COPPER ALLOY COATED WITH CERAMIC MATERIAL FOR LIQUID ROCKET ENGINE THRUST CHAMBERS APPLICATION.

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ABSTRACT

The aim of this work is present a methodology to characterize copper alloy samples coated with ceramic material, seeking their application in thrust chambers of liquid propellant rocket engine. Due to propellants combustion reactions, high temperatures acts in the walls of Liquid Rocket Engine (LRE) thrust chamber. One way to ensure the structural integrity of the chamber can be the use of a regenerative cooling cycle, where part of fuel is injected directly over the chamber walls to reduce the temperature until levels around 1000K. But this wall temperature isn't the ideal work condition to wall chamber. An alternative solution could be the use of ceramic materials for coating the inner walls of the chamber, acting as a thermal barrier. For over 20 years, Thermal Barrier Coatings (TBCs) have been used in aero turbine hot sections. The initial applications were driven by need to suppress component degradation caused by excessive thermal gradients in vane airfoils. TBCs consist of a bonding coat layer and a top layer. The bonding coat is a transition layer between the top layer and the base material. There are some studies about the possibility to apply TBCs over the internal surface of LREs wall thrust chamber. The purpose of this paper is study metallographic characteristics of cooper alloy samples (UNS C18200) coated with ceramic material, 8wt % yttria stabilized zirconia. Air Plasma Spray process was used to deposit the coating over the cooper alloy samples as an alternative to Electro Beam Physical Vapor Deposition – EB – PVD. Optical microscopy and scanning electron techniques were used to analyze the coating microstructure as well its adhesion to the substrate. The samples were submitted x-ray diffraction (XRD) to know crystalline phases, important factor to be examined to ensure the efficiency of coating. From this results will be possible know metallographic characteristics of Thermal Barrier Coatings manufactured by ceramics materials.

Topic 4: Ceramics Materials.

Key Words: Air Plasma Spray, Thrust Chambers, Thermal Barrier Coating, Zirconia

1. INTRODUCTION

The aim of this work is present a methodology to characterize copper alloy samples coated with ceramic material, seeking their application in thrust chambers of liquid propellant rocket engine. Due to propellants combustion reactions, high temperatures acts in the walls of Liquid Rocket Engine (LRE) thrust chamber. One way to ensure the structural integrity of the chamber can be the use of a regenerative cooling cycle, where part of fuel is injected directly over the chamber walls to reduce the temperature until levels around 1000K. But this wall temperature is not the ideal work condition to wall chamber. An alternative solution could be the use of ceramic materials for coating the inner walls of the chamber, acting as a thermal barrier. For over 20 years, Thermal Barrier Coatings (TBCs) have been used in aero turbine hot sections. The initial applications were driven by need to suppress component degradation caused by excessive thermal gradients in vane airfoils. TBCs consist of a bonding coat layer and a top layer. The bonding coat is a transition layer between the top layer and the base material. There are some studies about the possibility to apply TBCs over the internal surface of LREs wall thrust chamber. The purpose of this paper is to study metallographic characteristics of cooper alloy samples (UNS C18200) coated with ceramic material, 8wt % yttria stabilized zirconia. Air Plasma Spray process was used to deposit the coating over the cooper alloy samples as an alternative to Electro Beam Physical Vapor Deposition – EB/PVD. Optical microscopy and scanning electron techniques were used to analyze the coating microstructure as well its adhesion to the substrate. The samples were submitted x-ray diffraction (XRD) to know crystalline phases, important factor to be examined to ensure the efficiency of coating. From these results will be possible knowing metallographic characteristics of Thermal Barrier Coatings manufactured by ceramics materials.

2. THERMAL BARRIER COATINGS MANUFACTURED WITH ZIRCONIA STABILIZED WITH YTTRIA

According with Greuel et al., 2002 [2] a TBC consists of a bonding and a top layer. The bonding layer is a transition layer between the top layer and the metallic substrate material. Its function is to effectuate chemical adhesion of the top layer, to provide corrosion resistance of the coated metallic substrate and to compensate for the different thermal expansion coefficients of the top layer and metallic substrate.

