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USAGE OF THERMAL COATINGS FOR THE IMPROVEMENT OF MATERIAL PROPERTIES FOR BALLISTIC PROTECTION IN THE MILITARY FIELD. A REVIEW

BY

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Abstract. In this review, the impact on the ballistic protection properties for some materials used in the military field was analysed, in relation to the improvement of mechanical and microstructural properties.

The main objective was the ballistic protection materials with the potential to be used as ballistic protection for applications such as bulletproof vests.

In the addition to the evaluation related to improvement of the considered material properties, the impact on the improvement of the ballistic protection grades was also evaluated in relation with the test standards such as: NIJ, VPAM, NATO STANAG 4569 (Association of Test Laboratories for Attack Resistant Materials and Constructions, 2024; NATO Standardization Office NSDD, 2022; NIJ, 2023).

The evaluation that is subject of this paper, it consists of two types of processes: thermal coating using Atmospheric Plasma Spray (APS) method and coatings using Cold Spray method.

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Using these methods of improving the mechanical properties, the impact on ballistic protection grades was highlighted, considering both standards: (NIJ Standard 0101.07 (NIJ, 2023) and NIJ Standard 0123.00 (NIJ, 2023), which are defined in alignment with National Institute of Justice from USA. The impact of the materials was also evaluated in relation to the standard VPAM “Association of Test Laboratories for Attack Resistant Materials and Constructions” (Association of Test Laboratories for Attack Resistant Materials and Constructions, 2024) with intended use in Europe and also standard “NATO-Standardization Agreements” AEP-55 STANAG 4569 (NATO Standardization Office NSDD, 2022).

Keywords: APS; Cold Spray; Mechanical properties; Microstructural properties; Ballistic protection.

1. Introduction

Ballistic protection for people and military vehicles is one of the most important characteristics in the whole world considering the evolution of technologies in the military field these days. Ballistic protection is the main defence weapon against the enemy.

In this paper, the improvement of mechanical and microstructural properties was analysed for various materials with applicability in the military field and the impact on ballistic protection, as well as: steel 52100 (Lupu, 2024), steel ARMOX Advance (Coufal *et al.*, 2022), aluminium alloys 2024-T351, 6061-T651, 7075-T651 (Özşahin and Tolun, 2010), AW-5754-H111 (Lorenzo-Bañuelos *et al.*, 2021), ceramic B4C (Mi *et al.*, 2023), but also a combination of this materials.

Ballistic protection elements are divided into two categories:

- Soft ballistic elements
- Hard ballistic elements

The purpose of soft ballistic elements is to protect against projectiles from pistols and small-calibre machine guns. This type of protection can also incorporate protection against stabbing or impact.

The materials used for bulletproof vest, which fulfil this kind of ballistic protection element, are usually para-aramid and high-performance polyethylene (HPPE), (Mehler Protection ©, 2022).

Hard ballistic protection elements, on the other hand, are designed to protect against projectiles from large-calibre weapons. These elements can be used both individually and together with the soft ballistic protection elements, in order to achieve a higher level of protection.

The materials used for bulletproof vest, which fulfil this kind of superior ballistic protection, are usually aluminium oxide (Al₂O₃), silicon carbide (SiC), boron carbide (B₄C) or other type of ceramic materials.

The standards used to evaluate the level of protection are also divided according to each type of protection as follows (Mehler Systems ©, 2023):

For soft ballistic protection elements:

- NIJ (America) - NIJ I, NIJ II, NIJ IIA, NIJ IIIA
- VPAM (Europe)- VPAM 1, VPAM 2, VPAM 3, VPAM 4, VPAM 5
- CAST (England) - HO1, HO2, KR1
- TR (Germany) - SK1, SK2

For hard ballistic protection elements:

- NIJ (America) - NIJ III, NIJ IV
- VPAM (Europe) -VPAM 6, VPAM 7, VPAM 8, VPAM 9, VPAM 10
- CAST (England) - HO3, HO4, SG1, SP
- TR (Germany) - SK3, SK4

For the NIJ standard, starting from November 2023, there is a revision of the 0101.06 standard from 2008 (NIJ, 2008), to the new version 0101.07 (NIJ, 2023). Ballistic protection levels testing has been moved to “Specification for NIJ Ballistic Protection Levels and Associated Test Threats, NIJ Standard 0123.00” (NIJ, 2023), which is a new stand-alone document. The nomenclature of the test levels is also modified as described in the table below:

Table 1

NIJ ballistic protection standard differences (NIJ, 2023)

NIJ 0101.06 protection level	NIJ 0101.07 protection level	Notes
<i>NIJ II</i>	<i>HG1</i>	<i>HG=handgun</i>
<i>NIJ IIIA</i>	<i>HG2</i>	
<i>NIJ III</i>	<i>RF1</i>	<i>RF=rifle</i>
<i>NA</i>	<i>RF2</i>	
<i>NIJ IV</i>	<i>RF3</i>	

NIJ anticipates maintaining the 0101.06 product listing at least through the end of year 2027 (NIJ, 2023).

