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Microstructural aspects of the protective ceramic coatings applied on the surfaces of refractory alloys produced by additive manufacturing

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Abstract. The possibility of depositing multi layers made of metals/alloys and high temperature ceramics by electron beam physical evaporation process under high vacuum (EB-PVD) on the surface of a parallelepiped sample made by selective laser melting (SLM) from a Ni base refractory super alloy was experimentally tested. The SEM-EDAX micro structural analysis revealed the morphology and thickness of the coatings consisting of a NiCrAlY base alloy as bonding layer and three successive YSZ, LZO and GZO ceramic layers on the Ni-based super alloy substrate obtained by additive manufacturing. The adhesion of the layer deposited was evaluated by the scratch test method. The analysis highlighted the importance of pre-preparing the surface of the additive manufactured substrates, in order to control the adhesion and uniformity of the deposited layers.

Keywords: Ni-base superalloys / ceramic coatings / SLM / EB-PVD / scratch test

1 Introduction

Among the additive manufacturing (AM) techniques of metal parts, selective laser melting (SLM) is a technique with a sharp increase in the production of components with high complexity due to specific features like: building a part by layering allows for geometries that are not possible with conventional techniques, such as internal lattice structures or complex cooling channels; the precision of the processes allows for fine details which are extremely difficult to achieve with casting or machining; components can be fabricated in a single build; any material (powder) which is not fused can be recycled in the same process, thus providing huge feedstock waste reductions compared to machining. The utilization of SLM to manufacture components for high demanding industries is still limited and driven by the existing metal powder grades, efficiency and process cost. The SLM produced materials have a high level of anisotropy of structural and mechanical properties depending on the process parameters and build orientation [1,2]. The limited surface quality of parts obtained by SLM is one of the major drawbacks restricting its application. Deposition of thin films and coatings may be a very useful method to reduce this limitation [3–5].

The deposition of metallic or ceramic materials in vacuum in the form of thin films, by PVD (Physical Vapor Deposition) processes, on metallic surfaces obtained by conventional metallurgical processing methods (rolling, forging, casting) is frequently used to increase resistance to corrosion and erosion, reduce oxidation at high temperatures and increase operating temperature. However, the possibility of depositing thin films on other type of metal surfaces such as those obtained through 3D printing process was poorly investigated.

The vacuum deposition process by thermal evaporation using electron beam (EB-PVD) allows to obtain thin film and coatings with a granular-columnar structural morphology, perpendicular to the interface. This type of morphology maximizes the resistance to thermal stress that results from the differences between the coefficients of thermal expansion. Usually, successive layers of one or more ceramic materials are deposited on the substrate, having the role of thermal barrier coatings (TBC). The decrease of the thermal conductivity of the TBC is realized not only by the types of materials deposited on

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Table 1. Chemical composition of IN 625 metal powder.

Chemical elem.	Al	C	Co	Cr	Fe	Mn	Mo	Nb	Si	Ti	Ni
Specification [%wt]	<0.4	<0.1	<1.0	20–23	3–5	<0.5	8–10	3.15–4.15	<0.5	<0.4	Bal.

the substrate, but also by the micro structural defects (pores, micro-cracks) induced by the process of deposition EB-PVD, which represent obstacles in the way of the heat transfer.

For high-temperature applications such as land-based gas-turbine engines or jet engines, the substrate is generally based on Ni super alloy (commercially known as NIMONIC or INCONEL), which supports structural mechanical loads.

In the mid-1970s NASA introduced a two-layer TBC consisting of a porous atmospheric-pressure plasma-sprayed ZrO_2-Y_2O_3 ceramic over a plasma- sprayed NiCrAIY bond coat, successfully tested on the turbine blades. Y_2O_3-stabilized ZrO_2 (YSZ) was found to be the most suitable material for TBC applications, with an optimum amount Y_2O_3 around 7–8 wt.% (4–4.5 mol%). This composition offers a high degree of resistance to spallation and excellent thermal stability [6].

Rare-earth zirconates, such as $La_2Zr_2O_7$, $Nd_2Zr_2O_7$ and $Ga_2Zr_2O_7$ are now considered as emerging TBC materials for the future. These pyrochlore phases are stable up to the melting point (around 2300 °C), making them potential TBC materials for higher application temperatures. They also have a low intrinsic thermal conductivity, associated with the complexity of crystallographic structure and difference in the number and types of atoms in a unit cell [7,8].