The top layer act as the thermal barrier coating because it’s manufactured with ceramic material that perform the function of decrease the temperature acting over the wall thrust chamber. In function of the zirconia low thermal conductivity (about 1.5 W/mK) this material is used to manufacture the TBC top layer [2].

The first studies about ceramics films by MgO-ZrO_2 thermal spray application over NiCr substrate has began in the 70’s.. This coating had a limitation to the low life due to accelerated bond coat oxidation (interface between metallic substrate and top layer) when compared with yttria stabilized zirconia thermal barrier coatings applied by air plasma spray process over MCrAlY layer [4].

The zirconia when exposed to atmosphere pressure is polymorph, in high temperatures (> 2 370^{O}C) it’s possible to see a cubic structure (C), in intermediate temperatures it’s possible to see a tetragonal structure (1 200^{O}C – 2 370^{O}C) and in low temperatures it is possible to a monoclinic structure (< 950^{O}C) [5]. This description is according the diagram shown in figure 1.

Under equilibrium conditions yttria enters at zirconia solid solution and stabilizes its tetragonal crystal structure (t – YSZ) above about 1 050^{O}. During its cooling occurs a phase transformation from the tetragonal structure to a mixture monoclinic (m – YSZ) zirconia and a cubic (c – YSZ) zirconia. The tetragonal to monoclinic phase transformation during the cooling is martensitic in nature [6]. The recognition of the potential for enhanced fracture toughness that can be derived from controlled, stress – activated tetragonal (t) to monoclinic (m) transformation in ZrO_2 based ceramics ushered in new era in the development of the mechanical properties of engineering ceramics and provided a major impetus for broader – ranging research into the toughening mechanisms available to enhance the fracture properties of brittle – matrix materials. Small cracks can be generated by not ideal accommodation of the stresses generated by volumetric expansion, increase the mechanical strength reduction for TBCs manufactured with zirconia as only material [5]. For kinetic reasons associated with the relatively rapid deposition rate of the top coat, the deposited YSZ typically exists in a closely related but metastable tetragonal – prime (t’) structure rather than the stable tetragonal structure. Another important conclusion from this analysis is that t’ – YSZ does not undergo any transformation on cooling, even after an extended number of thermal cycles [6].

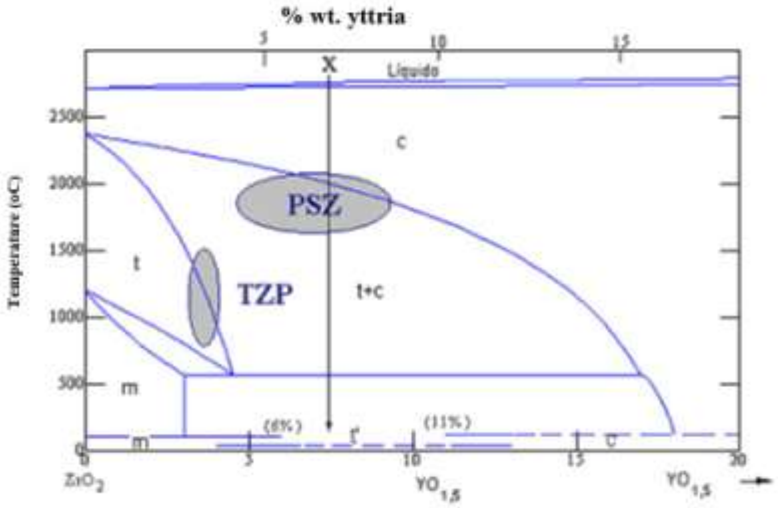

Figure 1: Part of the ZrO2 – YO1.5 system phase diagram [7].

For engineering applications it is necessary that the zirconia is stabilized or partially stabilized. The term “stabilized” originally is referred to partial stabilization of the cubic phase. Thus, the partially stabilized zirconia contains other phases [5]. The main feature of the zirconia – yttria binary diagram is the large tetragonal phase area that until nearly $YO_{1.5}$ 5% mol is in solid solution. This parameter associate with the low eutectoid transformation temperature (~ 5200 ^{O}C), enables the achievement of fully tetragonal zirconia or tetragonal zirconia policrystals (TZP). The zirconia – yttria system equilibrium phase diagram also shows a large region where it’s possible to see the t + c mixture, allowing obtaining the partially stabilized zirconia (PSZ) [8].

