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Reprocessable vitrimeric composites metallized via cold spray: A preliminary study on the feasibility of novel hybrid structures

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Abstract. Due to their excellent mechanical properties and lightweight, fibre-reinforced thermoset composites are appealing materials for high-demand industries like aerospace or automotive. However, the inability to be reprocessed and the difficulty in repairing and recycling the thermoset matrices raise serious environmental issues and greatly increase the cost of materials. In fact, as a result of the irreversible chemical bonds formed during the curing process, it is not possible to reshape the material once it is set into its final form. In this context, the novel vitrimer polymers, characterised by intriguing mechanical and chemical properties as well as the ability to be reprocessed and recycled, have sparked increased attention in the literature [1]. Nevertheless, those composites are still limited by their poor surface properties strongly limiting their functionalities. In this scenario, surface metallisation has proved to be an intriguing opportunity to overcome those issues. Among the metallisation technologies, in recent years Cold Gas Dynamic Spray (CGDS) was widely investigated in the literature, owing to its capacity to produce metallic layers on thermo-sensitive materials as it does not exploit thermal energy to create the coatings. In this work, the possibility of producing hybrid fibre-reinforced vitrimer-based composites coated with metallic particles is analysed.

Introduction

The use of carbon fibre-reinforced composites is widespread across industries thanks to their many favourable properties, including lightweight, high strength, resistance to corrosion and fatigue, and low thermal expansion [1,2]. The demand for these composites has been on the rise due to the need for materials that offer a high strength-to-weight ratio in various industrial applications [3,4].

Thermoset matrices are often chosen for these composites due to their impressive combination of characteristics, including a favourable stiffness-to-weight ratio, fatigue resistance, dimensional stability, thermal stability, mechanical strength, resistance to creep, electrical insulation, and chemical resistance [5,6].

Despite being widely used, carbon fibre-reinforced composites can experience mechanical damage in applications involving significant forces, high pressure, temperature, friction, and vibration [7,8]. This damage, which includes creeps, cracks, fractures, and punctures, decreases the lifespan of the product and raises the possibility of unforeseen failures.

Additionally, the insoluble and infusible properties of epoxy resins make it difficult to identify and fix microcracks. The irreversible chemical bonds formed during curing further limit recycling options, as existing techniques often lead to the degradation of the polymer matrix or the retrieval of just the fibres [9,10].

A potential solution to these challenges and the development of more sustainable methods involve the use of vitrimer materials as a viable alternative for recyclable thermoset composites [11]. These materials combine the resilience of thermosets with the ability to be reprocessed at high temperatures. One interesting approach to recycling thermoset composites is by customizing the chemical structure of the thermoset polymer matrix prior to its final production. Extensive efforts have been devoted to creating thermosets that are reprocessable, healable, and recyclable in the last twenty years [10,11]. This has involved incorporating reversible non-covalent interactions and reversible covalent exchanges into polymeric networks. Among these approaches, covalent adaptable networks (CANs) have emerged as a favourable option, as they offer a combination of strong mechanical integrity and thermoplastics-like behaviour at high temperatures [12].

Vitrimers were introduced in 2011 in the work of Leibler et al., as a novel type of polymeric material, utilizing associative covalent adaptable networks (CANs) [13]. These vitrimers were created by introducing a transesterification catalyst to an epoxy/acid polyester network, which allowed for control over the exchange kinetics. Considered the third class of polymer materials, alongside thermoplastics and thermosets, vitrimers exhibit similar thermal and mechanical properties to conventional thermosets at typical operating temperatures. However, when subjected to temperatures above the topology freezing transition temperature (Tv), vitrimers undergo rapid exchange reactions, resulting in a rearrangement of their molecular structure and quick stress relaxation [14,15]. Consequently, epoxy vitrimers can flow like a viscoelastic fluid when subjected to external forces, with their viscosity gradually decreasing as the temperature rises following an Arrhenius-type law.

In this work, experimental research was conducted on a novel epoxy vitrimer formulation optimized for compatibility with the fibres and the metallic coating. The composites produced were then metallized via CGDS employing aluminium powders. The samples produced were then analyzed in terms of surface properties. The influence of the fibres on the coating deposition process was thoroughly investigated.