The protective vest, as the general rule, consists of two elements, a cover and the protective element. Depending on the needs, it can also be extended with plate supports in relation to required applicability.

Protective vests are divided into several categories: covered vests and open vests (generally used by police and security agencies) and open vests with modular protective elements (used in the military field) (Mehler Protection ©, 2023).

In order to be compliant with ballistic protection standards such as NATO AEP-55 STANAG 4569, which aims to evaluate the protection of people and lightly armoured military vehicles against the penetration of projectiles, are used materials such as steel from the ARMOX Advance series (Coufal *et al.*, 2022).

Can be used as well a combined set of plates out of aluminium, steel, ceramics and even plastic which are bonded together (Tsirogiannis *et al.*, 2024).

Ballistic steel is produced by the casting process, followed by the cold rolling process in plates of various thicknesses. This type of material is known as rolled homogeneous armour (RHA) steel (Khan *et al.*, 2022).

Also, the plates are subjected to thermal processes of austenitizing, quenching and tempering processes, depending on the desired properties (Khan *et al.*, 2022).

2. Methods and materials used to perform thermal depositions

2.1. Thermal deposition method of Atmospheric Plasma Spray (APS)

The process occurs after the creation of an electric arc between a tungsten cathode electrode and a copper anode electrode. The two elements are cooled with water, and a gas circulates between the two electrodes (example: Helium, Hydrogen, Nitrogen or gas mixtures). When the circuit between the two electrodes is closed, due to the electric arc, the dissociation and ionization of the gases is created, thus the plasma is formed (Lupu, 2024; Ltd, AM Philpot (Hard Chrome)).

The thermal coating in the plasma jet is formed when the gas reaches temperatures of 7000-8000°C, in some applications even exceeding 10000°C (Lupu, 2024).

The sprayed material (in the form of powder) is injected into the spraying device, where it is melted and propelled at high speed towards a support surface. When it reaches this surface, the sprayed material cools down quickly and forms the coating layer. In order to achieve an even tighter bond between the base material and the coating material, an additional bond coat layer can be made beforehand with powders specially designed.

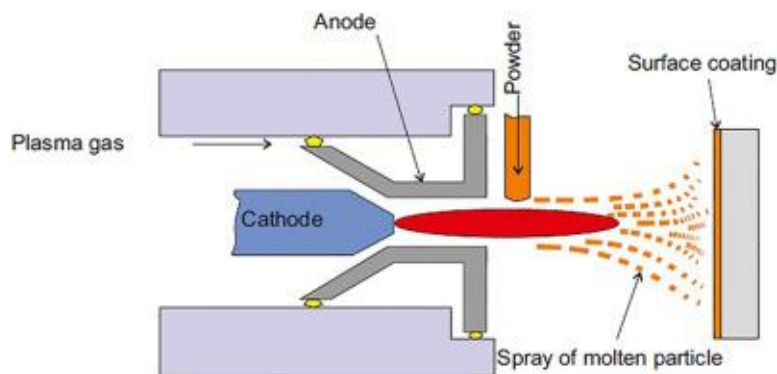


Fig. 1 – Schematic view of thermal coating plasma jet device (Devasia *et al.*, 2021).

2.2. Cold deposit method (Cold Spray)

During the cold deposition method, compared to the plasma jet deposition method, the sprayed material is not the result of combustion or ionization of the gas used in this deposition process.

The gas or mixture of gases used for this type of deposition is compressed to a pressure of 3.5 MPa and a temperature of approximately 700°C. The heated gas is introduced into the device through a system of Laval type nozzles (convergent-divergent), it expands thus reaching supersonic speeds. The powders are introduced into the device through a system of nozzles, then they are accelerated to adhere to the support surface, the process being carried out at temperatures below the melting point of the sprayed material. The particles used in the cold coating method, through the impact with the support surface, achieve a plastic deformation and the speed with which they are sprayed reaches values between 500-1500 m/s (Lupu, 2024).

