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Best available methods for developing ceramic coatings for high temperature applications

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Introduction

When choosing a material for an application it is essential to know what materials are available and how well they are suited to that specific purpose.

!!! WORKING ENVIRONMENT !!!

The same application working in different environments may require totally different materials.

It is foreseen a wide range of future opportunities related to high-temperature and harsh environment applications. The number of materials that can be used in extreme environments is very limited because they are restricted by some basic requirements.

Introduction

Understanding the behaviour of materials operating under various extreme environments (high/ low temperature, thermal shock, pressure, corrosion, erosion, radiation …) opens new opportunities in many technological fields: automotive, aerospace and defence industry, energy generation and storage, sensors, tools and machinery, chemistry and metallurgy, biotechnologies & biomaterials, etc.

In order to get closer to the intrinsic limits of the materials performance it is required:

- A deep understanding of atomic and molecular origins, on how the extreme environment affects the physical and chemical processes that occur in the volume or at the surface of different existing / newly developed material systems;
- Developing new methods for obtaining and characterizing bulk material systems or coatings for their rational use and for reducing the dependence on critical materials.

Materials

Materials in service under extreme environments:

a) metallic: refractory metals, stainless steels, high-temperature alloys.

+	-
- well studied - commercially available	- corrosion problems - critical materials

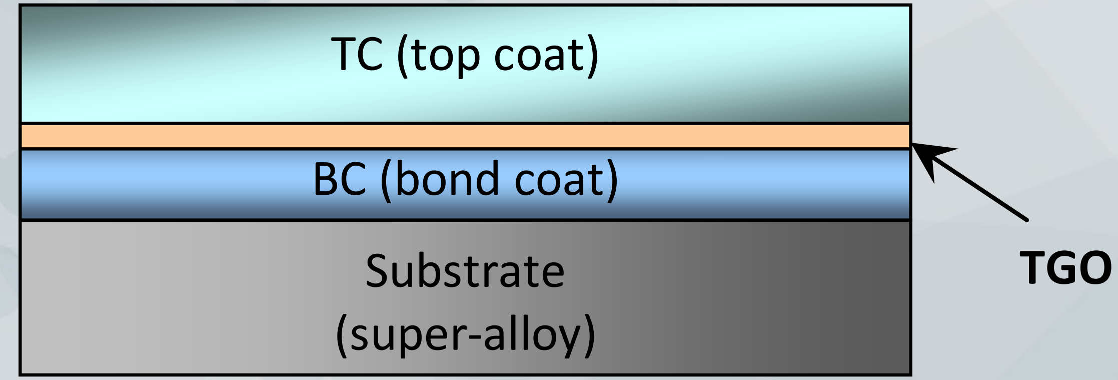
b) ceramic: UHTC (ultra high temperature ceramics), oxide materials, composites.

+	-
- less corrosion - low heat transfer - replace critical materials	- less studied - structure integrity

Materials

The most important applications for oxide materials in extreme environments are Thermal Barrier Coatings (TBC) and corrosion resistive coatings.

TBCs are multi-layered and multi-material coating systems used to lend thermal protection from hot gases in turbines and engines, and thus lower the surface temperature of the substrate components (Bose, 2007; Feuerstein et al., 2008). Conventional TBC systems consist of three layers over the superalloy substrate; a metallic bond coat (BC), an intermediate thermally grown oxide (TGO), and a ceramic top coat (TC). All these layers have distinct physical, mechanical, and thermal properties, which are strongly affected by the processing conditions (Karaoglanli, Ogawa, Turk, & Ozdemir, 2013).



Materials

The number of materials that can be used in extreme environments is very limited because they are restricted by some basic requirements:

- High melting point;
- Chemical inertness;
- Low thermal conductivity;
- No phase transformation between room temperature and operation temperature;
- Good adherence to the metallic substrate;
- Thermal expansion match with the metallic substrate;
- Low sintering rate of the porous microstructure.

Materials

Oxide coatings for extreme environments

(advantages and disadvantages of these materials compared with YSZ)

Materials	Advantages	Disadvantages
Alumina	High corrosion-resistance High hardness Not oxigen-transparent	Phase transformation (1273 K) High thermal conductivity Very low thermal expansion coefficient
7-8 YSZ	High thermal expansion coefficient Low thermal conductivity High thermal shock resistance	Sintering aboce 1473 K Phase transformation (1443 K) Corrosion Oxygen-transparent
YSZ + CeO2	High thermal expansion coefficient Low thermal conductivity High thermal shock resistance High corrosion-resistance Less phase transformation between m and t than YSZ	Increased sintering rate CeO_2 precipitation (> 1373 K) CeO_2-loss during spraying