Materials and Methods

For this experimental campaign, panels were produced using a combination of carbon fibres and a vitrimeric matrix. The formulation of the vitrimer was carefully studied and optimized to ensure compatibility with the fibres. The resin utilized is a combination of DGEBA (Bisphenol A diglycidyl ether), epoxy resin, THMPA (tetrahydro-methyl phthalic anhydride) curing agent, and of a 2,4,6-tris dimethylaminomethyl-phenol as catalyst, all obtained by Huntsman Corporation. To enhance the vitrimeric behaviour, anhydrous zinc acetate $Zn(Ac)_2$ is added as a transesterification catalyst to modify the standard epoxy system.

The formulation is prepared with equal amounts of epoxy and acyl, with a 10% weight of $Zn(Ac)_2$ relative to the total acyl groups. The manufacturing process involves mixing the epoxy resin and $Zn(Ac)_2$ powder by hand, followed by the addition of cross-linking anhydride and mixing using a planetary centrifugal mixer under vacuum at room temperature.

The accelerator (amine) is then added and further mixing is performed to achieve a homogeneous mixture. The mixture is then cast into Teflon moulds (by hand lay-up) and

reinforced with carbon fibres (carbon fibre fabric 3k T300 Twill 2×2 by Toray). The composite is then produced by hot curing the resin at 120 °C for 1 h 30 min and then continuing with a further cure phase at 140 °C for 2 h. The composite panels produced have dimensions of 100x100mm and a thickness of 3mm. Further information on the manufacturing of vitrimer-based composite are presented in previous works of the authors [16–18].

In order to determine the most suitable side for deposition, confocal analyses were carried out on the composite surface. This was done because each face of the surface exhibited different surface characteristics due to the contact with the Teflon mould. In fact, the surface characteristics of the substrate, could strongly influence the CS deposition, as assessed in previous studies [19].

Once the panels were formed, a metallization process was applied to them using Cold Spray (CS) technology. The chosen powders for the metallization were micrometric powders of AlSi10Mg (LPW South Group), specifically selected for their compatibility with composite materials based on previous experiments conducted by the authors [19,20]. These powders were found to be highly suitable for deposition on the panels, even at low temperatures.

The metallization process was carried out using a low-pressure cold spray machine, specifically the Dycomet 423 CS equipment. Nitrogen gas was used as the carrier gas in this process.

Based on a preliminary sensitivity analysis, not presented here for the sake of brevity, the most significant process parameters have been identified and are outlined in Table 1.

This analysis underscored the importance of temperature and Standoff Distance (SoD) in the deposition process for composite panels with a vitrimer matrix. Previous studies have confirmed that vitrimers exhibit enhanced flexibility when heated above their Tv, instead of becoming brittle [15,21]. Therefore, it is essential to employ a carrier gas at an appropriate temperature and distance from the nozzle to effectively heat the substrate and achieve the desired temperature.

Two temperature values, T_1=200 °C and T_2=300 °C, and two values of SoD, SO_1=70 mm and SO_2=100mm, have been selected, which represent the change in behaviour of the vitrimeric matrix.

Table 1 – Selected process parameters for CS deposition of AlSi10Mg powders on composite vitrimer-based substrates.

	C_{T1SO1}	C_{T2SO1}	C_{T1SO2}	C_{T2SO2}
Inlet gas temperature [°C]	200	300	200	300
Gas pressure [bar]	6	6	6	6
SoD [mm]	70	70	100	100
Gun traverse speed [mm/s]	1	1	1	1

A single layer of particles was deposited to the composite panel employing the four spraying conditions abovementioned, producing 50 mm long metal tracks.

To assess the characteristics of the metallized panels, various microscopic analysis techniques were employed. A Hirox ST-AS microscope was used to examine the coating width, while a confocal Olympus OLS5100 confocal microscope was utilized to assess variations in surface characteristics.

