ABSTRACT

In this doctoral thesis was done in the first place the study of the literature in order to identify the current state of the art in the field of thermal barrier coatings, in terms of the requirements for each component of the system and the new requirements and challenges in the field. Was determined the high-temperature performance of the proposed thermal barrier coating (TBC) systems through numerical simulation, by analyzing the temperature distribution in the system using the Ansys program. Was designed and manufacture support samples from the Nimonic 75 super alloy for the deposition of TBC systems in atmospheric conditions using the APS plasma jet spraying method. Was Analyzed the influence of the deposition process on the mechanical properties of the substrate by Vickers microhardness tests and the roughness of the samples after each deposited layer by roughness measurements. It was also done the development of a method for the quantitative evaluation of the pores and the area with thermally grown oxides (TGO) present in the system after isothermal oxidation by trinarization of optical and SEM microscopy images using the Scandium software. Was identifying the lifetime of the systems studied under conditions of cyclic isothermal oxidation at a temperature of 1150 °C and a holding time of 100h per cycle. Was done the evaluation of the lifetime of the TBC systems under simultaneous conditions of thermal shock and cyclic isothermal oxidation at 1200°C and 1250°C. Was determined the influence of cyclic isothermal oxidation on the densification of the component layers in the TBC system by quantitative evaluation of the pores and adhesion tests performed by the scratch method in cross section. Was done the evaluation the high-temperature corrosion behavior of the systems studied at temperatures of 900 °C and 1250 °C in environments rich in Na₂SO₄+V₂O₅ salts and Ca, Mg, Al and Si oxides, simulating the marine and desert environment in which these coatings can operate. Was designed an automated thermal shock and isothermal oxidation installation for testing thermal barrier coatings. Was submitted a patent application for the automated thermal shock and isothermal oxidation test installation for thermal barrier coatings.





ABSTRACT DOCTORAL THESIS

Studies and research on the development, testing and characterization of thermal barrier coatings (TBC)

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INTRODUCTION

The doctoral thesis addresses a field of interest for the aerospace industry and the scientific community by developing thermal barrier coatings (TBCs).

TBCs are advanced materials applied to the surface of components that operate at high temperatures, such as gas turbine and jet engine components. TBCs act as a barrier to protect the component material from heat and oxidation, significantly increasing the component's service life. TBCs are typically made from ceramic materials, such as yttrium-stabilized zirconia, which have excellent thermal insulation properties. They are applied using thermal spray or other coating techniques and must withstand thermal cycles and mechanical tests to be effective.

NASA published the article "History of Thermal Barrier Coatings for Gas Turbine Engines" in 2009 [1]. According to this, the history of TBCs dates back to 1947 with the publication of the work of Harrison and Moore "Review of an Investigation of Ceramic Coatings for Metallic Turbine Parts and Other High Temperature Applications". Research has continued, and in 1948 C.R. Morse presents the first tests with such coatings on the turbine blade in his work "Comparison of National Bureau of Standards ceramic coatings L-7C and A-417 on turbine blades in a turbojet engine". In 1953, Bartoo and Clure present the first record of a TBC applied to a turbine blade that lasted 100 hours in their work "Experimental Investigation of Air-Cooled Turbine Blades in a Turbojet Engine, XIII. Performance "Evaluation of Several Protective Coatings Applied to Turbine Blades of Nonstrategic Steels".



Top Edge of an Air-Cooled Blade



Figure 1: Image of the first functional turbine blade coated with TBC and its cross section.[2]

Research continued with notable results on several combinations of ceramic materials until 1976 when S. Stecura in his work "Two-Layer Thermal Barrier Coating for Turbine Airfoils— Furnace and Burner Rig Test Results" laid the foundation for the thermal barrier coating used predominantly today, consisting of yttrium-stabilized zirconium using a NiCrAlY substrate, succeeding in passing the tests with this coating on a J-75 engine.

The development and implementation of advances in both the metallic base and the upper ceramic layer will be explored. Evolution has included performance and durability improvements, process advances, and understanding and evolution of failure modes.

Recent efforts have focused on the future challenges of thermal barrier coatings to meet the ever-increasing operating temperature requirements of future applications.

In Figure 2 and Table 1, the evolution of the coating temperature used over the years can be observed. Only in the last 20 years has been a significant increase- over 500°C. Currently, rare earths are of great interest and represent a solution for improving these coatings.[6]



Figure 1 The evolution of TBC.[6]

To allow an increase in operating temperatures in a gas turbine additional protection of critical components, mainly turbine blades and combustion chamber, is needed. Together with advanced cooling systems (in the case of turbine blades), thermal barrier coatings (TBCs) are the most efficient methods for protecting the components of a gas turbine exposed to high temperatures and severe corrosive environments. The use of TBCs to protect critical components in a turboengine can allow an increase in operating temperature, without increasing the base material temperature, reduce the amount of air required for cooling while maintaining the operating temperature of the turboengine and improve the durability and reliability of the turboengine components.