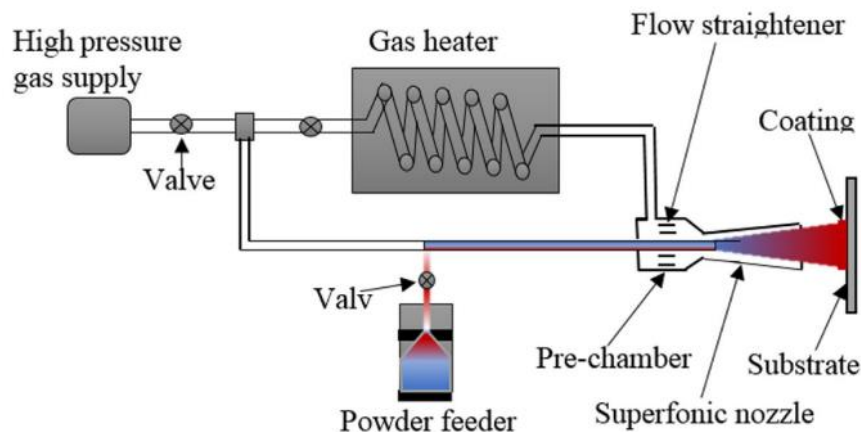


Fig. 2 – Cold deposit device scheme (Singh, 2023).

2.3. Types of powders used for deposition layers

2.3.1. Types of powders used for Atmospheric Plasma Spray deposition method

The recommended substrate for plasma jet thermal deposition applications must have a surface hardness of at most 55 HRC (Oerlikon Metco (US) Inc, 2022).

Depending on the characteristics that the protective layer must meet, the powders used are classified into several categories, as follows (Oerlikon Metco (US) Inc, 2024):

- Ceramic powders: alumina (Al_2O_3), zirconia (ZrO_2) and titania (TiO_2) which offers resistance to high temperatures, resistance to wear and thermal insulation properties.
- Metallic powders and alloys: nickel-based alloy, cobalt based alloy and stainless steel which offers corrosion protection and wear protection.
- Carbides powders: Tungsten carbide (WC), Chromium carbide (Cr_3C_2), Titanium carbide (TiC) which offer an improvement of surface hardness properties and wear resistance.

2.3.2. Types of powders used for Cold Spray deposition method

The powders used for the Cold Spray deposition method are also classified according to the type of application as follows (Solvus Global, 2024):

- a. Powders used for improving the mechanical properties of wear and impact:
 - WIP-BC1 – represents the bonding layer, based on chromium carbide and nickel agglomerates, defined to create the connection between the base material and the coating layer which follows to be created.
 - WIP-C1, WIP-C2 – Chromium carbide-based powders.
 - WIP-W1, WIP-W2 – Tungsten carbide-based powders.
- b. Aluminium-based powders for surface and dimensional repairs:
 - DARC-AL5056-G1H4
 - DARC-AL6061-G1H1
 - DARC-AL7075-G1H1
 - DARC-AL7075BC-G1H1 – additionally offers protection against corrosion.
- c. Powders used for improvement of corrosion protection properties and high temperature resistance:
 - HiT-718-B – nickel-based powder which contains ceramic constituents.
 - HiT-Nb – Niobium based powder.
 - HiT-Ta – Tantalum based powder.

3. Properties obtained by using thermal deposition methods

3.1. The properties of the coatings obtained by Atmospheric Plasma Spray deposition method (APS)

Miriam Lorenzo-Bañuelos and the collaborators evaluated the impact on thermal deposition with APS method, using as a base material the 5000 series aluminium alloy, AW-5754-H111, applying NiAl powder from Metco 450NS on the F4 plasma jet equipment of the manufacturer Oerlikon Metco, Switzerland,

using nitrogen cooling and having the theoretical value of the plasma temperature of 11,000°C. Through this process, the aim was to improve wear properties, resistance to high temperatures and corrosion properties.

Regarding the evaluation of the results, for SPT - Small Punch Test ((CEN) European Committee for Standardization, 2019) was used 430KN MTS-Criterion equipment, Vickers HV0.3 surface microhardness was evaluated according to ASTM E384-17 and the roughness of the resulted surfaces was also evaluated according ISO 4287-1997 using the Mitutoyo Surftest SJ210 measuring instrument (Lorenzo-Bañuelos *et al.*, 2021).

The Small Punch Test (SPT) is based on the punching of a 0.5mm thin plate until it breaks, by means of a punch, while the edges of the plate are rigidly clamped at the top and bottom surfaces. By performing the test, it is evaluated the load and displacement of the punch, where P_{max} represents the maximum load, $P_y/(t/10)$ represents the yield load (the load corresponding to the maximum displacement at the yield limit) and ΔP_{max} represents the displacement corresponding to the maximum load (Lorenzo-Bañuelos *et al.*, 2021; (CEN) European Committee for Standardization, 2019).

Several deposits were made, resulting in a total of 15 combinations of surfaces.

In the interpretation of the results, the variables of three process parameters were taken into account as impact for the mechanical and quality properties of the coating layer: spraying distance, argon gas flow rate and transverse spraying speed, resulting in a response surface methodology (RSM) and the variables were used as input being coded to obtain a cubic design of experiments (DoE) (Lorenzo-Bañuelos *et al.*, 2021; Azarmi *et al.*, 2008).