Results and Discussion

As highlighted in the previous section, it is crucial to determine the surface on which to deposit. In fact, the presence of the Teflon mould ensures different surface properties for the top face and the back face. The acquisitions of height surfaces through confocal microscopy of the two surfaces before deposition are shown in Fig.1.

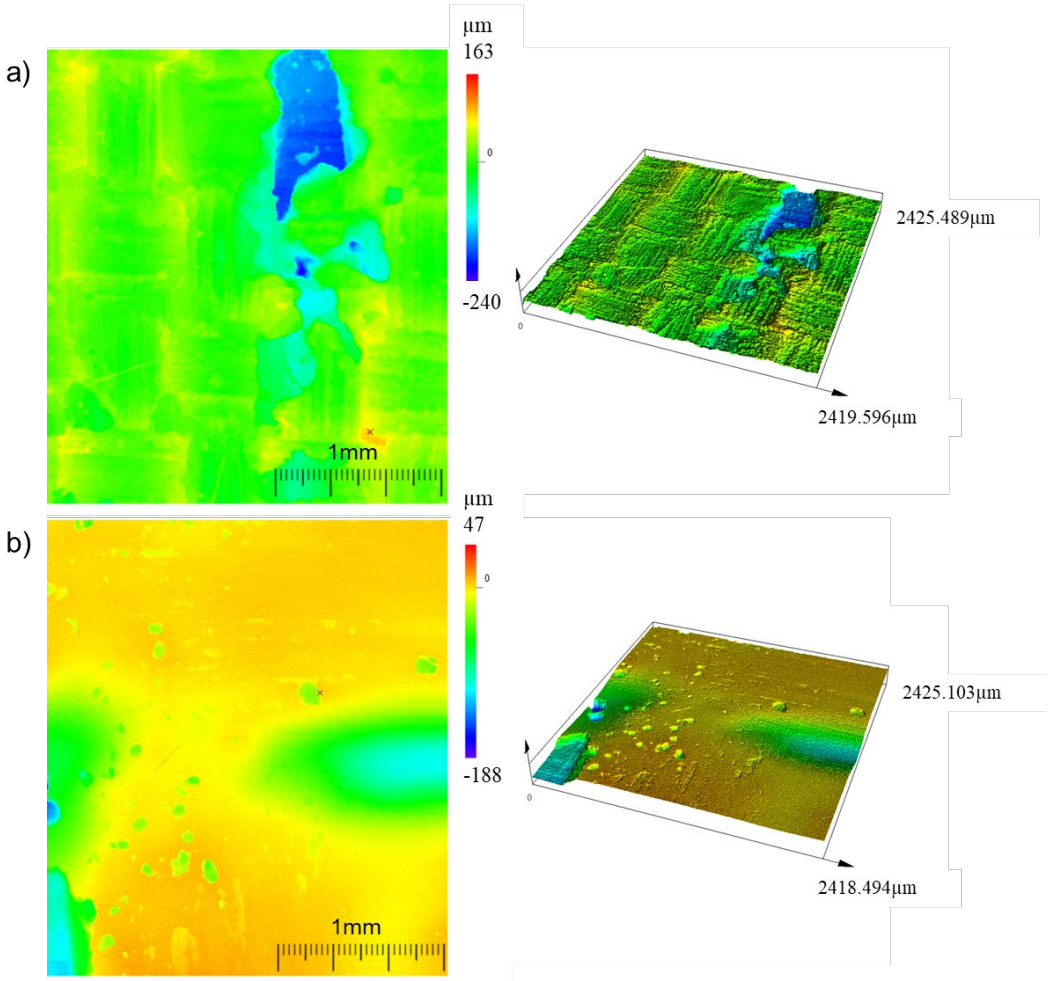

Fig.1 – Confocal acquisition of the surface of the bare composite before the CS deposition a) rough back surface b) smooth top surface of the composite

Upon examination of the image and analyzing the values of Arithmetical Mean Height (Sa) of the surfaces, it can be concluded that the lower surface shown in Fig.1a, which is in contact with the mould, appears to be rougher. (Sa=28.80 µm). Furthermore, it is possible to notice from the figure that the presence of fibres is clearly visible. This could hinder the deposition process and potentially cause damage to the fibres, thereby reducing the composite's properties. Conversely, the other surface appears to be smoother (Sa=18.73 µm) and therefore better suited for CS deposition.