The most commonly used deposition technologies, thermal spray and electron beam – physical vapor deposition (EB-PVD), result in different types of coating microstructures. The deposition with EB-PVD typically leads to columnar structures with good thermo-mechanical performance [9]. LO/YSZ/DLC (diamond-like carbon) coating shows obvious feathery nanostructure and intra-columnar pores also showed a relativity low thermal conductivity ($0.864\,W\,m^{-1}\,K^{-1}$ at 1200 °C) and high thermal cycling lifetime (1535 cycles) [10]. The thermal conductivity of the LZO and YSZ composite ceramic value is in the range of 1.7745–2.3076 $W\,m^{-1}\,K^{-1}$ for temperatures from 200 °C to 1000 °C, which is between those of YSZ and LZO respectively. The trend in the thermal conductivity of the composite ceramic is similar to that of YSZ with increasing temperature [11].

MCrAlY-type coatings have been widely used to protect nickel based super alloy substrates used in gas turbines from oxidation and hot corrosion. This type of coatings is usually preferred for TBC systems. In MCrAlY-type coatings, M refers to either cobalt or nickel, or both [12–14]. Al and Cr are added in the composition of bond coat to increase oxidation and hot corrosion resistance, while Y is added to enhance the toughness and improve adhesion [15–17]. During the oxidation of MCrAlY- type metallic bond coats, a thermally grown oxide layer (TGO) forms on the coating surface, consisting mostly of alpha-alumina and trace amounts of different oxides [18,19–21].

Such ceramic coatings with very high melting points are generally deposited with two deposition techniques. The first method is Atmospheric Plasma Spray (APS) as the most commonly known, cost-efficient and applicable method. The latter is the electron beam physical vapor deposition (EB-PVD) technique, which is a more expensive and more complex process. As an innovative technique with an increasing application field, EB-PVD process involves deposition of less porous coatings [25]. Moreover, in this technique, the deposition process results in a coating with columnar microstructure. As a consequence of the expansion tolerance provided by EB-PVD process, strains that arise during thermal cyclic oxidation of TBCs are tolerated to a greater extent [22–24].

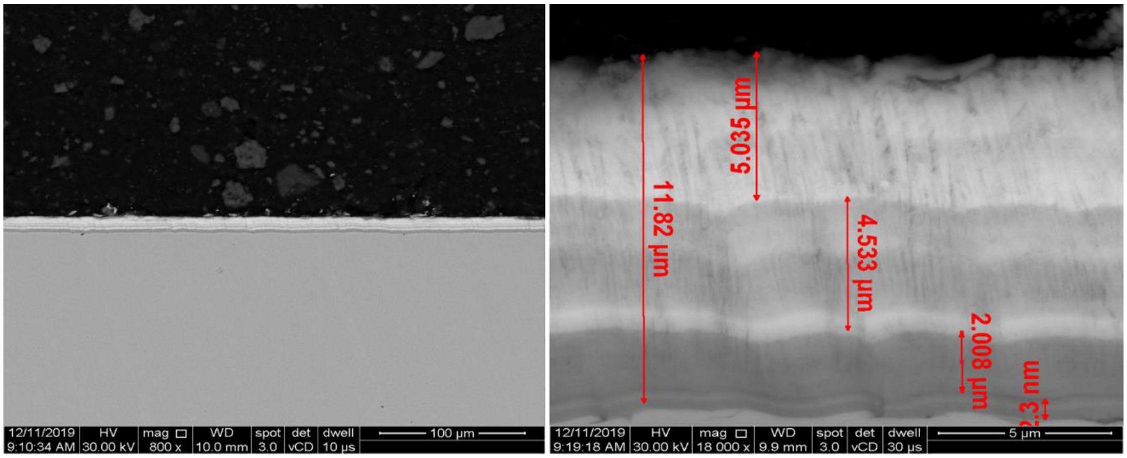
The aim of this paper is to obtain by EB-PVD process advanced TBC coatings consisting of NiCrAlY- base alloy as bonding layer and three successive YSZ, LZO and GZO ceramic layers on the Ni-based super alloy substrate obtained by additive manufacturing and evaluate their morphology in order to control the adhesion and uniformity of the deposited layers.