X.Q. Cao, R. Vassen, D.Stoever., Ceramic materials for thermal barrier coatings., Journal of the European Ceramic Society 24 (2014)

Materials

Oxide coatings for extreme environments

(advantages and disadvantages of these materials compared with YSZ)

Materials	Advantages	Disadvantages
$La_2Zr_2O_7$	Very high thermal stability Low thermal conductivity Low sintering Not oxigen-transparent	Relatively low thermal expansion coefficient
Mullite	High corrosion-resistance Low thermal conductivity Good thermal-shock resistance below 1273 K Not oxygen-transparent	Crystallization (1023-1273 K) Very low thermal expansion coefficient
Silicates	Cheap, readily available High corrosion-resistance	Decomposition into ZrO_2 and SiO_2 during thermal spraying Very low thermal expansion coefficient

X.Q. Cao, R. Vassen, D.Stoever., Ceramic materials for thermal barrier coatings., Journal of the European Ceramic Society 24 (2014)

Deposition processes

In general, deposition processes may principally be divided into two groups:

- those involving droplet transfer such as plasma spraying, arc spraying, wire-explosion spraying, and detonation gun coating;
- those involving an atom-by-atom transfer mode such as the PVD processes of evaporation, cathodic arc deposition and sputtering, chemical vapor deposition (CVD), and electrodeposition.

The main disadvantage of the droplet transfer process is the porosity in the final deposit, which affects the properties.

Deposition processes

There are three steps in the formation of any deposit:

1. Synthesis of the material to be deposited:

(a) transition from a condensed phase (solid or liquid) to the vapor phase

(b) for deposition of compounds, a reaction between the components of the compound, some of which may be introduced into the chamber as a gas or vapor.

