



Coating by the Cold Spray Process: a state of the art

Ramin Ghelichi, Mario Guagliano

Dipartimento di Meccanica, Politecnico di Milano, Via La Masa 1, 20156 Milan, Italy

RIASSUNTO. Si descrive il processo di cold-spray per l'ottenimento di rivestimenti di superfici metalliche e non metalliche. La memoria, dopo una parte introduttiva relativa alle applicazioni del processo, intende discutere criticamente le attuali conoscenze al riguardo, principalmente indirizzate all'influenza dei parametri di processo sull'efficienza di deposizione (DE). Si focalizza l'attenzione su tutti i parametri di interesse ed è indirizzata, in particolare, all'analisi dell'influenza della rugosità della superficie del substrato sull'efficienza di deposizione. Vengono poi analizzati i principali effetti del cold-spray sulle proprietà del substrato. Infine, sulla base delle attuali conoscenze si tracciano e sottolineano alcuni possibili sviluppi di ricerca in questo settore.

ABSTRACT. A brief description of cold spray coating process is presented. This paper intends to review some the previous works which are mostly about the influences of the cold spray parameters, mostly the surface of the substrate, on the deposition efficiency (DE). Almost all the important parameters, with more focus on the roughness of the substrate, on increasing the DE are briefly studied; this review also includes a description of application of cold spray and of some important effect of this method on substrate properties. On this basis, some possible development in this field of research are drawn and discussed.

KEYWORDS: Cold spray coating, Surface treatments, Thermal coating

INTRODUCTION

The ever increasing demand to manufacture weight efficient structures that are damage tolerant and can operate at elevated temperatures has fueled the development of novel alloy compositions and radically different processing approaches over the last decades. 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.

The limitation some coating types (for instance HVOF process, Plasma spray systems, thermal spray technology of coating, etc) 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.

Furthermore, cold spray is known to present other characteristics that offer unique advantages compared to existing spray technology:

- The coatings can exhibit wrought-like microstructures with near theoretical density values;
- The spray trace is small (typically 1-25 mm²) and well defined allowing for precise control on the area of deposition;
- The coatings can be produced with compressive stresses, thus ultra thick (5-50 μm) coatings can be built-up without adhesion failure;
- Coatings can be deposited on temperature-sensitive materials such as glass or polymers[1].

Cold gas-dynamic spray (or simply cold spray) is a process of applying coatings by exposing a metallic or dielectric substrate to a high velocity (300–1200 m/s) jet of small (1–50 μm) particles accelerated by a supersonic jet of compressed gas at a temperature that is always lower than the melting point of the material, resulting in coating formation from



particles in the solid state. The general principle of cold spraying has been described elsewhere in more detail [2-4]. This process is based on the selection of the combination of particle temperature, velocity, and size that allows spraying at the lowest temperature possible. As a consequence, the deleterious effects of high-temperature oxidation, evaporation, melting, crystallization, residual stresses, debonding, gas release, and other common problems for traditional thermal spray methods are minimized or eliminated.

Cold-sprayed coatings can be processed with very low numbers of defects and low oxygen contents, and therefore exhibit bulk like properties with respect to electrical or thermal conductivity that are not attainable by normal thermal spray processes [4].

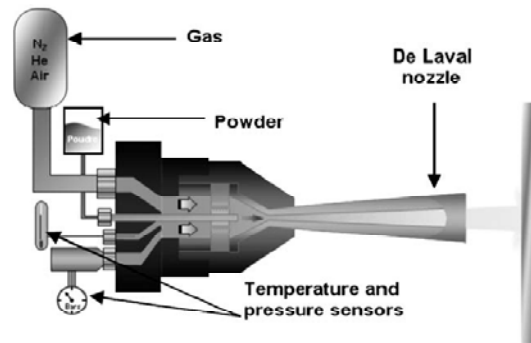


Figure 1: The schematic drawing of cold gas spray apparatuses [3].

APPLICATION

The cold spray cost model was exercised to predict the “should” cost of making deposits of various complexities. Sensitivity of these “should” costs to input variables such as powder cost, utility and shop rates, deposition precision, etc., was also carried out. This study showed that manufacturing using the cold spray process attacks many aspects of the value simultaneously. Judged against the value stream results, use of this technique accomplished. [5]

- Reduction in material input;
- Elimination of mold and melt pour cost;
- Reduction in rework;
- Reduction in finishing;
- Large increase in material utilization (cold spray has deposition efficiency of 60-95%).

These estimated deposition costs were then used to help develop business cases to show that a cost advantage could be obtained by fabricating parts using the cold spray process [5]. Cold spray technology can be used to produce both protective coatings and prototyping/freeform fabrication in not only strategic industries such as defense and aerospace, but also in various other general industries such as steel, utilities, paper and pulp, etc. High performance materials such as superalloys, MMCs and nanostructured materials are used to produce complex and intricate components of various high tech industries. Established cold spray process can cater to economical and fast prototyping and fabrication of these components. For instance, aluminum and aluminum alloy coatings are being investigated for repair/refurbishment of space shuttle solid rocket boosters and others (aerospace), repair and retrieval of parts and plate stocks used in aircraft structures (aircraft industry), repair/refurbishment of casings (gas turbine), corrosion protection coatings (petrochemicals), brazing/joining (utility) and others. Similar to aluminum, it is being pursued with copper (steel, electronics, aerospace), titanium and tantalum (electronics, bioengineering), etc. There are many other applications for cold spray coating some of them as below [5]:

- Corrosion Resistant Coatings (Zn, Al)
- Dimensional Restoration and Repair (Ni, Stainless Steel, Titanium, Aluminum)
- Wear Resistant Coatings (CrC-NiCr, WC-Co, WCu)
- Portable Units for Field Repair
- Biomedical – prostheses with improved wear
- Aerospace – fatigue-resistant coatings
- Chemical – improved corrosion resistance
- Mineral processing – improved corrosion and erosion resistance
- Die casting – extending die life
- Electronics – creating a heat sink or superconductive, magnetostrictive surfaces

- Printing – copper coating on rollers
- Oil and gas – improved corrosion resistance
- Glass – platinum coating.

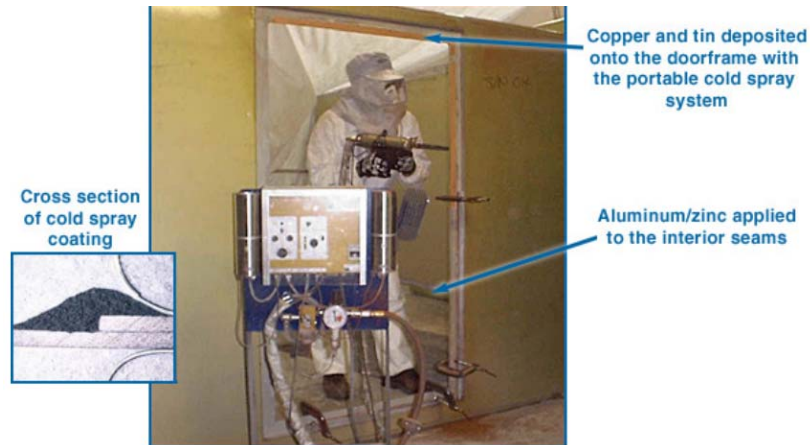


Figure 2: an example of the CGDS applications [6].