2 Experimental procedure

To achieve the supports (substrates $30 \times 50 \times 3$ mm) through the 3D printing process, commercially IN 625 metal powder with the chemical composition presented in Table 1 were used. The 3D printing system was a Lasertec 30 SLM (DMG Mori, Germany) equipped with a 600 W Yb: YAG fiber laser. The Lasertec 30 SLM machine has a building volume of $300 \times 300 \times 300$ mm and an Ar flow system which keeping the working area under oxygen level as low as 0.2% to avoid metals oxidation. The IN625 supports were manufactured with the following process parameters: 750 mm/s laser speed, 250W laser power, 70 μm spot size, 50 layers thickness and 0.11 mm hatch distance. The layers were scanned using a 90° scanning strategy rotated with 90° between two successive layers and the temperature of building plate was 80 °C.

Commercial NiCrAlY powders (Amperit 413) containing – 67 wt.% Ni was used to deposit the bond coat prior to deposit the ceramic layer. Commercially 8% Y_2O_3 partially stabilized micro-sized ZrO_2 powders – YSZ (Metco 204NS-G), $La_2Zr_2O_7$ (LZO) granulated powders (grain sizes 30–120 μm) and $Gd_2Zr_2O_7$ (GZO) granulated powders (grain sizes 45–140 μm) from Trans-Tech Ceramics and Advanced Materials USA were used to deposit the ceramic layers.

Coating process was developed in a special designed combinatorial EB-PVD thin film coating equipment



(a) (b)

Fig. 1. SEM analysis – morphological aspect of the films deposited by EB- PVD on a Ni base super alloy substrate manufactured by 3D printing – (a) ×800; (b) ×18000.

(Torr Inc., USA) endowed with quartz sensors (QCM) and software for monitoring the deposition rate. It has a 3 m^3 vacuum chamber with 4 independent 10 kW e-beam guns working under high vacuum of over $3 \times 10e^{-7}$ Torr (4.0×10^{-5} Pa) that may be reached by the help of two cryogenic pumps. Each evaporation source has 4 crucibles of 75 cm^3 each that can be rotated continuously around e-beam source. Possibility of depositing multilayer thin film coatings of up to 16 elements in the same batch or co-deposition by evaporating up to 4 different elements at the same time. Two substrate holders enabling horizontal rotation with possibility of depositing on several small or single square piece of 350 mm with high uniformity or vertical rotation for coating cylinders of up to 350 mm in length are available. The substrates may be heated during deposition up to 400 °C with the help of 8 infrared heating lamps. Computer-assisted installation, allows the creation of complex deposition recipes. Preliminary tests have been performed to establish the influence of process parameters such as evaporation rate, substrate temperature and distance between substrate and evaporation source on the layer thickness calculated from the quartz sensor on line data and adherence of coatings for bonding layer and ceramic layers respectively. The materials used for the deposit are in the order of their deposition: NiCrAlY bonding coat/ YSZ/ LZO/ GZO. Based on the preliminary tests, the substrate was heated to approx. 300 °C and the depositing materials that were previously loaded into crucibles, were evaporated in high vacuum (6.67×10^{-5} Pa), using a 10 kW power electron gun, accelerating voltage 10 kV, and the beam current varied between 0 and 1 A. After depositing, the microstructure and microcomposition of samples were investigated by scanning electron microscopy (SEM) using a FEI F50 Inspect scanning electron microscope equipped with an EDAX Apollo X silicon drift detector energy dispersive X-ray spectroscopy (EDS) system. The scratch tests were performed with a Revetest Scratch Tester RST3, (Anton Paar, Switzerland) with load range 0.5–200 N and equipped with a Rockwell C diamond, $R = 200$ µm, cone angle 120°. The scratch testing consisted of scratching on the surface of samples with a progressive load of 100 N/min, scratch speed of 10 mm/min and scratch distance of 4 mm, according ISO 20502/2005.

3 Results and discussions

The SEM micro structural analysis performed in the cross section of the sample, highlights the individual heterogeneous morphological aspect of the four layers of thin films deposited. The evaporation process under the high vacuum took place at a deposition rate of 0.8–1.2 $\text{Å}s^{-1}$ leading to continuous films with good thickness uniformity for each layer. It may be also observed that thin films deposited by the EB-PVD process contains micro-pores and micro-cracks and the films topology follow the contour of the substrate surface (Fig. 1a). The total thickness of the films deposited on the surface of the substrate is about 12 µm (Fig. 1b). The qualitative EDAX analysis in the cross-section presented in Figure 2, shows the distribution of the elements from all materials deposited by thermal evaporation EB-PVD respectively: Ni-MCrAlY; YSZ; LZO and GZO. The elements from each film is cleared evidenced and no diffusion of the elements from the ceramic layers in the substrate took place.

