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Structural analysis and mechanical properties of some coatings obtained by cold spray method. A review

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Abstract. In this paper a documentation was made to highlight the characteristics obtained on surface modifications by means of the Cold Spray, using different powders based on tungsten carbide (WC) and agglomerated with nickel, sprayed on different materials, as well as the possibility of using 52100 steel, which is often used in the manufacture of rolling bearings and which has acquired high performances both in terms of wear and fatigue and in terms of high resistance due to the alloying with chromium and the high percentage of carbon. Studies on the use of WIP-C1 powders, powders attributed exclusively to the cold spraying process, and the prior use of WIP-BC1 powders, intended to establish a stronger bond between the substrate and the base layer, have shown that good wear and impact resistance is obtained and the risk of delamination and interfacial porosity has been minimised. Studies with different coating compositions using several methods to improve surface quality by surface spraying, namely HVOF (high velocity oxygen fuel), CGDS (cold gas dynamic sterilization) and CS (cold spray), led to an improvement in performance, with the cold spray process showing improved scratch resistance, good adhesion between the substrate and the sprayed layer and higher hardness. Surface spraying is an efficient process to obtain additional characteristics, improving mechanical, tribological, corrosion and erosion properties, and of all the other techniques, Cold Spray becomes competitive because it is the only technology that deposits particles below the melting point.

1. Introduction

Cold Spray technology is a method of processing solid state particles through which thermal spraying, based on the dynamic increase of gas acceleration to supersonic speeds, leads to obtaining kinetic energies with values raised [1], [2].

This method of cold spraying was developed around the 1980s in Russia by AP Alkhimov and his colleagues during aerospace applications at the Institute of Theoretical and Applied Mechanics in Novosibirsk. During the experiments, metal particles were used and it was observed that the particles adhered to the surface of the vehicle forming a coating instead of eroding it. This cold gas spray technology was patented in 1994 in the USA and in 1995 in Europe. The diagram of the principle of operation of the cold spraying installation is illustrated in figure 1 [3], [4], [5], [6].

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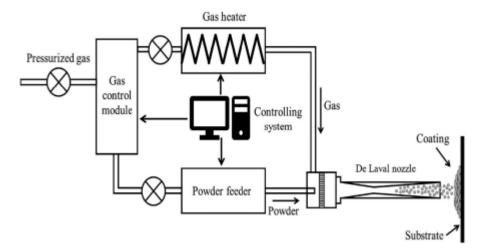


Figure 1. The cold spray installation

2. Properties of 52100 steel

This type of steel, called ASTM A295 52100, is alloyed with Chrome and has a high carbon content, which gives it a high hardness and is characterized by high resistance to wear and fatigue, thus managing to meet standards such as ASTM and SAE. Steel 52100 has a density of $7.81~\rm g/cm^2$ and a melting point of $1424~\rm ^{\circ}$ C [7], [8]. The exposition of the physical properties, respectively of the alloying elements that enter the composition of 52100 steel, as well as of the equivalents together with their standards are specified in the table 1.

Standard	Quality	C (%)	Mn (%)	P (%)	S (%)	Si (%)	Ni (%)	Cr (%)	Cu (%)	Mo (%)
ASTM A295 (SUA)	52100	0.93- 1.05	0.25- 0.45	0.025	0.015	0.15- 0.35	0.25	1.35- 1.60	0.30	0.10
DIN 17230 (Germany)	100Cr6/ 1.3505	0.90- 1.05	0.25- 0.45	0.030	0.025	0.15- 0.35	0.30	1.35- 1.65	0.30	-
IT G4805 (Japan)	SUJ2	0.95- 1.10	0.50	0.025	0.025	0.15- 0.35	-	1.30- 1.60	-	-
BS 970 (UK)	535A99 / EN 31	0.95- 0.10	0.40- 0.70	-	-	0.10- 0.35	-	1.20- 1.60	-	-

Table 1. Percentage of steel alloying elements 52100 together with equivalent

A factor that contributes to highlighting the superior qualities of 52100 steel, characterized by mechanical properties in terms of elastic rigidity is the modulus of elasticity that reaches high values, respectively 210 GPa, making it a rigid material, responding well to processing processes , also having important characteristics on the compressive strength, which for example, unlike most aluminum alloys, is almost twice as strong with a bulk modulus value of 160 GPa. Through these properties, both physical and mechanical, performance is created that makes 52100 steel an ideal steel for extremely demanding parts such as aircraft bearings, ball screws, etc. [8], [9], [10].

In the literature, between the 1940 and the 1990, it was found that in rolling bearing steels, during cyclic loading, due to rolling stresses, a strong contact fatigue stress (RCF) occurs resulting in substantial microstructural changes [11]. Around the 1980s and 1990s, research conducted by numerous institutes on heat treatment concluded that fatigue performance is undoubtedly influenced

by the condition of the material and some studies show that surface hardening leads to a longer life (RCF) unlike fully reinforced elements [12], [13].