The addition of Ta_2O_5, Nb_2O_5 and HfO_2 to the bulk Y_2O_3 stabilized tetragonal ZrO_2 increases the transformability (t to m transformation temperature) of the resulting zirconia ceramics. The enhanced transformability is related to the alloying effect on the tetragonality (c/a – cell parameters ratio) of stabilized tetragonal ZrO_2 (figure 2), so the addiction of these oxides increases the tetragonal distortion of the cubic lattice [1].

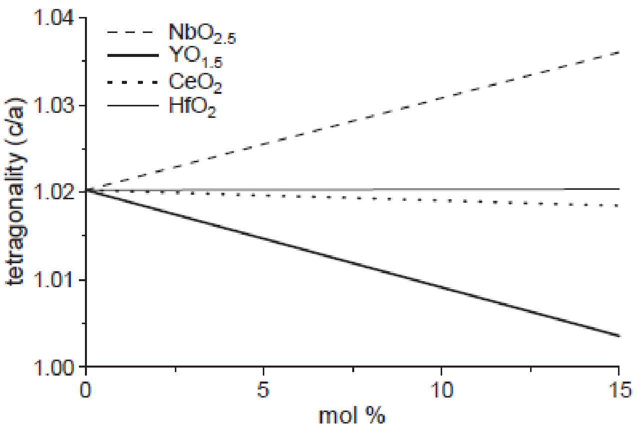

Figure 2: Influence of the alloying oxide in the c/a axial ratio of bulk zirconia – based ceramics [9].

Increasing the tetragonality, parameter shown in figure 2, due to alloying is consistent with the increase in the fracture toughness and increase in the t to m transformation temperature [1].

The thermal and mechanics properties of ceramic coatings of yttria-stabilized zirconia are: low thermal conductivity, high permeability with respect to oxygen and high thermal expansion coefficient. Due to this high permeability for oxygen is required a protection layer over bond coat or metallic layer in order to avoid its oxidation [6].

Due to the bond coat layer is very rich in aluminum, it's associated to oxide, TGO (Thermal Oxide Growth) between the top layer and bond coat layer [6].

The weakest part of a thermal barrier system is the planar region between the top layer and bond coat layer. Both phase and volume changes during the thermal cycles from the thermal expansion coefficient differences can lead to detachment of the Thermal Barrier Coating [10].

3. MATERIALS AND METHODOLOGY

The samples used in this work were manufactured sectioning a UNS C18200 copper alloy circular billet. Samples were prepared to application of ceramics coatings, zirconia stabilized with 8 wt.% yttria, by solid blasting process and after was deposited the coatings by the Air Plasma Process (Figure 3), widespread thermal spray process.

The plasma generator consists of a circular anode, usually made of copper and cathode of throated tungsten. The electric arc discharge supported by a generator through the connectors heats up the working gases, which expand to the atmosphere a jet. The powder, suspended in a carrier gas, is injected in the flame. The particles of the powder after being melted and accelerated in the plasma impact the substrate and form the coating [11].

The microstructure of thermally sprayed coatings has a lot of characteristics that have been discussed previously, making it difficult to select an appropriate investigation method. One other hand, microstructure research is an intermediate and necessary step between the processing of the coating and the selection of the spray parameters, and the achievements of their desired functional property [11]. To characterize Thermal Barrier Coatings (TBC) requires modern materials characterization techniques, like X – ray diffraction and metallographic characterization using the X – ray diffraction is a powerful technique used to identify the crystalline phases present in a material and also to estimate the structural properties of a material. It's possible to use the X-ray diffraction to determine the thickness films and structures with multiples layers, as well as atomic arrangements in amorphous structures [12]. The principle of the method consists of the determination of the diffraction angle Θ that is related to the d – spacings characterizing phase, between the difracting crystalographic planes, following the Bragg's equation (1):

$$2d\sin\theta = \lambda \qquad (1)$$

where λ is the used X – ray wave length. The d – spacings pattern can be atributted to phase with the use of actualized yearly standard JCPDS (Joint Commitee on Powder Diffraction Standards, USA) index cards [13].

The coating must be crushed prior to the XRD test. The method enables identifying of the phases of minimum content in the sample of about 5 wt. % [12].