2. Transport of the vapors between the source and substrate.

3. Condensation of vapors (and gases) followed by film nucleation and growth.

Deposition processes

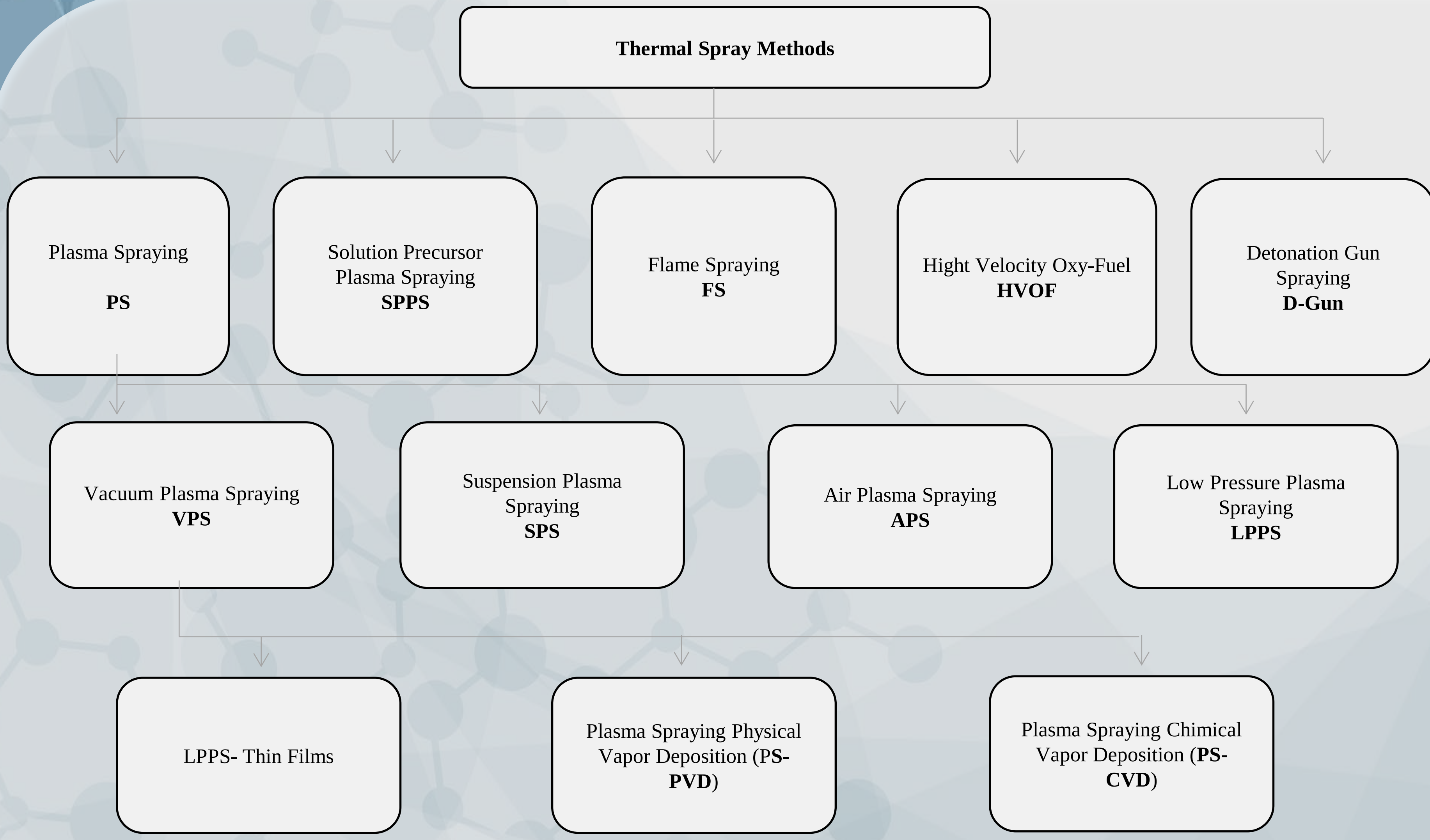
ICARUS SUPERMAT

Main deposition processes used for obtaing oxide coatings

Criteria for deposition processes	Deposition processes				
	PVD			**CVD**	**Thermal spray**
	E-beam evaporation	RF Sputtering	Cathodic arc	PECVD	APS/SPPS
Mechanism of production of depositiong species	Thermal energy	Momentum transfer	Thermal energy	Chemical reaction	Flames or plasma
Deposition rate	Can be very high (up to 750000 Å/min)	Low	Can be very high	Moderate (200-2500 Å/min)	Very high
Deposition species	Atoms & ions	Atoms & ions	Ions	Atoms	Droplets
Uniformity for complex shaped objects	Poor, line of sight coverage except by gas scattering	Good, nonuniform, uniform thickness distributions	Good, but nonuniform thickness distribution	Good	No
Energy of deposited species	Low (~0.1-0.5 eV)	Can be high (1-100 eV)	Very high	Can be high	Very high
Bombardment of substrate/deposit by inert gas ions	Generally no	Yes or no, depending on geometry	Yes	Possible	Yes
Substrate heating (by external means)	Yes, normally	Yes or no	Yes or no	Yes	Not normally

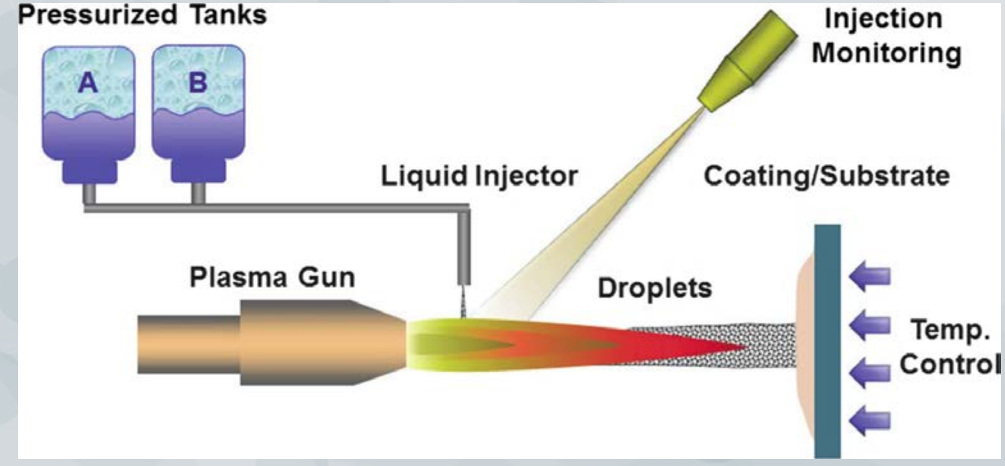
Peter M. Martin., Handbook of Deposition Technologies for Films and Coatings, Third Edition, Elsevier, 2010

Deposition processes



Deposition processes

From all of these thermal spray methods the APS and SPPS are the most widely used for manufacturing TBC coatings. Solution precursor plasma spray (SPPS) unitizes liquid chemical solutions injected into plasma or combustion jet in place of powder to create coatings. The process is schematically shown in the figure below. A related method is suspension plasma spray (SPS) in which solid particles are suspended in a liquid and injected into the thermal jet.



Deposition processes

Chemical Vapor Deposition (CVD) is a process in which the substrate is exposed to one or more volatile precursors, which react and/or decompose on the substrate surface to produce the desired thin film deposit.