The coatings deposited on turbine blades must meet the following requirements:

- Provide resistance to hot corrosion, oxidation and erosion when exposed to the flow of hot gasses;
- Resist the static and dynamic loads applied to the blades, thus the material from which the coatings are made must present a combination of strength and ductility;
- Show good stability and not degrade at contact with the substrate;
- Must not degrade the mechanical properties of the blades.

It has been found that even after a long period of operation, turbine blades have superior mechanical properties to those that are not coated.

The main objective of the doctoral thesis is to develop thermal barrier coatings (TBCs) through APS thermal spray technology for use in high-temperature applications, such as gas turbine components.

In order to achieve the main objective, a research methodology has been developed through which the following steps will be taken:

- Analysis of the current state of the art in the realization and testing of thermal barrier coatings systems for parts and subassemblies used in the aeronautical industry;
- Behavior assessment of the proposed superalloys through high-temperature corrosion tests in order to use them in thermal barrier coating (TBC) systems;

- Design of new TBC systems with rare earths using APS thermal spray technology;
- Evaluation of the high-temperature behavior of the systems by numerical simulation of the temperature distribution along them;
- Evaluation of the influence of the deposition process on the substrate and the final roughness;
- Determination of the performance of the proposed systems by subjecting them to thermal shock tests, isothermal oxidation tests and high-temperature corrosion tests.

PART I. DOCUMENTARY ANALYSIS OF THE CURRENT STATE REGARDING THE CONSTRUCTION AND TESTING OF COATING SYSTEMS AS A THERMAL BARRIER OF PARTS AND SUBASSEMBLIES USED IN THE AIRCRAFT INDUSTRY

CHAPTER 1. GENERAL ASPECTS REGARDING THERMAL BARRIER COATING SYSTEMS

1.1 The composition of covering systems with the role of a thermal barrier

A thermal barrier coating (TBC) system is composed of several components, of which the most important are:

Bond coat: This layer is responsible for ensuring the adhesion of the ceramic layer to the substrate. The bond coat is usually made from a metallic material, such as nickel aluminide or MCrAIY (where M is an element such as cobalt or nickel), which provides excellent adhesion to the substrate and also offers a level of protection against oxidation and corrosion.

Thermal insulation layer: This layer is responsible for providing the thermal insulation properties. The thermal insulation layer is usually made from a ceramic material, such as yttrium-stabilized zirconia (YSZ), which has a very low thermal conductivity and can withstand high temperatures. The layer is usually applied as a thin coating, with a thickness usually in the range of 50-300 microns.

Currently, thermal barrier coatings (TBCs) are widely used in gas turbines to provide protection against corrosion, high-temperature oxidation, and to extend the operating life and/or increase the operating temperatures while keeping the substrate (the material from which the components are made) at an optimal temperature to maintain the properties necessary for normal operation.

By analyzing Figure 1.1, it can be observed that TBC coatings are a multilayer system consisting of a metallic substrate (Ni-based superalloy), an oxidation and corrosion resistant bond coat, an intermediate oxide layer with a diffusion barrier role that appears during exposure to high temperatures (TGO - Thermally grown oxide) and an outer ceramic layer (top coat) with a thermal barrier role that can allow a reduction in the temperature at the surface of the component.



Figure 1.1 A cross-section of a turbofan and a blade with a TBC coating, with its components seen under an electron microscope. [8,9]

CHAPTER 2. DEFINING THE REQUIREMENTS NECESSARY FOR THE DEVELOPMENT OF A NEW TBC SYSTEM AND DEPOSIT TECHNIQUES OF THERMAL BARRIER COATING SYSTEMS

2.1 Defining the requirements necessary for the development of a new TBC system

Based on these considerations, the study carried out in this stage to identify new solutions for improving the characteristics and service life of current TBC coatings has highlighted the possibility of developing new TBC coatings based on oxides with pyrochlore structure, such as lanthanum (La₂Zr₂O₇) and gadolinium (Ga₂ZrO₇) zirconates, which would allow an increase in durability and operating temperatures up to 1300 °C. The choice of lanthanum (La₂Zr₂O₇) and gadolinium (Ga₂ZrO₇) zirconates for use in the upper layer of a coating was based on the following selection criteria for the most promising materials:

- Reduced thermal conductivity;
- Thermal shock resistance;
- High melting point;
- Thermal expansion coefficient close to that of the metallic layer;
- No phase transformation between ambient temperature and high temperatures of over 1200°C;
- Corrosion and oxidation resistance at high temperatures;
- Chemical compatibility with the metallic layer and TGO layer;
- Low sintering rate;

2.2 Techniques for depositing thermal barrier coating systems

In order to deposit the layers that form the thermal barrier coating (TBC) system, yttriastabilized zirconia (YSZ) or any other ceramic used poses the most problems in the coating process. The zirconia deposition process must supply enough heat to melt, evaporate, or cause chemical fragmentation of the raw materials. The main challenge of the deposition process is to ensure the yttria content in the zirconia, which is about 7% by weight. Conventionally, two commercial deposition techniques are currently used to produce high-performance TBCs, namely electron beam physical vapor deposition (EB-PVD) and atmospheric plasma spraying (APS).

