 (priority year 1990) (Ref 12). The gas dynamic spraying method invented by Alkhimov et al. (assignee Anatoly Papyrin) uses a supersonic gas flow to entrain powder particles (metal, alloy, polymer, or a mixture thereof) at such velocity (typically between 300 and 1200 m/s) that by impinging on an article these particles make a coating while remaining at temperatures below their melting point. The particle size utilized to obtain a coating is in the 1-50 μm range. In order to increase the gas

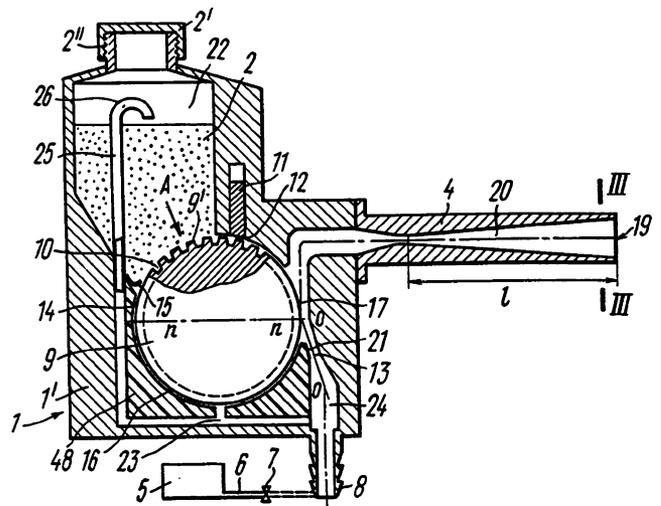


Fig. 15 A technical drawing taken from Alkhimov et al. (Ref 12) US patent. Although this patent differs in detail, the method proposed is the one presented in the Russian patents (Ref 6, 7) filed in 1986 and issued in 1991

velocity, it can be preheated up to 400 $^{\circ}\text{C}$. Figure 15 shows that the powder is injected in the high-pressure zone prior to the convergent part of the nozzle. Cold Gas Technology GmbH (CGT) (Ref 46), a Germany-based company, currently makes commercial systems based on this patent.

Improvement to this system (illustrated in Fig. 16) was proposed by Kay and Karthikeyan (Ref 47, 48). They disclosed a novel nozzle design and a new system arrangement that allows overcoming some inherent limitations of the prior patent.

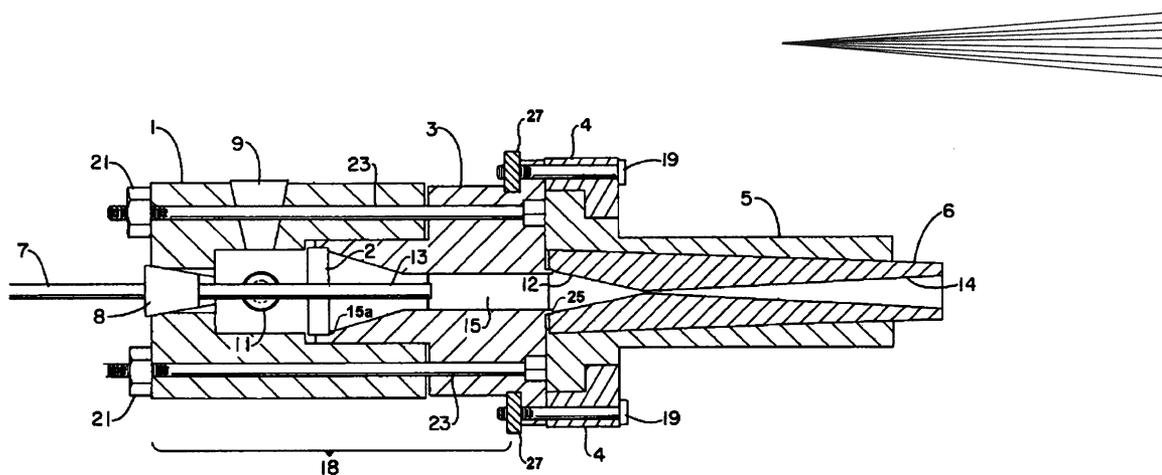


Fig. 16 Redesigned cold spray nozzle minimizing warpage at operating temperatures and improving leak-tight characteristics (Ref 47, 48)

