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Cold-spray deposition of Ti₂AlC coatings

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Abstract: Ti₂AlC coatings have been fabricated by cold-spray deposition. The microstructure evolution as a function of basic spray parameters temperature and pressure onto AA6060 aluminium alloy and 1.0037 steel substrates has been studied. Adherent and dense 50-80 µm thick Ti₂AlC coatings were deposited on soft AA6060 substrates under gas temperature and pressure of 600 °C and 3.4 MPa, respectively, whilst comparable results were obtained on harder 1.0037 steel by using higher temperature (800 °C) and pressure (3.9 MPa).

Keywords: MAX-phase; cold-spray deposition; coating

MAX phases [1,2] are a family of ternary carbides and nitrides (“X”) of transition metals (“M”) interleaved with group 12-16 elements (“A”, e.g. Al or Si) that have gained much interest in the last 15 years because of their interesting combination of ceramic and metallic properties. They are resistant to oxidation and corrosion, elastically stiff as well as machinable and thermally and electrically conductive [3]. Physical vapour deposition, especially magnetron sputtering, has emerged as the most commonly used technique [4-11] for thin-film deposition of MAX phase including Ti_2AlC , a material exhibiting a ceramic-like behaviour with hardness of 5.5 GPa [12]. For thicker MAX-phase coatings, spraying techniques have been also investigated [13], most notably High Velocity Oxy-Fuel (HVOF) [14,15]. This technique is industrially used to coat large areas, but typically produces coatings with a significant fraction of oxides because of the high temperatures of the process [14]. This study is focussed on deposition of thick Ti_2AlC coatings by a particular thermal spray deposition technique called “cold gas dynamic spray” from MAXTHAL 211® powder. Besides some preliminary results [16], until recently this technique has not been substantially studied for deposition of MAX-phase materials. It has nevertheless drawn interest among the scientific community as testified by the results obtained by Gutzmann *et al.* in a paper published during the later stages of the review process of the present paper [17].

The cold spray technique uses a high-pressure gas jet to accelerate particles to supersonic speed through a convergent-divergent De Laval nozzle so that the particles achieve sufficient kinetic energy to undergo plastic deformation at the impact. The gas temperature is typically between 200 and 800 °C but the particle temperature is significantly lower because of the short time they stay in contact with the gas. Thus, no particle melting is involved in the process [18,19] and the low temperature of the process enables to produce coatings with low residual stress [20], low porosity, and low oxygen content [21]. Cold spray deposition of ductile materials like aluminium and copper is widely reported in previous studies [22,23]. Harder and less ductile metallic materials like Ni, Ti (and their respectively alloys), and stainless steel can with some difficulties also be cold sprayed to

obtain compact coatings with low porosity and good mechanical properties [23,24]. Finally, cold spray deposition of ceramic powders has been considered difficult due to limited particle plastic deformation [25]. Here, we demonstrate the feasibility of depositing Ti_2AlC MAX phase powder by cold spray.

MAXTHAL® 211 (Ti_2AlC MAX-Phase) powder, supplied by Sandvik AB, with a nominal grain size of $40+25\ \mu\text{m}$ was used as feedstock for the cold-spray process. Spraying was performed by a CGT-Kinetiks 4000 cold spray system (CGT Cold Gas Technology GmbH, Ampfing, Germany) using nitrogen as carrier-gas. The gun was provided with a commercial type-24 nozzle and a 100-mm-long prechamber. The coatings were deposited on AA6060 alloy (Si 0.30-0.60%, Mg 0.30-0.060%) and 1.0037 steel (C <0.19%, P < 0.045%, S < 0.045%, N < 0.011%) 60x500x5mm plate substrates whose microhardness was $90.9\pm 5.1\ \text{HV}0.05$ and $197.5\pm 7.4\ \text{HV}0.05$, respectively. Steel substrates were grit blasted (with corindone 16 MESH) prior to coating ($R_a=15.75\pm 7.22\ \mu\text{m}$) while the aluminium alloy substrate was not pretreated (tool-finishing: $R_a=0.45\pm 0.14\ \mu\text{m}$). In order to study the effects of different cold spray deposition parameters, a set of samples was coated according to Table 1. The other parameters were kept constant: standoff distance was 20 mm; powder flow rate about 0.1 g/s, and the carrier gas flow in the powder feeder $2.3\ \text{m}^3/\text{h}$.