In a first stage, the maximum load from the Small Punch Test (SPT) was evaluated, which shows:

- A short spray distance leads to an increase in the maximum load from the SPT.
- A moderate argon flow rate of 55 slpm, together with medium to short spray distances, leads to higher P_{max} values.

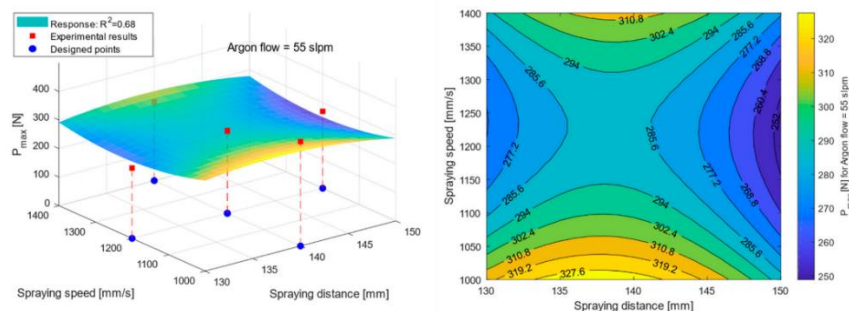


Fig. 3 – Resulted surface in relation to P_{max} for Argon gas flow of 55 slpm (Standard Liters Per Minute), (Lorenzo-Bañuelos *et al.*, 2021).

In the second stage, was evaluated the impact in terms of the thickness of the coating layer, which shows the following:

- The greater the spraying distance together with the high concentration of argon gas, the greater the thickness of the deposited layer.
- For moderate flow rate of 55 slpm, the thicker coating is obtained using maximum spraying distances and moderate spraying speeds.

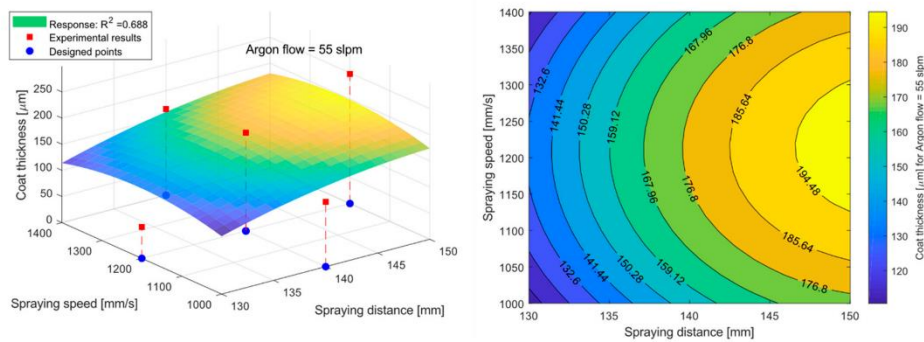


Fig. 4 – Resulted surface in relation to thickness of deposited layer for Argon gas flow of 55 slpm (Standard Liters Per Minute), (Lorenzo-Bañuelos *et al.*, 2021).

In the third stage, the impact was evaluated in relation to the microhardness of the surface, which shows:

- The higher the microhardness of the surface, the greater, within defined limits, the spraying distance.

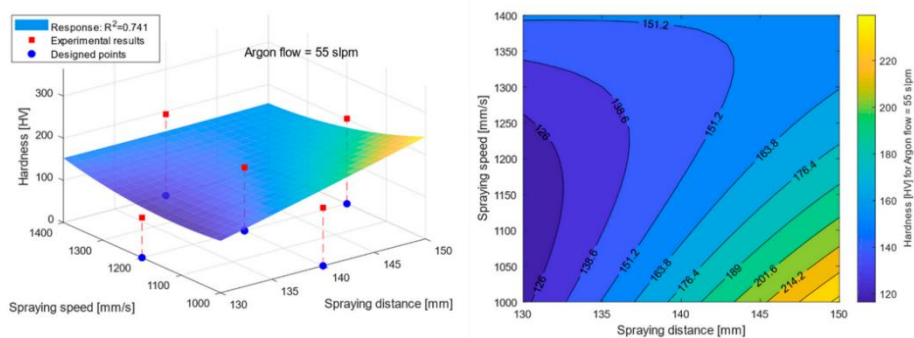


Fig. 5 – Resulted surface in relation to microhardness value of deposited layer for Argon gas flow rate of 55 slpm (Standard Liters Per Minute), (Lorenzo-Bañuelos *et al.*, 2021).

In the fourth stage, the impact of the average roughness R_a of the resulted surface of deposited layer was evaluated, through which it is observed:

- The high flow of argon leads to the appearance of high values of the average roughness R_a .