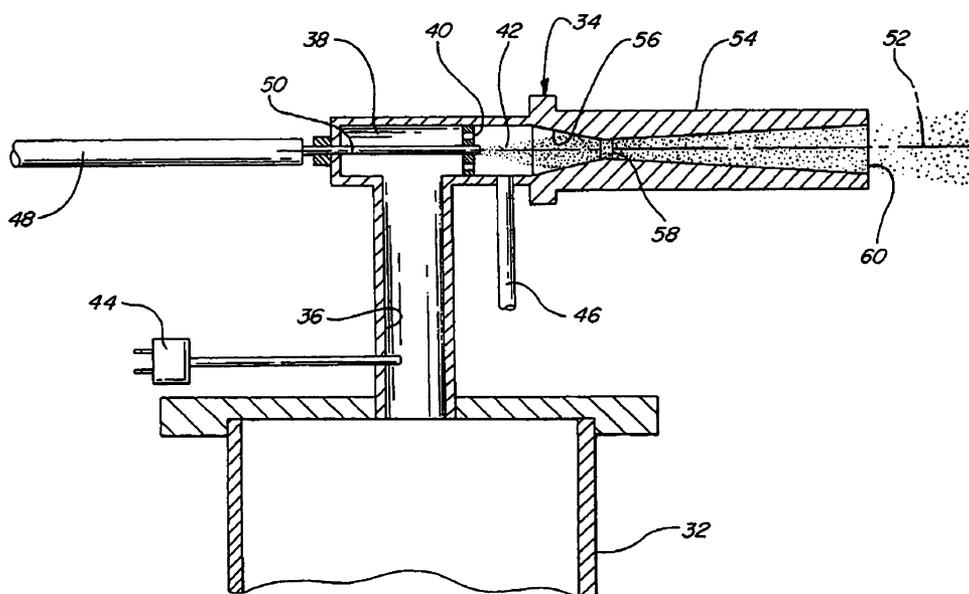


Fig. 17 Kinetic spray apparatus schematic (Ref 51). The system is designed to deposit particles larger than 50 μm in diameter which is outside the range of particle size included in earlier patents

The “Kinetic Spray” apparatus developed by Van Steenkiste et al. (Ref 49, 50), shown in Fig. 17, uses a supersonic jet to entrain powder particles ranging in size from 50 to 106 μm . In this system, a very small powder particle injector is utilized and the air passage to the injector area ratio is of at least 80/1. This ratio is significantly higher than that of the invention disclosed by Alkhimov et al. or the system developed in NCMS. Improvement of this apparatus with a longer nozzle (200-400 mm) makes it possible to increase the range of particle sizes that can be used for coatings to up to 250 μm (Ref 51).

The electric gas heating unit is replaced in one patent by a plasma torch that produces a very high temperature plasma flame. A cold high-pressure gas entrains powder particles to converge coaxially into the high-pressure plasma flame and mixing therewith, which causes the powder particles and the cold gas flow to be heated. The

particles are heated to a point below which thermal softening or melting can occur. The increased gas temperature allows for higher velocity flowing into the supersonic nozzle, thus increasing the particle velocity (Ref 52).

Cold Spray System with Sonic or Subsonic Gas Velocity: Tapphorn and Gabel (Ref 53) (assignee Innovative Technology Inc.) have developed an apparatus and process for solid-state deposition and consolidation of powder particles entrained in a subsonic or sonic gas jet onto the surface of an object, called the kinetic metallization system (Fig. 18). It innovates by using lower gas velocity and compensates for the lower particle impact kinetic energy by increasing the powder temperature, which can then deform plastically more easily. Innovative Technology Inc. (Ref 54), known as Inovati, is a USA company that makes a commercial system based on this patent.