Hence, the depositions were performed on the upper surface. As mentioned previously, process parameters were utilized to emphasize the shift of the vitrimer's behaviour from being glass-like to becoming ductile. This transition can be clearly observed by examining the images captured by a confocal microscope, as depicted in Fig. 2.

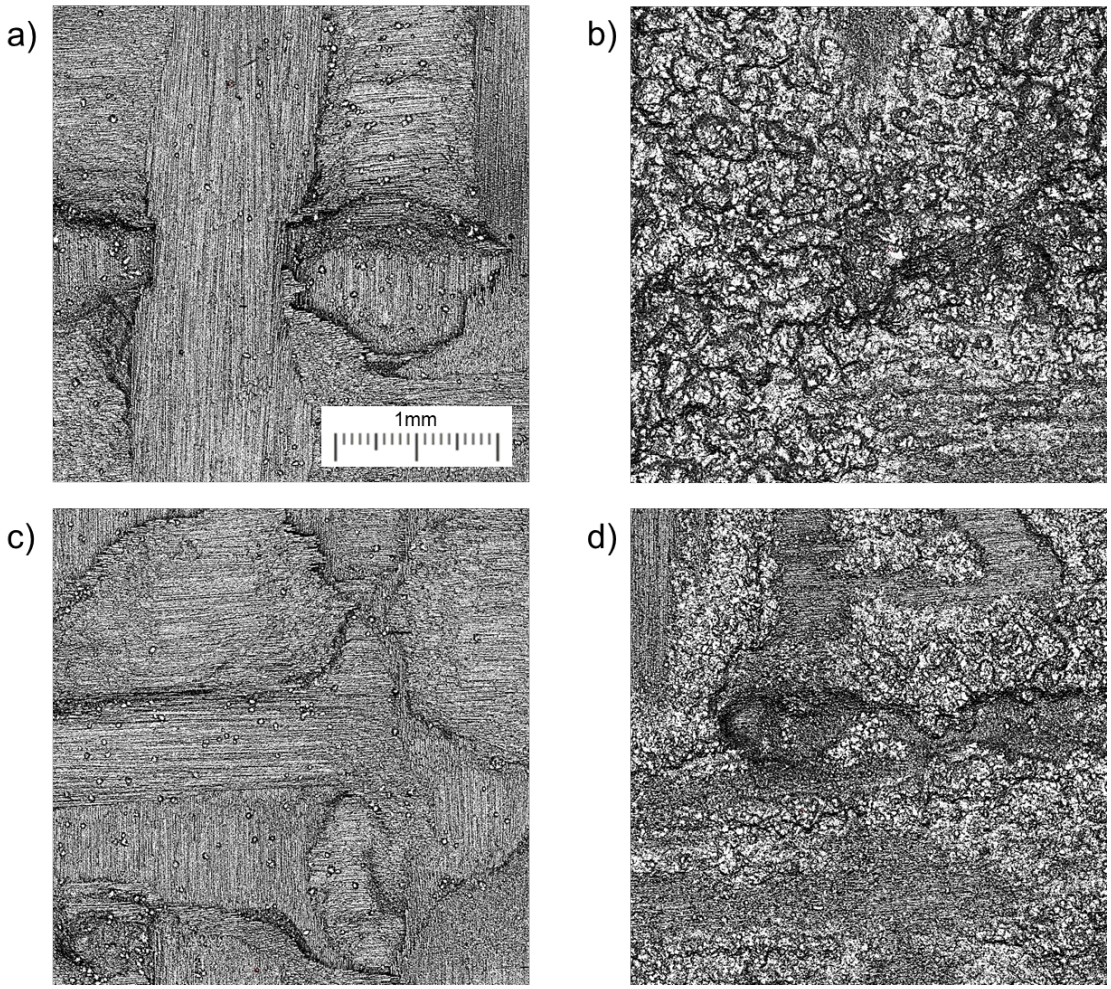

Fig.2 – Confocal images of the coated panels: a) Specimen C_{T1SO1} b) Specimen C_{T2SO1} c) Specimen C_{T1SO2} d) Specimen C_{T2SO2}