CVD is parent to a family of processes whereby a solid material is deposited from a vapor by a chemical reaction occurring on or in the vicinity of a normally heated substrate surface. The resulting solid material is in the form of a thin film, powder, or single crystal. By varying experimental conditions, including substrate material, substrate temperature, and composition of the reaction gas mixture, total pressure gas flows, etc., materials with a wide range of physical, tribological, and chemical properties can be grown. A characteristic feature of the CVD technique is its excellent throwing power, enabling the production of coatings of uniform thickness and properties with a low porosity even on substrates of complicated shape. Another important feature is the capability of localized, selective deposition, on patterned substrates.

Deposition processes

In thermally activated CVD (TACVD), the deposition is initiated and maintained by heat. However, photons, electrons, and ions, as well as a combination of these (plasma activated CVD), may induce and maintain CVD reactions.

There are three **PVD processes**, namely:

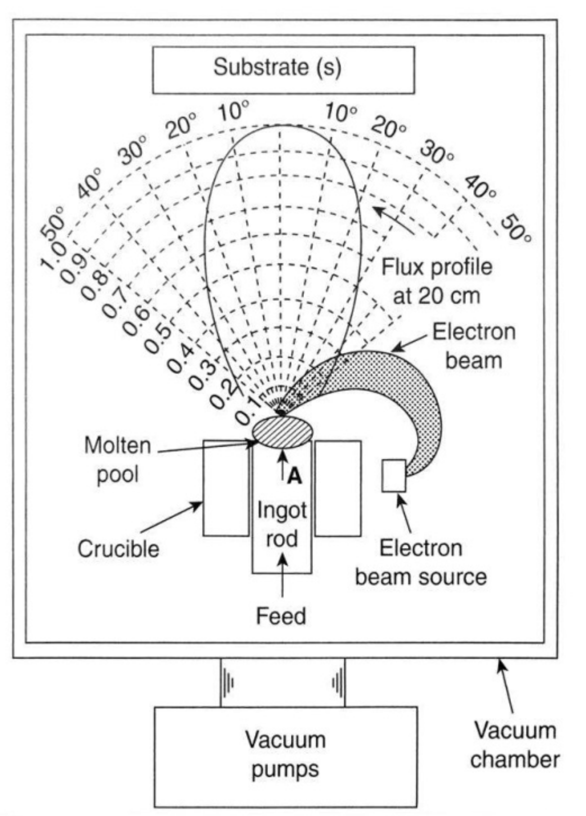
- sputtering.
- cathodic arc deposition
- evaporation

In the **sputtering process**, positive gas ions (usually argon ions) produced in a glow discharge (gas pressure 20-150 mtorr) bombard the target material (also called the cathode). dislodging groups of atoms which then pass into the vapor phase and deposit onto the substrate.

In **Cathodic arc deposition** (Arc-PVD) the target material is a cathode which is varorized with the help of an electric arc.

Deposition processes

In the **evaporation process**, vapors are produced from a material located in a source which is heated by direct resistance, radiation, eddy currents, e-beam, laser beam, or an arc discharge. The process is usually carried out in vacuum (typically 10 -10^{-6} torr) so that the evaporated atoms undergo an essentially collisionless line-of-sight transport prior to condensation on the substrate.