COLD SPRAY IMPORTANT PARAMETERS

Deposition efficiency

One of the most important characteristics of cold gas dynamic spray (CGDS), as well as of any other methods of powder spray, is deposition efficiency; there are many reasons that make it practically impossible to obtain a deposition efficiency that is equal to unity. First, polydisperse powders are usually used. As the jet during its impingement is spreading along the substrate surface, the finest particles either do not reach the surface at all or impact at acute angles, which deteriorate particle attachment. Although the largest particles are incident at a close-to-normal angle (i.e., the angle between the particle impact velocity and the substrate surface is close to 90°), their velocities may be insufficient for particle attachment. Second, the particle velocity at the jet periphery can be lower than it must be for particle attachment. In addition, if the velocity is not sufficiently high, the surface should be self-activated by the impacted particles.

Due to the sufficiently complicated nature of CGDS, it is rather difficult to measure the deposition efficiency; first, three main stages (see Fig. 3) of the spray process may be identified. At the initial stage, some time is required for surface preparation (i.e., the induction time), when only erosion occurs without any deposition. At the second stage, a thin layer of the particle material (hereinafter referred to as the first layer) is formed on the substrate surface. This stage is characterized by the interaction of particles with the substrate surface, and it depends on the preparation level and properties of the surface material. The third stage, which can be conventionally called the build-up stage, is characterized by the growing thickness of the coating layer. In this case, the particles interact with the surface formed by previously incident particles. Thus, it is clear why there is some uncertainty in measuring the powder deposition efficiency. [7]

Second, adhesion of particles depends on many factors: area of the contact surface, crater depth, plastic strain, yield stress, pressure and temperature at the contact boundary, etc. In turn, these factors are affected by the impact velocity of the particle. Therefore, it seems logical to assume that these parameters reach their critical values at velocities close to the critical one or their dependence on velocity becomes different. Postulating of some adhesion criterion requires these critical values and conditions to be determined [8]. But in the simplest way the deposition efficiency calculated experimentally as follow:

$$kd = \Delta ms / Mp \quad (1)$$

where Δms is change of weight of a substrate and Mp is weight of all particles interacting with a substrate.

As it is known up to now, the most important parameter in not only deposition efficiency and also in cold spray procedure per-se is the velocity of the particles. Since the particle velocity exceeds the critical value v_{cr1} , the coating



process begins. The deposition efficiency rapidly increases to 50–70% as the particle velocity significantly exceeds the critical value.

The other important parameter which has a great influence on deposition it is simply concluded that the particle and substrate temperatures have also a significant effect on the spraying process; as the air temperature in the pre-chamber increases, both the particle velocity and the particle and substrate temperatures increase.

During the first stage, the particles interact with the substrate, and this process determines the quality of the interface and coating adhesion. To improve adhesion, sand blasting is commonly used under thermal spraying. However, this method has certain disadvantages including the effect of interface contamination due to penetration of sand blasting particles into the substrate, especially for soft substrate materials. Sand blasting is undesirable in many applications, for example, in spraying on parts with thin walls, parts already coated, parts made of brittle materials, etc. In the cold spray process, the sprayed particles are in the solid state, and in some cases they can be used for preliminary treatment and preparation of the substrate, in particular, when the use of sand blasting is unacceptable. The first stage of coating spraying turns out to be more complicated, because it depends on particle and substrate parameters (e.g., roughness, hardness, temperature, etc.) and on the state of the surface, which is obviously changed as the number of particle impacts increases. This change, in turn, leads to changes in conditions of particle–substrate interaction and, consequently, to unsteady growth of the coating [1].

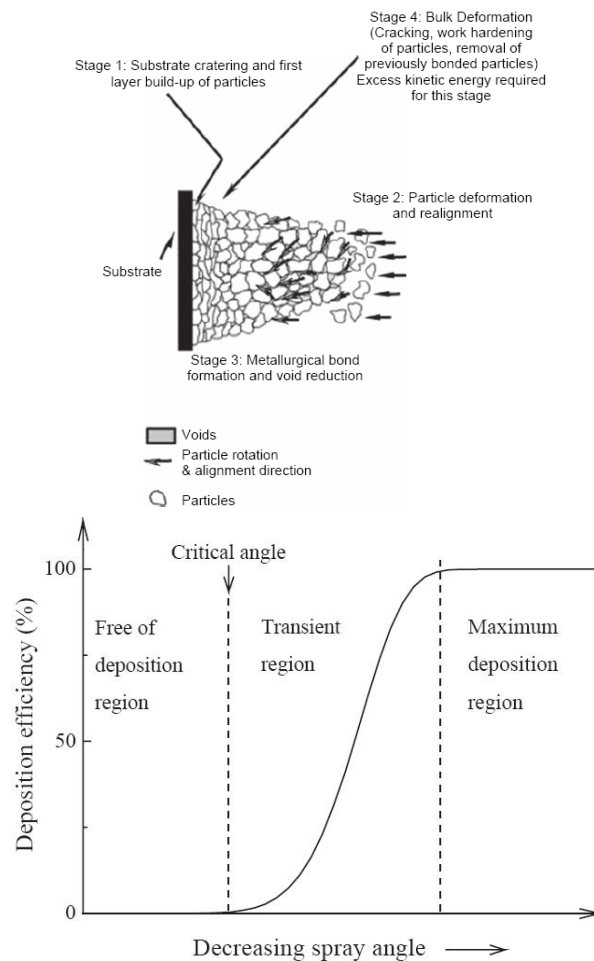


Figure 3: The schematic view of different region of particles on substrate [1].

Before the first stage there is an induction or delay time is the time between the beginning of surface treatment by the flow of particles and the beginning of particle attachment to the surface. There are three characteristic regions of particle–substrate interaction, divided by two values of particle velocity: v_{cr1} and v_{cr2} (Fig. 4). In region 1, with v_p higher than v_{cr2} (850 m/s), particles adhere to the initial surface without any delay. As the particle velocity decreases, the situation is changed. In region 2, located between v_{cr1} and v_{cr2} , particles cannot adhere to the initial (original) surface. They start to



adhere to the surface only after some delay, when the surface state is changed because of its treatment by the first impinging particles. In this region, the first particles rebound, thus, preparing the surface, only after, that does the coating start to form [1].

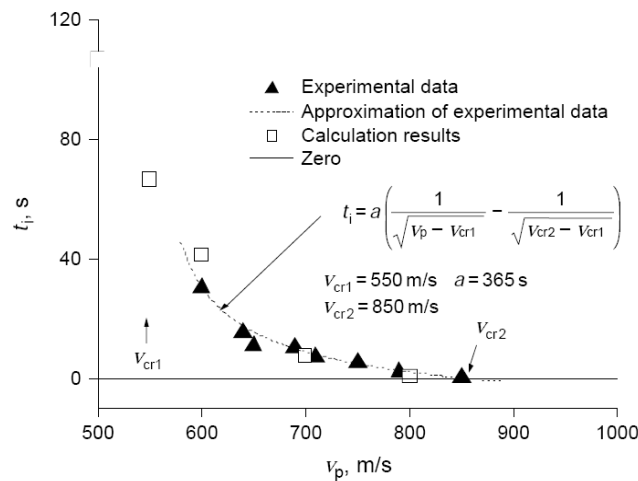


Figure 4: Induction (deposition delay) time versus the mean impact velocity of aluminum particles on a polished copper substrate [1].

Thus, it is clear that the surface, before the second region, was exposed to a large number of particle impacts before particles start to adhere to the surface. The results presented show that the sprayed particles in the cold spray process can play an important role in the preparation and activation of the substrate surface and this effect can be used in applications when utilization of sand blasting is unacceptable or undesirable. In this case, however, additional effects associated with a delay of spraying of the first layer should be taken into account in the coating formation process analysis.