The coating and powder microstructure were investigated by light optical microscopy (LOM) (DM6000M, Leica) and scanning electron microscopy (SEM) (VEGA LMU, TESCAN). The metallographic samples for coating structure evaluation were cut from sections of both specimens (AA6060 and 1.0037 steel substrates) and mounted using an automatic mounting press (MEGAPOL P320, Presi). Grinding was performed using different grades of abrasive papers and polishing was carried out using diamond suspensions down to $3\ \mu\text{m}$ in size for the final stage.

X-ray diffraction (XRD) was performed in θ - 2θ geometry in a Philips diffractometer with a CuK α source. Microhardness measurements on metallographically prepared cross-section samples were performed by a microhardness tester (VMHTAUTO, Leica). The Vickers 50 g load (or 10 g in the case of powder) indentations (15 measurements) were performed inside every coating and substrate. Starting from these measures, the average microhardness and the standard deviation was reported. The average microhardness and the standard deviation of different phases in the coating are also reported.

Figure 1 shows that the shape of the used MAXTHAL® 211 particles is flake-like and irregular. They exhibit both a coarse and fine (Fig.1, inset) lamellar microstructure. The average microhardness of the powders is 570.3 ± 120.9 HV0.01. XRD θ - 2θ diffraction of the feedstock powders (not shown, essentially identical to Fig. 1 in Ref. 14) showed that they consist mainly of Ti₂AlC, with some Ti₃AlC₂ (also a MAX phase) and a very small amount of TiC_x.

Figure 2 shows SEM images (backscattered electrons) of the 6 representative deposition tests carried out on AA6060 (labelled Al 1-3) and 1.0037 steel (labelled Fe 1-3) substrates as reported in Table 1. The first set of depositions was performed on AA6060 substrate in order to verify the feasibility to obtain thick Ti₂AlC coating by cold spray. Aluminium alloy was selected because of its high plasticity and consequent promotion of coating growth and adhesion in cold spray deposition [18]. Although the primary gas temperature was only varied by 100 °C between Al2 (600 °C) and Al1 (500 °C), the difference in the coatings is rather dramatic. The coating deposited by the Al1 process (Fig. 2.a) exhibits a clear double-layer structure: two single-particle thick layers stacked one upon the other. The layers display a good inter-locking and no delamination although they are clearly separated by a continuous transversal crack. This indicates weak particle cohesion and consequently difficulty to increase the coating's thickness. The Al2 process yielded the coating in Fig.2b: it is ~50 μ m thick, well adhered to the substrate and, despite the presence of non-

continuous cracks, reasonably compact. In both cases (Fig. 2) a remarkable deformation of the sprayed particles is visible. While this deformation is an essential factor for cold-spray deposition, the experiments Al1 and Al2 demonstrate that the Ti_2AlC powder is usable for cold spray deposition. Further increase of gas temperature, as in Al3, although leading to higher coating thickness, produces a noticeable lamellar detachment (spalling) of the coating on large areas ($>1\text{mm}^2$) during the deposition process. This is because of tensile stress on the aluminium substrate generated by the high process gas temperature.