2.2.1 APS plasma jet spraying

In the case of atmospheric plasma spraying (APS), the plasma spray flame is based on the Gerdien-type plasma generator (Gerdien and Lotz, 1922). The plasma spray process using a plasma was patented by Gageet et al. (1962), as well as by Giannini and Ducati (1960).[75] APS is a jet plasma spraying method that is carried out in atmospheric air. APS can also be deposited in low-pressure (also known as LPPS) and vacuum (also known as VPS) conditions [57]. In a typical APS deposition process shown schematically and in Figure 2.3, the coating material is in powder form and is sprayed into the hottest region of the plasma. The molten particles are then transported by the plasma to the substrate surface [70,76].





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CHAPTER 3. METHODS OF INSPECTION, CHARACTERIZATION AND TESTING OF COATING SYSTEMS AS A THERMAL BARRIER

3.2 Characterization and testing of thermal barrier coating systems

Testing these coating systems helps to determine their suitability and performance in realworld conditions, ensuring that they provide effective thermal protection to gas turbine components.

The most common analyses and tests for TBC include:

- Optical microscopy and scanning electron microscopy morphological analysis of the coatings.
- High-temperature exposure test exposes the coated component to high temperatures for a specified period of time to test its durability and resistance to thermal degradation.
- Adhesion test measures the bonding strength between the TBC and the substrate.
- Thermal shock test involves rapid heating and cooling cycles to test the TBC's ability to withstand thermal stress.
- Corrosion resistance test measures the system's resistance to exposure to high temperatures in the presence of various corrosive compounds found in the atmosphere in marine, desert or fuel residues.
- Thermal conductivity test measures the amount of heat transmitted through the coating material.
- Impact resistance test measures the ability of the coating layer to withstand mechanical impacts or shocks.

PART II. OWN EXPERIMENTAL RESEARCH FOR THE REALIZATION OF A NEW COATING SYSTEM AS A THERMAL BARRIER

CHAPTER 4. EXPERIMENTAL RESEARCH ON THE SIMULATION, FABRICATION AND CHARACTERIZATION OF THERMAL BARRIER COATING SYSTEMS

4.1 Experimental research on choice of super alloy for substrate based on high temperature corrosion resistance

Corrosion at high temperatures has been a serious problem since the 1940s. It became especially important during the Vietnam War, when parts of helicopter engines flying over or near the sea were corroded. TBC coatings are currently used to protect the outer surfaces of super-alloy components, but the inner surfaces are still exposed to high-temperature corrosion.

A new corrosion test at 900 °C was carried out using a mixture of corrosive salts in powder form consisting of 50 % Na₂SO₄ and 50 % V₂O₅ with a purity of 99 % and 99.6 %, purchased from Carlo Erba Reagents SAS. The amount of corrosive powder was ~5 mg/cm2.

The weight gain after the 900 °C corrosion tests is shown in Table 4.2, it was measured by the difference between the initial and final state. A similar trend in the samples was observed in the

case of the superalloy In625, with a slightly higher gain for the In625 SLM samples. The weight gain is higher for In625 samples, especially those obtained by SLM, compared to those obtained conventionally with 37.4 % after 8 hours, 3.98 % after 24 hours, 4.46 % after 48 hours and 5.8 % after 96 hours. In the case of the superalloy Nimonic 75, the weight gain is lower than that of the superalloy In625 by up to 177.67 %.

These results suggest that TBC coatings are not sufficient to protect the inner surfaces of superalloy components from high-temperature corrosion. New protection strategies are needed to prevent the degradation of these components.Tabelul 4.2. Weight gain of samples following corrosion tests.[153]

Specimen	Weight gain, [mg/cm ²]				
	8 h	48 h	96 h		
IN625	27.80 ± 0.2	107.68 ± 0.12	228.90 ± 0.02		
IN625 SLM	38.20 ± 0.12	112.49 ± 0.04	242.20 ± 0.12		
Nimonic 75	7.85 ± 0.04	11.34 ± 0.12	14.32 ± 0.2		

Investigations by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) were performed on the cross-sections of the samples to observe the sample-coating interface, as well as the distribution of elements in the sample and coating. A thicker coating can be observed on the Nimonic 75 samples. A more compact coating similar to the one formed by oxidation is formed on the surface of the Nimonic 75 samples (Figure 4.3 c).