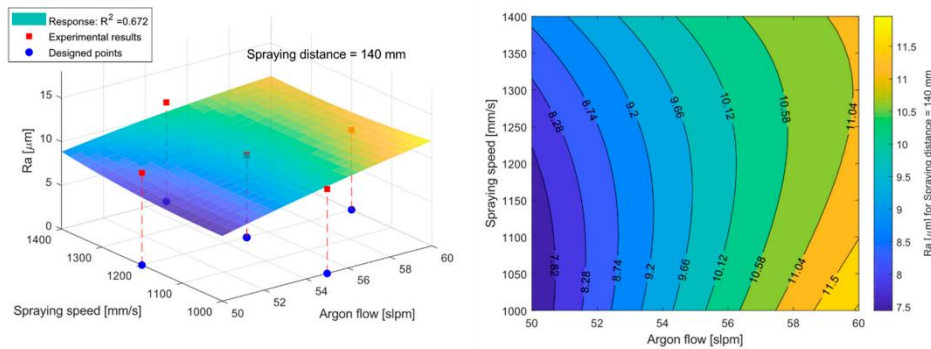


Fig. 6 – Resulted surface in relation to average roughness R_a obtained for deposited layer for a spraying distance of 140 mm (Lorenzo-Bañuelos *et al.*, 2021).

The main conclusions show that in order to obtain a surface with the highest possible hardness, based on the experimental results of the present study, it is recommended to use a lower spraying speed and an increased spraying distance using an intermediate Argon flow rate.

On the other hand, Evren Özşahin and his collaborators evaluated the influence of surface coating for aluminium plates subjected to high velocity impact loads in relation to ballistic performances, using the plasma jet thermal deposition method.

AA 6061 T651 aluminium alloy plates were used, 6.35 mm and 8 mm thick, together with two types of protective layers with a thickness of approximately 0.762 mm: Metco 68F-NS-1 (cobalt, molybdenum, chrome, powder that offers an improvement of mechanical resistance but also wear and corrosion properties) and Metco 201NS (zirconium oxide, powder that offers improvement properties for: thermal shock, corrosion and sulphation at high temperatures). The equipment used for deposition is Metco 9 MB with Argon and Hydrogen gas mix (Oerlikon Metco (US) Inc, 2024; Özşahin and Tolun, 2010a, b).

For the ballistic testing part, Full Metal Jacket (FMJ) bullets of 9 mm diameter and 19 mm length were used, having a weight of 8 ± 0.075 g and a firing speed of 370 ± 10 m/s, the speed being monitored with optical devices: photoelectric Model 55 and chronograph Model 35P (Özşahin and Tolun, 2010a, b).

To evaluate the protective layer, Vicker microhardness measurements were made using the LEICA WHHT MOT device under a load of 200 g for 12 s, and to evaluate the impact test, the displacement of the plates in the back area and the penetration depth in the front area were measured using 3D- CMM.

Evren Özşahin and collaborators, additionally performed a comparative study to evaluate the impact of the previously described protective layers, on the

impact at high speed, for two other aluminium alloys used as base material: AA2024-T351 and AA7075-T651 (Özşahin and Tolun, 2010a, b).

Following the impact tests on the used samples, the following experimental data resulted:

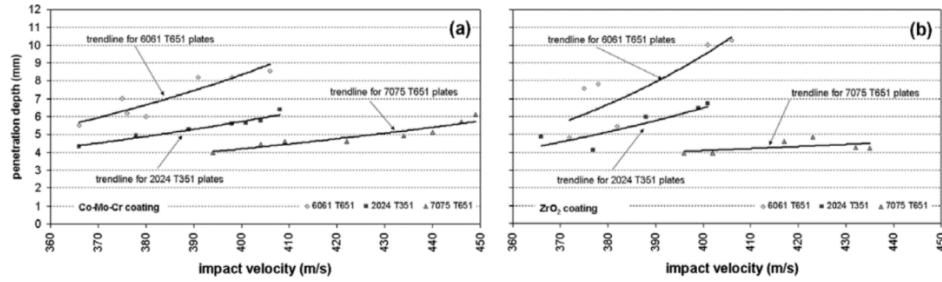


Fig. 7 – Evaluation of the penetration depth in the front area of the coated plates (a) Metco 68F-NS-1 powder (b) Metco 201NS powder (Özşahin and Tolun, 2010a, b).

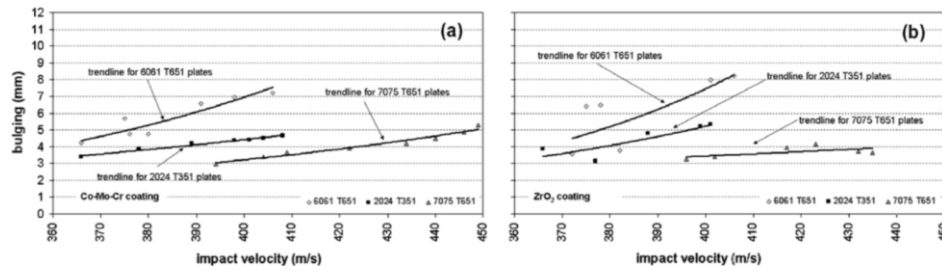


Fig. 8 – Evaluation of the displacement in the back area of the coated plates (a) Metco 68F-NS-1 powder (b) Metco 201NS powder (Özşahin and Tolun, 2010a, b).