It can be observed that when the lowest temperature is selected (Fig.2a and Fig.2c), only a small number of particles can be seen on the vitrimer substrate. In fact, this temperature of 200 °C is actually lower than the vitrimer's topology freezing transition temperature; therefore, the vitrimer vitrimer will not be able to deform enough to accommodate the impinging particles properly. As a result, cracks could form on the surface resulting in poor adhesion.

On the other hand, when higher temperatures (namely 300 °C) are employed and Tv is reached a rather homogeneous coating can be observed on the entire surface(Fig.2b and Fig.2d). Specifically when a lower standoff value is used (Fig.2b), the coating appears even thicker and more uniform. This is because the vitrimer is heated further, allowing it to better accommodate the particles. It is important to note that lower standoff values can also lead to surface degradation, so finding the right balance is crucial. This can be further confirmed by observing the height acquisitions of the surfaces of the coating, presented in Fig.3.

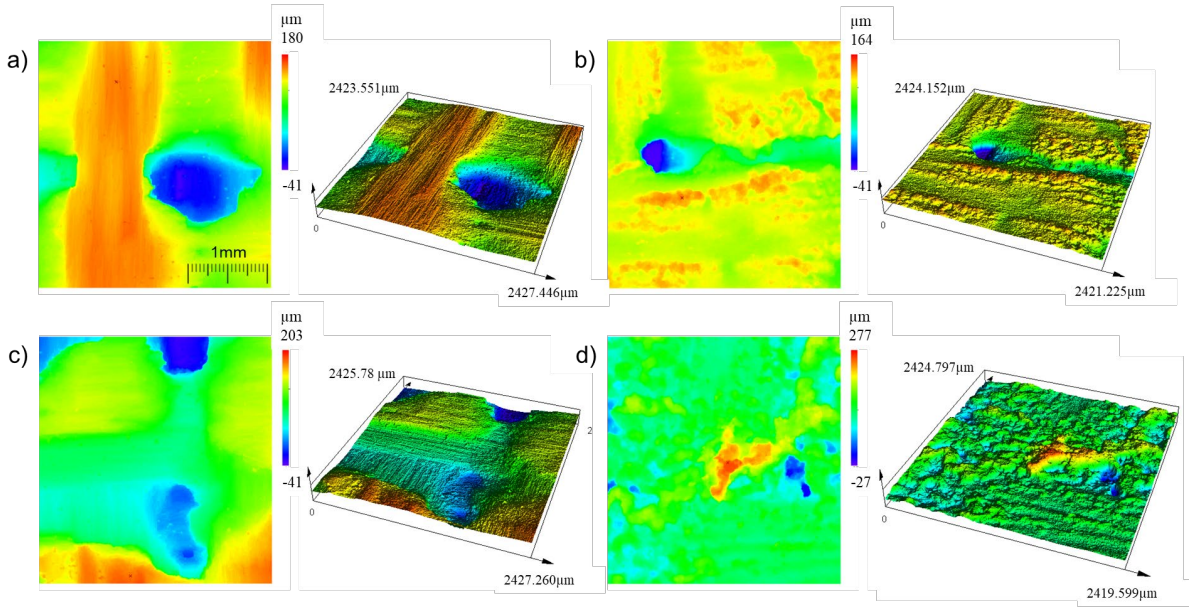

Fig.3 – Confocal acquisition of the surface of the coated panels: a) Specimen C_{T1SO1} (Sa=86.34 µm) b) Specimen C_{T2SO1} (Sa=41.37 µm) c) Specimen C_{T1SO2} (Sa=92.87 µm) d) Specimen C_{T2SO2} (Sa=39.33 µm)

It is noticeable that all process parameters result in higher Sa values compared to uncoated surfaces. This indicates that even in cases where the coating is not successfully produced (Fig.3a and Fig.3c), the surface still experiences damage and the formation of cracks, leading to an increase in the depth of the surface valleys.