Viktorija et al. [11] conducted research on the microstructure of 52100 steel including a common joint heat treatment process with austenitizing at 830-860 °C, followed by extinction in oil at 60 °C and quenching for 2 hours at 170-220 °C thereafter, the samples were analysed by scanning electron microscopy and it was observed that the steel has a microstructure composed of martensite hardening and primary spheroidised carbides with a homogeneous distribution (Fe, Cr) 3C, tempered carbides and in a percentage of 10-12 % retained austenite. By means of SEM SE and BSE images, the primary (Fe, Cr) 3C spheroidized carbides are exemplified with arrows, these primary iron-chromium spheroidized carbides being unaltered, as shown in figure 2.

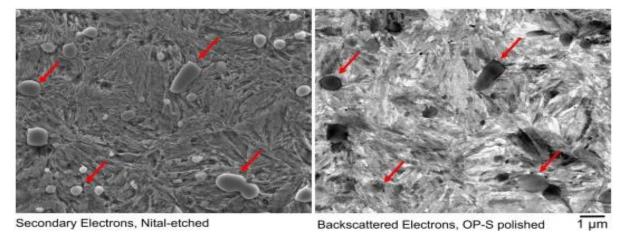


Figure 2. Images taken to observe the microstructure of 52100 steel

3. Improving resistance using the cold spray process

The realization of the gluing of the particles by cold spraying (Cold spray), is due to the process of high speed impact of the particles and their plastic deformation at the moment of consolidation on the sprayed surface [14], [15].

WIP-C1 powder is a material based on chromium carbide and agglomerated with nickel with a melting point of 1455 ° C and the percentage of elements that are part of it being 66-72% Cr, 3% C and 25-31% Ni, elements that confer a high resistance to wear and impact, this type of powder being specially designed for cold spraying (with nitrogen or helium) and also, to achieve maximum performance, it is necessary a preliminary stage of preparation which consists in a first hard bonding layer using WIP-BC1 powder. It is advisable to use this material when a hard substrate is desired, with the role of establishing a stronger bond between the substrate and the coating, being an material based on chromium carbide and nickel that uses an optimized particle size distribution, having a high fluidity giving a proper preparation of the base substrate to which powders such as WIP-C1, respectively WIP-C2 and WIP-W1 adhere very well to this layer and through which the risk of delamination and interfacial porosity is eliminated. With the help of the scanning electron microscope, images of the WIP - C1 (a) and WIP - BC1 (b) powders were obtained, they are presented in figure 3 [14], [16], [17].

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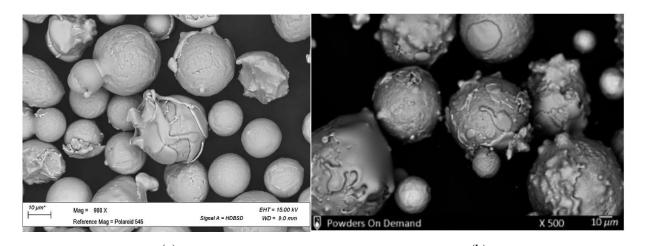


Figure 3. SEM images of WIP - C1 (a) and WIP - BC1 (b) powders

Aaron Nardi and collaborators at the U.S. Army CCDC Research Laboratory (also known as Devcom), studied the effects of cold spray coatings to restore and perfect the quality of various military technical components using WIP powder coatings. Several types of powders were used in the study, namely WIP - BC1 powder as the first base layer (bonding layer), followed by the second WIP-C1 powder and the component that was studied for spraying being made of AISI 4340 alloy steel. The findings of the research led to a similar and even better wear performance than the chromium (Cr) plating, increasing the surface quality for high impact conditions, and shear tests led to an increase in hardness from 17 HRC of the base material to 40-44 HRC, and the surface porosity resulting from sputtering was 1.5 - 3 % in case of nitrogen (N2) spraying and below 1 % using helium (He). Observations of the surface sputtering with WIP - C1 powder as well as the base substrate sputtered as a binder layer with WIP - BC1 powder are exemplified in figure 4 [18].

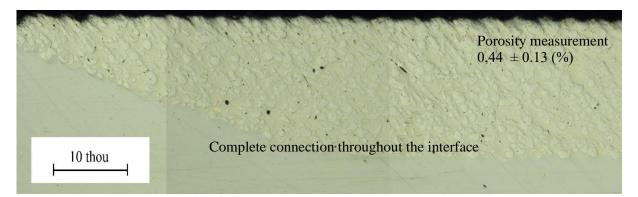


Figure 4. Surface sprayed using WIP - BC1 and WIP - C1 powders

In an article published by the US federal news program Phillips, the materials scientist in the army, Dr. Victor Champagne, who in 2001 set up the Cold Spray Center within the army research laboratory, claims about the spray technology (Cold spray) is a revolutionary one due to the fact that the improvement of the powders has led to the spraying of materials that were impossible to achieve. This technology proves to be quite efficient in view of the technological processes of repair of the various components, so that it determines a continuous development of both the spraying technology and the powder used in this process [19].