Appropriate material

Polycrystalline solids are classified into isomechanical groups, i.e., groups that possess similar mechanical properties. The most important isomechanical groups of metals are: aluminum, copper, silver, gold, platinum, nickel, and gamma-iron (face-centered cubic (FCC) lattice); tungsten, tantalum, molybdenum, niobium, vanadium, chromium, alpha-iron, and beta-titanium (bulk-centered cubic (BCC) lattice); and cadmium, zinc, cobalt, magnesium, and titanium (hexagonal lattice, which is the densest packing). Metals with the FCC lattice have the greatest number of slipping planes, which is responsible for their high plasticity; metals with the hexagonal structure have much fewer slipping planes, which yield a lower plasticity; and metals with the BCC lattice have the lowest plasticity among the three types. Groups of tetragonal or trigonal crystalline systems include oxides that are not suitable for cold spray because of their low plasticity (this issue has not been adequately addressed to definitely state inapplicability of all oxides and ceramics for cold spray). If we plot the homological temperature (ratio of temperature to the melting point) on the x axis and the product of the shear modulus and compression modulus on the y axis and mark points corresponding to various metals in the diagram, it turns out that more plastic materials are located in the right side of the diagram close to the x axis, whereas less plastic materials can be found in the left side of the diagram close to the y axis. This positioning allows us to classify materials from the viewpoint of their suitability for cold spray. Copper is considered as an almost ideal material, which has a low resistance to strain and a melting point below 1100°C. Materials with a low melting point can be readily compacted. In general, cold spray treatment of BCC metals involves more difficulties, because the mobility of spiral dislocations under strains with high rates is limited by Peierls stresses [9]. From the viewpoint of material science, the suitability of materials for cold spray could be related to Peierls stress. Peierls stress is the force, first discovered by Rudolph Peierls and modified by Frank Nabarro, needed to move a dislocation within a plane of atoms in the unit cell. The magnitude varies periodically as the dislocation moves within the plane. Peierls stress depends on the size and width of a dislocation and the distance between planes. Because of this, Peierls stress decreases with increasing distance between atomic planes. Yet since the distance between planes increases with planar density, slip of the dislocation is preferred on closely packed planes, but available publications are insufficient to draw this conclusion.

But based on the results of many researchers, it seems somehow obvious that particle adhesion is primarily related to the readiness of the substrate and particle to deform, and adhesion is assumed to be possible if the particle is substantially more plastic than the substrate.



The result of R. Gr. Maev and V. Leshchynsky [10] work shows that the main characteristics of GDS such as deposition efficiency and average single pass thickness depend on the kinetics of adiabatic shear band formation following the Arrhenius flow law. Localized plastic deformation at the particle-substrate interface appears to be necessary for the coating formation. For this reason, successful powders and substrates for GDS are mostly metals with relatively high plasticity.

L. Ajdelsztajn et al. [11] show that the localized adiabatic shear instability at the particles boundaries helps the creation of intimate contact between clean surfaces that result in a metallurgical bonding at the particle/particle surfaces. One can speculate that the adiabatic regimen created during the impact could raise particle temperatures close to the glass transition temperature (T_g) of the amorphous alloys, leading to particle softening and making it possible to achieve very high densities in the coating. It is proposed that for the soft substrates and hard particles used in this work, the first impacts will primarily confine the deformation to the substrate material, and after the first layer of undeformed hard particles are created the subsequent impacts provide severe plastic deformation on both substrate and impacting particles.

The effect of velocity on DE

For a given material, successful deposition requires a certain minimum particle velocity or “critical velocity,” the value of which depends most significantly on the thermo-mechanical properties of the powder and substrate materials [12-18]; below this critical velocity, impacting particles are generally observed to cause erosion of the substrate. Normally, a feedstock powder will contain a range of particle sizes and consequently a distribution of particle velocities a large number of studies have suggested that the particle deposition behavior is influenced significantly by the particle velocity prior to impact with the substrate. Particle velocity is a function of the spray process conditions, including gas type, pressure, and temperature, and materials properties, such as particle diameter, density, and morphology [19-21]. The relationships between the deposition efficiencies and particle velocity (Fig. 5) were investigated [23, 24]. Assadi et al. [26] have used numerical simulation to work out the effect of various material properties on the critical velocity in cold spraying. They summarized these effects into a simple expression for the critical velocity. François Raletz et al [3] present an imaging technique that allows a fast measurement of critical velocity. The measuring method is first evaluated by comparing the critical velocity of copper (sprayed on copper substrate) found in the literature, with the measured one. Its accuracy is then tested with other materials and, finally, some improvements of the method are proposed. In Development of a generalized parameter window for cold spray deposition Tobias Schmidt et al calculate the critical velocity based on particles size. They developed a CFD analysis for thermal solution.

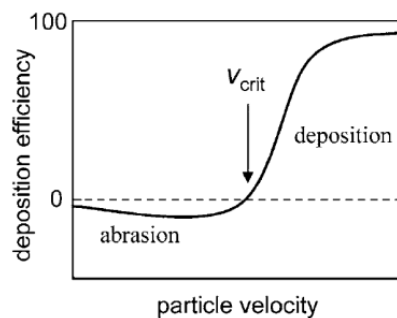


Figure 5: The effect of particle velocity on deposition efficiency in CGDS [22].

Papyrin et al. [28] modeled the impact of a plastic particle onto a rigid substrate at velocities that are commonly achieved in the cold spray process. The calculated distribution of the radial component of velocity indicated that metal jetting could take place. However, they also demonstrated that under certain conditions, melting may occur on the surface of the particle in the contact zone but suggested that since this was limited to only a very thin layer, it would not significantly affect the properties of the coating. The modeling of particle impact is used to provide a better understanding of the bonding mechanisms, and to estimate critical velocities for bonding particles of different materials. By means of a so-far widely accepted model, bonding in cold spraying can be explained by the occurrence of local shear instabilities at particle-substrate and particle-particle interfaces due to thermal softening, as first shown by Assadi et al. [29]. Based on the concept of bonding by shear instabilities and by combining the results from modeling and experimental investigations, analytical expressions were recently developed to predict the ranges of optimum spray conditions with respect to the mechanical properties of spray materials, spray particle sizes, and particle temperatures [25]. Hidemasa Takana et al [27] survey a real-time computational simulation on the entire cold spray process by the integrated model of compressible flow field, splat formation model, and coating formation model, in order to provide the fundamental data for the advanced

high performance cold gas dynamic spray process with electrostatic acceleration. In this computation, viscous drag force, flow acceleration added mass, gravity, Basset history force, Saffman lift force, Brownian motion, and electrostatic force are all considered in the particle equation of motion for the more realistic prediction of in-flight nano/microparticle characteristics with electrostatic force and also for the detailed analysis of particle-shock-wave-substrate interaction. Computational results show that electrostatic acceleration can broaden the smallest size of applicable particle diameter for successful adhesion; as a result, wider coating can be realized. The utilization of electrostatic acceleration enhances the performance of cold dynamic spray process even under the presence of unavoidable shock wave.