Considering the experimental results from the present study, from ballistic protection performance point of view, the uncoated material with the best performance was AA7075-T651, followed by AA2024-T351, the lowest being the AA6061-T651. On the other hand, the coating layer of Metco 68F-NS-1 has a higher efficiency for the front penetration depth and the displacement of the back surface of AA6061-T651 and AA2024-T351 plates, while the coating layer of Metco 201NS is superior to the layer Metco 68F-NS-1, when used with material AA7075-T651 (Özşahin and Tolun, 2010a, b).

Regarding the ceramic materials, with applicability in the military field for bulletproof vests, Pengbo Mi and collaborators (Mi *et al.*, 2023), carried out studies which evaluates the impact on the dynamic compressive properties of boron carbide B₄C ceramic matrix by applying multilayer coatings using plasma jet spraying method.

Cobalt-Nickel alloy powder, Titanium powder and Graphite powder are used, resulting in the Co/Ni-(Ti-graphite) powder mix. Co/Ni-(Ti-graphite) powder is sprayed on B4C to create the Co/Ni-TiCN (Cobalt/Nickel - Titanium-Carbon-Nitride) layer. Initially, an additional bond layer was sprayed between the B4C material and the Co/Ni-TiCN layer, using Ni/Al powder. Thus, multilayer coatings were created with Co/Ni-TiCN in two layers, four layers and gradient layer with different values of the wt% (percentage by weight) of Ti-graphite agglomerated powders (Mi *et al.*, 2023).

The samples were morphologically analysed using SEM images with a JSM-6510A LaB6 microscope (Mi *et al.*, 2023), as a result was evaluated the true stress-strain curves using Split Hopkinson Pressure Bar (SHPB) method (Alaghmandfard *et al.*, 2022; Mi *et al.*, 2023):

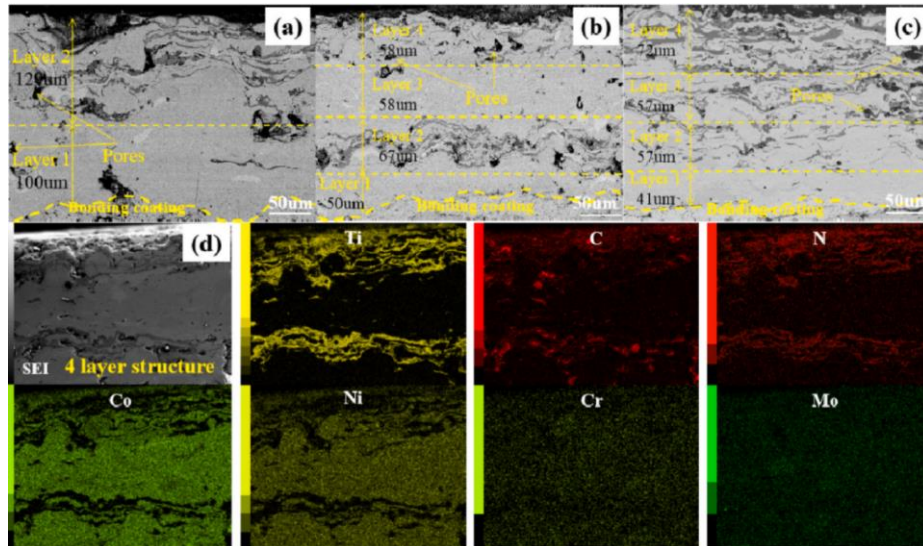


Fig. 9 – SEM morphology for: (a) two layer Co/Ni-TiCN coating, (b) four layer Co/Ni-TiCN coating, (c) gradient structure Co/Ni-TiCN coating, (d) the distribution of the elements on the four layers Co/Ni-TiCN coating (Mi *et al.*, 2023).