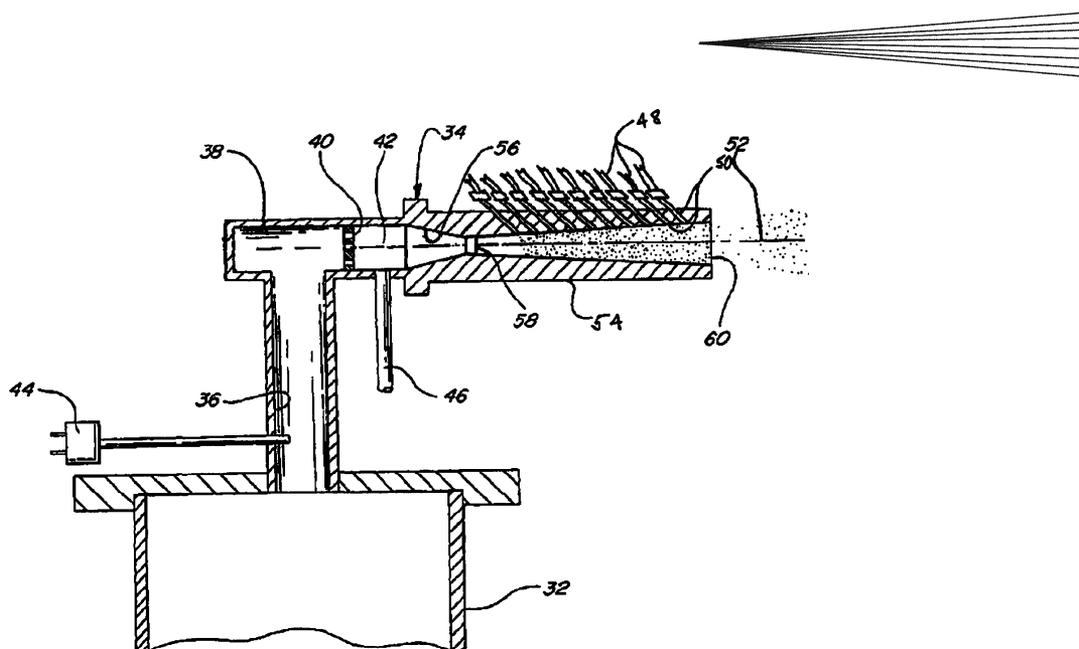


Fig. 20 Low pressure kinetic spray nozzle schematic (Ref 57, 58). The powder particles are injected in the divergent part of the nozzle at a position where the pressure is slightly above atmospheric

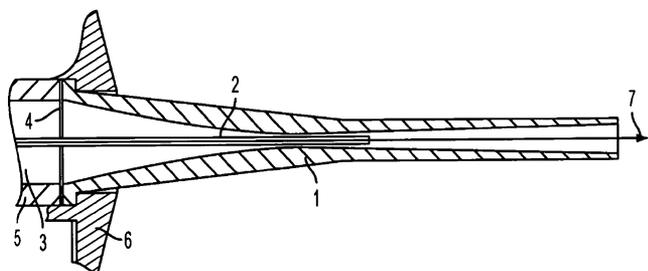


Fig. 21 Low pressure axial injection powder nozzle schematic (Ref 61). The injection of powder particles is improved by the feeding made on the axis directly in the core of the gas flow

softened prior to application. It is claimed to increase the versatility of the spray nozzle and addresses several problems inherent in kinetic spray applied coatings.

Heinrich et al. (Ref 61) patented a De Laval nozzle with a powder tube which enables the particles to be injected axially into the expansion region as illustrated in Fig. 21. Such a design makes it possible to use a low-pressure powder feeder while preserving the advantage of injecting the particles directly in the center of the gas flow.

Krysa et al. (Ref 23) have patented a method and apparatus that uses the dual nozzle discussed in the Russian section (Fig. 9). Their new system includes a compressed air supply, a heating unit, a mixing chamber, a powder dosing feeder, a powder bunker with a dosing device, and a nozzle unit. The propelling gas and the powder within the carrier gas are delivered independently to two accelerating nozzles by sprayers that are able to rotate, providing easy adjustment of the angle at which the gas flow is supplied to each nozzle. The outlet nozzle sections are located in the same plane and directed toward an ejection cap placed in the outlet of the nozzle unit. The

system is designed to be built smaller than other spray systems and is designed to operate with powder having a wide range of particle sizes. Rus Sonic Technology Inc. (Ref 62) is an American company that makes a portable low-pressure cold spray system based on this invention.

It is important to mention that for optimal performance in terms of material eligibility, coating adhesion, deposition efficiency, coating properties, etc., some of the low-pressure cold spray systems require the use of hard-ductile material mixtures.