Metallographic is the study of the morphology and structure of materials. To perform the analysis, the sample is cut in the plane interest, sanded, polished and attacked with chemical reagent in order to reveal the interfaces between the different elements that compose the studied material [14].

The SEM is one of the most common techniques for microstructure characterization currently known, finding application in various fields of knowledge. In the SEM an electron beam of energy up to 50 keV and diameter down to 5 nm is focused on the surface of the sample. The electron beam ionizes the atoms near to the surface and this result in an emission of secondary electrons (SE) of energy up to 50 eV, which enables surface topology to be observed [12].

Figure 3: Coatings process application (DUROTEC Ltd).

The surfaces of specimens for SEM investigation must be electrically conducting. Insulating materials have to be covered with a thin conducting film of evaporated carbon or sputtered gold. The fracturing of the observed surfaces should be done shortly before the SEM investigation in order to minimize the contact with the environment [12].

4. RESULTS

The diffractogram obtained from analysis by X – ray diffraction is shown in figure 4. Looking at the index cards from JCPDF to tetragonal zirconia phase, expected for this ceramic coating due to their stability with 8 wt.% can be identified diffraction peaks, which are presented in figure 4.

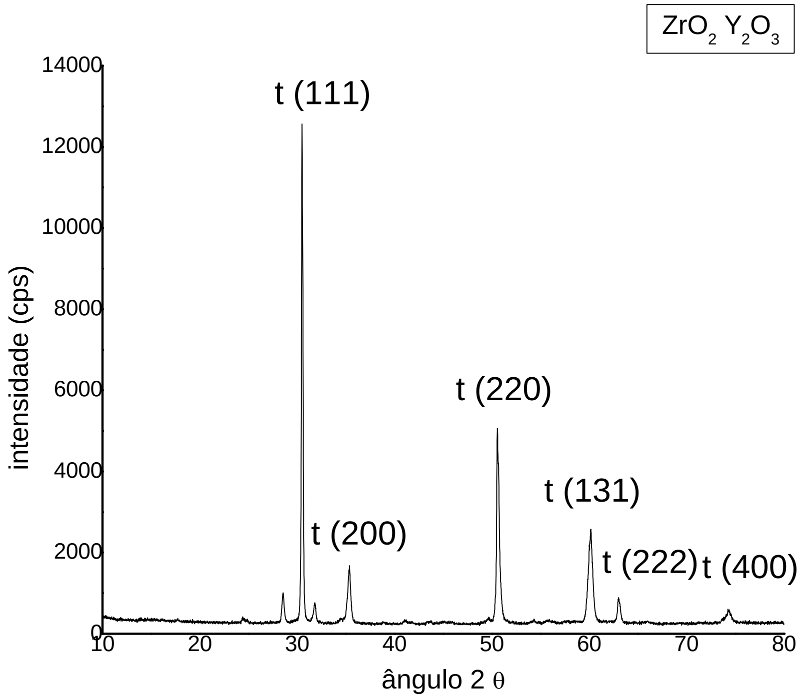

Figure 4: X – ray diffractogram of a UNS C 18200 copper alloy sample coated with zirconia stabilized with 8 wt.% yttria.

However, the X – ray diffraction technique allows determining, with sufficient precision the position of the peaks, the position of the peaks is correlated with crystalline cell lattice parameters and these vary strongly with the chemical composition of the coatings [1].

Taking as reference a = 5.104 Å, c = 5.102 Å, as record analysis zirconia tetragonal JPCDF index card the tetragonality results 1.011, confirming the existence of a tetragonal phase in the studied coating.

The samples were cut and embedded and in a first step were analyzed using the optical microscopy technique with the purpose to make a qualitative analysis about the quality of the coatings applied.

In the sequence the coated samples were analyzed using a scanning electron microscopy technique, where it’s possible to see the details of the deposition of the coating over the metallic substrate. The figures 4 and 5 show these details of the coating deposition over the metallic substrate, enabling the determination of the ideal applying process conditions.