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4. Mechanical, tribological, corrosion and erosion properties of deposits using the cold spray method

D. Lioma and collaborators carried out a very interesting study on the hardness of cold spray deposition with low pressure of WC - Ni and WC - 12Co - Ni powders with different percentages of Ni (4, 10, 25, 50%) on a mild steel. Following the tests performed, analyzing the results of SEM and XRD, it was found that during the formation of the coating by the excellent refining of the granules and a low porosity (up to 1.47%) as well as by means of a small percentage of Ni, unlike the coatings with other values of the percentage, for WC - 4% Ni and WC - 12Co - 4% Ni a high hardness is obtained. From a total of 8 combinations made in the study, for the powder WC - Ni, respectively WC - 4% Ni, the maximum hardness value of 459.2 HV was obtained, however, this is not a very satisfactory value as compared to the general average values of other coating techniques such as CGDS (cold gas dynamic sterilization) and HVOF (high velocity oxygen fuel) which reach values of approximately 1135 HV. Microstructures having the composition WC - Ni (a, b, c, d) and WC - 12Co - Ni (e, f, g, h), where the colour white phase represents WC, the light colour grey phase represents Co and the dark grey colour phase expresses the Ni matrix, are shown in Figure 5. The morphology of Ni powder (a), WC powder (b) and WC - 12Co powder are shown in figure 6 [20], [21], [22].

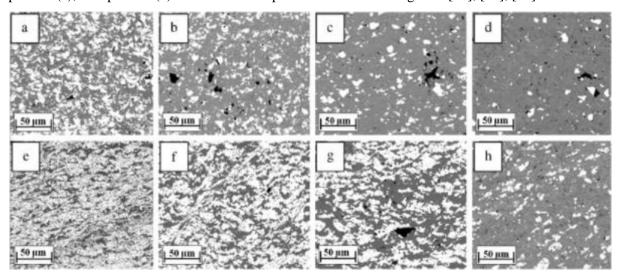


Figure 5. Microstructure of WC - Ni and WC - 12Co - Ni powders

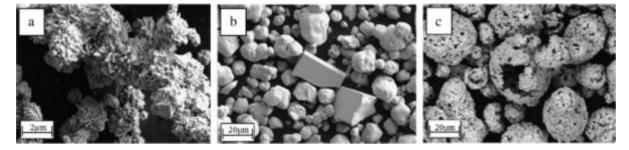


Figure 6. Morphology of Ni, WC and WC powders - 12Co

NM Melendez et al conducted research on the wear behavior on a low carbon steel substrate of tungsten carbide (Ni) and Ni coated metal matrix coatings made by low pressure cold spraying, percentage of WC of these coating - Ni being 7% WC, 19% WC, 56% WC and 66% WC, also performing spray tests with a layer of pure nickel, subsequently, the samples being subjecte to the standard ASTM G65 test of abrasion wear dry. Following the analysis, it was found that for the WC - Ni samples, a significant decrease in wear is observed as WC increases in quantity, which expresses

the fact that the improvement of wear is driven by the increase in the quantity of WC, and as regards the sample sprayed with pure nickel, due to the observation of an increase in the crack network, the lack of WC armouring proved to be harmful. The worn surface of the samples subjected to coating with 7 % WC (a), 19 % WC (b), 56 % WC (c), 66 % WC (d) and the worn surface sprayed with pure nickel (e), are shown in the figure. 7 [23], [24].