Vacuum Cold Spray System: Muehlberger (Ref 63) obtained a patent for the vacuum cold spray system in 2004. It is claimed that the cold spray process is improved by coating an article in a low ambient pressure environment in which the pressure is substantially less than the atmospheric pressure. The low ambient pressure environment is provided by a vacuum tank coupled to a vacuum pump and having both the workpiece and a cold spray gun located therein, as shown in Fig. 22. The vacuum tank allows for gas recovery and for powder overspray collection.

It is worth noting that a similar design has already been disclosed by Akedo and his coworkers in the so-called aerosol deposition method (ADM) in which nanoparticles were sprayed in a vacuum chamber using a propellant gas flow of helium or air (Ref 64). In this method, the propellant gas is also below atmosphere and the velocity reached is lower than that for cold spray. This process reduces significantly the bow shock effect, making it possible to deposit very small particles.

Other Methods and Apparatus: The nozzle clogging issue, which is sometimes a concern when spraying metallic powders, was addressed in a patent describing a method in which a mixture of particles with two particle

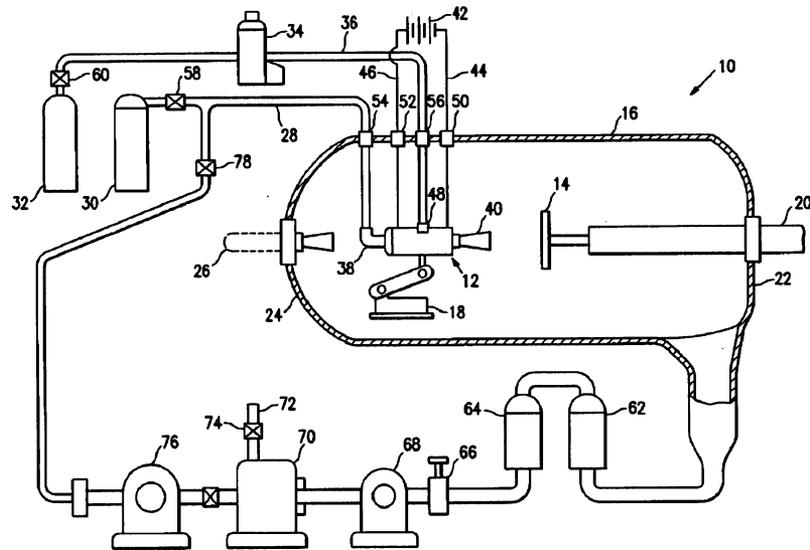


Fig. 22 Vacuum cold spray system schematic patented by Muehlberger (Ref 63). This system makes it possible to reach higher particle velocity with lower inlet gas pressure. The spray process is totally contained allowing for gas recovery and powder overspray collection

populations is used (Ref 60, 65). The operating conditions are selected such that the second particle population is not accelerated to a velocity sufficient to result in adherence when it impacts the substrate. The second population can be chosen to differ from the first in terms of yield stress, average particle size, or material nature. The inclusion of the second particle population maintains the supersonic nozzle in a non-obstructed condition and also enables one to raise the main gas operating temperature to a much higher level, thereby increasing the deposition efficiency of the first particle population.

For cold spraying at the highest velocity, which is needed for materials having very high critical velocity, it could be useful to spray with helium as the propellant gas. To address the problem associated with prohibitive helium cost, two gas recovery systems have been developed, one with pressure swing adsorption (PSA) technology (Ref 66) and the other with membrane technology (Ref 67, 68).

One of the advantages of cold spray is to produce patterned coatings with narrow lateral dimension, which is possible because of the relatively narrow particle beam of a few millimeters that is delivered by the De Laval nozzle. In the patent filed by Brockmann et al. (Ref 69), a focused beam generator is placed after the supersonic nozzle to produce an even more tightly focused particle beam with a spatial resolution of 0.8 mm (Fig. 23).

Particles that do not adhere to the substrate simply bounce back; thus, for expensive materials or for low deposition efficiency conditions, it becomes interesting to recover the materials that normally are lost during the process by not being deposited. A cold spray apparatus with debris recovery has been proposed by Gabel and Tapphorn (Ref 70, 71) in order to retrieve excess or ejected material from the substrate. It is claimed also that this system allows for triboelectrically charging the projected particles to support forming the coating.