The second set of coatings was deposited on steel 1.0037 substrates, initially prepared by sandblasting to improve coating adhesion [26]. In this case the first layer of the deposit was affected by strong erosion from subsequently impinging particles leading to extensive delamination. As a result (see Fig.2.d) it was possible to deposit only a single layer of particles consisting of fractured particle debris. The dramatically different behaviour is due to the higher hardness of the steel to the aluminium substrate resulting in increasing of rebounded Ti_2AlC particles and to lower substrate ductility, which in turns leads to a poor interface adhesion. An attempt (Fe2 sample) to overcome this problem by simply changing the deposition strategy (traverse gun movements in the pattern of deposition) was ineffective as shown in Fig 2.e. Thicker coatings, $\sim 80\text{ }\mu\text{m}$ thick, was obtained on the steel substrates with the process Fe3 (Fig. 2.f) that employs the maximum gas temperature and pressure allowed by the cold spray system used here. In this respect, the increase of both gas pressure and temperature contributes to the increase of particles velocity, whereas the increase of just the gas temperature enhances the thermal input to the powder [20] promoting the growth of cohesive coatings on the hard substrate.

The coatings on AA6060 and 1.0037 steel, realized by the respectively optimized cold spray process (Al2 and Fe3) were characterized by structural and microhardness analysis. Both coatings as reported in Fig.3, exhibit the presence of two distinct phase structures, the main lamellar MAX

phase from Ti_2AlC and some Ti_3AlC_2 , and a titanium aluminide, as shown by XRD below. The coating of Fig.3.a, deposited on the aluminium alloy substrate (Al2 cold spray process of Table 1), presents some cracks parallel to the substrate. In the same manner, the coating on steel substrate (Fe3 cold spray process) exhibits the same defects (Fig. 3.b). The difference between coating cracks on the two samples consists primarily in the extension of the cracks and secondary in their width. While the cracks in the Al2 coating are 20 – 40 μm large and closed, the cracks in the Fe3 coating are continuous, in some cases up to 0.5 mm long, and they are 'open', which means particle detachment and delamination.

The intermediate ceramic and metallic character of MAX phase material is highlighted by its reaction as a consequence of the high velocity impact on a metal substrate. On one side, MAX exhibits a ceramic-like behavior for high velocity impact (Fe3) with particles fragmentation during impact and consequent formation of debris embedded in the coating microstructure as reported in figure 2.f. On the other side, MAX exhibits a metal-like behavior in case of relatively low impact velocity (Al2) with a deformation of particles during the impact and a moderate variation of the aspect ratio of the initial powders with respect to the coating microstructure. Neither debris nor fragmentation during spray is observed at these conditions. The mechanical properties of the substrate material could further exacerbate these effects in the deposition of the first layer of coating. The impact on a hard and high strength substrate such as steel is more violent and could promote ceramic-like behavior whilst in the case of a ductile metal, such as aluminum, the plastic deformation of the substrate material allow the loss of initial particle energy, which in turn promotes a mechanical interlock and a sub-implantation of the impinging particle. In the case of steel substrate higher particle velocity are necessary to obtain the interlocking between MAX-Phase and grit blasted 1.0037 substrate.

XRD patterns of the coating Fe3 show the characteristic peaks of Ti_2AlC phase (see Fig.4). Ti_3AlC_2 is also present with a strong peak evident at $2\theta = 9.5^\circ$ and with lower intensity at 18.5° . The remaining peaks in the diffractogram are due to small amounts of the binary phases TiC and Ti_yAl_x .

Unlike HVOF spraying processes [14], the cold spray process clearly does not induce substantial phase transformation and avoids degradation, as it possible to see by comparing the XRD of the coatings with the one of feedstock powder [14].

The measured MAXTHAL® 211 powder hardness - 570.3 ± 120.9 HV0.01 - is in good agreement with the bulk Ti_2AlC hardness [26]. Papyrin *et al.* [18] reported a hardness increase in the coating with respect to the feedstock powder for metallic material after cold spraying. This phenomenon was explained by work hardening of the metals because of the high plastic deformation and peening effect of the particle during deposition. The same 'hardening', was identified in our MAX-phase depositions depending on the cold-spray process parameters and, secondarily, on the substrate mechanical properties. From the powder to the coating deposited using the parameters of process Al2 the average microhardness remains almost unchanged: 570.3 ± 120.9 HV0.01 to 608.4 ± 118.5 HV0.05. An increment, about the 35-40% with respect the powder, was noticed in the coating realized on 1.0037 steel (Fe3), whose average microhardness stood at 786.7 ± 130.7 HV0.05.