Figure 4.3 Cross-sectional SEM image of In625 (a), In625 SLM (b) and Nimonic 75 (c) samples after 96 h exposure.[153]

A quantitative analysis of the corrosion layers was performed. Two points were selected for investigation, the first (1) closer to the coating surface, and the second closer to the substrate (2), (Figure 4.3, Table 4.3). The results show a clear difference in chemical composition between the two selected zones, so there is a chemical composition gradient, but in a small amount, such as Cr2O3 [161].

Zone		Chemical composition [%]								
	0	Ni	Cr	Мо	Nb	Fe	Mn	S	Na	V
IN625 - 1	18.31	23.54	10.90	26.11	4.52	2.68	-	11.86	1.16	0.93
IN625 - 2	24.74	22.07	20.47	15.20	4.45	4.13	-	6.82	1.30	0.81
In625 SLM - 1	18.92	25.11	13.80	22.75	3.88	2.83	-	10.42	1.21	1.08
In625 SLM - 2	13.26	26.87	27.72	12.19	9.32	3.28	-	5.15	0.93	1.28
Nimonic 75 - 1	24.64	27.92	41.33	-	-	3.98	2.14	-	-	-
Nimonic 75 - 2	15.76	67.82	14.15	-	-	1.30	0.97	-	-	-

Table 4.3 Chemical composition measured by EDS in the two zones of the layer formed after 90 h corrosion.[153]

A possible degradation mechanism that can influence the corrosion rate of the material is based on the amount of "spinel" NiCr2O4 phase, formed on the surface of the samples from the interaction of chromium and nickel oxides. The phase is formed in the presence of Cr2O3 and NiO, which subsequently prevents the diffusion of oxygen into the coating, thus reducing the corrosion rate [169].NiCr2O4 can be present in a larger amount in the case of the superalloy Nimonic 75 compared to In625 SLM and IN625 due to the higher amounts of Ni, Cr and O elements that can form Cr2O3 and NiO leading to the formation of the NiCr2O4 spinel phase. The main degradation mechanism that could explain the difference between In625 SLM, IN625 and Nimonic 75 could be the presence of the Mo element in the composition of the superalloys. Being the 3rd element present in the composition of the layers formed after corrosion in the case of the superalloy In625 shows an intense reaction with corrosive salts and hence the drastic weight gain.

4.2.1 Microstructural analysis

A microstructural analysis of the LZO and GZO zirconia oxide coatings revealed similarities in structure to nano-YSZ coatings. The LZO/GZO zirconia oxide coatings are also homogeneous in composition, without the identification of material inclusions.

This microstructural analysis of the LZO and GZO zirconia oxide coatings provides essential information about the structure and characteristics of these coatings, contributing to the understanding of their performance in specific applications.

Unlike single-material coatings, composite coatings obtained by mixing YSZ and LZO or GZO show a higher level of defects such as pores, cracks, material segregation, and lack of adhesion, which can have effects on the high-temperature behavior of the coatings. Although it is preferable for a TBC coating to have a high level of porosity, when the pore size is too large (on the order of tens of microns) the adhesion/cohesion strength decreases significantly, especially if the coating is subjected to mechanical stresses.



Figure 4.18SEM images of TBC systems, YSZ nano (a, b), 50% YSZ nano + GZO (c, d) and 50% YSZ nano + LZO (e, f).

CHAPTER 5. EXPERIMENTAL RESEARCH ON THE TESTING OF COATING SYSTEMS AS A THERMAL BARRIER

5.1 Testing the adhesion of the component layers of the thermal barrier coating system

The adhesion of the layers of the thermal barrier coating system was tested by a scratch test in the cross-section of the coating, measuring the scratch left by the indenter to evaluate the

behavior of a coating by analyzing the image of the scratch zone and measuring the projected cone area.

Figure 5.3 shows an example for each proposed system with the method of measuring the projected cone area.

The average projected cone area was summarized in Figure 5.4 and it showed that the nano-YSZ ceramic layer has the best cohesion strength. It can also be noted that all system variants showed a cohesive failure even at 40N, which indicates a very good adhesion obtained after the coating process and thus validates the deposition parameters.



Figure 5.3 Optical microscopy images at 100x magnification of the projected area of the cone after scratching tests performed with 40 N, YSZ nano (a), YSZ nano + 50% LZO (b) and YSZ nano + 50% GZO (c)



Figure 5.4: Graph of the average adhesion strength of the TBC systems.