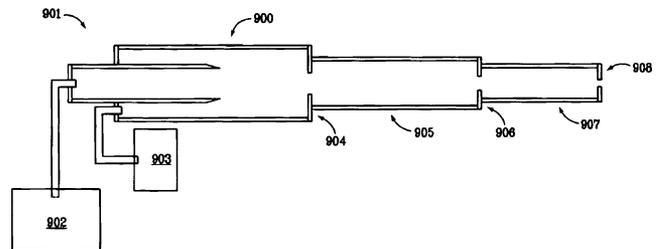
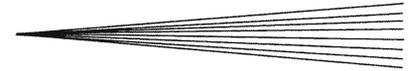


Fig. 23 Focused beam generator schematic making it possible to reduce the spray trace down to 0.8 mm in diameter (Ref 69)

3.2.2 Patents Related to Cold Spray Coatings and Repairs.

Some patents take advantage of the below-melting temperature particle characteristics of the cold spray process to produce functional coatings without melting or oxidizing the projected powder particles. For example, in the patent filed by Popoola et al. (Ref 72), a powder mixture of metal and foaming agent is cold sprayed to obtain, after appropriate heat treatment, a foam metal coating. In another patent, a magnetostrictive composite coating is cold sprayed on an automobile steering shaft to serve as a portion of a torque sensor device (Ref 73). The idea of cold spraying particles on a plastic material to obtain, for example, electrical connection or solderable pads has been also patented by Van Steenkiste et al. (Ref 74).

Some patented ideas take advantage of the better coating quality (i.e., low porosity, high hardness, etc.) that can be obtained by cold spray as compared to other thermal spray technologies. For example, the processes of applying abrasable (Ref 75), thermal barrier (Ref 76), or wear and erosion protection (Ref 77, 78) coatings using cold spray have been patented.



Further advantages of cold spray over thermal spray proceeded to protected ideas such as the possibility to spray on temperature-sensitive materials without damaging the parts to be coated as well as repairing such parts more easily at lower cost. For example, in a patent filed by Hu et al. (Ref 79), a method for repairing damaged engine components that involved heat treatment and hot isostatic pressing (HIP) after cold spraying is proposed. Patents on cold spray processing for repairing turbines (Ref 80) and damaged thermally spray coated machine tools or dies (Ref 81) have been issued. Two patents focusing on corrosion protection were issued recently. One patent covers localized coatings, for instance the repair of coating on parts that have already been coated but subsequently have been compromised by manufacturing method such as cutting or welding (Ref 82). Another patent covers a corrosion protection coating on different types of weld (Ref 83). Finally, one patent is based on the development of selected ceramic-metal mixed powders to produce coatings with high gas impermeability (Ref 84).

3.2.3 Patents Related to Free Forms and Devices. The cold spray process offers two unique characteristics over other thermal spray technologies that make it especially suitable for the fabrication of free forms and devices: (1) it allows for the deposition of very thick layers of materials and (2) the spray trace is very well defined.

The ability of the cold spray technique to build thick and dense coatings has been exploited to produce free-form shapes that can be further machined or deformed to obtain a final product (Ref 85). An extension of this concept was used for the development of a method and apparatus for directly making rapid prototype tooling from a computer model having a free-form shape (Ref 86). The possibility of directly applying materials to a localized area of a substrate resulted in two patents: the application of brazing materials directly on components (Ref 87) and the integration into the fabrication process of components such as heat exchangers (Ref 88). This ability to deposit materials on dissimilar substrates with low heat input was exploited in a patent describing a microelectronic sealed package using a cold spray metal seal deposited around a transparent window (Ref 89) and to make circuits using a polymer aerosol masking technique (Ref 90). The ability to spray coating on dielectric materials as well as the possibility to form metal matrix composites were exploited to fabricate heat sinks (Ref 91). The low oxide content in the deposited coatings enables excellent electrical conductivity of the deposited layers. This led to patents regarding electrical contacts (Ref 92, 93) and fabrication of electrical commutators (Ref 94). The control of the oxide level in metallic coatings enables the formation of metal oxide catalysts such as CuO that can be used to reduce the amount of low atmosphere ozone. Many metallic catalysts can also be used and applied, for instance on automotive radiator fins (Ref 95). Spraying of composite materials constituted of soft magnetic metals and hard permanent ceramic materials combined with the ability to control the spray pattern enables the fabrication of electromagnetic devices as disclosed in patents (Ref 96-99). Finally, the ability to control the porosity

without reaching high temperature during spraying enables the development of medical components that can even include drugs (Ref 100, 101).