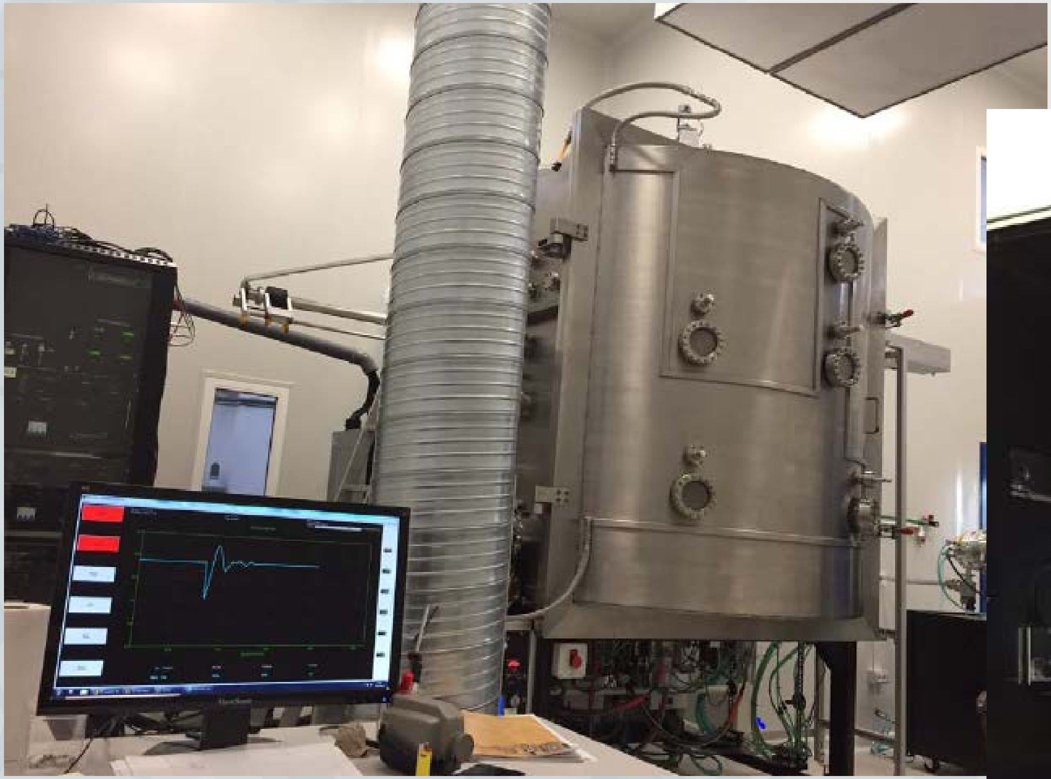


Vacuum evaporation system with e-beam heating.

It must be noticed that the deposit thickness is greatest directly above the center-line of the source and decreases away from it