5.2 Determination of oxidation resistance of thermal barrier systems

In order to carry out the isothermal oxidation resistance tests, samples of approximately 15x15 mm were cut and placed in an alumina crucible for each temperature range. For their evaluation, the criterion was used by which the ceramic coating is considered to be degraded when the exfoliation is more than 30%.

Isothermal oxidation resistance tests were performed with the help of the Nabertherm electric furnace model N 17/HR with Tmax=1400°C.

The following parameters were used for testing the samples:

- Heating rate: 5 °C/min;
- Test temperature: 1150 °C;
- Cycle duration: 100 h.

After the isothermal oxidation resistance tests (Table 5.1), it was found that the conventional YSZ nano coating withstood the 8 cycles without showing the exfoliation of the layer by more than 30% as the condition was imposed, while the unconventional coatings with rare earths did not withstand any cycle.

In Figures 5.5-5.7, images of the surface of the samples subjected to isothermal oxidation cycles can be seen as well as optical microscopy images with the cross-section of these. Following the microscopic analysis after the first cycle, the rare earth coatings systems lost more than 70% of the ceramic layer, leaving only areas with a thickness of up to 80% of the initial layer. It can also be underlined that the main degradation factor was the tension produced in the ceramic layer. This tension can be explained by a deposition of the ceramic layer with inappropriate parameters or by an incompatibility of the two ceramics in a 50-50% proportion. In the case of the conventional coating, it does not show any reduction in the ceramic layer, but it can be mentioned that the isothermal oxidation process of 800h oxidized more than 60% of the bond layer by forming the TGO (thermal grow oxide) layer, which according to the literature can have a negative impact on the resistance of the TBC system due to the stresses induced in the system after its growth. The main hypothesis that can explain the behavior of the ceramic layer is that the thickness of the TGO layer remained at low values of ~ 4um due to the large surface of oxidation of the bond layer created by the lack of adhesion of the deposited layers during manufacture, which created a network-type oxidation that managed to release the stresses produced by the growth of the TGO layer. Normally, the TGO layer appears at the interface between the ceramic layer and the metal bond layer and its growth produces a delamination of the ceramic layer due to the stresses produced by growth.



100h

Figure 5.5: Images of the surface and cross-section of the YSZ nano + 50% GZO coated sample after isothermal oxidation tests.



100h

Figure 5.6: Images of the surface and cross-section of the YSZ nano + 50% LZO coated sample after isothermal oxidation tests.



300h





400h





600h







800h Figure 5.7 Surface images and cross sections of the YSZ nano coated sample after isothermal oxidation tests.

5.2.1 The influence of isothermal oxidation on the porosity of the adhesion layer and ceramic.

Table 5.3 shows the average of 10 zones of the results of the percentage measurement by trinarization of porosity and the area affected by TGO. The surface area of the TGO layer is 37.11% at 400 h, and 51.84% at 800 h. The porosity of the bond layer decreases from 14.42% to 1.62% after 800 h of cyclic isothermal oxidation.

	Initial state	400h	800h
Area TGO [%]	0	37.11	51.84
Porosity [%]	14.42	2.74	1.62

Table 5.3 Average po	prosity and TGO affected	area in the tie layer.
----------------------	--------------------------	------------------------

As the temperature and oxidation time increase, the porosity of the bond layer decreases. During oxidation, oxygen infiltrates into the pores and micro-cracks of the TGO layer, leading to the formation of internal oxides in the bond layer. In addition, the pores tend to be filled with internal oxides, such as Al2O3 and mixed oxides, at longer oxidation times [183-184].

Figure 5.12 shows scanning electron microscopy images of the ceramic layer in crosssection in the initial state and after 400 h and 800 h of cyclic isothermal oxidation. The overall appearance of the ceramic layer is similar, with the particularity of the presence of a greater amount of cracks and pores formed as a result of the rupture of the material due to the propagated cracks after cyclic isothermal oxidation.



Figure 5.12 SEM images of the ceramic layer in cross section after 400h and 800h of cyclic isothermal oxidation.

The results of the porosity determination by binarization of 10 zones for each sample in Table 5.4 showed that after 400 hours, densification occurs as a result of cyclic isothermal oxidation due to the sintering phenomenon, while after 800 hours, the porosity increases due to the grinding of the ceramic layer as a result of the propagation of cracks in the layer, maintaining a high density.

Table 5.4 Average porosity for each ceramic layer.

	01	5	<i>.</i>	
YSZ nano		Initial state	400h	800h
Porosity [%]		20.08	17.84	20.43

5.2.2 Analysis of the influence of isothermal oxidation on the adhesion of layers

Figure 5.14 shows the results of the adhesion testing of the YSZ nano system according to the procedure presented in subchapter 5.1.

The adhesion test results indicate that after cyclic isothermal oxidation, the ceramic layer is densified, which leads to an increase in strength, explained by the fact that the projected cone area decreases.