3.3 New Inventions—US Patent Applications

This section presents US patent applications exclusive to cold spray technology for which the corresponding patents were not yet issued at the moment of the preparation of this article. Despite the fact that no critical review of these documents has been done, this section gives an indication of the latest trends in the IP related to cold spray. The reader can refer also to Kosarev et al. (Ref 102) for a detailed review on recent patented inventions related to cold spray.

3.3.1 USA Patent Applications Related to Apparatus and Method. The issue of recovery of overspray material is addressed in the application filed by Baran (Ref 103) in 2006 who proposes a new spray nozzle design coupled with a collection assembly for collecting the non-deposited powder particles during cold spraying. The idea of assisting the cold spray process by using a laser to increase the temperature of the deposited layer or to increase the density of the coating is presented in one patent application (Ref 104). Increasing the powder temperature may result in higher deposition efficiency, especially for materials that are usually difficult to cold spray. Heating of the powder particles was therefore proposed by different innovative approaches. One method involved heating of the powders into the nozzle using microwaves (Ref 105). Heating was also accomplished by modifying the gun through the addition of a pre-chamber between the nozzle and the gas/powder mixing chamber in order to increase the transit time of the particles in the hot gas (Ref 106, 107). Another approach involved adding a powder pre-heating device to the cold spray apparatus (Ref 108). In this latter invention, a high-pressure gas heater is mounted in the spray gun. To reduce the gas consumption and improve efficiency, a hybrid plasma-cold spray apparatus and method is proposed in which the process gas is ionized by means of electric arcs (Ref 109). Improvements to the low-pressure portable spray gun are proposed in Ref 110, where the powder and gas flow rates are continuously monitored in order to control the deposition efficiency. In another application, an improved powder injector is proposed to reduce clogging problems while spraying atypical powder materials (Ref 111). Vacuum cold spray systems are described in two patent applications that both were filed before the vacuum cold spray system patent was published (Ref 112, 113). A cold spray apparatus having pulsed powder injection and pulsed gas heating device capabilities is proposed to improve the deposition process (Ref 114). Nozzle design is a very active axis of development both for high-pressure and low-pressure systems with many applications (Ref 115-125) related to innovative designs. Some USA patent applications show nozzles designed for the cold spraying of inner surfaces of long articles. In one patent application, the nozzle is angled at $30^\circ \pm 15^\circ$ allowing for coating a liner in a cylinder of an aluminum engine block (Ref 126). In another application,

a curvilinear extension is added to the conventional DeLaval nozzle, which has a larger diameter than the nozzle in order to minimize clogging (Ref 127). Finally, in a third patent application, a curvilinear nozzle is proposed for coating bore surfaces (Ref 124).

3.3.2 USA Patent Applications Related to Coating and Repair. Cold spray technology has been reported to be successful in producing coatings using a large variety of metals and this has been exposed in numerous patent applications regarding coatings and repair techniques.

Patent applications for bond coatings (Ref 128) and platinum aluminide coatings (Ref 129) have been filed as well as applications for high strength copper (Ref 130), amorphous or microcrystalline materials (Ref 131). Two patent applications describe methods for applying or producing a ceramics-based photocatalytically active layer or polymer (Ref 132, 133). In the aerospace industry, numerous applications related to turbine repair involving cold spray have been found: titanium part repair (Ref 134), blade platform repair (Ref 135), and engine airfoil repair followed by post-treatment using HIP (Ref 136). Application of a repair technique involving powder preheating has also been filed (Ref 137). As well, repair techniques of super alloys (Ref 138), Al (Ref 139), and Mg (Ref 140) parts have been the object of patent applications. Repair of thermal spray coatings using cold spray (Ref 141) and thin wall housing (Ref 142) have also been the object of patent applications. Several applications have been filed for wear resistant coatings (Ref 143) on Al substrates (Ref 144), on turbine engine (Ref 145), or on blade materials (Ref 146). Abrasive and environment resistant coatings have also been applied for coating a surface of a turbine component (Ref 147). A method for producing an arc-erosion resistant coating is proposed in Ref 148 and a method for repairing a metallic surface wetted by a radioactive fluid and susceptible to stress corrosion cracking in a nuclear reactor has been proposed in Ref 149. Patent applications were filed for porous metallic coating (Ref 150, 151) and functionally graded material coating (Ref 152), one for which the compositional gradient is varied laterally instead of through the coating thickness (Ref 153). A method for applying an alloy coating on turbine engine components is proposed in Ref 154 where the powder, composed of a mixture comprising all the alloy elements, is cold sprayed followed by an appropriate heat treatment until the alloy elements inter-diffuse and form the alloy. Finally, a patent application describing the use of agglomerated powders for deposition of thin coatings is presented in Ref 155.