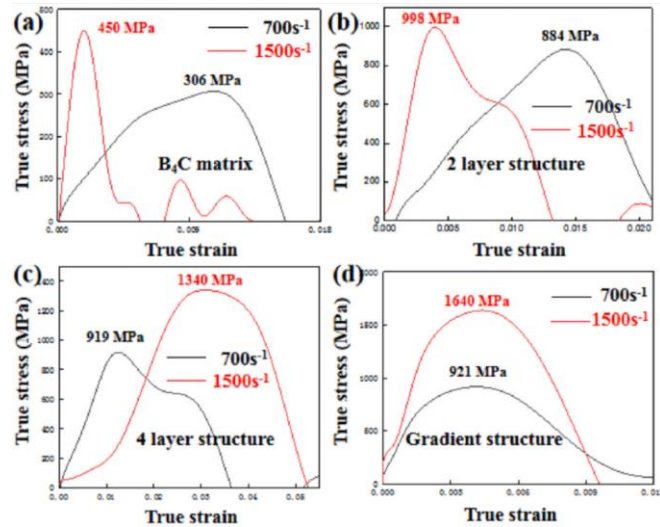


Fig. 10 – The true stress-strain curves for B₄C with Co/Ni–TiCN coating: (a) B₄C without coating, (b) two layers, (c) four layers, (c) gradient structure (Mi *et al.*, 2023).

According to the previously presented experimental data, a considerable increase in the maximum stress value can be observed, both for the deformation rate of 700 1/s and for 1500 1/s, taking into account the properties of the material without coating in relation to the coatings in two layers, four layers and gradient layer. This suggests that multilayer coatings can improve the dynamic compressive properties of B₄C material.

3.2. The properties of the coatings obtained by cold deposition using the Cold Spray method

Fabian Cezar Lupu and the collaborators evaluated the improvement of wear and corrosion properties, for military steel 52100 by applying a layer of Ni/CrC (WIP-C1), (Solvus Global, 2024) as well as an intermediate bond layer (WIP-BC1), (Solvus Global, 2024) using VRC equipment, Gen-III CS, by the Cold Spray method (Lupu *et al.*, 2024).

The morphological analysis of the surfaces was carried out using the SEM Quanta 200 3D 20 kV device and with the CETR UMT-2 tribometer the following proprieties were evaluated: hardness according to ASTM E18, micro scratch resistance according to ASTM D7187 and friction tests according to the ASTM 132 standard. For corrosion property evaluation, an electrochemical test was performed using the Parstat 4000 station (Lupu *et al.*, 2024).

For surface hardness evaluation, microindentation tests were performed (Lupu *et al.*, 2024):

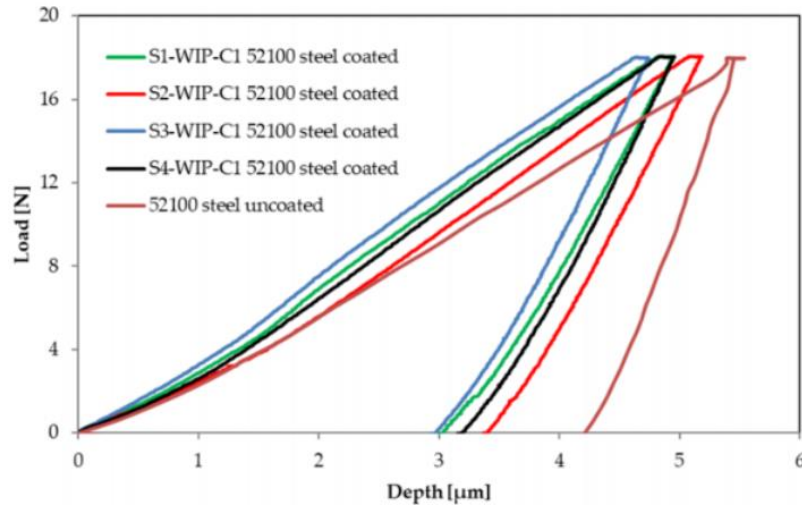


Fig. 11 – Microindentation test results, considering 20N load, in relation with penetration depth (Lupu *et al.*, 2024).

Regarding the evaluation of the microscratch tests, 4 sample test were performed where the coefficient of friction COF was evaluated for linear loads, applying a force from 1 N to 10 N in an interval of 60 s, and constant loads, with a force of 10 N, the results being presented in the following Fig. 12:

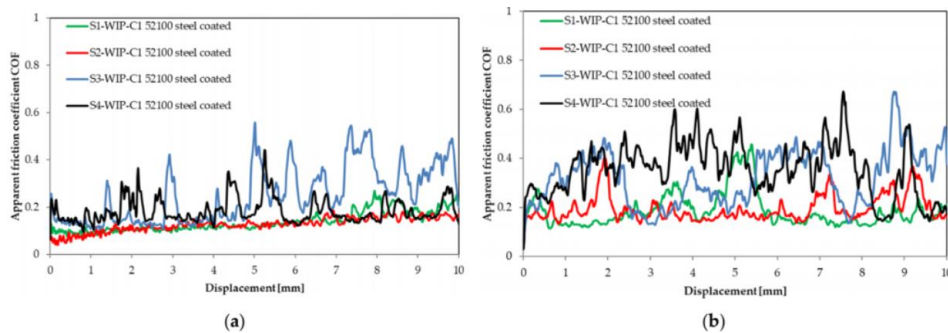


Fig. 12 – Microscratch test results for: applying a linear loads (a), applying a constant loads (b) (Lupu *et al.*, 2024).