The surface topography and temperature of the substrate

Some authors have examined the role of substrate surface topography on the formation of a bond between incoming particles and substrate. Tokarev et al. [30] have suggested that particles impacting a substrate in cold spraying first activate the substrate by roughening it; only once this has occurred is a coating able to initiate and grow. It has also been reported that, with a greater roughening of the substrate surface (going from polished to grit-blasted), deposition efficiency of metallic powders increases slightly [7]. J.G. Legoux et al surveyed [31] the change in temperature of the substrate during the deposition process was measured by means of a high speed IR camera. The coating formation was investigated as a function of (1) the measured surface temperature of the substrate during deposition, (2) the gun transverse speed, and (3) the particle velocity. Both single particle impact samples and thick coatings were produced and characterized. From the results obtained, based on Fig. 6 it was quite noticeable that the higher substrate temperature brought about a higher deposition rate of Cu particles, even under the condition where particles were kept at room temperature [31].

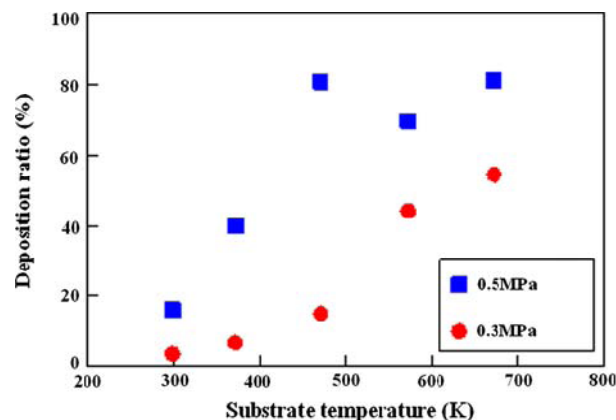


Figure 6: Relation between deposition ratio and both substrate temperature and gas pressure [27].

Vicek et al. [33] have discussed the bonding of particles in cold spraying primarily on the relative deformability of the particles and the substrate. They indicated that as the substrate deformability decreased, the ease with which particles bond to the surface also decreased. D. Zhang et al. [34] have work on spraying Aluminum powder a range of substrates. The substrates examined include metals with a range of hardness, polymers, and ceramics. The substrate surfaces had low roughness ($R_a < 0.1 \mu\text{m}$) before deposition of aluminum. It has been shown that initiation of deposition depends critically upon substrate type. A number of phenomena have been observed following spraying onto various substrates, such as substrate melting, substrate and particle deformation, and evidence for the formation of a metal-jet. Such phenomena have been related to the processes occurring during impact of the particles on the substrate. Metallic substrates which are mostly harder than the aluminum particles generally promoted deposition. Initiation was seen to be rapid on hard metallic substrates, even when deformation of the substrate was not visible. It may be concluded that the most successful initiation of bonding of Al. particles onto substrates of low roughness by cold spraying requires a metallic surface with hardness higher than that of the particles. The results of their work are completely opposite with the results of Vicek et al. [33].

Jianhong He et al. [35] worked on the influence of grit blasting, feedstock powder, and thermal spraying technology on the performance near the surface on the substrates side. The experimental results show that both the grit-blasting process and thermal spraying process harden the substrate and microhardness on or near the surface was noticeably increased. Grit blasting created deformed regions next to the surface of the substrate and interface between entrapped grits and substrate. When fine ferrite grain regions or pearlite phase were indented, higher hardness were obtained. While coarse ferrite grains created lower hardness value. Therefore, a fluctuation of hardness was observed in the hardness profiles. There are always fine grain zones near the surface because of higher cooling rates after hot rolling of the plate.

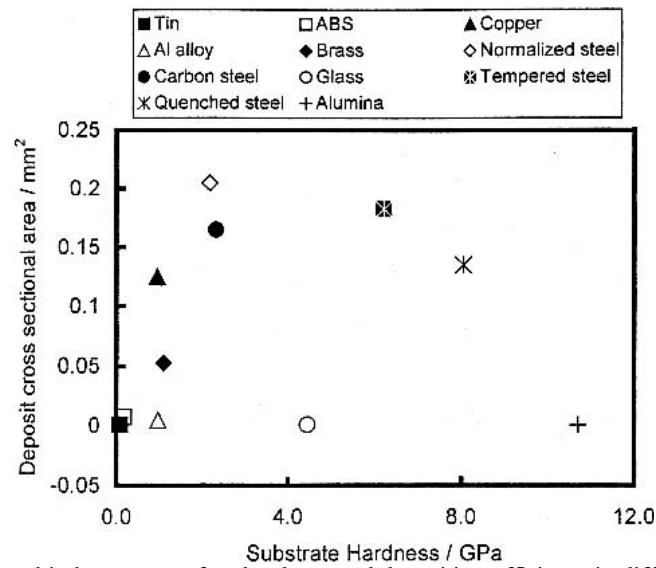


Figure 7: The relationship between surface hardness and deposition efficiency in different substrate [34].

Stephan Siegmann et al. [36] work shows that the topography of a roughened substrate (or bond coat) plays a key role in coating adhesion, and in phenomena which can influence adhesion. It is known that the complex nature of the substrate topographies cannot be adequately characterized over the entire range by conventional methods such as average roughness. The adhesive strength should be expressed as:

$$HA = m (S/A) (M/P) \quad (2)$$

where HA is the adhesive strength, m is a number between 0 and 1 that represents the fraction of the bond sites that are active, S is the characteristic strength of an individual, fundamental bond, A is the characteristic area of an individual, fundamental bond, M is the apparent area of the substrate surface measured at the scale of the characteristic area of an individual bond, and P is the nominal, or projected, area of the surface. The M/P ratio is the relative area at a particular characteristic area or scale, and it is always equal to or greater than 1. The M/P ratio is proposed to be a parameter for relating the texture to the actual adhesive bonding, whereas the droplet impact, spreading and wetting will influence the number of active bond sites, and hence the factor m. In this Paper they calculate the adhesion strength for thermal coating based on microstructures. This work shows that the relative area at scales below about $100 \mu\text{m}^2$ can be a good predictor of adhesive strength.

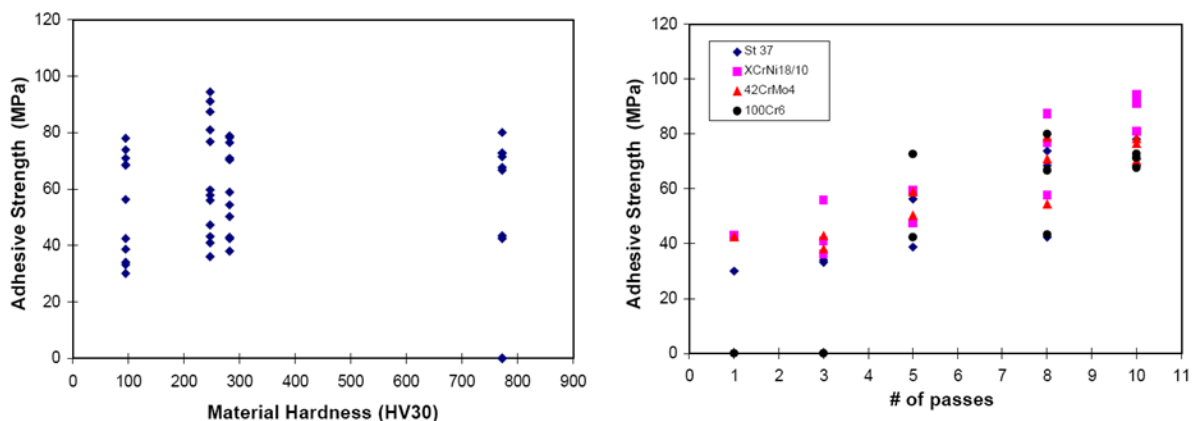


Figure 8: Tensile adhesive strength as a function of the substrate materials hardness and number of grit blast passes [36].