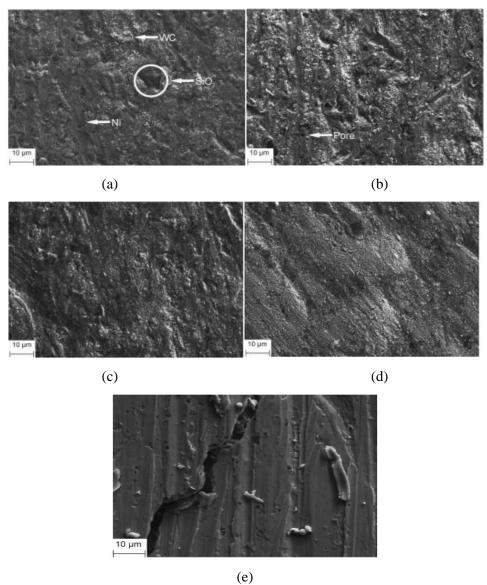


Figure 7. Worn surface of WC covers - Ni and pure nickel coating

Sima Ahmad Alidokht and colleagues conducted research into the performance of erosive wear of the WC effect on Ni and Ni deposits - 10.5% WC on a mild steel performing SPE (solid particle erosion) tests in an angle erosion system of 30 ° and 90 ° of solid particles by gas explosion made to order in accordance with the ASTM G76 standard. Following the SPE tests, it was observed that at the 30° impact angle, for the two coatings was obtained a similar erosion resistance, both showing a higher erosion rate under this oblique angle of impact while for the 90° angle, it was observed that the erosion resistance decreases with the addition of WC in Ni due to the presence of cracks but also due to the limited deformability that caused the WC to break. Fluctuation of erosion level as a function of

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test duration for Ni and Ni - WC deposition performed under 90° impact angle (a) and 30° impact angle (b) are illustrated in figure 8 [25].

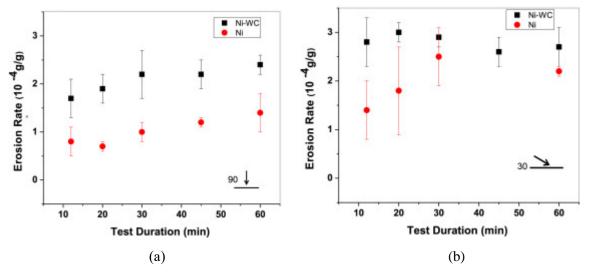


Figure 8. Erosion variation of Ni and Ni WC at an angle of 90 $^{\circ}$ (a) and 30 $^{\circ}$ (b)

Fs. da Silva et al. conducted a research on the improvement of corrosion characteristics by cold-sprayed WC-Co coatings on an AA 7075-T6 aluminum alloy (used in industries such as aeronautics) where due to alloying elements such as Mg, Zn and Cu, the predisposition to corrosion is high. Tests on samples covered with WC-25Co showed that a very good corrosion resistance was obtained, confirmed by the results obtained where 700 hours of immersion in 3.5% NaCl solution were exceeded and in the case of spraying with salt with 5% neutral NaCl the sample withstood an exposure of 3000 hours [26], [27].

Manoj Kumar and colleagues conducted a comparative research of the hardness and wear characteristics of coatings on SA516 boiler steel with Ni-Cr powders using HVOF (high speed oxygen fuel) and CGDS (cold gas dynamics sterilization) methods as surface spray technologies. Following the study, it was concluded that in the case of cold spraying a better improvement of scratch resistance was obtained, unlike HVOF, presenting a good adhesion of the base substrate as well as a higher hardness, namely 456 - 601 Hv compared to 506 - 525 in the case of HVOF, at the same time, a decrease in roughness was observed due to the increase in nanoparticle content for both methods [28].

5. Conclusions

Cold spray technology, through the qualities it incorporates, leads to a significant improvement in the properties of the materials where research has shown that by processing the particles in a solid state, they adhere to the surface instead of eroding it.

Steel 52100, with its high chromium alloying potential and high carbon content, is an ideal material for highly stressed parts and surface spraying leads to a longer service life as opposed to integral hardening.

The use of WIP powders based on chromium carbide and agglomerated with nickel led to superior characteristics, where after studying the coating of AISI 4340 steel sample with WIP-C1 powders and previously bonding the sputtered layer with WIP-BC1, the increase in the degree of resistance to strong impact was generated, and from the data obtained in terms of hardness increase, values of up to 40-44 HRC were obtained as opposed to 17 HRC as the base material and porosity values of 1. 5-3% for nitrogen spraying and below 1% using helium.

In research using WC-Ni and WC-12-Ni powders in a low-pressure cold spray process, a maximum hardness value of 459.2 HV was obtained, which is not very satisfactory compared to other techniques

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such as CGDS (cold gas dynamic sterilization) and HVOF (high velocity oxygen fuel) which reach values of about 1135 HV.

Following the comparative study of coatings on SA516 boiler steel with Ni-Cr powders, a slightly higher hardness was obtained for the CGDS technique, namely 456-601 Hv, unlike HVOF where the resulting value was 506-525 Hv, however, a better scratch resistance was observed in the case of the CGDS technique which also showed an improvement of the base substrate.

The approach to cold spray coatings shows that there are improvements in characteristics, while also showing the advantage of the wide variety of materials that can be sprayed, but for a better perception of the potential of cold spray, it would be very helpful to further investigate adhesion and cohesion properties, as well as studies to obtain a thicker layer that is significant..

Cold spraying is proving to be an efficient technique to improve properties and confirmed by its integration in different fields of industry, becoming competitive by being the only technology that deposits particles below the melting point.

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