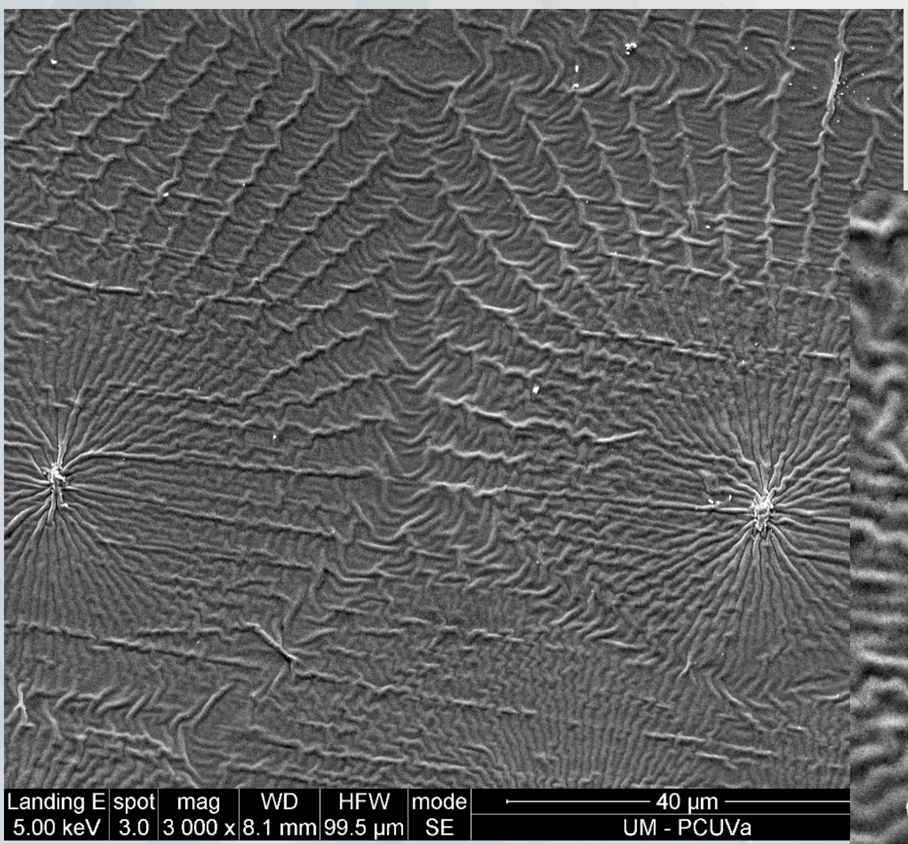
Experimental results

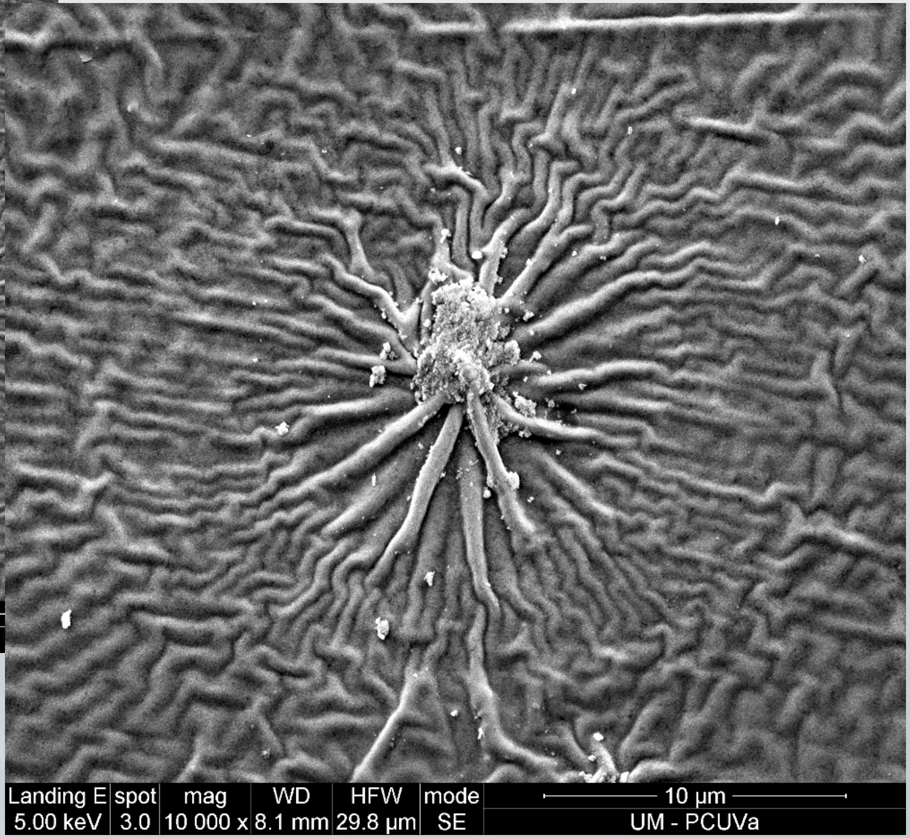
IMNR infrastructure: EB-PVD thin film coating equipment



Experimental results

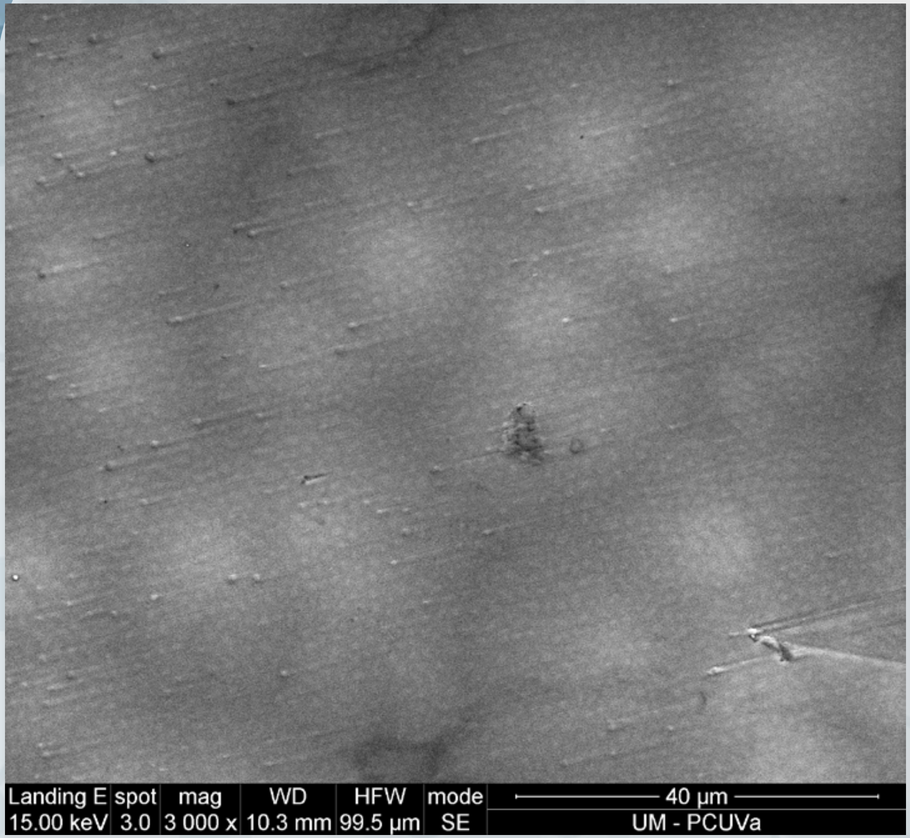
BaZrO3 coating deposited by EB-PVD on nimonic substrate - HR-SEM micrographs