The adhesive strength as a function of substrate material hardness showed no strong correlation for all grit blast conditions. This means that the surface hardness itself is not a limiting factor for good adhesion, if surface preparation is

done properly. Adhesive strengths of at least 80 MPa could be achieved for all materials, even for the hardened steel, also it will increase by increasing the number of passes (Fig. 8).

In [37] which introduce a experimental way to calculate the adhesion strength, the tensile adhesion is RH is the strength obtained in the tension test, calculated from the quotient of the maximum load F_m and the cross-section of the specimen at the fractured face. Compared to the AISI 304 substrate, extreme roughening was recognized on the A6063 substrate surface. This is simply attributed to the lower hardness of A6063 substrate compared to AISI 304 substrate. From the observation results on the cross-section microstructure for both substrates, it was revealed that the adhered copper particles deformed themselves on the harder AISI 304 substrate while both particles and substrate deformed each other on the softer A6063 substrate surface [31].

On the other hand, the successful building up of coating at high deposition efficiency depends on the design of powder porous structure [39] it was found that the WC-Co cermet particles with the porosities of 30% and 44% could be deposited on the substrate of different hardness from 200 to 800 kgf/mm². The deposition of the particles is mainly attributed to the deformation of powders themselves. The properly designed porous cermet powder with certain hardness is necessary to deposit hard WC-Co cermet coating. In HP powders it is evident that the layer becomes more uniform with the increase of substrate hardness. But in MP powders the fracture of powder particles likely occurred compared the spherical morphology of the starting powder with the relative rough one; the deposited particles are relatively complete. LP powder, it was observed that with stainless steel substrate the particles penetrated into the substrate to certain depth, depending on the particle size and subsequently particle velocity. On the other hand, with the Ni40 and Ni60 substrates only craters were observed on the surface [40].

M. Kulmala worked on [42]. A laser-assisted low-pressure cold spraying (LALPCS) is a one-step coating process in which the laser irradiation interacts simultaneously with the spraying spot on the substrate or deposited coating surface in order to improve coating properties. It is expected that the LALPCS could be an effective method to improve a low-pressure cold sprayed coating deposition efficiency and denseness. The Results showed that laser irradiation improved the copper coating denseness and also enhanced deposition efficiency. The coating thickness increased mainly in the function of the laser power.

Z.D. Xiang et al. [43] showed that it seems reasonable to expect that the coating would grow faster in a steel surface with a finer grain structure if the coating growth process can be significantly influenced by the diffusion through grain boundaries and microstructural defects. Indeed, it has been demonstrated recently that the solid-state diffusion process at low temperatures can be substantially enhanced in the plastically deformed steel surface in which grain sizes are reduced to the range of nanometers and large numbers of microstructure defects are simultaneously generated by a cold working process termed surface mechanical attrition treatment. The shot peened surface would have a microstructure that differs significantly from that of the bulk. It would contain a large number of grain boundaries and lattice defects such as dislocations.

T. Marrocco et al. [55] shows that the bond strength between a coating (deposited with CTi at 29 bar) and substrate, as a function of substrate surface condition, is shown in Fig. 9. It can be seen that the grit-blasted surface condition resulted in the lowest bond strength, with an average strength of 8 MPa, while the polished and ground surfaces resulted in higher bond strengths of 22 MPa.

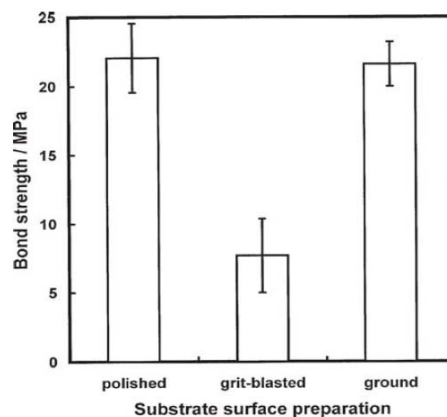


Figure 9: Bar chart showing the effect of substrate condition on the bond strength of deposits sprayed at 29 bar gas pressure using CTi powder(course powder) (error bars represent the standard error of the mean)[55].



Surface preparation	R_a , μm	R_z , μm	R_k , μm
Ground	0.21 ± 0.03	1.57 ± 0.16	0.73 ± 0.06
Polished	0.046 ± 0.002	0.46 ± 0.09	0.101 ± 0.005
Grit blasted	2.66 ± 0.06	17.03 ± 0.39	9.13 ± 0.31

Table 1: Parameters describing the surface profile of the substrates as a function of surface preparation method [55]. Values are the average of three measurements, with standard error of the mean indicated.

Other important parameters

There are many other important parameters which have a great influences on cold spray process. S. Barradas et al. [44] developed an experimental simulation of the particle-substrate reactions at the particle impingement. This simulation is based on original flier impact experiments from laser shock acceleration. Relevant interaction phenomena were featured and studied as a function of shearing, plastic deformation, phase transformation primarily. They applied a FEM analysis for cold spray coating. The ALE method provides a suitable way to examine the particle deformation in cold spraying. Moreover, the numerical results also show that there exists the similarity for the deformation of particles of different diameters [45]. Viecek et al. [33] have examined the impact of a range of powder types onto a range of substrate materials in cold spraying. They explained differences in the ability of particles to deposit in terms of the mechanical properties of the particles and substrate and the specific impulse of the impact. They related bonding primarily to the relative ease of deformation of the substrate and particle, and concluded that if the particle was significantly more deformable than the substrate, then adhesion was not possible.

Van Steenkiste et al. [46] described the deposition of large aluminum particles ($> 50 \mu\text{m}$) onto a brass substrate by cold spraying; they argued that particle melting does not occur, with bonding resulting from severe deformation and subsequent disruption of oxide films on metallic particles allowing nascent metal surfaces to come into contact. Bolesta et al. [47] deposited aluminum by cold spraying onto a nickel substrate. Using x-ray diffraction, they detected the formation of Ni_3Al and suggested that the interface phase was in the region of 200 to 500 Å in thickness. This indicates that melting may occur as a precursor to the formation of the new phase; such bonding was referred to as a chemisorptional bond.

Wen-Ya Li et al. [48]. The microhardness of the as-sprayed and annealed Cu coating is shown in Fig. 10. The microhardness of the as-sprayed Cu coating was about 132 $\text{HV}_{0.2}$, which was consistent with those reported by Borchers et al. [49, 50] and McCune et al. [51].

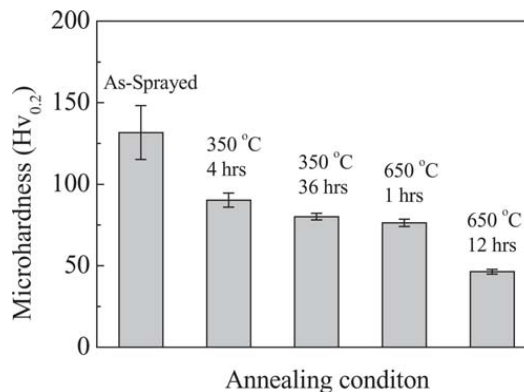


Figure 10: The effect of annealing on microhardness of the coated specimen [48].

H. Lee et al. [52] worked on the effect of pressure on Al coating. In the case of hardness, the coating of Al at low pressure condition had higher hardness because of work hardening (peening effect) resulted from bounced-off Al particles (0.7 MPa). Therefore, it was found that the gas pressure as a processing parameter could have an influence on Al coating's properties. The results of their work are shown in Fig. 11.