The densification, according to the results, takes place in the first cycles and is maintained even up to 800 hours.



Figure 5.14 Evolution of the projected area of the cone following cyclic isothermal oxidation.

5.3 Determination of thermal shock resistance of thermal barrier systems

To validate the thermal barrier coating systems, they were subjected to a thermal shock test that simulates the real operating conditions of the coated components of the hot section of the gas turbine, specifically the moment of takeoff where the temperature suddenly increases or at landing where an aggressive cooling is produced from temperatures of over 1200°C to room temperature. These tests are vital in the validation of these TBC systems due to their low resistance to the internal stresses created in each layer as well as between layers after thermal shocks.

Figure 5.16 shows the installation at INCDT COMOTI that will be used for future experiments. The thermal shock installation consists of a Nabertherm furnace capable of heating up to 1400°C with an 80 mm access slot in the upper part where the samples enter the furnace, a Yamaha motorized axis connected to a PLC and a compressor for cooling the samples. In Figure 5.16, top right, the sample holding device can be seen, consisting of a thermocouple, support rod and two caps, cooling pipes connected to the compressor and the access slot in the heated enclosure of the furnace.

For the evaluation of these, the criterion was used by which the ceramic coating is considered to have failed at the moment of peeling with more than 30%.



Figure 5.16 Picture of the sample testing facility.

To test the samples, the following parameters were used and the thermal shock cycle diagram is shown in Figure 5.17:

- Test temperature: 1200 °C and 1250 °C;
- Heating time to plateau: 60 sec;
- Plateau holding time: 100 sec;
- Sample cooling temperature: 90 °C;
- Cooling time: 120 sec;
- Cooling air pressure: 3.5 Bar.

Figure 5.18 shows images of the appearance of the ceramic layer after thermal shock testing at 1200°C and 1250 °C.





5.4 Corrosion resistance testing of TBC systems

In order to perform the high-temperature corrosion resistance tests, samples of approximately 15x15 mm were cut and placed in an alumina crucible. For testing, two corrosive mixtures were used, a mixture of salts in powder form consisting of 50% Na2SO4 and 50% V2O5 with a purity of 99% and 99.6% and the second mixture consisting of oxides CaO-MgO-Al2O3-SiO2 with a purity of over 99%, purchased from Carlo Erba Reagents SAS. The amount of corrosive powder was ~5 mg/cm2 in the case of the salt mixture and 20 mg/cm2 in the case of the oxide mixture. The corrosive powder mixture was spread on the surface of the samples. The crucibles were weighed with the analytical balance Pioneer PX224 with a precision of 10-4 g.

The isothermal oxidation resistance tests were carried out with the help of the Nabertherm electric furnace model N 17/HR with Tmax=1400°C.

The following parameters were used to test the samples:

Heating and cooling rate: 5 °C/min

Test temperature: 900°C and 1250°C

Cycle hold time: 8 hours

In Figure 5.20, the weight gain of the TBC systems after being subjected to cyclic corrosion at 900°C can be observed. The weight gain is the result of the interaction of the corrosive salts with the ceramic layer, and a reduced reaction indicates that the ceramic layer is chemically stable to the interaction with the corrosive salts and, in practice, the corrosion resistance is higher. According to the literature, it is known that the use of rare earths in the production of these TBC systems improves corrosion resistance and increases the service life of components that operate in corrosive environments. This fact is validated by these tests, where a difference of up to 20% can be observed between the conventional system alternative with YSZ and the one with the addition of rare earth GZO.



Figure 5.20 Variation of weight gain of samples after corrosion tests.

Figure 5.23 shows the graph of the weight gain of the TBC systems after being exposed to cyclic corrosion at 1250°C with the CMAS oxide mixture. The tests were stopped after 24 hours due to the high degree of exfoliation of the YSZ nano system. The weight gain reflects

the interaction between the corrosive salts and the ceramic layer, and a lower weight gain indicates a higher chemical stability of the ceramic layer in contact with the corrosive salts, which denotes a higher corrosion resistance. According to the literature, it is known that the use of rare earths in these TBC systems improves corrosion resistance and extends the service life of components that operate in corrosive environments. This finding is validated by the results of these tests, where a difference of up to 10% can be observed between the conventional system variant with YSZ and the one with the addition of rare earth LZO.



Figure 5.23 Variation of weight gain of samples after corrosion tests.