When the coating is successfully applied on the surfaces, lower Sa values can be observed compared to those obtained with the lowest temperature values. For instance, comparing Fig.3a and Fig.3b it is possible to observe lower Sa value for the second set of process parameters. This is due to a homogeneous arrangement of the coating on the entire surface. However, the Sa value of Fig.3b is still higher than that of the bare surface, suggesting that the particles are unable to deform enough to create a completely continuous coating.

In order to compare the quality and characteristics of the produced coatings, obtained with the most effective process parameters (samples C_{T2SO1} and C_{T2SO2}) further analyses were carried out using a Hirox microscope. The images of the coatings are presented in Fig.4.

Fig.4 – Hirox image of the Aluminium coating on vitrimer-based panel a) C_{T2SO1} coating obtained with T=300 °C and S.O=70 mm b) C_{T2SO2} coating obtained with T=300 °C and S.O=100 mm

It is possible to observe that the coating obtained at the lowest standoff distance value appears to cover the surface more thoroughly. In fact, when the distance of the nozzle from the substrate is low the combined effect of the ductile matrix accommodating the impacting particles and the stiffening of the panel due to the presence of fibres leads to a more homogeneous coating where the particles are able to deform and produce the coating.

On the other hand, for the highest standoff value, only the areas between the fibres appear to be coated. These areas are indeed richer in vitrimeric matrix, which becomes ductile at high temperatures. The particles, for such high standoff values, do not seem to have enough energy to effectively adhere to the surface. Further analyses of the produced coatings under the Hirox microscope are shown in Fig.5 and Fig.6.

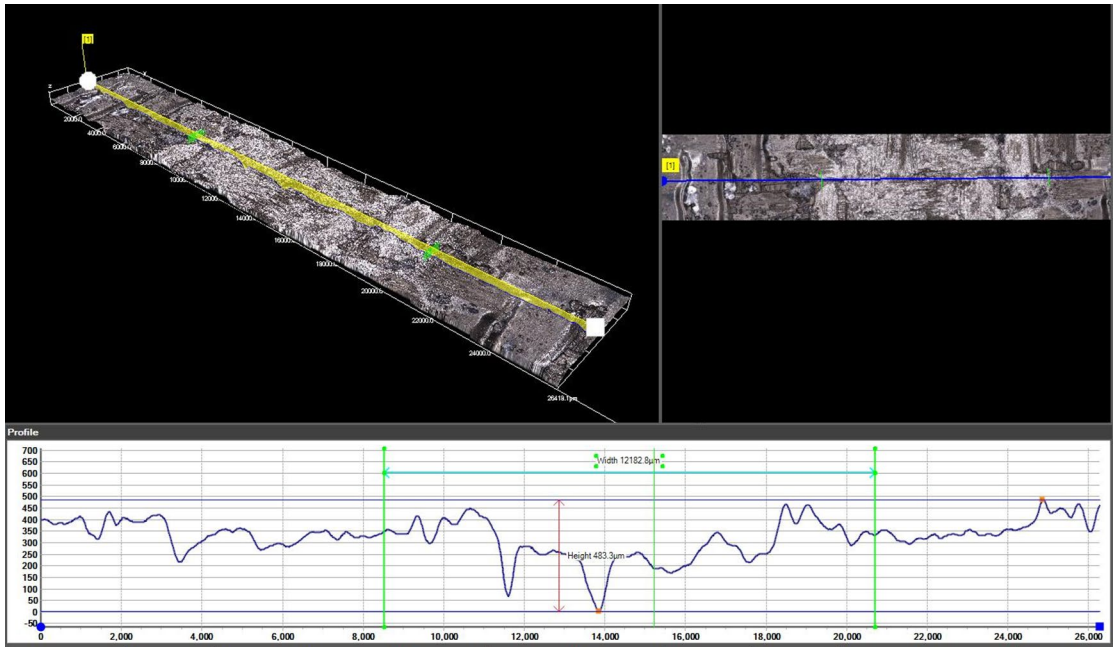

Fig.5 - Hirox 3D image and coating height of the specimen obtained with spraying condition T=300 °C and S.O=70 mm