Eric Irissou et al. [47] found out coatings with the starting powder based on the larger Al particles are systematically harder than coatings made with the smaller size Al powder mixtures. This is likely due to the larger peening effect of the large particles due to their higher kinetic energy. The addition of Al_2O_3 to the Al powders helps improving the coating deposition. Because Al_2O_3 particles alone cannot form a coating in our experimental conditions, they play only a role of peening and roughening of the layers during deposition. The addition of Al_2O_3 to Al powder increased the adhesion of the coating on the substrate.

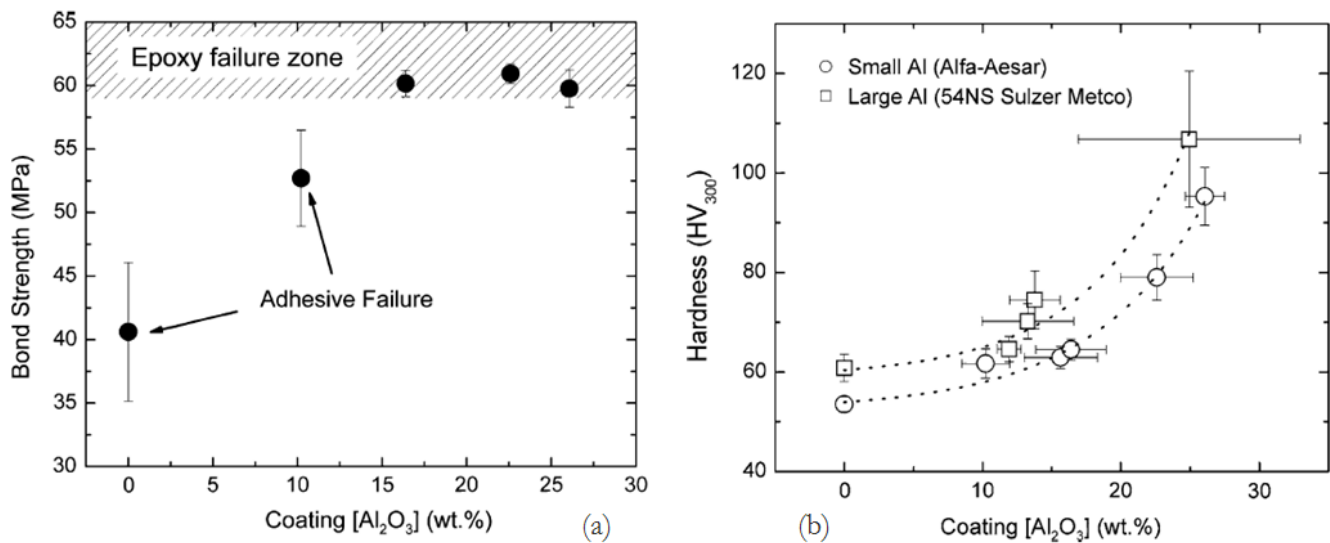


Figure 11: a) Bond strength against coating Al₂O₃ concentration;
b) Vickers hardness measurements against Al₂O₃ concentration [52].

T.S. Price et al [53] described a method for characterizing the bonding between aluminum and copper particles following deposition by cold spraying. The degree of bonding between particles within cold-sprayed deposits is of great importance as it affects their mechanical and physical properties. This has shown that on impact, high plastic strain rates can occur in the immediate vicinity of the contact zone which lead to adiabatic heating, localized softening of the material and the formation of what are termed shear instabilities. It was found that at inter-particle boundaries oxides were identified that appeared to have originated from the original feedstock. Although evidence of ruptured surface oxides was found, which allowed true metal-to metal contact to occur at points along particle interfaces, true metal to metal bonding was incomplete [54]. In this respect the occurrence of shear instabilities when high velocity particle impact occurs has a key role in breaking down oxide films and creating intimate metallic contact which will favor atomic level bonding during elevated temperature annealing. The increase in fractional interface coverage with increasing primary gas pressure, which was measured in this work, can presumably be attributed to more extensive breakdown of oxide films at the higher pressure. In this work, it was noted that an increase in bonding pressure increased the area over which intermetallics formed, because of increased oxide break-up. The intermetallic layer development during elevated temperature annealing can be explained in terms of a solute diffusion controlled process.

Between the other parameters residual stress of coating is more interesting. W.B. Choi et al. [41] discuss and evaluate the relationships between the microstructure, properties and residual stresses in CS Al coatings, combining indentation, dilatometry, resistivity measurements and neutron diffraction techniques. The results show that:

- 1) Residual stresses in CS Al are virtually non-existent and in fact are lower than the peening stresses induced during surface roughening.
- 2) Elastic modulus of CS Al is lower than bulk by approximately a factor of 2, attributed to incomplete bonding between particles. Annealing might decrease modulus presumably due to weakening of the oxide interphases. This damage is ameliorated during annealing in air, likely due to compression from further oxidation.
- 3) As-sprayed CS Al has a higher flow stress than bulk Al, due to hardening of particles. In addition, plastic behavior is brittle, as evidenced by cracking observed underneath indents. Annealing softens particles enough to promote ductile behavior, and flow stress is lowered below bulk. The nature of the brittle to ductile transition is interesting and warrants further study.
- 4) Thermal expansion of the coating is increased by oxidation and decreased by the presence of oxides. The only CS coatings that exhibit CTE closely matching bulk values were those annealed in argon.
- 5) Electrical resistivity displays some anisotropy (i.e. higher through-thickness than in-plane), as one would expect. Annealing in air increases and decreases resistivity for coatings from non-oxidized (spherical) and pre-oxidized (globular) feedstocks, respectively. This is likely due to more oxidation in the former and a greater extent of annealing in the latter coatings. Annealing in Ar causes an anisotropy reversal in the coatings from pre-oxidized feedstock, presumably due to more "vertical" than "horizontal" micro-damage.

THE EFFECT OF CGDS ON SUBSTRATE PROPERTIES

The effect cold spray coating process on many substrate properties specially the fatigue behavior was studied by many authors. T.S. Price et al. [56] studied the Effect of Cold Spray Deposition of a Titanium Coating on Fatigue Behavior. Thus, Coatings were deposited onto samples with two different surface preparation methods (as-received and grit-blasted). The fatigue life of the as-received and grit-blasted materials, both before and after coating was measured. A 15% reduction in fatigue endurance limit was observed after application of the coating to the as-received substrate, but no significant reduction was observed on its application to the grit-blasted substrate. It has been shown that CGDS titanium coatings have a detrimental effect on the fatigue endurance limit of Ti6Al4V. Compressive stresses found within a coating are usually associated with increased fatigue endurance limits; however, those found within CGDS titanium coatings are too low to prevent fatigue crack formation, and these lead to premature fracture.

Surface Finish	Surface Roughness, Ra, μm	Fatigue endurance limit, MPa	Modulus, GPa
As-received	2.7	633	107
As-received and sprayed	8.6	537	20
Grit-Blasted	3.5	507	107
Grit-blasted and sprayed	8.5	512	19

Table 2: Effect of surface finish on fatigue endurance limit [56].

E. Sansoucy et al. [57] work on in particular the bending fatigue and the bond strength, of the Al-Co-Ce coatings. The results show that the Al-Co-Ce coatings improved the fatigue behavior of AA 2024-T3 specimens when compared to uncoated and Alclad specimens. It is suggested that the increase in the fatigue properties of the specimens can be attributed to the residual compressive stresses induced in the coatings and to the high adhesion strength of the coatings to the substrates. The fatigue results can be rationalized on the basis of two important factors: the existence of residual compressive stresses, and the high adhesion of the coatings to the substrate. The high velocity impacts of particles cause plastic deformation of the underlying layers and generate compressive residual stresses.