A good microscratch resistance was observed, COF values having average values above 0.2. It was also observed that the microscratch marks affected only the protective layer, the base material remained untouched.

Regarding corrosion resistance, the electrochemical corrosion process was evaluated through the linear polarization and Tafel extrapolation technique.

Following parameters was analysed: corrosion potential (E_{corr}), corrosion current density (I_{corr}) and the corrosion rate.

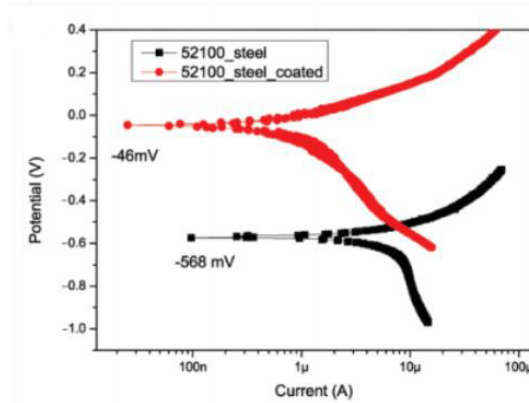


Fig. 13 – Tafel plot (Lupu *et al.*, 2024).

Table 2
Obtained parameters from Tafel plot (Lupu et al., 2024)

Sample	E_0 (mV)	I_{corr} (mA)	Corrosion rate (mpy)
Steel 52100 substrate	-568	18.37	88.48
Steel 52100 substrate with Ni/CrC coating	-46	3.9	18.95

Considering the results especially regarding the corrosion rate, significant improvements can be observed by using the Ni/CrC coating layer.

4. Conclusions

Author conclusion out of current paper is that ballistic protection level is significantly improved by applying deposition coatings using both Cold Spray and Atmospheric Plasma Spray processes.

Considering the experimental results evaluated in the presented studies, using both the APS deposition method and the Cold Spray deposition method, significant improvements of the material properties in terms of hardness, abrasion resistance, dynamic response and corrosion was observed, properties which have direct contribution for ballistic protection.

In order to obtain relevant results from research studies regarding the subject of this review, a good knowledge of the properties and characteristics of the powders that we propose to use is necessary, as well as the correct use of the parameters for the deposition processes.

Regarding future research perspectives, direction is to evaluate the improvements in the properties of materials used in the military field, with an impact on bulletproof vests, for materials such as ARMOX steels (SSAB, 2024), in direct relation to the international testing standards mentioned in the introductory part, by improving properties that have a direct impact on ballistic protection.

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UTILIZAREA ACOPERIRILOR TERMICE PENTRU ÎMBUNĂȚIREA
PROPRIETĂȚILOR MATERIALELOR DESTINATE PROTECȚIEI BALISTICE
DIN DOMENIUL MILITAR. O REVIZUIRE

(Rezumat)

În această revizuire, a fost analizat impactul asupra proprietăților de protecție balistică ale unor materiale folosite în domeniul militar, în raport cu îmbunătățirea proprietăților mecanice și microstructurale.

Obiectivul principal au fost materialele de protecție balistică cu potențial de a fi utilizate ca protecție balistică pentru aplicații precum vestele antiglonț.

Pe lângă evaluarea îmbunătățirii proprietăților mecanice și microstructurale ale materialelor considerate, a fost evaluat și impactul asupra îmbunătățirii protecției balistice în raport cu standardele de testare precum: NIJ, VPAM, NATO STANAG 4569 (Association of Test Laboratories for Attack Resistant Materials and Constructions, 2024; NATO Standardization Office NSDD, 2022; NIJ, 2023).

Evaluarea care face obiectul acestei revizuii, este reprezentată de folosirea a două metode de depuneri: metoda de depunere termică Arc Plasma Spray (APS) și metoda de depunere la rece Cold Spray.

Folosind aceste metode de îmbunătățire a proprietăților mecanice, a fost evidențiat impactul asupra gradelor de protecție balistică considerând atât standarde precum NIJ Standard 0101.07 (NIJ, 2023) și NIJ Standard 0123.00 (NIJ, 2023), care sunt definite în aliniere cu Institutul Național de Justiție al SUA. De asemenea, au fost evaluate proprietățile materialelor raportat la standardul VPAM “Association of Test Laboratories for Attack Resistant Materials and Constructions” (Association of Test Laboratories for Attack Resistant Materials and Constructions, 2024) folosit în Europa, dar și cu standardele “NATO-STANdardization AGreements” AEP-55 STANAG 4569 (NATO Standardization Office NSDD, 2022).