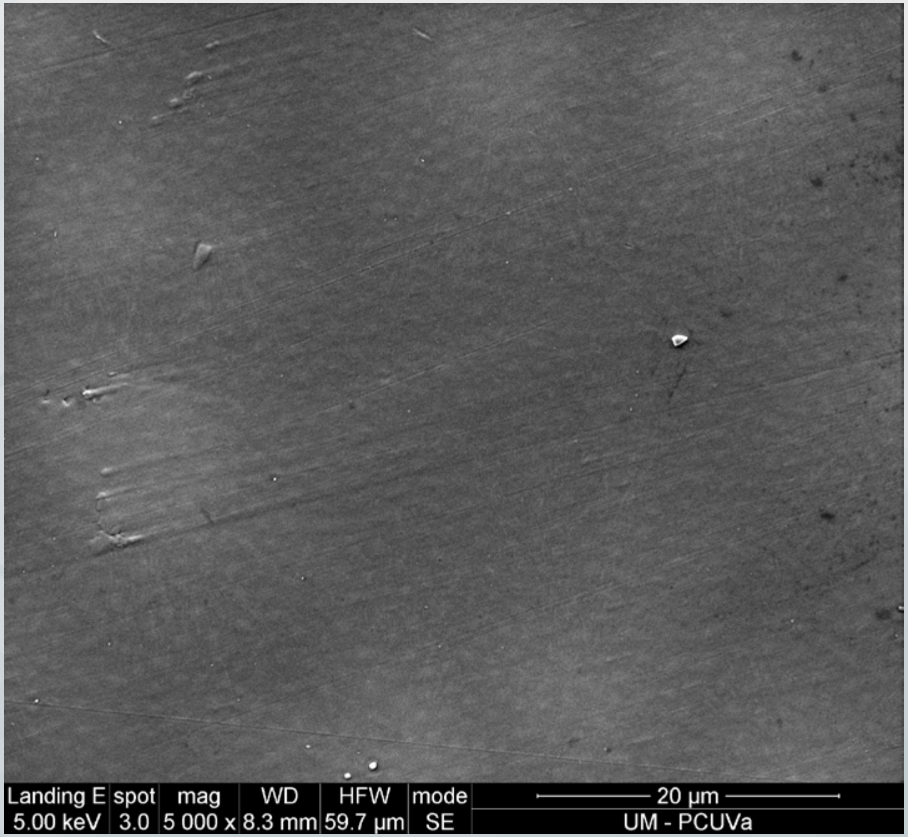




Experimental results

NiCr+BaZrO3 coating deposited by EB-PVD on nimonic substrate - HR-SEM micrographs