Referring to the hardness of the two major phases of MAXTHAL® 211, which are identified in the powder and in the coatings, readable Vickers indentation marks with low load ($<10g$) could not be obtained for the powder. However, an interesting change was observed in the MAX phase of the coating that reaches the high value of 1033.3 ± 155.7 HV0.01 in the process Fe3: 30% higher than the value on Al2 coating (790.7 ± 171.0 HV0.01). The anisotropic lamellar structure of the powder particles is organized in domains with coherent planar direction (see Fig 1). The increment of microhardness might be attributed to the rearrangement of these domains upon deposition caused by

the powder impact with the substrate and the subsequent peening effect of the other incident particles that leads to the intensification of kink bands as proposed by Barsoum *et al.*[27]. According to this mechanism, the stretching and the compressive stress of the domains are principally ruled by the particle velocity at the impact that, in turns, grows with the pressure and temperature of the gas carrier, therefore leading to the increase in the MAX-phase hardness as observed in our experiments.

In conclusion, MAX-phase Ti_2AlC coatings have been deposited by cold spray of MAXTHAL® 211 powder both on aluminium (AA6060) and steel (1.0037 steel) substrates. The results show that the substrate hardness plays a major role in the quality of the coatings. Specifically, 50 μm thick adherent MAX-phase Ti_2AlC can be deposited on soft AA6060 substrates under mild deposition parameters (gas temperature and pressure of 600 °C and 3.4 MPa, respectively). Comparable results are obtained for harder 1.0037 steel only by using higher temperature and pressure (800 °C and 3.9 MPa) and by sandblasting preparation of the substrate to obtain mechanical interlocking. The low-temperature approach provided by cold spray has been confirmed as an excellent tool for obtaining compact coatings preserving the initial composition and structure. No MAX-phase deterioration or coating oxidation was observed up to 800 °C process gas temperature. However, the coating growth is limited to 50-80 μm and the occurrence of cracks in the coating microstructure is detrimental for coating performances. Further experiments are in progress to overcome these limitations for industrially-applicable cold-sprayed MAX-phase coatings.

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Table1. Cold spray deposition parameters.

AA6060 Substrate				
Process*	N2 Gas pressure	N2 Gas temperature	Gun Traverse	Pass distance**
ID	[MPa]	[°C]	speed [mm/s]	[mm]
Al1	3.4	500	50	1
Al2	3.4	600	50	1
Al3	3.9	800	50	1
1.0037 steel Alumina-grit blasted (16MESH) Substrate				
Fe1	3.4	600	10	1
Fe2	3.4	600	10	5
Fe3	3.9	800	10	1

* The same ID identifies also the coating obtained using the relative process.

** Distance between two next traverse gun movements in the pattern of deposition.

Figure 1. SEM micrograph of MAXTHAL® 211 Ti_2AlC powder showing coarse lamellar structure and finer lamellar structure in flake-like grains (inset).

Figure 2: SEM (backscattered electron) micrographs of cold sprayed Ti_2AlC coatings on aluminium alloy AA6060 substrate: process Al1 a), Al2 b) and Al3 c); and on steel 1.0037 substrate: process Fe1 d), Fe2 e), and Fe3 f).

Figure 3: SEM (backscattered imaging) micrographs of thicker Ti_2AlC coating deposited on a) aluminium alloy AA6060 substrate (Al2) and b) 1.0037 steel after sand blasting (Fe3). The red ellipses highlight an intermetallic phase. The green circle shows crushed particles, and the arrows indicate cracks.

Figure 4: XRD patterns of the coatings with phases indicated.