The formation of micro-pores and micro-cracks may locally reduce the adhesion of the films during mechanical or thermal stresses. Adhesion testing should be used to evaluate the coating performances and reproducibility. They are generally used to provide comparative measurements and are not meant to gibe absolute measurement, different tests giving different values. In case of scratch test method used according to method previously described, the failure mode of the film is observed under a microscope and a critical load at failure is assigned for each film [25]. The scratch test performed on the surface of coated sample revealed that the films deposited are adherent to the substrate (Fig. 3). At a force of about 23 N, the exfoliation of the oxide films deposited on the substrate of the Ni base super alloy obtained by additive manufacturing occurs.

The scratch test confirms the thickness of the film deposited by about 12 μm, evidenced by the SEM analysis and composed of the multilayers of oxides deposited by e-beam and which is adherent to a force up to about 23 N.

The scratch test performed with a Revetest Scratch Tester RST3 on the same films of ceramic materials deposited in the same conditions on Inconel supports, made by two different process of the type: SLM and rolling respectively, present close values (Fig. 4).

Generally, the results of the scratch test methods depend very much on the hardness of the substrate that influence the cracking of the coating during testing [25]. In the case of the LZO and GZO layers deposited by EB-PVD on INCONEL substrate obtained by traditional metallurgical process and 3D printing respectively, no significant variation of the scratch resistance may be observed.

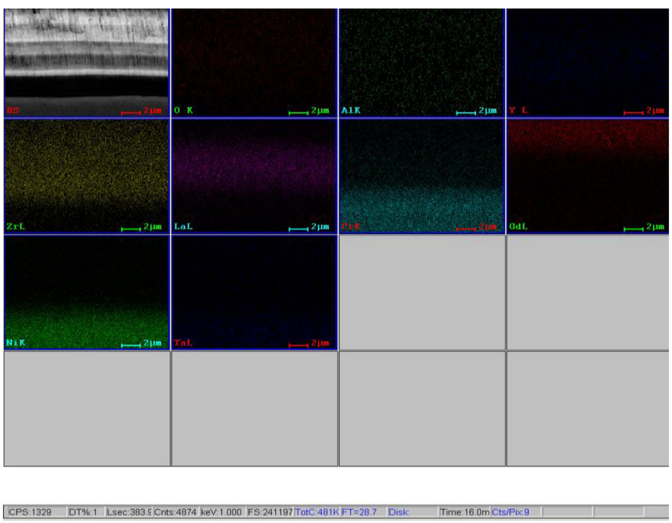


Fig. 2. EDS elemental maps of the films deposited by EB-PVD on a Ni base super alloy support manufactured by 3D printing.

Comparing the results obtained for flatness and surface roughness obtained by 3D printing, we may conclude that the structure and porosity of deposit materials (metal and ceramic) by EB-PVD follow the topology of the substrate surface and the coating method enables efficient surface protection.

Based on these results future works are under development to optimize the coating properties by studying the influence of the substrate heating temperature and deposition time on the kinetics of the films' growth and morphology.

4 Conclusions and future prospects

The aim of the research performed is to improve the high temperature performances of the products obtained by 3D printing of INCONEL powders by surface engineering methods.

The obtained results show that the successive ceramic layers deposited from: YSZ, LZO and GZO are adherent on the surface of the substrate from Inconel made by the SLM process. The aspect of depositing ceramic films on the 3D printed support at the macroscopic level is homogeneous, while at the microscopic level a heterogeneous aspect is highlighted.

The scratch tests results show that coatings are adherent and exfoliation process take may be observed starting from about 23 N.

The analysis of the roughness of samples show that the surface of the substrate has a large influence on the morphology and growth of the ceramic coatings.