3.3.3 USA Patent Applications Related to Free Forms and Devices. The narrow spray jet in cold spray can produce sharp and well-defined deposits that can be used to develop a method for directly applying a knife edge on a turbine rotor for sealing function (Ref 156) or a ridge for producing gas turbine blade tip (Ref 157). The ability of forming thick coatings with various materials and composites resulted in two patent applications (Ref 158, 159), one for the production of functionally graded materials combined with cold isostatic pressing of the final shape

and then sintering using field activated sintering (Ref 159). Many patent applications have been filed on the usage of cold spray for bonding of parts: Directly for two dielectric electrodes (Ref 160), for bonding parts using an electrical conductor for the fabrication of multi-cell batteries (Ref 161), or by the application of the braze materials to the part (Ref 162, 163) that can lead to the formation of an assembly such as heat exchanger (Ref 164) and even combined with other thermal spray processes for the fabrication of high-performance thermal stack (Ref 165). Methods for joining a metallic part to a ceramics part (Ref 166) or to a composites part (Ref 167) have also been filed. Cold spray can also be used to promote bonding of polymers (Ref 168). The ability of cold spray to form patterns over different surfaces enables, when combined with plasma spray, the fabrication of strain gages directly on polymer surfaces (Ref 169). Cold spray can also be employed for applications involving energy generation using fuel cells where it can be used to form a layer of corrosion-resistant material over bipolar plates (Ref 170). It can also be used to form surfaces preventing coking for hydrogen converters (Ref 171). Cold spray patent applications were filed targeting the microelectronic industry to make wiring boards (Ref 172) or to make an electro-static chuck with non-sintered AlN as dielectric material (Ref 173). Concerning the application of conductive materials, the adhesion of cold spray copper can be promoted using a bond layer (Ref 174). Conductor coatings can also be applied directly on ceramic where the technique can even be used to deposit different materials for electrical conductivity (Al) and to incorporate welding areas (Cu) (Ref 175). Also, the thermal conductivity property of as-deposited cold spray coatings is exploited in Ref 176. Finally, a patent application describing a process for manufacturing structures for guiding electromagnetic waves, such as telecommunication cables which comprise the step of applying a conductive coating by cold spray is described in Ref 177.

4. Author's Notes on the Present Patent Situation

In view of the extensive patent review presented in this article, one can be tempted to conclude that some sort of patent race took place during the last few years. This phenomenon has worried many industrialists who have interest in this technology, especially in the USA where the implementation of cold spray equipment for commercial usage has been limited as compared to Europe or Asia. The question that arises most frequently is "Will I be allowed to use this technology for my application if I buy this equipment?"

We would like to address this question in three points:

- Firstly, some of the recent USA patents and patent applications related to cold spray contain claims that are well within the grasp of a person having ordinary skill in the relevant art. To illustrate one situation, it



has been clearly established since the first divulgations regarding the cold spray process (Ref 12) that cold spray is a tool for applying a metallic coating to an article. It is also well known that an Al or Zn metallic coating can provide galvanic corrosion protection to an article. A patent that would only protect the idea of using cold spray for applying an Al or Zn metallic coating to an article for corrosion protection will appear to a person with skill in the relevant art obvious. However, a number of patents and patent applications contain such claims, where the novelty seems disputable. The §103 of the Patent Act forbids issuance of a patent when “the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art.” Moreover, the Supreme Court of the United States has attempted to define obviousness for decades. Its recent judgement (No. 04-1350, decided April 30, 2007) will, it is believed, restrain to a greater degree the possibility of issuing patents that combine elements from different pre-existing patents. Consequently, current cold spray patents based on such combination of pre-existing patents might be weakened and new patents of this type should now be more difficult to obtain.