Qiang Zhang et al. [58] nanostructured NiCrAlY bond coating was deposited after that a shot-peening treatment was applied to the as-sprayed coating to modify the coating surface morphology. It was found that a uniform oxide layer was formed on the surface of the shot-peened nanostructured NiCrAlY coating during oxidation at temperatures of 900 °C and 1000 °C. The surface geometry of the cold-sprayed NiCrAlY coating must be modified to promote formation of a protective oxide film during oxidation, through application of a post-treatment process such as shot-peening. The surface of as-sprayed coating was very rough, and some protrudings presented on the surface of bond coating, as shown in Fig. 12. However, after shot-peening treatment, the surface of bond coating was uniform and smooth, and compacted, as shown in Fig. 12. The surface roughness was significantly reduced from $R_a=5.6\pm 1.2 \mu\text{m}$ ($R_z=26.2 \pm 3.5 \mu\text{m}$) at the as-sprayed state to $R_a=3.1\pm 0.6 \mu\text{m}$ ($R_z=14.1\pm 1.3 \mu\text{m}$) at the shot-peened state.

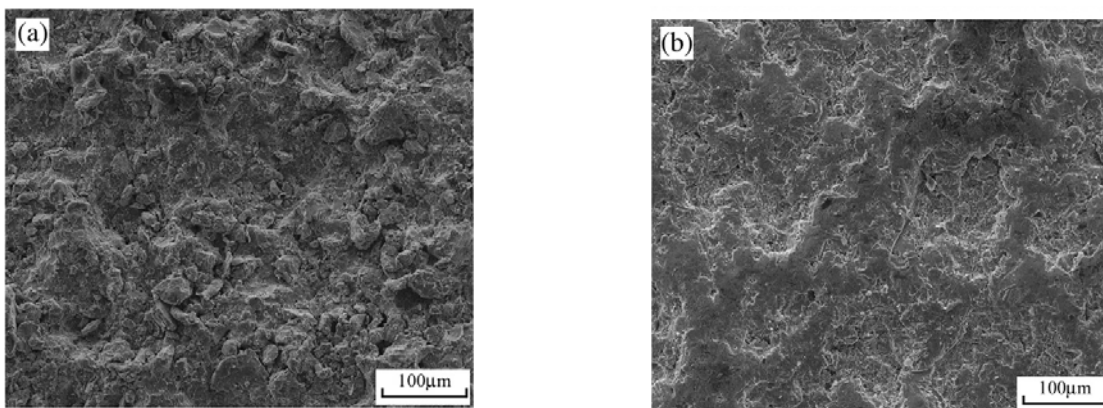


Figure 12: Surface morphology of as-sprayed NiCrAlY bond coating (a) and after shot-peened NiCrAlY bond coating (b)[58].

And finally the effect of cold spray on residual stress in substrate is shown in Fig. 13. This graph displays in-plane stresses in the substrate before deposition and the coating–substrate system after deposition. The bare substrate exhibits ~ 90 MPa in compression at the surface, presumably due to peening effects of sand blasting. This is partially balanced by a tensile region (max 50 MPa) in the interior. Cold spray deposition induces a slight (average 10 MPa) compressive stress through the thickness of the coating, which thus reduces the near-surface substrate stress magnitude [60].

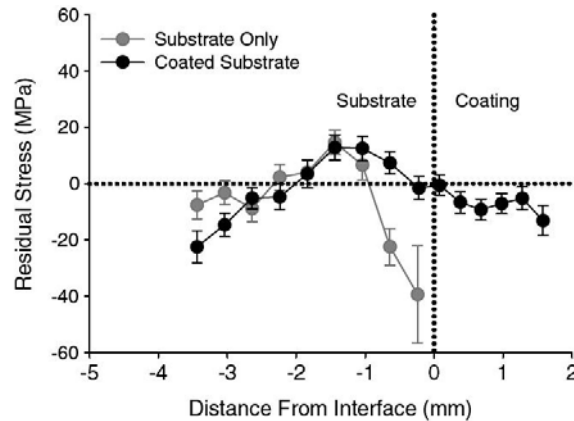


Figure 13: Residual stress measurement of CS Al coating [60].

CONCLUSIONS

Many studies have been conducted since ten odd years ago about the cold spray coating and its related parameter. Many reviewers, as it is mentioned above, have been trying to survey different factors about CGDS such as calculation deposition efficiency, find a way, for example by changing the parameters, to increase the DE, critical velocity for different materials, effect of thermal annealing on cold spray, etc. Although the authors believe that the most important question remained vague is the main reason of bounding of the particles to the substrate, there are a lot of books and articles in this regard.

In this point of view, there is still a field which is missed and it is rarely to find references about the effect of shot peening on cold spray coating. The authors believe that Shot-peening which is very famous in increasing the fatigue limit by applying the residual stress on the surface of specimen, might have appreciable effects on the CGDS parameters. It seems necessary to find the answers of the following questions:

- What are the results of applying shot-peening before cold spray coating on substrate on the CGDS factors such as deposition efficiency, critical velocity, bounding strength, etc. This answer might be different for different materials, thus it should be experimented for many materials which are suitable for CGDS.
- Are the important parameters of substrate (For instance, physical properties of substrate such as electrical and thermal conductivity, fatigue limits which somehow directly related to residual stress on the surface, ductility behavior of substrate) will change by shot-peening before and after the CGDS?

These questions should be answered by both experimental test and numerical solution.

REFERENCES

- [1] A.Papryin, V.Kosarev, S.Klinkov, A.Alkhimov, V.Fomin, Elsevier, (2006).
- [2] R.C. McCune, A.N. Papyrin, J.N. Hall, W.L. Riggs II, P.H. Zajchowski, Houston, ASM (1995), 1-5.
- [3] François Raletz, Michel Vardelle, Guillaume Ezo'o, *Surface & Coatings Technology* 201 (2006) 1942–1947.
- [4] A.P. Alkhimov, S.V. Klinkov, V.F. Kosarev, A.N. Paprin, *J. Appl. Mech. Phys.* (1997) 176-183.
- [5] J. Karthikeyan, *Cold Spray Technology: International Status and USA*, (2000).
- [6] US army laboratory WebPages, Cold Spray Coating application.
- [7] T. Stoltenhoff, H. Kreye, H.J. Richter, (2002) 542-550.
- [8] S.V. Klinkov, V.F. Kosarev, *Journal of Thermal Spray Technology*, (2006) 364.
- [9] A.A. Deribas, I.D. Zakharenko, *Fisika Goreniya I Vzryva.*, (1974) 409–421.