CHAPTER 6. DEVELOPMENT OF AN AUTOMATED STAND FOR TESTING RESISTANCE TO OXIDATION AND THERMAL SHOCK OF LAYERS DEPOSITED AS A THERMAL BARRIER

The development of the stand was aimed at using it to simulate the real operating conditions of these coatings, which are mainly intended for the aerospace industry, in order to determine their performance and limitations, which are necessary in the research, design and development stages of thermal barrier coatings superior to the current ones. The stand in Figure 6.1 consists of six graphite blocks (1) which provide a channel for heating the sample (5) with a resistor (4), two channels for cooling the sample (6) and the substrate (7), four channels for the exhaust of hot/cold air (11), two holes for contact thermocouples used to identify the temperature at the surface of the sample (2) and the substrate temperature (3), a slot for positioning the sample (10), vertical (8) and horizontal (9) channels used for the recovery of thermal energy, three ventilation systems (12) for the realization of the hot and cold air flow.





b)



Figure 6.1 Overview of the test stand.

The facility is used to simulate the actual operating conditions of the deposited layers according to EN ISO 13123:2011, which are used in particular in the aerospace industry. This test determines the performance or/and limitations of the layers, and the results are useful in the design and development stages of new thermal barrier coating systems.

Currently, there are various test stands for testing the oxidation and thermal shock resistance of thermal barrier coatings, all of which have in common a heating and cooling source, a temperature measurement and control system, a sample gripping system and an incinerator.

The facility presented in this article solves three technical problems:

It ensures the cooling of the substrate in the case of testing thermal barrier coating systems;

It has reduced construction and operation costs, as it does not have complex handling or sample gripping systems;

It is built and configured to provide the possibility of complete and independent automation.

The development of the automated test stand for testing the oxidation and thermal shock resistance of the deposited thermal barrier coatings led to the filing of a patent application with OSIM with number A2023/00129.

CHAPTER 7. GENERAL CONCLUSIONS AND OWN CONTRIBUTIONS

7.1 General conclusions

Experimental research was carried out on the selection of the superalloy for the substrate based on the high-temperature corrosion resistance.

Following the experiments on the high-temperature corrosion resistance of the superalloys In625, In625 SLM and Nimonic 75, it was found that the superalloy Nimonic 75 has a resistance of up to 178% compared to the superalloy In625 SLM.

Three mechanisms of superalloy degradation due to hot corrosion were identified based on the analysis of the results and the literature:

The presence of the Mo element in the composition of the superalloys, being the 3rd element present in the composition of the layers formed after corrosion.

The presence of the spinel NiCr2O4 phase formed from Cr2O3 and NiO, which reduces oxygen penetration and the corrosive activity of salts.

A fine and compact structure can slow down the corrosion process by dispersing the same amount of corrosive salts over a larger surface. This is due to the infiltration of corrosive salts at the grain boundary, and through a larger grain boundary, the contact surface with the salts increases and gives the superalloy time to produce enough protective phase to slow down or cancel out the corrosive activity of the salts.

Three variants of TBC systems were studied for the purpose of numerical simulation, manufacturing and characterization, consisting of a substrate of superalloy Nimonic 75, a metal

layer of superalloy NiCrAlY and a ceramic layer of nano-YSZ, nano-YSZ + 50% GZO and nano-YSZ + 50% LZO.

Following the numerical simulations, it was found that system 3 with a ceramic layer made of nano-YSZ + 50% LZO reduces the surface temperature of the substrate by about 12 $^{\circ}$ C compared to the conventional nano-YSZ variant and 150°C compared to the variant without TBC system.

In all three systems, the microstructural analysis revealed a significant amount of pores, inclusions and unmelted or partially melted particles both in the metal layer and in the ceramic layer. At the same time, it can be observed that the layers are not adhered in the ceramic and in the metal layer. In all variants, the sandblasting marks are quite pronounced and no cracks are observed at the substrate-metal layer interface. The layer thicknesses vary within the range of 10-15%, totaling approximately 600-650 µm.

Following the analysis of the influence of the deposition process on the substrate, it was found that the thermal influence during the deposition of the coatings on the substrate is present up to a depth of approximately 0.3 mm and brings an increase in hardness up to 152 HV03. The difference decreases significantly to 65 HV03 after the TBC system is subjected to a temperature of 1250 °C, the operating temperature of the system under normal conditions.

Analyzing the influence of the deposition process on the final roughness of the sample after each deposition step, it was found that there is an increase of up to 5 times in the roughness compared to the non-coated sample.

Tests to determine the porosity of the ceramic layer in the initial state have summarized that the nano-YSZ layer has a porosity of 20.26%, nano-YSZ + 50% GZO 23.71% and nano-YSZ + 50% LZO 17.30%.

Tests to determine the porosity of the metal layer in the initial state have summarized that the nano-YSZ layer has a porosity of 14.42%, nano-YSZ + 50% GZO 18.21% and nano-YSZ + 50% LZO 17.18%.

Tests to determine the adhesion strength of the ceramic layer in the initial state concluded that the nano-YSZ layer has the best strength followed by the nano-YSZ + 50% GZO and nano-YSZ + 50% LZO layers.