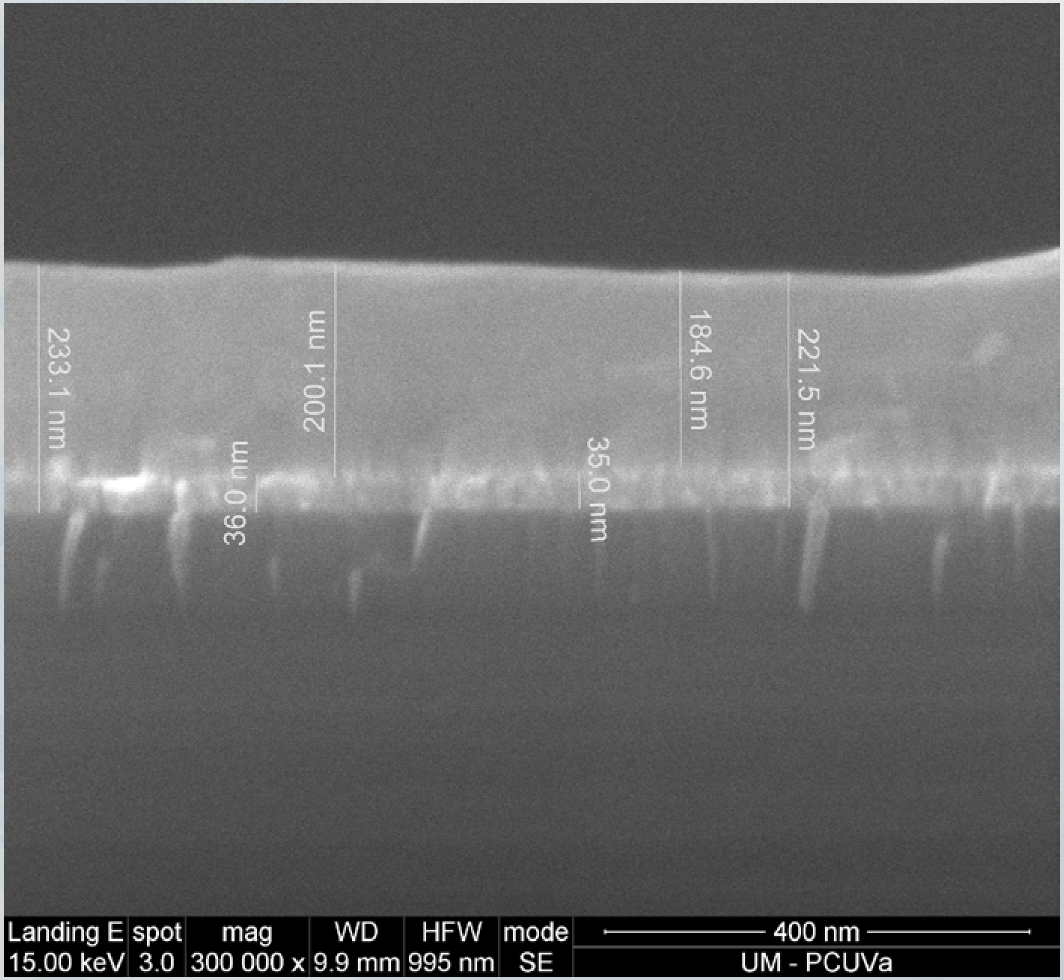




Experimental results

NiCr+BaZrO3 coating (cross-section)

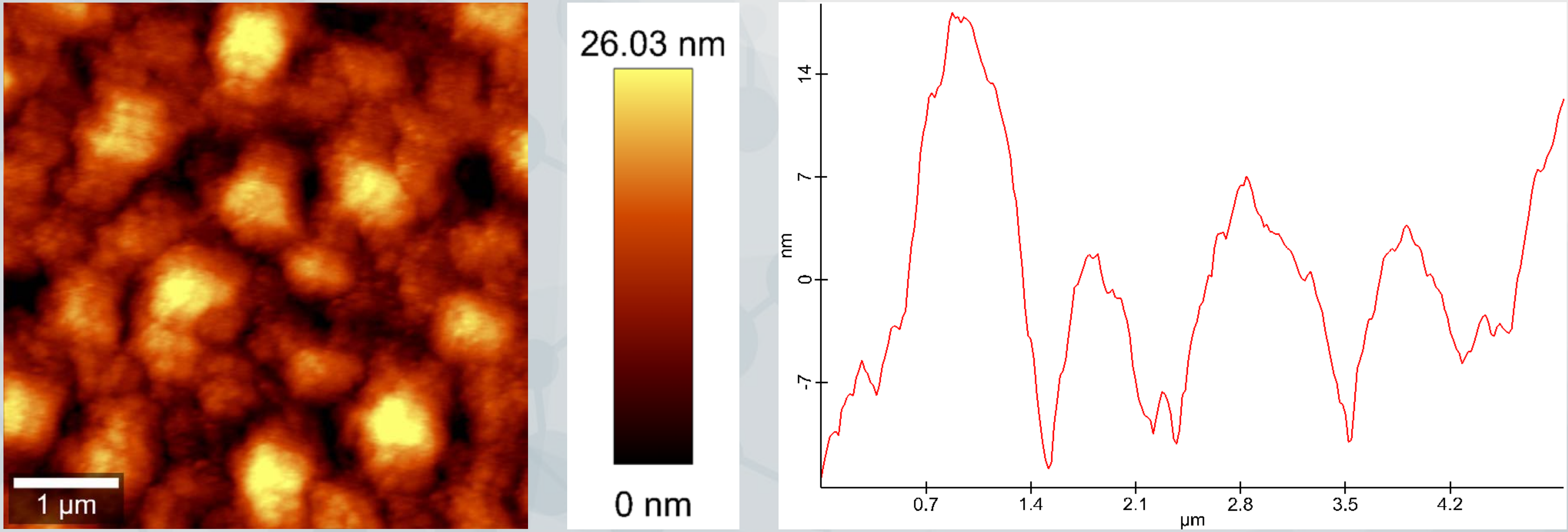
deposited by EB-PVD on silicon substrate - SEM micrograph



Experimental results

NiCr+BaZrO3 coating deposited by EB-PVD on silicon substrate

AFM measurement



All SEM and AFM investigations presented, were performed at University of Burgos - ICCRAM (Spain)

Conclusions

Differnt oxide materials with various structures are availabe to obtian coatings with designed properties for extreme environments applications. The best available technologies are those that allow to control in a reproducible and convenient way the structure, properties and adhseion of the coatings assuring an economical implementation in the desired applicaitons.

For these materials thermal spraying and EB-PVD seems to be the most preferred method.

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