- [10] R. Gr. Maev, V. Leshchynsky, *Journal of Thermal Spray Technology*, (2006) 198.
- [11] L. Ajdelsztajn, B. Jodoin, P. Richer, E. Sansoucy, E.J. Lavernia, *Thermal Spray Technology Volume* (2006) 495.
- [12] P.O. Kettunen, *Physical Metallurgy*. IMS Tampere University (1995).
- [13] R.C. McCune, A.N. Papyrin, J.N. Hall, W.L. Riggs II, P.H. Zajchowski, C.C. Berndt and S. Sampath, (1995) 1-5.
- [14] R.C. Dykhuizen, M.F. Smith, D.L. Gilmore, R.A. Neiser, X. Jiang, S. Sampath, *Impact of High J. Therm. Spray Technol.*, (1999) 559-564.
- [15] K. Sakaki, N. Huruhashi, K. Tamaki, Y. Shimizu, E. Lugscheider and C.C. Berndt, Ed., (2002) 385-389.
- [16] J. Vlcek, L. Gimeno, H. Huber, E. Lugscheider, *Thermal Spray* (2003) 37-44.
- [17] V.F. Kosarev, S.V. Klinkov, A.P. Alkhimov, A.N. Papyrin, *J. Therm. Spray Technol.*, (2003) 265-281.
- [18] F. Gurtner, C. Borchers, T. Stoltenhoff, H. Kreye, H. Assadi, *Thermal Spray* (2003) 1-8.
- [19] K. Sakaki, T. Tajima, H. Li, S. Shinkai, and Y. Shimizu, *Thermal Spray* (2004) 358-362.
- [20] D.L. Gilmore, R.C. Dykhuizen, R.A. Neiser, T.J. Roemer, M.F. Smith, *J. Therm. Spray Technol.*, (1999) 576-582.
- [21] R.C. McCune, A.N. Papyrin, J.N. Hall, P.H. Zajchowski, C.C. Berndt, S. Sampath, (1995) 1-5.
- [22] D. Zhang, P.H. Shipway, D.G. McCartney, *J. Therm. Spray Technol.*, (2005) 109-116.
- [23] Frank Gurtner, Thorsten Stoltenhoff, Tobias Schmidt, Heinrich Kreye, *Journal of Thermal Spray Technology* (2006) 223.
- [24] R.C. McCune and A.N. Papyrin, J.N. Hall, W.L. Riggs II, P.H. Zajchowski, (1995).
- [25] D.L. Gilmore, R.C. Dykhuizen, R.A. Neiser, T.J. Roemer, M.F. Smith, *J. Thermal Spray Technol.*, (1999) 576-582.
- [26] T. Schmidt, F. Gurtner, H. Assadi, H. Kreye, *Acta, Mater.*, (2006) 729-742.
- [27] Hidemasa Takana, Kazuhiro Ogawa, Tetsuo Shoji, Hideya Nishiyama, *Journal of Fluids Engineering*, (2008).
- [28] A.N. Papyrin, V.F. Kosarev, S.V. Klinkov, A.P. Alkhimov, *DVS* (2002) 380-384.
- [29] T. Stoltenhoff, H. Kreye, H.J. Richter, H. Assadi, *ASM International*, (2001) 409-416.
- [30] A.O. Tokarev, *Metal Sci. Heat Treatment*, (1996) 135-139.
- [31] J.G. Legoux, E. Irissou, C. Moreau, *Journal of Thermal Spray Technology* (2007) 619.
- [32] M. Fukumoto, H. Wada, K. Tanabe, M. Yamada, E. Yamaguchi, A. Niwa, M. Sugimoto, M. Izawa, *Journal of Thermal Spray* (2007) 643.
- [33] J. Vlcek, H. Huber, H. Voggenreiter, A. Fischer, E. Lugscheider, H. Hallén, G. Pache, *Thermal Spray*, (2001) 417-422.
- [34] D. Zhang, P.H. Shipway, D.G. McCartney, *J. Therm. Spray Technol.*, (2005) 109-116.
- [35] Jianhong He, Bruce Dulin, Thomas Wolfe, *J. Thermal Spray Technology* (2008) 214.
- [36] Stephan Siegmann, EMPA Thun, Thun, Switzerland Christopher A. Brown, *Surface Metrology Laboratory, WPI*, (1999) 355-360.
- [37] EN 582- Thermal spraying; determination of tensile adhesive strength (1993-10).
- [38] Junji Morimoto, Tetuya Onoda, Yoh Sasaki, Nobuyuki Abe, *Elsevier* (2004) 527-532.
- [39] Pei-Hu Gao, Yi-Gong Li, Chang-Jiu Li, Guan-Jun Yang, Cheng-Xin Li, *Journal of Thermal Spray Technology* (2008) 742.
- [40] Pei-Hu Gao, Chang-Jiu Li, Guan-Jun Yang, Yi-Gong Li, Cheng-Xin Li, *Surface & Coatings Technology* (2008) 384-390.
- [41] W.B. Choi, L. Li, V. Luzin, R. Neiser, T. Gnaupel-Herold, H.J. Prask, S. Sampath, A. Gouldstone, *Acta Materialia* (2007) 857-866.
- [42] M. Kulmala, P. Vuoristo, *Surface & Coatings Technology* (2008) 4503-4508.
- [43] Z.D. Xiang, P.K. Datta, *Scripta Materialia* (2006) 1151-1154.
- [44] S. Barradas, V. Guipont, R. Molins, M. Jeandin, M. Arrigoni, M. Boustie, C. Bolis, L. Berthe, M. Ducos, *Journal of Thermal Spray Technology*, (2007) 548.
- [45] Wen-Ya Li, Hanlin Liao, Chang-Jiu Li, Gang Li, Christian Coddet, Xiaofang Wang, *Applied Surface* (2006) 2852-2862.
- [46] T.H. Van Steenkiste, J.R. Smith, R.E. Teets, *Surf. Coat. Technol.*, (2002) 237-252.
- [47] A.V. Bolesta, V.M. Fomin, M.R. Sharafutdinov, B.P. Tolochko, *Nucle. Instrum. Meth., Phys. Res. A*, (2001) 249-252.
- [48] Wen-Ya Li, Chang-Jiu Li, Hanlin Liao, *Journal of Thermal Spray Technology*, (2006) 206.
- [49] C. Borchers, F. Gurtner, T. Stoltenhoff, H. Assadi, H. Kreye, *Appl. Phys.*, (2003) 10064-10070.
- [50] C. Borchers, F. Gurtner, T. Stoltenhoff, H. Kreye, *Acta Mater.*, (2005) 2991-3000.
- [51] R.C. McCune, W.T. Donlon, O.O. Popoola, E.L. Cartwright, *J. Therm. Spray Technol.*, (2000) 73-82.
- [52] H. Lee, H. Shin, S. Lee, K. Ko, *Materials Letters* (2008) 1579-1581.
- [53] T.S. Price, P.H. Shipway, D.G. McCartney, E. Calla, *D. Journal of Thermal Spray Technology* (2007) 566-570.
- [54] K. Balani, A. Agarwal, S. Seal, J. Karthikeyan, *Scripta Mater.*, (2005) 845-850.



- [55] T. Marrocco, D.G. McCartney, P.H. Shipway, A.J. Sturgeon, *Journal of Thermal Spray Technology*, (2006) 263.
- [56] T.S. Price, P.H. Shipway, D.G. McCartney, *J.of Thermal Spray Technology* (2006) 507.
- [57] E. Sansoucy, G.E. Kim, A.L. Moran, B. Jodoin, *J. Thermal Spray Technology* (2007) 651.
- [58] Qiang Zhang, Chang-Jiu Li, Cheng-Xin Li, Guan-Jun Yang, Siu-Ching Lui, *Surface & Coatings Technology* (2008) 3378–3384.
- [59] P. Bansal, P.H. Shipway, S.B. Leen, (2006) 5318 – 5327.
- [60] W. B. Choi, L. Li, V. Luzin, R. Neiser, T. Gnaupel-Herold, H. J. Prask, S. Sampath. A. Gouldstone, , *Acta Materialia* 55 (2007) 857-866.