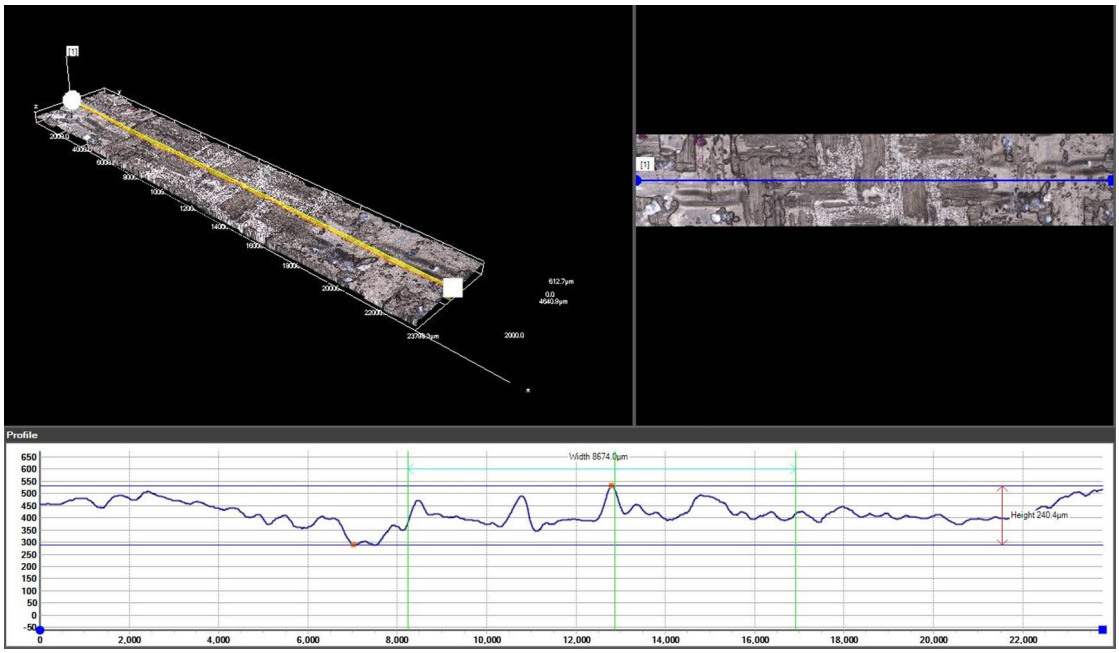

Fig.6 - Hirox 3D image and coating height of the specimen obtained with spraying condition T=300 °C and S.O=100 mm

Through analysis of the Hirox 3D images, one can examine the width of the coating profiles. Comparing Fig.5 and Fig.6 it can be observed that the coating trace on the C_{T2SO1} sample is wider than that on the C_{T2SO2} sample. This is because as the Standoff Distance (SoD) increases, the particles impact at lower velocities and it is more likely that the particles in the peripheral zones of the flow (which impact with a velocity component perpendicular to the substrate) will have a lower velocity than the critical velocity, which is the minimum velocity required for coating adhesion [22].

Conclusions

Based on the findings and discussions from the conducted experiments, it can be inferred that:

- The process of cold spray deposition successfully applied aluminium particles onto composite panels containing a vitrimer material as the matrix.
- The use of epoxy vitrimer as the matrix material appeared to be promising for cold spray metallization, as it exhibited similar properties to a thermoplastic material above its transition temperature (Tv), while still maintaining its mechanical and thermal characteristics below this temperature.
- Two key factors for achieving successful deposition on vitrimer-based composites were identified as the gas temperature and standoff distance. Specifically, it was crucial for the gas temperature to be above the topology freezing transition temperature.
- For temperatures lower than the transition temperature, it is not possible to achieve a homogeneous coating on the surface, which is damaged by the impacting particles.
- Using lower standoff values, however, increases the likelihood of achieving a more uniform coating and wider metallized traces, as it allows for a greater number of particles to have velocities higher than the critical velocity.

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