After carrying out the isothermal oxidation resistance tests, it was found that the conventional was able to withstand a maintenance of 800h at 1150°C without showing the exfoliation of the layer while the unconventional variants with LZO and GZO did not withstand after the first cycle of 100h, noting that no peeling was actually produced but a grinding of the ceramic layer remaining a small amount in the continuation on the surface of ~ 10-20%.

Following the thermal shock resistance tests carried out at 1200 °C and 1250 °C, it was found that the conventional YSZ nano coating has the best resistance, followed by the unconventional GZO and LZO coatings.

After carrying out the corrosion resistance tests at a temperature of 900 °C for up to 96 hours, it was found that the conventional YSZ nano coating has the best resistance to degradation, while the coating with the rare earth mix GZO has the best corrosion resistance in terms of interaction with corrosive salts.

Corrosion resistance tests with the CMAS oxide mixture at a temperature of 1250 °C for 24 hours showed a better resistance of systems with rare earths compared to the version without them.

A stand was developed for the automatic testing of the oxidation and thermal shock resistance of the deposited coatings with a thermal barrier role, which has three advantages:

The facility ensures the cooling of the substrate during testing.

It has reduced construction and operation costs, as it does not have complex handling or sample gripping systems and is equipped with energy recovery channels.

It is designed and configured in order to provide the possibility of complete and independent automation.

7.2 Own contributions

Study the literature in order to identify the current state of the art in the field of thermal barrier coatings, in terms of the requirements for each component of the system and the new requirements and challenges in the field.

Determine the high-temperature performance of the proposed thermal barrier coating (TBC) systems through numerical simulation, by analyzing the temperature distribution in the system using the Ansys program.

Design and manufacture support samples from the Nimonic 75 super alloy for the deposition of TBC systems in atmospheric conditions using the APS plasma jet spraying method.

Analyze the influence of the deposition process on the mechanical properties of the substrate by Vickers microhardness tests and the roughness of the samples after each deposited layer by roughness measurements.

Develop a method for the quantitative evaluation of the pores and the area with thermally grown oxides (TGO) present in the system after isothermal oxidation by trinarization of optical and SEM microscopy images using the Scandium software.

Identify the lifetime of the systems studied under conditions of cyclic isothermal oxidation at a temperature of 1150 °C and a holding time of 100h per cycle.

Evaluate the lifetime of the TBC systems under simultaneous conditions of thermal shock and cyclic isothermal oxidation at 1200°C and 1250°C.

Determine the influence of cyclic isothermal oxidation on the densification of the component layers in the TBC system by quantitative evaluation of the pores and adhesion tests performed by the scratch method in cross section.

Evaluate the high-temperature corrosion behavior of the systems studied at temperatures of 900 °C and 1250 °C in environments rich in Na2SO4+V2O5 salts and Ca, Mg, Al and Si oxides, simulating the marine and desert environment in which these coatings can operate.

Design an automated thermal shock and isothermal oxidation installation for testing thermal barrier coatings.

Submit a patent application for the automated thermal shock and isothermal oxidation test installation for thermal barrier coatings.

7.3 Future research directions

Manufacture a substrate for current thermal barrier and environmental coatings made of a silicon carbide composite reinforced with continuous or chopped silicon carbide fibers by the SPS sintering method.

Manufacture current thermal barrier and environmental coatings from Yb2Si2O7 and 3Al2O3 -2SiO2 by the APS plasma jet spraying method in atmospheric air.

Test the substrate for chemical stability to oxidation and corrosion at high temperatures

Test the new coating concepts to determine the lifetime under isothermal oxidation, corrosion and thermal shock conditions at temperatures above 1300°C, but also from a mechanical point of view regarding the cohesion strength and toughness.

Commissioning the automated thermal shock and isothermal oxidation installation for testing thermal barrier coatings.

DISSEMINATION OF RESEARCH RESULTS

Presentations given at international conferences:

- 12th International Advances in Applied Physics & Materials Science Congress & Exhibition (APMAS 2022 Microstructural and mechanical properties of plasmasprayed thermal barrier coatings Alexandru Paraschiv, Mihaela Raluca Condruz, Teodor Adrian Badea
- 2. Mihaela Raluca CONDRUZ, Tiberius-Florian FRIGIOESCU, Ionut Sebastian VINTILA, **Teodor-Adrian BADEA**, Alexandra ADIACONITEI (2021), Computational and experimental study on investment cast micro-turbopump impeller, lucrare acceptată pentru prezentare orala în cadrul conferinței Thirteenth Conference of the Euro-American Consortium for Promoting the Application of Mathematics in Technical and Natural Sciences, Albena, Bulgaria, June 24-29.
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