Further works are under development to improves the adhesion of the deposited layers by controlling the heating

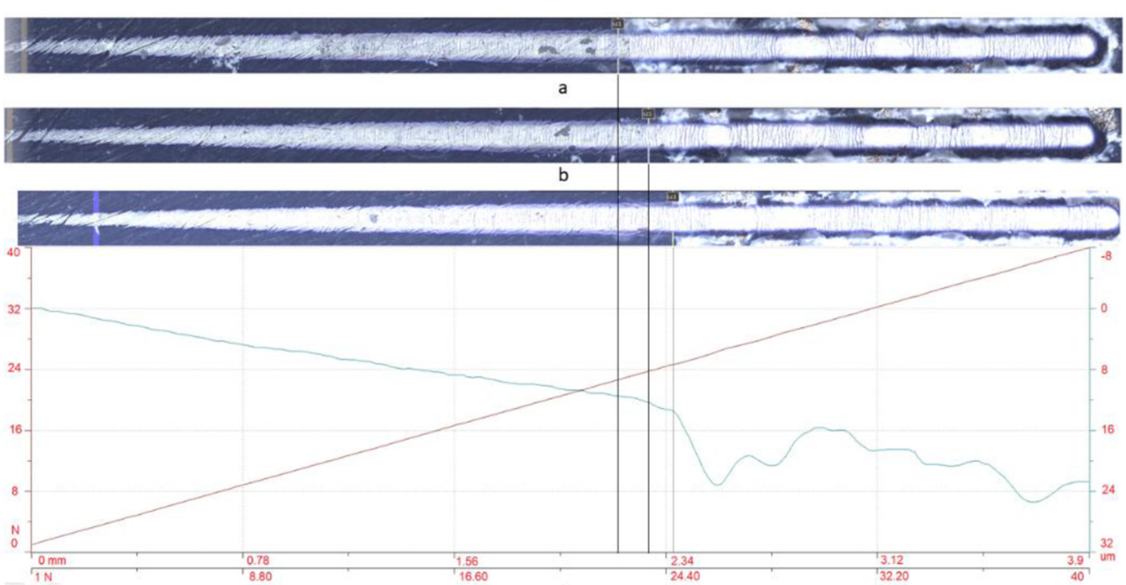


Fig. 3. Scratch test on the substrate manufactured by 3D printed process from Ni based superalloy and coated by EB-PVD with a multilayer film of oxides.

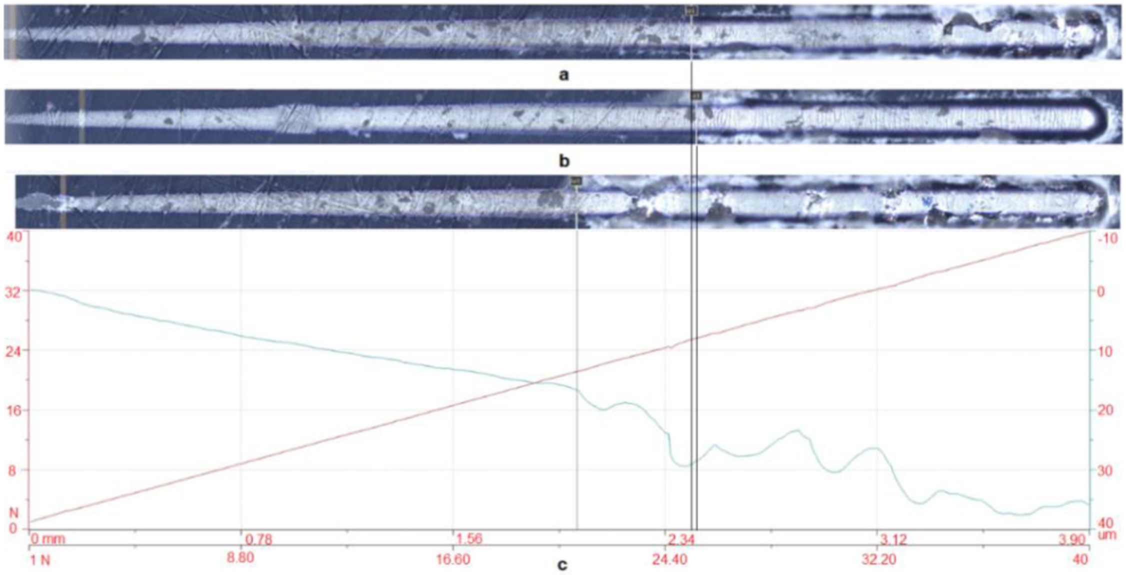


Fig. 4. Scratch test on the substrate manufactured by rolling process from Ni based superalloy and coated by EB-PVD with a multilayer film of oxides.

substrate temperature during EB-PVD deposition and assess the functional properties of high refractory oxide coatings on parts obtained by SLM for energy applications.

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