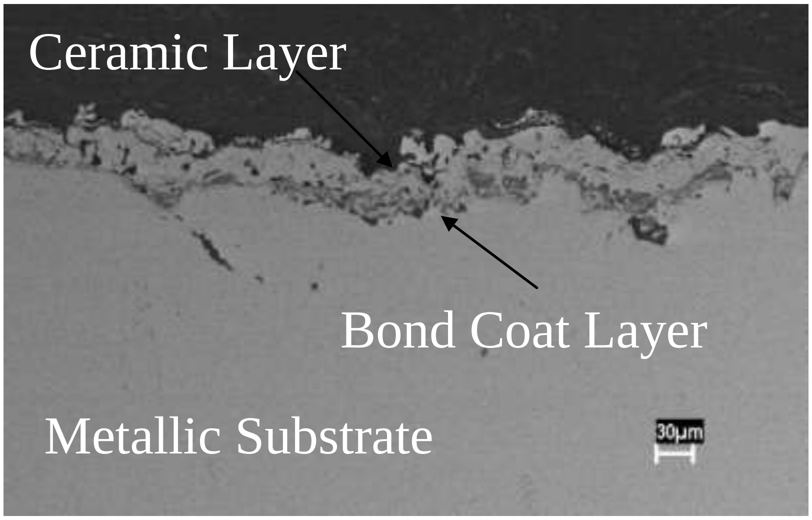

Figure 5: SEM of Air Plasma Spray coating cross section.

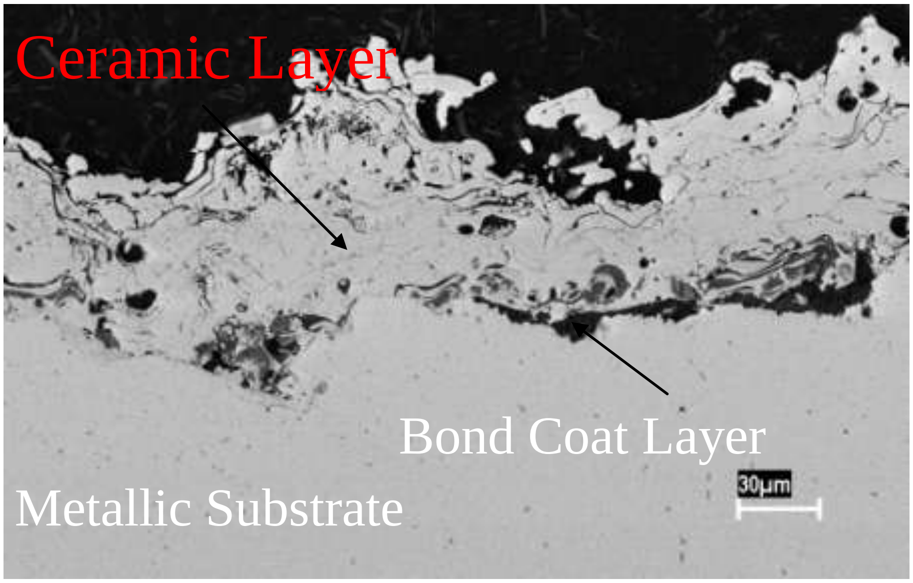

Figure 6: SEM of Air Plasma Spray coating cross section.

Up to figures 5 and 6 is evident that the coatings obtained are satisfactory, but it's necessary observe some manufacturing parameters like the distance between plasma torch and the metal substrate at the time of application that should be as uniform as possible, this parameter is subject to detailed study, because it influences the speed which the particles of coating material in molten state will collide on the substrate and consequently the coating adhesion, creating or not manufacturing defects such as delaminations and porosities.

The gas that generates the plasma from the torch application deserves attention because it may be associated with the oxidation process during application of coatings.

5. CONCLUSIONS

The automatic application process is recommemded since it allows for greater uniformity of the coating deposited on the substrate, as this consistency depends on the distance of the plasma torch relative to the metalic substrate, with is easier to be controlled in automatic process.

Manufaturing defects such as delaminations and porosity depend on the impact velocity of the molten particle over the methalic substrate. This parameter of the process of thermal spraying depends on the distance between the plasma torch and metalic substrate.

It's possible the occurrence of the oxidation phenomenom before and during application of the coatings, mainly for the situation that metallic substrate to be a copper alloy, a material that oxidizes easily at high temperatures. In this case it's necessary a rigorous analisys of the gas that generate the plasma used in the cotings application process.

6. ACKNOWLEDGEMENTS

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