- Secondly, in addition to the obviousness issue, there is also an anteriority issue. Indeed, the cold spray technology originates from the former Soviet Union and many inventions related to cold spray were patented only in Russia as described in this review. Many innovative ideas were therefore disclosed and are freely exploitable for the rest of the world. This review summarized some ideas that were up to now only published in Russian. For this reason, it is not surprising to find USA patents based on similar inventions patented in Russia where they were divulged years ago. In such a context, some USA patents could be invalidated on the basis of the Russian patent anteriority.
- Thirdly, there are at least five different commercial cold spray systems on the market from five different companies based in four countries all owning patents or license to protect their technology and to ensure the right to their clients to use this process for what the technology is claimed to do, namely producing coatings from powder feedstock. This situation favors price competitiveness and continuing improvements of design and performance for cold spray equipment in the future. Furthermore, the first USA patent (Ref 12) describing the method of cold spray will expire in 2011 opening even more the market. These three points combined with the very rapidly expanding common knowledge developed by the scientific community, which is the object of the second part of this review, create favorable conditions for the commercial exploitation of the cold spray technology worldwide.

5. Conclusion

As early as 1900, the idea of applying a metal layer upon another metal to enhance its properties, using a blast of pressurized gas, was patented by H.S. Thurston. However, this concept was translated into a feasible process only 80 years later, as a team of former Soviet scientists led by A. Papyrin rediscovered the idea by accident, and was able to develop it into a working process helped by the advances of technology. By using a high-pressure gas together with an appropriate converging-diverging nozzle and a powder feeder able to withstand and operate at high pressure, the cold spray process succeeded for the first time in the production of coatings from a broad range of materials. Cold spray is one of the various names for describing an all-solid-state coating process that uses a high-speed gas jet to accelerate powder particles toward a substrate where they plastically deform and consolidate upon impact. Cold gas dynamic spray, kinetic spray, supersonic particle deposition, dynamic metallization or kinetic metallization are all terminologies found in the literature that designate the above-defined cold spray coating process.

This article covered all English and Russian written patents, found through databases from 78 patent authorities, protecting an idea that uses exclusively cold spray as part of the invention. A total of 164 patents and patent applications were reviewed and this extensive survey has allowed establishing a precise historical perspective of the technology development. In Russia, three groups of researchers have significantly contributed to the early development of the cold spray technology. The original experimental and theoretical work occurred in the 1980s at the Institute of Theoretical and Applied Mechanics of the Siberian Branch of the Russian Academy of Sciences. In the 1990s, the Obninsk Center for Powder Spraying brought noteworthy developments to the cold spray technology and it became leading Russian company manufacturing DYMET® gas-dynamic coating equipment. Researchers formerly from the Moscow Aviation Institute (State University of Aerospace Technologies) have also participated significantly in the development of the cold spray technology during the 1990s.

In the USA, the development effort on cold spray started a few years after the 1994 patent by Alkimov et al. was issued, with the work of the National Center for Manufacturing Sciences consortium (with Flame Spray Industries, Ford Motor Company, General Electric – Aircraft Engines, General Motors Corporation, the Naval Aviation Depot, TubalCain Company and the Pratt and Whitney Division of United Technologies Corporation as members). From 2000 to 2003, a Cooperative Research and Development Agreement (funded by Alcoa, ASB Industries, Ford Motor, K-Tech, Pratt & Whitney and Siemens Westinghouse) also worked on the cold spray technology. ASB Industries and K-Tech have also contributed to the development of cold spray in the USA by working with the aerospace industries to develop coatings for the aerospace and gas turbine industries. The real

surge for cold spray technology in the USA arises after 2003 with the number of patent applications increasing exponentially since then.

This thorough review allows concluding that the numerous patents and patent applications resulting from a tremendous amount of work performed by many research institutions and individuals over the last three decades have led to both the extensive development of the cold spray equipment and to the demonstration of the process capabilities. As such, it has been shown that cold spray can be used as a tool for coating unconventional materials, as a spray forming process, for device fabrication or for repairs. This in turn has brought the cold spray technology to a convincing maturity, although improvement can still be envisioned.

As cold spray is progressively introduced in industries and thermal spray job shops, it is foreseen that many new innovative application ideas will be implemented in production, establishing cold spray technology as an inevitable member of the thermal spray family.

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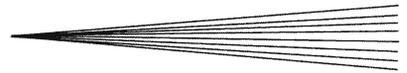
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